NANO-ENGINEERED POLYMER COMPOSITES

SYNTHESIZED BY SI-ATRP – FROM

SYNTHESIS TO NOVEL MATERIALS

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Preface

Radical polymerization (RP) is widely employed in industry since it can polymerize a wide range of vinyl monomers and tolerate water/protic impurities. However, RP is accompanied by an unavoidable termination process that limits the control over molecular weight (MW), molecular weight distribution (MWD) and chain end functionality. The development of reversible-deactivation radical polymerization (RDRP) methods during the past three decades have overcome many of these limitations and facilitated access to polymers with precisely controlled MW, compositions, topologies, and functionalities. Atom transfer radical polymerization (ATRP), developed in 1995 in our laboratories, is among one of the most robust RDRP techniques and has been successfully utilized for the preparation of polymer/inorganic (hybrid) nanocomposites (NCs).

ATRP is superior to other RDRPs for preparation of homopolymers and copolymers from a wide range of monomers and provides a simple procedure to introduce additional functionality onto the well-preserved chain-end functionality. More importantly, compared to agents required for other RDRPs, most of the required ATRP reagents are currently commercially available which simplifies the scaling of ATRP for industrial production. Although ATRP is currently the most frequently used RDRP method to synthesize NCs in the published literature, some challenges remain. Challenges included the surface confinement effect that may diminish the reactants' diffusion rate and hence control over the polymerization kinetics from surfaces, unavoidable termination reactions that limit the MW of surface-initiated ATRP (SI-ATRP), and side reactions that form new chains or introduce branching into the growing chain. This dissertation therefore focuses on the investigation of the kinetics of conducting ATRP from solid inorganic surfaces of various curvatures and size. It also focuses on the development of new polymerization methods that allow the syntheses of high MW tethered polymer chains, on understanding the effects of side reactions and the final structure of the synthesized NCs on the properties of the novel hybrid composite materials prepared using these methods.

Chapter I reviews the development of hybrid NCs since their introduction. Also the benefits and limitations of various RDRPs are compared and discussed while focusing on the fundamentals of ATRP. Specifically, the development of SI-ATRP is discussed and the recent advancements using SI-ATRP for the preparation of nano-engineered hybrid composites for a spectrum of diverse applications is presented.

Chapters II and III present the major challenges that SI-ATRP faced, including the surface congestion effect which affects the polymerization kinetics and unavoidable termination reactions that limited the MW of polymers tethered

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on surfaces. Specifically, Chapter II focuses on the surface congestion effect, a subject that has been seriously debated during the last decade. This was resolved by an examination of the kinetics of grafting methyl methacrylate (MMA) from surfaces of particles with a range of sizes in bulk. The fact that identical MWs were obtained in all cases, indicated that polymerization kinetics are not influenced to any significant degree by grafting from convex surfaces. To broaden the scope of the analysis, n-butyl acrylate (BA) was simultaneously grafted from the interior and exterior of silica nanotubes. Since there are both concave and convex surfaces on nanotubes the objective of the study was to reveal the greatest difference in confinement effects. The results showed similar polymerization kinetics on both surfaces thereby proving that confinement effects are not a serious problem in traditional SI-ATRP systems. However, there are exceptions, for example macromonomers such as oligo(ethylene glycol) methyl ether methactylate (M_n = 475, OEGMA₄₇₅) are not grafted efficiently from silica nanoparticles (SiO₂). This is most likely due to the fact these monomers are long, sterically bulky and contain hydrophilic ethylene glycol groups. Grafting a thin layer of di(ethylene glycol) methyl ether methacrylate (MEO₂MA) from silica particle surfaces before continuing the grafting from reaction with OEOMA475 showed a dramatic improvement in OEOMA475 conversion using SI-ATRP. These products have found utility as low as 0.005 wt% in stabilizing 50:50 xylene in water Pickering Emulsions that have remained stable for more than 1.5 years.

Chapter III discusses three methodologies for the preparing high MW grafted SiO₂ nanoparticles. Typically, high MW is difficult to achieve in radical polymerization methods owing to unavoidable termination reactions. However, the termination rate can be diminished while increasing the propagation rate when the polymerization is carried out at high pressure since termination is under diffusion control but propagation is not. Therefore high pressure was used first to polymerize MMA and butyl methacrylate (BMA) in a grafting from SiO₂ ATRP under 6 kbar pressure, allowing the preparation of polymers with $M_n > 10^6$, even at ambient temperatures. The retention of high chain end functionality was proved by successful chain extension. However, since large-scale high-pressure facilities are generally not commercially available, a high particle dilution approach was developed to achieve high MW. The idea was to reduce the radical concentration in the beginning of the reaction, so inter-particle termination would be dramatically diminished. Reactions were then conducted at a faster rate as monomer conversion and MW increased owing to the reduction in termination reactions expected from the increase in viscosity in the polymerization medium. Although radical concentration was increased during the higher monomer conversion range, the high MW of the tethered polymers limited termination since termination is diffusion controlled. Conducting SI-ATRP of MMA using this high-dilution strategy also achieved $M_{\rm h} > 10^6$. Increasing the temperature provided faster reactions with better control in MWD. This is probably because increasing the temperature can also increase k_p/k_t . Thus, by combing both high particle dilution and hightemperature high MW of a low k_p monomer, e.g. styrene (S), was also achieved by utilizing SI-ATRP regardless of the fact that many untethered polymer chains were generated by thermal self-initiation of S at elevated temperature. These untethered chains were removed by centrifugation, and hybrid particles with PS of $M_n \sim 0.3 \times 10^6$ were obtained. Further optimization of reaction conditions may be needed for faster reaction rates and higher MW production.

Chapters IV and V discuss the use of nanofillers to build novel functional materials, in addition to improving and expanding the fundamental understanding of SI-ATRP. Chapter IV focuses on the preparation of traditional filler-matrix composites. The chapter discusses the introduction of enthalpy interactions in the system to provide better filler dispersibility, and filler loadings up to 70 wt% were achieved without scarifying mechanical or thermal stability. More impressively, this type of material could be conceived as optically transparent, when the NC's refractive index was adjusted to match with the matrix using the Maxwell-Garnett theory. An interesting observation was that the material exhibited a 200% strain when the material was tested at 50 °C. Although it was shown that blending of fillers in a matrix is easier when exploiting enthalpy interactions, a multi-step synthesis and post-polymerization processing is usually required. Therefore, Chapter V presents the synthesis of a new class of materials that do not require blending, are procesesable and are self-assemblable hybrid NCs. This material was facilitated by nanofiller (NF) self-assembly and brush entanglement generating a uniform NF dispersion in a monolayer film with zero aggregation, as observed by transmission electron microscopy. This innovative material is referred

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to as a particle-brush material. The regular self-induced uniform packing of the hybrid NF particles also provide a photonic effect from this material.

Chapters VI, VII, and VIII further expand the scope of both filler-matrix and particle-brush materials. Chapter VI studies the structure-properties relationships of the particle-brush systems and establishes that the polymer conformation and interface strength are the keys to attaining various enhanced properties. Chapter VII discusses the effects of thermal self-initiation of S monomer on the properties of particle-brush materials formed in a grafting from reaction with S at elevated temperatures. Chapter VIII discusses the use of the particle-brush materials to synthesize functional porous nanocarbons.

Abstract

This thesis describes the design and use of nanofillers (NFs) synthesized by surface-initiated atom transfer radical polymerization (SI-ATRP). The history of polymer/inorganic (hybrid) nanocomposites (NCs), the development and fundamentals of SI-ATRP are discussed in the introductory chapter.

Chapters II and III present the major challenges in SI-ATRP, including the surface confinement effect that influences the polymerization kinetics and unavoidable termination reactions that limit the molecular weight of polymers tethered on surfaces. Chapter II discusses the experiments that demonstrate the surface confinement effects which were found to be a minor contributor to controlled chain growth in normal SI-ATRP, with one exception, when one attempts to polymerize sterically bulky and hydrophilic monomers. Chapter III discusses ways to suppress termination reactions that contribute to molecular weight limitations by carrying out the reactions under high-pressure, high-dilution, or/and at high-temperature.

In addition to extend the fundamental understanding and improvements of SI-ATRP, Chapters IV and V discuss the use of NFs to create novel nanostructured functional materials. Chapter IV focuses on the preparation of traditional filler-matrix composites. Mechanically and thermally stable films with silica nanoparticle (SiO₂) filler loadings up to 70 wt% were achieved by introducing enthalpy

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interactions to improve the dispersibility of SiO₂ in a selected matrix. Chapter V presents approaches that allow preparation of a processable self-assembled film of hybrid NCs that do not require blending with a host matrix. This class of material was created by NF self-assembly and interparticle brush entanglement which provided uniform NF dispersion in a monolayer film with zero aggregation, as observed by transmission electron microscopy.

Chapter VI, VII, and VIII further expands the scope of materials designed in Chapter IV and V. Chapter VI specifically studies the structure-properties relationship of the particle-brush composites and the confirmation that controls the polymer conformation and interface strength which are the keys for various enhanced properties. Chapter VII discusses the effects of thermal self-initiation of styrene (S) on the properties of particle-brush materials. Chapter VIII discusses the use of particle-brush hybrid particles to synthesize porous nanocarbons.

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Abbreviations

4VP = 4-vinylpyridine =

- a =length of a repeat unit
- AA = acrylic acid = он

AGET = activator generated by electron transfer

 $AI_2O_3 = alumina$

aq = aqueous

ARGET = activators regenerated by electron transfer



AsAc = ascrobic acid

ATRP = atom transfer radical polymerization



BMA = butyl methacrylate =

bpy = 2,2'-bipyridine =
$$\sqrt{N}$$

CIPBrMP = 3-(chlorodimethylsilyl)propyl 2-bromo-2-methylpropionate

CI Si O Br

=

CPB = concentrated polymer brush

CRP = controlled radical polymerization

Cu = copper

CuBr = copper (I) bromide

 $CuBr_2 = copper$ (II) bromide

CuCl = copper (I) chloride

 $CuCl_2 = copper$ (II) chloride

d = interparticle distance

D = polymer length dispersity (previously termed as polydispersity or M_n / M_w)

DC model = Dauod-Cotton model

DCF = dead chain fraction

 $D_{n,DLS}$ = hydrodynamic diameter measured by DLS

DLS = dynamic light scattering

DMF = dimethylformamide = H

$$C_{9}H_{19}$$

 $C_{9}H_{19}$
 $C_{9}H_{19}$
 $C_{9}H_{19}$
 $C_{9}H_{19}$
 N

DP = degree of polymerization

eATRP = electrochemically mediated ATRP, see ATRP



EC = ethylene carbonate = $\sqrt{}$

- FITC = fluorescein isothiocycnate
- FRET = fluorescence resonance energy transfer
- FRP = conventional free radical polymerization
- GC = gas chromatography
- GPC = gel permeation chromatography see SEC
- HF = hydrofluoric acid

HMTETA - 1,1,4,7,10,10-hexamethyltriethylenetetramine =



hybrid = materials that consisted of both organic and inorganic components

ICAR = initiators for continuous activator regeneration

IPA-ST-L or 50 SiO₂ = SiO₂ ca. 29.6 nm of 30% solution in isopropanol

IPA-ST-ZL or $120SiO_2 = SiO_2 ca. 56.6 nm of 30\%$ solution in isopropanol

- k_{act} = activation rate coefficient
- $K_{\text{ATRP}} = \text{ATRP}$ equilibrium constant ($k_{\text{act}}/k_{\text{deact}}$)
- k_{da} = deactivation rate coefficient
- k_i = initiation rate coefficient
- $k_{\rm p}$ = propagation rate coefficient
- $k_{\rm p}/k_{\rm t}$ = propagation to termination rate coefficient ratio
- $k_{\rm t}$ = termination rate coefficient
- L = ligand
- M = monomer

MA = methyl acrylate =

MALLS = multi-angle laser light scattering

MC = fluorescent merocyanine, see Scheme I-11

Me₆TREN = Tris(2-dimethylaminoethyl)amine =

MI = macroinitiator

MIBK-ST or $8SiO_2 = SiO_2$ ca. 7.7 nm of 30% solution in methyl isobutyl ketone

MMA = methyl methacrylate = $\sqrt{}$

 M_n = number average molecular weight

- MW = molecular weight
- M_w = weight average molecular weight
- MWD = molecular weight distribution

NBDAE = 4-(2-acryloyloxyethylamino)-7-nitro-2,1,3-benzoxadiazole, see Scheme

I-11

NC = nanocomposite

NF = nanofiller

 $N_{\rm G}$ = grafted degree of polymerization of polymer brush

NIPAM = N-isopropylacrylamide =

NMP = nitrox-mediate polymerization

NMR = nuclear magnetic resonance

NT-Br = silica nanotube functionalized with ATRP initiator sites

OEOMA₄₇₅ = oligo(ethylene glycol) methyl ether methactylate with M_n = 475 =

$$H_3C \left[O \right]_n CH_2 CH_2$$

OM-TiO₂ = organized mesoporous titania

PAA = poly(acrylic acid)

particle-brush = polymer-grafted particle

PEO = poly(ethylene oxide)

PIL = poly(ionic liquid)

PMDETA = N, N, N', N'', N''-pentamethyldiethylenetriamine $\overline{}^{\dot{N}}$

POEMA = poly(oxyethylene methacrylate) = $\int_{CH_3}^{H_2C} \int_{CH_3}^{O} \int_{CH_3}^{OH} dt$

polymer brush = surface-tethered polymer

R.T. = room temperature

 R_0 = particle core radius

 $R_{0,\text{TEM}}$ = radius of particle measured by TEM

RAFT = reversible addition-fragmentation chain transfer polymerization

RDRP = reversible deactivation radical polymerization

 $R_{\rm e}$ = polymer chain end-to-end distance

RI = refractive index

RP = radical polymerization

SAN or PSAN = poly(styrene-*r*-acrylonitrile)

SARA = supplemental activator and reducing agent

SDPB = semi-diluted polymer brush

SEC Size exclusion chromatography

SI-ATRP = surface-initiated atom transfer radical polymerization

SiO₂ = silica nanoparticle

SiO₂ = silica nanoparticles

SiO₂-Br = silica nanoparticle functionalized with ATRP initiator sites

SIO2P050 or $500SiO_2 = SiO_2$ ca. 233.2 nm of 30% solution in methyl isobutyl

ketone

SiO₂-PBMA = poly(butyl methacrylate)-grafted silica nanoparticle

SiO₂-PMMA = poly(methyl methacrylate)-grafted silica nanoparticle

SiO₂-polymer = polymer-grafted silica nanoparticle

SiO₂-PS = polystyrene-grafted silica nanoparticle

SiO₂-PSAN = poly(methyl methacrylate)-grafted silica nanoparticle

SIP = surface initiated polymerization

$$Sn(EH)_{2} = tin(II) 2-ethylhexanoate = 2^{2}$$

SP = nonfluorescent spiropyran, see Scheme I-11

ssDSSCs = solid-state dye-sensitized solar cells

t = reaction time

T = temperature

tBA = tert-butyl acrylate =

TEM = transmission electron microscopy

=

TES-HBMP

6-(triethoxysilyl)hexyl 2-bromo-2-methylpropanoate =



 T_g = glass transition temperature

TGA = thermogravimetric analysis

 $TiO_2 = titania$



TPMA = tris(2-pyridylmethyl)amine =



TTIP = titanium (IV) isopropoxide =

WSC = Wigner-Seitz cell

 β -CD = β -cyclodextrin

- K_{p} = plate compressibility
- $\sigma \textit{ or } \rho_{s}$ = grafting density of surface-grafted chains
- v^* = reduced excluded volume parameter
- σ^* = reduced grafting density

List of Schemes

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hydrolysis. Reproduced from reference 90 with permission from [Nature Publishing Group]......41

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represent *d* determined byTEM of particle monolayers shown in panels a–h; blue squares (8SiO₂-PS*N*) and open circles (8SiO₂-PS*N* determined from reference 9) represent $R_{\rm H} - R_0$ determined by DLS in toluene solution. The particle surface-tosurface distance and the brush height are found to scale with the degree of polymerizationas $d \approx N^{0.8}$ and $(R_{\rm H} - R_0) \approx N_G^{0.98}$ (CPB regime) and $d \approx N_G^{0.52}$ and $(R_{\rm H} - R_0) \approx N_G^{0.58}$ (SDPB regime), respectively. The good agreement between the predicted and experimentally observed CPB \rightarrow SDPB

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Chapter I

Surface-Initiated Polymerization as an Enabling Tool for Multifunctional (Nano-)Engineered Hybrid Materials

I.1. Initial development of polymer/inorganic (hybrid) nanocomposites (NCs)

The distinct differences in properties between soft elastic organic polymers and rigid inorganic nanofillers (NFs) has led to an increased level of attention focused on the properties of composite materials resulting from a combination of these two materials.¹ The obtained polymer/inorganic (hybrid) nanocomposites (NCs) offer unique mechanical,² thermal,³ and optoelectrical properties.⁴ While natural hybrid NCs have existed in our body for a long time (e.g. teeth and bone), the earliest attempts to blend polymers and inorganic NFs can be traced back to

^{*} Work in this chapter has been partially published in the following paper: Hui, C. M.; Pietrasik, J.; Schmitt, M.; Mahoney, C.; Choi, J.; Bockstaller, M. R.; Matyjaszewski, K., Surface-Initiated Polymerization as an Enabling Tool for Multifunctional (Nano-)Engineered Hybrid Materials. *Chemistry of Materials* **2014**, *26* (1), 745-762. Copyright © 2014 American Chemical Society.

1700 years ago. These early examples include the Lycurgus cup created in 400 A.D. and Maya Blue invented in 800 A.D., today both are referred as ancient arts but were actually the earliest examples of hybrid NCs.⁵ In the former case, gold and silver NFs were embedded inside a glass matrix so the glass displayed two distinct colors, depending on whether light was transmitting through the composite or not. In the second case, an inorganic mineral clay was added to an organic Indigo dye and utilized for painting, and the color remained fresh, despite passage of time and harsh weather conditions. Some paintings with Maya Blue were even reported as chemical resistant.

Notwithstanding the fact that hybrid NCs were used over a long timeframe, there was no literature reports of hybrid NCs until the middle of 19th century, when Charles Goodyear first toughened vulcanized tire rubber with magnesia.⁶ Afterwards, a few industrial applications of nanocomposites were proposed,⁷ but were not extensively studied until the early 1990s when the development of nylon/clay composite that provided a hybrid material with a significant increase of mechanical strength, thermal properties, and flame retardant properties was reported in Japan, and utilized in the automotive industry.⁸

I.2. Choice of nanofillers (NFs)

In fact, the success of nylon/clay composites was claimed to be due to the selection of NF with an appropriate shape. For instance, the proposed mechanism of flame retardation by the nano-clay composites was that the clay layers survive

and grow throughout the combustion process, yielding a char-barrier that insulates the bulk polymer against heat and prevents the transportation of volatile products generated by the polymer decomposition to the flame interface.⁹ The mechanism for production of the nanocomposite is illustrated in Scheme I-1.



Scheme I-1. First step: quaternary ammonium ions replace the cations on the clay surface. Second step: caprolactam was mixed with the swollen clay then polymerized.

Not only are the shapes of the NFs important but specific properties are also directly inherited from the incorporated inorganic substances.¹⁰ Table I-1 lists some commercial examples of NFs and their applications. For instance, zinc oxide (ZnO) with a wide band-gap, which can absorb UV light, is used in optical protectors, and silver nanoparticles, that can suppress mold growth, is widely used in antimicrobial coatings.

Nanofillers	Property enhancements	Application/utility
Exfoliated clay	Flame resistance, barrier, and mechanical improvement	Automotive and construction materials
CNT Graphene	Electrical conductivity and charge transport	Electronics/optpelectronics
Silver	Antimicrobial	Medical coatings
CdSe, CdTe	Charge transport	Solar cells
ZnO	UV absorption	UV screens and protectors
Silica	Viscosity modification	Paints and adhesives
POSS	Improved stability, flammability resistance	Sensors, LEDs
Iron	Electrical and environmentally friendly catalysts	Electronics and heterogeneous catalysts

Table I-1.Commercially applications of NFs and reasons for utilities.

I.3. Minimizing NF aggregation and ways to disperse NFs

Despite many advantages of incorporating inorganic NFs into polymer matrices, NFs tend to aggregate to minimize surface energy, which results in loss of transparency and mechanical robustness.¹⁰ Therefore, procedures improvement NF dispersion in a selected matrix have received increased attention in the research and industrial communities during the past two decades. One of the most widely used methodologies to suppress NF aggregation is to incorporate additional polymer ligands on the inorganic surface prior to processing the NCs. The polymer ligands can either act as a binder to enhance miscibility between the

NF and the matrix (enthalpy approach), or as a bumper that separates the NFs by steric hindrance (entropy approach).

Three different strategies can be utilized for attachment of polymeric ligands, as shown in Scheme I-2. The earliest approach was physisorption of polymer ligands directly onto the NF surfaces. For instance, the development of block copolymers that were adsorbed onto selected surfaces in selective solvents significantly improved the properties of the product while maintaining the reversibility of physisorption.¹¹ However, the long term properties of products synthesized by polymer ligand physisorption were generally compromised by progressive phase separation of NFs during use, which is due to weak interactions between the NF and matrix.^{1a} The aging problems associated with the physisorption approach were soon overcome by development of the "grafting onto" method.¹² In this innovative method, polymer ligands form covalent bonds with reactive groups on NF surfaces instead of relying on physisorption. The stronger chemical bonds thus facilitated a more stable dispersion of the filer in the matrix. However, grafting onto also suffered from a steric limitation, resulting in low grafting density (σ , the real number of growing chains / substrate surface area) since bulky polymers were concurrently being tethered to the surface, and the amount of tethered polymers was restricted by steric crowding that build up on the surfaces. For this reason, the "grafting from" procedure that gradually grows polymer chains from the surfaces represents a more attractive approach. Since grafting from only involves diffusion of monomers, not steric-bulky polymeric

ligands onto the surfaces, a product with significant higher σ can be easily produced.^{13,14} A high value for σ can enhance the separation of NFs and introduce special mechanical properties. Poly(methyl methacrylate) films grafted from silica wafer (Si-PMMA) using surface-initiated atom transfer radical polymerization (SI-ATRP, more details in section "The development of SI-ATRP") were subjected to the glass transition temperature (T_{g}) and the plate compressibility (κ_{p}) measurements.¹⁵ In the T_g measurement, grafted films with different thicknesses were tested. It was reported that the T_g of the grafted films are at least 8 °C higher than that of the spin-casted films. In addition, T_{g} sharply increased when grafted film thicknesses decreased, suggesting that the increase in T_g is due to the restricted mobility of the tethered chains close to the surface of the solid substrate. $\kappa_{\rm p}$ of Si-PMMA was also tested, and it was observed that $\kappa_{\rm p}$ of the grafted film is ca. 30 - 40% lower than the spin-casted film. The magnitude of the κ_p is probably due to the high σ and to the highly stretched chain architectures synthesized by grafting from method. An additional reason of the increased of use of grafting from technique was the invention of reversible deactivation radical polymerizations (RDRPs) procedures that require mild reaction conditions and provide the capability to polymerize a wide range of vinyl polymers with controlled degree of polymerization of polymer grafts ($N_{\rm G}$) under scalable conditions.



I.4. Surface-initiated radical polymerizations

I.4.1. Surface-initiated conventional/free radical polymerization (SI-FRP)

Conventional free radical polymerization (FRP) has many advantages over the other polymerization techniques, including its tolerance of impurities, its ability to polymerize a wide range of vinyl monomers combined with the ease of copolymerization and tolerance of substituents with a wide range of functionalities, as well as its simple set up and mild reaction temperatures. Hence, FRP has become the leading procedure employed in industrial polymer production. Surface initiated FRP (SI-FRP) was first reported in 1998, started with a monolayer of AIBN-type azo initiator grafted onto a surface.¹⁷ It was found that molecular weight (MW) of the tethered polystyrene (PS) chains using this method steadily increased with increasing conversion of the initiator, while MW of the free polymer remained constant. At that time, this observation was solely attributed to less coupling termination due to diffusion control. However, according to our recent studies, thermal-self initiation of S is probably another reason, as will be discussed in Chapter VII. Alternatively, SI-FRP from silica nanoparticles (SiO₂) with tethered and polymerizable double bonds was also reported.¹⁸ S was then grafted through the double-bond functionalized SiO₂ in an emulsion polymerization and formed an interesting flower-like structure. However, SI-FRP procedures usually resulted in a graft density less than 0.2 chains/nm² in addition to low chain-end functionality, and high MW dispersity (*Đ*) due to low initiator efficiency ($k_i < k_p$) and unavoidable termination processes. For this reason, alternative methods that can provide a targeted DP, well-controlled molecular weight distribution, composition, high chain-end functionality, and higher σ were desired.

SI-nitroxide mediated polymerization (SI-NMP), SI-reversible addition fragmentation transfer polymerization (SI-RAFT), and SI-atom transfer radical polymerization (SI-ATRP), all procedures that can control the initiation/propagation rate and minimize termination reactions were highly attractive alternatives. Since all these 3 methods rely on the similar reversible deactivation of radical to control instantaneous radical concentration, they are also called reversible-deactivation radical polymerizations (RDRPs), and were previously referred as "controlled radical polymerizations" (CRP) due to their controlled quasi-living kinetic features.

I.4.2. Surface-initiated nitroxide-mediated polymerization (SI-NMP)

The mechanism of nitroxide-mediated polymerization (NMP) is based on reversible capping of the active chain-end radical with a stable nitroxide leaving

group therefore the procedure is also called stable free radical polymerization, as shown in Scheme I-3. An example resulting in formation of hybrid NCs via SI-NMP was grafting PS brushes from alkoxyamine initiator modified silicon wafers.¹⁹ However, the use of surface-tethered initiators on a flat surface alone did not provide controlled polymerization kinetics since the concentration of TEMPO in the contacting medium was too low to provide sufficient concentration of free TEMPO persistent radical in the contacting solution to deactivate all radical chain ends. For this reason, structurally similarly untethered initiators were added to the reaction solution, and better control over the polymerization was achieved. Unfortunately, NMP is mainly limited to styrenic monomers, since NMP of other monomers usually provides polymers with low MW and relatively high D.²⁰ For example, β -H elimination of the growing polymer chain occurs simultaneously during chain growth and NMP reversible deactivation in the NMP of acrylic and methacrylic monomers.²¹



Scheme I-3. Illustration of SI-NMP grafting polymerization reaction of styrene from surface.¹⁹

I.4.3. Surface-initiated reversible addition fragmentation transfer polymerization (SI-RAFT)

Reversible addition fragmentation transfer polymerization (RAFT) is also mediated by a capping agent. The capping agent in RAFT polymerizations is a chain transfer agent (CTA). The CTA is used to protect and unprotect radicals by a series of chain transfer reactions, as shown in Scheme I-4. Therefore, SI-RAFT polymerizations are apposite to grow polymer on two different types of functional surfaces, one a surface that can generate radicals and the other a surface with tethered RAFT agents. The former case has an advantage since tethered FRP initiators can be directly converted into a RAFT process by simply adding an appropriate amount of a CTA, such as dithioester, dithiocarbamate, or dithiocarbonate, etc. It was demonstrated that SI-RAFT from azo-initiator modified silica surfaces in the presence of dithiobenzonate enabled the formation of homopolymers and block copolymers with controlled thickness.²² SI-RAFT from a reported,²³ CTA-modified surface was also in this case smethoxycarbonylphenylmethyl dithiobenzoate was tethered to a methyl-abromophenyl acetate modified SiO₂ and was used to grow polymer chains. However, it was claimed that chain transfer reaction efficiency and σ are limited in SI-RAFT procedures owing to the surface steric hindrance. Similar to the situation with NMP the addition of a small amounts of unterthered initiators, in both strategies, were found useful in facilitating better growth of brushes in SI-RAFT. When compared to NMP, RAFT polymerizations are more versatile and tolerate a wider

range of functional groups however, unfortunately, each CTA is limited to a certain class of monomers, and not all the desired CTAs are commercially available.



Scheme I-4. Illustration of SI-RAFT grafting reaction of methyl methacrylate from surface.

I.4.4. Surface-initiated atom transfer radical polymerizations (SI-ATRP)

ATRP is superior to NMP and RAFT for preparation of homopolymers and copolymers from wide range of monomers, and provides a simple procedure to introduce additional functionality onto the well-preserved chain-end functionality and has been successfully employed to prepare different hybrid NCs.²⁴ More importantly, most of the necessary ATRP reagents are currently commercially available compared to agents required for other RDRPs which provides ATRP a bigger potential in industrial production.²⁵ Additionally, activators regenerated by electron transfer (ARGET) and activator generated by electron transfer (AGET) ATRP allow conducting the polymerization in the presence of a small residual trace of oxygen. Therefore, ATRP was selected to be used for the synthesis of NCs in this thesis based on its ability to polymerize a wide range of monomers and functional groups in a range of reaction media.

I.5. The development of SI-ATRP

I.5.1. Development of ATRP

ATRP is among the most efficient and robust RDRP techniques.²⁶ It provides access to previously inaccessible polymeric materials and various hybrids.^{24b, 27} As shown in Scheme I-5, in ATRP alkyl (pseudo)halide initiators (RX) / dormant species (P_{n-}X) react with activators, typically complexes of Cu^I halides with various N-containing ligands, to reversibly form propagating radicals (Pn[•]), and deactivators, complexes of Cu^{II} halides.^{27a, 28} The dormant species in this ATRP equilibrium can be polymer chains able to grow in one or many directions, or polymers attached to functional colloidal particles, surfaces, biomolecules, etc. The upper right part of Scheme I-5 shows a typical dependence of polymerization rate (R_p) and dispersity (M_w/M_h or D) on kinetic parameters and reagent concentrations. R_p depends on the propagation rate constant k_p , and the ratio of the rate constants of activation (k_a) and deactivation (k_{da}) and on the concentrations of involved reagents. D decreases with faster deactivation (catalysts with a higher value of k_{da} and at higher deactivator concentrations). The D decreases with the monomer conversion and is lower for polymerizations targeting higher molecular weight (smaller [Pn-X]0).^{27a}



Scheme I-5. General scheme for ATRP and low-ppm Cu-ATRP.

Originally, ATRP was carried out with a relatively high catalyst concentration to compensate for unavoidable radical termination because every act of termination irreversibly consumed an equivalent amount of the lower oxidation state activator catalyst complex. Therefore, the catalyst concentration was in the range of 0.1 to 1 mol% vs. monomer.²⁹ However, during the last several years, it became possible to reduce the amount of catalysts to a few parts per million (ppm) in the presence of various reducing agents.³⁰ These processes are shown at the bottom part of Scheme I-5. In ARGET ATRP (activators regenerated by electron transfer) reducing agents such as ascorbic acid, sugars, tin(II) octanoate, sulfites, or amines can be employed.³¹ In ICAR ATRP (initiators for continuous activator regeneration), conventional radical initiators are used.^{31b} SARA ATRP (supplemental activators and reducing agents) is based on the dual role of zerovalent metals.³² Electrochemistry that can be run under either potentiostatic or galvanostatic conditions is used in eATRP.³³ Some Cu^{II} complexes can be photoreduced by irradiation at the ligand-metal charge transfer region (usually at $\lambda < 450$ nm).³⁴ In all these systems, the amount of catalyst can be significantly diminished to ppm level. However, an excessive decrease of catalyst concentration beyond a certain value, for lower activity catalysts, may be accompanied by increase of *D* of formed polymers, according the second equation in Scheme I-5. On the other hand, this opens possibility of synthesis of polymers with designed *D* that can have novel morphological features. For example, block copolymers with one segment of narrow and the other of broad MWD, can phase-separate into a bicontinuous morphology of hexagonally perforated lamellae rather than typical cylinders at ca. 1/2 volume ratio.³⁵

If the contribution of radical termination would be very small, in principle, it should be possible to reduce catalyst concentration even without adding reducing agents. Since k_p/k_t values are 30 times larger in polymerization of acrylates than those of methacrylates, there is much less termination and lower amount of Cu catalyst could be used.³⁶ It is also possible to increase k_p/k_t ratios by conducting the polymerizations at higher temperature and at higher pressure.³⁷ Termination but macroscopic gelation can be avoided in polymerizations conducted in confined systems such as miniemulsion.³⁸

One of the advantages of ATRP is a possibility to precisely control polymer architecture, not only in terms of MW and MWD, but also in terms of the shape or topology of polymer chains, exemplified by linear, cyclic, branched (also regular combs or stars), networks and (hyper)branched polymers; chain composition, as in segmented copolymers (blocks and grafts), as well as gradient, periodic and statistical copolymers; chain functionality, represented by mono- or difunctional telechelics, macromonomers, linear polymers with various side groups, multifunctional (hyper)branched polymers or stars prepared from functional monomers or initiators but also capping agents, as well as via various postpolymerization techniques.^{27b, 39}

I.5.2. Fundamentals of SI-ATRP

SI-ATRP the predominant SI-RDRP is method to prepare polymeric/inorganic hybrid materials.^{14, 24b, 40} SI-ATRP utilizes the same mechanism as a conventional ATRP from an untethered initiator, which involves initiation, propagation, activation/deactivation and termination processes. However, there are several differences due to the existence of the functionalized inorganic surface. First, initiators are immobilized onto the surface by coupling techniques prior to polymerization.⁴¹ Second, since the chains grow from the surface the rate of propagation could be limited due to the need for diffusion of monomer to the chain ends, affecting polymerization kinetics.^{24a} Third, the addition of sacrificial initiator⁴² or deactivator^{24a} is required in SI-ATRP from flat surfaces, because of

the slow spontaneous generation of deactivators from the very low concentration of surface-bound initiator. If the deactivator concentration is low, then no reversible deactivation occurs and irreversible radical termination should dominate. On a flat surface, this may result only in on-surface termination⁴³ but, as predicted by Flory's gelation theory, the occurrence of only ca. 0.1% of termination in an inter-particle fashion could produce macroscopic gels in SI-ATRP from nanoparticles (NPs) with thousands tethered chains.³⁸

The selection of an inorganic surface for SI-ATRP depends on the targeted application. SI-ATRP has been applied to various substrates, including silica, germanium, alumina, titanium oxide, iron oxides, gold, guantum dots, as well as a range of organic and biological materials in order to fulfill different needs.^{40a} Inorganic substrates with different surface geometries have been selected to fit different applications. However, different surface geometries may affect SI-ATRP in different ways. As noted above, the concentration of tethered initiator on a flat substrate is usually very low and it does not provide enough cleavable polymer for MW and MWD measurement by size exclusion chromatography (SEC). On the other hand, although convex systems, e.g. functionalized NPs, have much higher initiator/grafting density and can provide enough polymer for SEC, the higher radical concentration can cause macroscopic gelation.³⁸ In concave systems, the growing chains will experience confinement effects which could reduce the level of control over MW and MWD if the reaction conditions are not appropriately selected.44

I.5.2a. Initiation

SI-ATRP has been applied to many different inorganic substrates,^{40a} and some examples are illustrated in Scheme I-6. Among these substrates, silica and metals (oxides) are the most commonly reported surfaces for SI-ATRP, due to their market availability and novel physical properties. The silanol (Si-OH) functionalities on the silica surface can easily react with related reactive groups (e.g. CI-Si-, MeO-Si-, EtO-Si-) which form stable siloxane bonds. In addition, the possibility of forming a network of silsesquioxanes (e.g. Cl₃-Si-, (MeO)₃-Si-, (EtO)₃-Si-) could permit generation of multiple-attachments to the surface, providing better stability, compared to single bond attachment. Multiple-attachments are especially important for weaker bondings, e.g. thiol-gold bonding.⁴⁵ It was reported that monopodal thiol-gold bonding is very unstable, but its tripodal version dramatically improved the stability of the complex formed after immobilization of oligonucleotides. Modification of metal (oxide) surfaces should follow Pearson's hard/soft-acid/base (HSAB) principle.⁴⁶ Thus, hard-hard (ionic character) and softsoft (covalent character) acid-ligand interactions are more stable than the opposite approaches. For example, phosphoric acid, carboxylic acid, catechol, or acyl halides are suitable functional groups to modify an iron surface and form a stable Fe-O bond. Selection of appropriate anchoring groups therefore can selectively graft an initiator or polymer on the desire surface. It was recently reported that catechol-terminated initiator only attached to the alumina side of the alumina-silica halloysite clay nanotubes due to the low binding energy to silica.⁴⁷ This was further

proved by SI-ATRP of MMA from the nanotubes and TEM revealed that PMMA are only grafted from the alumina side.



Scheme I-6. Examples of anchoring groups for surface modification (a) and a strategy to control grafting density via inactive ("dummy") initiators (b).

The properties of the resulting hybrid materials can be finely tuned by controlling the grafting density.^{14, 48} Generally, initiator density is controlled during the synthetic procedures employed for the functionalization of the surface, thereby controlling the final grafting density. Scheme I-6b illustrates a typical procedure employed for tuning grafting density by conducting the surface modification with the mixture of active and inactive ("dummy") tetherable ATRP initiators to control the concentration of initiating sites on the surface.^{48c, 49} Alternatively, ATRP initiators can be partly destroyed by high energy irradiation.⁵⁰

Similar to conventional ATRP initiators used in bulk/solution polymerization, the appropriate ATRP initiating functionality on a tetherable initiator should be selected to assure a rate of activation at least as fast as the rate of propagation. This is a prerequisite to provide high initiation efficiency and narrow MWD. Generally, the activation rate constant increases with initiator substitution from primary to tertiary, and increases with better radical stabilizing groups; $CN > Ph > C(O)OR.^{51}$

I.5.2b. Propagation

As noted above, some unterhered (sacrificial) initiators are often added, when grafting from flat surface systems. The MW and MWD from these unterthered polymer chains can be used to provide approximate values for the MW and MWD of tethered polymer chains and, hence, graft density for a specific polymer layer thickness.¹⁴ However, both higher/lower MW and different^{44, 52} or similar⁵³ MW and MWD of the tethered polymers relative to untethered polymers were reported. Specifically, a term called "confinement effect" was used to describe the complications associated with monomer and catalyst delivery, as well as chain crowding effects.⁵⁴ Scheme I-7 illustrates the decrease of accessible volume (highlighted in pink) and increase in confinement, when the curvature of a substrate changes. Simulations suggested that when confinement increased, either through change of curvature or increase of grafting density, the MW and MWD could be affected.^{24a, 55} The experimental results show that in some cases concurrent growth from the surface and in solution provides very similar polymers but in other cases MW of polymers formed by SI-ATRP are lower than in solution. This could be due to the particular choice of initiators, catalysts and reaction
conditions, such as solvent, targeted MW, temperature, concentration, etc. In the case of convex surfaces (e.g. spherical NPs), confinement effect is less of a concern and tethered chains generally have the same MW and MWD as the untethered chains.¹⁴



*Above illustrated same thickness (red arrow) and equal inter-chain distance.

Scheme I-7. Illustration of confinement effect (accessible volume for grafted chains is highlighted in pink) in SI-ATRP system.

I.5.2c. Exchange reactions

Control over the concentration of the deactivator in a SI-ATRP is crucial to regulate the lifetime of the radical and provide a controlled/living character to the polymerization. The equation in Scheme I-5 quantitatively shows how the control of MWD can be affected by the concentration of deactivator. During the polymerization from convex curved surfaces, there could be enough spontaneously formed deactivator via a radical termination process to assure appropriate rate of exchange. However, during the growth from flat surfaces, the concentration of tethered-initiators is very small and a sufficient amount of the deactivator cannot be generated. One approach to resolve this problem is to add

sacrificial initiator, which can generate deactivator during the polymerization.⁴² Another preferred method, is to add a fraction of the deactivator at the beginning of the reaction.^{24a} Results of simulations of these two methods in SI-ATRP show that the addition of deactivator at the beginning of polymerization provides instantaneous control over the polymerization that is retained during the entire polymerization. It provides more uniform growth, higher grafting density and thicker films.^{43b} When sacrificial initiators are used, deactivators accumulate during the polymerization but their concentrations are low at the beginning of the reaction, resulting in inferior control. The decay of initiator concentration by termination reactions decreased the grafting density, and the excessive consumption of monomer by sacrificial initiators decreased the thickness growth rate. Thus, the initially added deactivator provides a better-controlled process and thicker films.

I.5.2d. Termination

Termination in SI-ATRP decreases the chain end functionality on all kinds of surfaces and may produce macroscopic gelation during growth from NPs. The termination mechanism during grafting from flat surface is complex.^{43b} A typical surface-initiated polymerization system is illustrated in Scheme I-8, in which the hypothetical grafting density is ca. 1 chain/nm² and radical concentration is 10⁻⁶ chains/nm². These values correspond to ca. 1 nm and 1000 nm inter-chain and inter-radical distance, respectively. Hence, direct bimolecular chain termination between radicals separated by 1000 nm is impossible and termination can occur only when an activator activates a dormant chain adjacent to an existing radical.

Then, the two radicals should terminate instantaneously, via a so called "migration effect".^{43b} Therefore, it has been proposed that the termination rate coefficient should be proportional to the catalyst concentration, meaning that a high catalyst concentration may cause more termination.^{43b}



Scheme I-8. Schematic illustration of the population of dormant (blue dots) and radical species (red dots) in a typical SI-ATRP system. Bimolecular termination happens only when a dormant chain end close to a radical is activated.

Since nanoparticle (NP) (convex) systems have a very high surface area and a high number of initiating sites per particle, the consequence of inter-particle termination reactions during grafting from NP could be the formation of a macroscopic gel. A NP with $R_0 = 10$ nm has a surface area ca. 1200 nm² and over 1000 initiation sites. Thus, according to Flory's gelation theory,³⁸ the macroscopic gel point occurs when only 2/1000 = 0.2% of the chains terminate in an interparticle fashion. The concentration of terminated chains can be diminished when the reaction is conducted under conditions that reduce the concentration of radicals, e.g. the polymerization is conducted at a slower rate, up to a limited monomer conversion or to a reduced targeted degree of polymerization.^{36, 56} However, this is still challenging for monomers with low k_p/k_t ratio (e.g. styrene or MMA).⁵⁷ High dilution and low monomer conversion may not be desired. Recent advances in preparation of hybrid particles by using SI-ATRP in mini-emulsion or under high pressure can overcome this problem. Compartmentalization of the particles effectively entraps the multifunctional species, such as stars and NPs, in each miniemulsion droplet and they are not able to react between droplets and percolate to form a macroscopic gel. Inter-particle termination within a droplet can lead to the formation of small amounts of linked dimers and trimers.³⁸ When ATRP is carried out under high-pressure, the propagation rate constants increase and the termination rate constants decrease, resulting in a relatively fast polymerization with retained control over polymer architecture without sacrificing MW or conversion.⁵⁸ In such a way, at 6 kbar pressure, hybrid particles with PMMA or PBMA grafts with $M_0 > 10^6$ were prepared even at room temperature in a relatively short time. The reaction process is illustrated in Scheme I-9.



Scheme I-9. Schematic illustration of a) the procedure of high pressure AGET SI-ATRP and b) the SEC traces of the chain extension of PMMA (M_n = 1,610,000) with methacrylate (MA) block copolymer (M_n = 2,400,000).⁵⁸ (reprinted with permission from reference, Copyright Macromolecular Rapid Communications, 2011.)

Some additional side reactions can also affect MW and MWD in hybrid systems. They may include not only termination but also transfer or self-initiation. The effect of thermal-self initiation (TSI) of styrene (S) in SI-ATRP from silica NPs was recently reported.⁵⁹ During SI-ATRP of S from silica NPs, the TSI of S generated additional untethered polymer chains in solution. These untethered chains, analyzed by SEC, had lower MW and broader MWD than chains attached to SiO₂, because they were continuously generated by TSI. The selection of a more active Cu catalyst (Cu/PMDETA vs Cu/dNbpy) and a lower polymerization temperature (70 °C vs 90 °C) resulted in a reduction of the fraction of unattached PS generated by TSI from 17.2% to 4.2%.

I.5.2e. Control parameters

Several critical aspects of polymeric/inorganic hybrid materials can be controlled by the appropriate selection of inorganic substrates. Major tools of macromolecular engineering such as MW, MWD, topology, functionality, and composition, are shown in Scheme I-10. They also include various copolymers as well as brushes with bimodal distribution of chains, binary (miktoarm) brushes that can be separated to form Janus particles and brushes with a thin crosslinked layer next to the surface of the NP.

The addition of a reducing agent allows the reaction to be started from oxidatively stable Cu^{II} species while high pressure significantly increased the k_p/k_t ratio which facilitated higher MW and allowed the production of poly(methyl methacrylate) (PMMA) with MW > 10⁶ and PMA with MW > 1.5 10⁶. The samples of PMMA⁶⁰ and PS⁶¹ prepared under 6 kbar pressure from untethered initiator produced polymers with MW ca. 10⁶ in a few hours at room temperature. The high-pressure SI-ATRP applied to SiO₂ systems also yielded well-defined brushes with very high MW.⁵⁸



The MWD and *Đ* of grafted chains can be fine-tuned by varying [Cu^{II}LnX], according to the equation in Scheme I-5. This is very easily achieved in ARGET, ICAR or eATRP processes. However, sometimes broad MWD, or even bimodal distribution may be desired. NPs with long polymer chains can be dispersed better even in high MW matrices and could enhance mechanical properties by entanglement, while those with short chains can screen the particles and prevent their aggregation.⁶² Such systems were recently prepared by SI-RAFT technique.⁶³

I.5.2f. Controlling polymer architectures

ATRP is a versatile method that allows polymerization of a wide range of monomers with controlled polymer composition and architecture.^{27b} Thus, SI-ATRP has been applied to grow block,^{24a, 57} statistical,⁶⁴ and gradient⁶⁵ copolymers from various inorganic substrates. In addition to predetermined control over chemical composition, polymers with different topologies were also prepared by SI-ATRP. They include (hyper)branched and cross-linked brush grafted from/onto surfaces. Hyperbranched polymer hybrids were prepared by grafting a selfcondensing AB* inimer, which had both polymerizable acrylic group and an initiating group, from silica particles via ATRP.⁶⁶ This hyperbranched hybrids has a 3D globular structure which has an increased number of chain end functionalities formed during the synthesis. A miktoarm hybrid system is composed of two types of polymer chains and can be used to create surfaces responding to various solvents.⁶⁷ Miktoarm systems have been prepared by grafting onto⁶⁸ and grafting from.⁶⁹ These methods provided limited grafting density. Higher density can be reached using asymmetric Y-shaped difunctional initiators and sequential grafting two brushes by different RDRP procedures, e.g. via SI-ATRP and SI-NMP.⁷⁰ Another approach was the use of a two-step reverse ATRP method, in which the polymerization was initiated from azo-initiators attached to the surface, forming brushes with different composition.⁷¹ The chemical composition and grafting density of the polymer brushes was controlled through temperature and time of decomposition of the tethered initiators during the synthesis of the first generation of grafted chains. A crosslinked brush architecture was prepared via homo- or

copolymerization of a difunctional crosslinker with or without an additional monomer. A one-pot SI-ATRP grafting of BA and a dimethacrylate-based crosslinker from gold NPs was reported.⁷² The higher reactivity of the dimethacrylate crosslinker enabled the formation of a thin crosslinked polymer shell around the surface of the Au-NP, before the growth of linear polymer chains from the *in situ* formed shell. This crosslinked polymer shell served as a robust protective layer and prevented detachment of polymer chains as seen with chains weakly anchored to Au solely via thiol groups. It provided the hybrid Au-NPs with excellent thermal stability at elevated temperatures (i.e., over 24 h at 110 °C) with preserved plasmon resonance effect.

Due to the ability to control and precisely tune the chemical nature and architecture of the tethered brushes by SI-ATRP the formed polymeric/inorganic hybrids may exhibit new properties. They can serve as a platform for the synthesis of a range of other microstructured functional materials. For example, the surface hydrophilicity can be tuned by pretreatment with different solutions in the case a gradient copolymer grafted system.⁶⁵ The polymer brush reorganization was confirmed by NMR in binary brush systems prepared using the Y-shape initiators.⁷⁰ The miktoarm brushes could self-segregate and form Janus particles.⁷³ The preparation of stimuli-responsive Janus particles by sequential SI-ATRP and grafting onto was reported.⁷⁴ In the first step, amino-groups were introduced onto the surface of silica NPs. The coated particles were then assembled around wax colloidosomes and the exposed faces of the NPs were selectively modified by

deposition of ATRP initiators. A first polymer was grafted from the surface by SI-ATRP, and a second polymer was grafted onto the remaining amino-groups.

I.6. From nano-engineering hybrid particles by ATRP and other RDRP methods to applications

Excellent control over the architecture, composition, and distribution of polymer grafts, facilitated by SI-ATRP (and other SI-RDRP techniques), provide new opportunities to tailor the interaction parameters, assembly, and properties of particle-brush based materials. In addition to providing insights into the physics of nanostructured hybrid materials the studies also provide an opportunity to evaluate the properties of the novel functional materials in specific applications.

I.6.1. Anisotropic self-assembly of NFs

SI-ATRP and other SI-RDRPs can prepare well-defined hybrid NFs with high σ that have the potential to control dispersion of NFs in a range of matrix materials. This was first demonstrated by controlling the polymer loading on the spherical NPs.⁷⁵ PS was grafted from the spherical NPs by SI-RAFT, and the polymer loading was controlled by both M_h and σ . Interestingly, the NPs did not instantly uniformly disperse into a matrix when polymer loading increased, but formed four distinct morphologies of NP arrays. First, NPs were strongly aggregated when the polymer loading is low, since NPs tried to minimize the interaction with the matrix. Then, when the polymer loading increased slightly, the

NPs formed sheet-like and string-like structures. This is because the polymer chains started to redistribute and tried to separate the particle aggregates, but this additional entropy still was not enough to overcome the demixing of the NP/matrix interfaces. For this reason, a real dispersed state in entropy driven system required very high polymer loading and is actually a disadvantage when high inorganic loading material is desired. Introducing enthalpic interactions provided a remarkable opportunity to overcome this limitation.⁷⁶ This was exemplified by mixing PS-b-poly(ethylene) (PS-b-PEP) with the aliphatic coated smaller gold NPs and larger silica NPs, in which, both NPs preferred to stay in the PEP phase.77 Therefore, NP dispersions were organized by the controlled phase separation (enthalpy driven) morphology. In addition, the contribution of entropy interactions was not negligible, and the smaller gold NPs were pushed into the intermaterial dividing surfaces while the segregated larger silica NPs resided in the middle of the PEP phase. This is because the decrease in conformational entropy of the respective polymer subchains upon particle sequestration is dominant for larger NPs, whereas the decrease in entropy is outweighed by the NPs' translational entropy. The recognition that the combination of both enthalpy and entropy contribute to particle dispersion in the final hybrid materials therefore provides a brand new approach to engineering high-performance composite materials one in which the distributed particles are located in regions that allow efficient capitalization of their characteristic properties. Other enthalpic interactions such as hydrogen bonding will be further discussed in Chapter IV.

Furthermore, NPs' distribution can also be regulated by external stimulus. The organization of magnetite NPs by magnetic fields is one of the simplest and widely applied examples, but the induced structure usually breaks down when the external field is removed. This led to the recent development of an innovative locking mechanism, one that can fix the distribution of the NPs'.⁷⁸ Poly(ethyleneoxide)-b-poly(2-vinylpyridine) (PEO-b-P2VP) was grafted onto magnetite NPs, and NPs were first aligned via the external magnetic field. Afterwards, the pH was adjusted to lock and unlock the distributed NPs. At low pH, the P2VP segment was protonated so both PEO and P2VP blocks are soluble in water and no locking of the distribution of the NP was observed. However, once the pH was increased beyond 4, NPs were locked together since P2VP became hydrophobic at pH > 4, and NPs tended to aggregate at the hydrophobic sites. The balance between this additional hydrophobic "like dissolves like" interactions and the strength of the magnetic field allows the creation of NCs with well-defined size, shape, and morphology.

I.6.2. NFs in industrial coatings

Uniform dispersion of NFs is of great importance in industrial coatings. The simplest groups of NFs employed in industrial coatings are pigments and pigment molecules but aggregation in a polymeric matrix reduces their efficiency. Grafting polymers from/onto pigment surfaces can prevent agglomeration that is induced by osmotic and entropic effects.⁷⁹ To overcome this limitation two sizes of pigment molecules (specific surface areas of 94 and 15 m²/g respectively) were decorated

by poly(butyl acrylate)-b-poly(2-dimethylaminoethyl methacrylate) (PDMAEMA) and both hybrid pigment particles were much better dispersed in a matrix than pigments without polymer decoration. In addition, it was found that the smaller pigment particle required longer PBA stabilizer block for better dispersion while DP was not as critical in the case of larger pigment particle. This is likely because there is a greater driving force for the smaller pigment particles to aggregate due to their higher surface area. Similarly, dyes can be attached to a non-colored inorganic core. This was done by grafting both tetherable ATRP initiators and fluorescein isothiocyanate (FITC) onto SiO₂ using a silane linking units. Afterwards, poly(2-(diethylamino)ethyl methacrylate) (PDEAEMA) was grown from the ATRP initiators, and the PDMAEMA grafted fluorescein NPs were used to write on a glass substrate. The NPs adsorbed onto the substrate strongly, even when washed with neutral and basic solutions, since PDEAEMA segments are mostly deprotonated under these conditions and are hydrophobic in character. In order to remove the writing, the PDEAEMA was protonated and stretched by washing with an acid solution so NPs became charged and hydrophilic, and were removed from the surface. Alternatively, functional small pigment particles can be copolymerized into the polymer chains. For instance, thermoresponsive poly(N-isopropylacrylamide) (PNIPAM) brushes with inner and outer layers selectively labeled with fluorescence resonance energy transfer (FRET) donors and acceptors were synthesized via SI-ATRP, Scheme I-11.⁸⁰ Uniform dispersion of FRET dye show 36% transfer efficiency at R.T., and up to 67% when temperature was increased to 37 °C since PNIPAM can collapse at high temperature and reduce the distance

between FRET donors and acceptors. Therefore, this type of hybrid NPs can potentially serve as a fluorescence thermometer. In another example, the FRET acceptor was incorporated into polymer brushes and was reversibly interchangeable from the nonfluorescent spiropyran (SP) form to the fluorescent merocyanine (MC) structure upon irradiation with UV or visible light, which changed the color emission. Indeed special NCs that can show four different colors upon temperature and light stimuli were synthesized.



Scheme I-11. a) Illustration of the synthesis of fluorescence resonance energy transfer (FRET) donor/acceptor loaded polymer-grafted particles (particle brushes). The dye has 2 parts, the donor 4-(2acryloyloxyethylamino)-7-nitro-2,1,3-benzoxadiazole (NBDAE) and acceptor nonfluorescent spiropyran (SP). They were both loaded onto the particlebrushes via copolymerization with = N-isopropylacrylamide (NIPAM) using SI-ATRP. When PNIPAM was heated, PNIPAMA was collapsed and acceptordonor distance decreased so color became more intensive. When SP was irradiated with UV or visible light, it will reversibly transfer from SP to the fluorescent merocyanine (MC) structure. Therefore, the synthesized hybrid materials can produce 4 different color based on the combination of temperature and photo stimuli.

Creation of a colored coating does not necessarily require dye molecules. NPs with sizes in sub-nanometer range can change the motion of photons and create beautiful color effects. A liquid suspension of a high concentration SiO₂ with a shell of well-defined PMMA synthesized via SI-ATRP was found to progress from a disordered fluid to a colloidal crystal system with a face-centered cubic structure, Scheme I-12.⁸¹ This created long-range periodic optical nanostructures with two identified dielectric areas that affected the electron motion by defining allowed and forbidden band gaps. The proposed "colloidal crystals" system has the potential to tune the band gap by changing MW of the tethered PMMA, the size of SiO₂, and should also be controlled by selecting other types of polymers and NPs.



Scheme I-12. Left: photographs of PMMA-grafted SiO₂ (SiO₂-PMMA) suspensions in the mixed solvent (1,2-dichloroethane/chlorobenzene/odichlorobenzene in 53/20/27 volume ratio) illuminated from behind by white light. The showed pictures were taken 7 days after sample preparation. M_w of the PMMA grafts is 158 000 and the diameter of the SiO₂ core is 130 nm. Samples with various SiO₂-PMMA volume fractions increases from 0.0785 (leftmost) to 0.111 (rightmost). Right: confocal laser scanning microscopic images of SiO₂-PMMA crystals. (Reproduced from reference 81 with permission from [American Chemical Society].)

The influence of incorporated nanoparticles on a coating is not limited to coloring, other types of coatings include anti-contaminate and anti-icing surfaces were also recently synthesized by SI-ATRP.⁸² Both systems attempted to mimic the superhydrophobicity of lotus leaves by creating a rough surface using SiO₂ based hybrid NCs. In order to make the surface more hydrophobic or amiphiphobic, fluoro vinyl monomers were grafted from the SiO₂NPs. In one case, tri(isopropyloxy)silylpropyl methacrylate was copolymerized with fluroro monomers and was further hydrolyzed to cross-link and maintain the rough structure. This approach provided a superamphiphobic coating for both glass and cotton fabric

surfaces. In another example, with a different fluoro monomer but without crosslinker, a maximum contact angle of water on a treated glass surface was 170.3°, Scheme I-13. In the presence of such a high value for the contact angle condensed water on the treated surface displayed 50 times slower crystallization rate than that on an untreated glass when both of the samples were held at -18 °C. This observation was attributed to the minimized contact area on the superhydrophobic surface retarding the heterogeneous nucleation of freezing.



Scheme I-13. Illustration of anti-icing properties of polymer-grafted SiO₂ (particle-brushes) when coated on surface swith various monomers. a & b show the contact angle measurements of these samples. Both rough surface created by SiO₂ and the copolymerize segment of fluoro monomer facilitated a superhydrophilic coating on a glass surface with contact angle 170.3 °. Therefore, 50 times slower freezing rate compare with an untreated surface was achieved at -18 °C. SEM images of the surface with 2 magnitudes was shown in c. (Reproduced from reference 82b with permission from [Royal Society of Chemistry].)

I.6.3. NFs as templates for novel materials

Hybrid NCs can serve also as templates for the preparation of novel nanostructured carbons, metals, and metal hybrids. The inorganic materials are employed as structural templates and the polymeric materials serve as the nanocarbon precursor in the synthesis of porous nanocarbons. Thus, polyacrylonitrile (PAN) was grafted from convex silica NPs⁸³ and also from mesoporous silica materials.⁸⁴ The substrates were used as the sacrificial phase allowing, after graphitization, the preparation of well-defined nano-structured carbons. An alternative approach employed poly(ethylene oxide) (PEO)/PAN diblock copolymers that were used directly as supramolecular templates for preparation of mesoporous silica and as precursors for mesoporous carbons.⁸⁵ Poly(styrene-*r*-acrylonitrile) (PSAN) copolymers⁸⁶ and carbonyl cross-linked polystyrene (PS)⁸⁶ can also be used as carbon precursors. The thermally decomposable S units in PSAN generated additional micropores, and the carbonyl cross-linked PS was successfully converted to carbon. The nanostructured carbons with N-preserved sites can be used for membranes suitable for gas adsorption, filtration, and separation or as electronic materials.

Hybrid NCs can also be used as templates for nanostructured metals, in which, the inorganic cores are still employed as structural templates, while the polymer shell is used to shelter metal ions before metal fabrication. This is exemplified by the synthesis of mesoporous titania (TiO₂) in a process that is comparable to the synthesis of mesoporous carbons, Scheme I-14.⁸⁷ For example,

alumina NPs with hydrophilic poly(oxyethylene) methacrylate (POEMA) grafts were first synthesized by SI-ATRP, then self-assembled forming highly-organized packing of the particles. Additionally, hydrophilic titanium(IV) isopropoxide was selectively combined with POEMA brushes using a sol-gel process. Afterwards, the organic precursor was removed by calcination and the alumina inorganic core was removed by sodium hydroxide solution resulting in an organized mesoporous TiO₂ (OM-TiO₂) structure based on the initial hybrid template. A high energy conversion efficiency of 7.3% at 100 mW cm⁻² was reported by fabricating the OM-TiO₂ into the solid-state dye-sensitized solar cells (ssDSSCs) with loaded polymerized ionic liquid (PIL). This is one of the highest recorded values for any ssDSSCs. The exceptional cell performance was due to the well-organized structure, resulting in improved dye loading, excellent pore filling by the electrolyte, enhanced light harvesting, and reduced charge recombination. Likewise, it was found that PS core could also serve as the structural template allowing the synthesis of hollow TiO₂ particles with controlled void size and shell thickness.⁸⁸.



Scheme I-14. Illustration of synthesizing organized mesoporous titania (OM-TiO₂). Poly(oxyethylene) methacrylate (POEMA) was first grafted from alumina (Al₂O₃) particles via SI-ATRP. Hydrophilic titanium (IV) isopropoxide (TTIP) was then loaded on to the hydrophilic POEMA through hydrogen bonding interactions. Afterwards, the organic precursor was removed by calcination and the Al₂O₃ inorganic core was removed by sodium hydroxide solution to form the targeted material. Reproduced from reference 87 with permission from [John Wiley and Sons].

However, the removal of organic components is not a requirement for utility in selected applications and nanostructured NCs with functional polymer brushes can be synthesized. For instance, TiO₂ NPs that generate a hydrophobic core with a biocompatible polymer shell were synthesized.⁸⁹ First, a PEO-*b*-PDMAEMA-*b*-PS triblock copolymer was synthesized using ATRP and self-assembled to form a three-layer core-shell NP. The aromatic interacting PS blocks formed the core layer, while hydrophilic PEO and PDMAEMA blocks formed the corona and shell layers, respectively. Next, hydrophobic precursors of TiO₂ were added and enriched the two inner layers. Finally, the precursor was hydrolyzed to TiO₂ through self-catalysis in the PDMAEMA layer. The transmittance of 0.01 mg/mL hybrid NCs at 245 nm is 69.8% lower than 0.03 mg/mL commercially available P25 TiO₂. Moreover, since it was not necessary to remove the PDMAEMA and PEO blocks, the PDMAEMA helped to block electron emission from TiO₂ and the PEO outermost layer increased biocompatibility of the hybrid particle, thus, the formed NCs have potential in UV-screening cosmetic products.

Last but not least, a similar method was recently applied to the synthesis of nearly monodisperse sub-nanometer inorganic NPs and NCs.⁹⁰ Normally, the syntheses of inorganic monodisperse NPs is difficult, since there are many variables including the fabrication temperature, stirring rate, and the amount of reactants and surfactants that are added to the reaction. Therefore, converting an already monodisperse star-like copolymer to an inorganic NPs is a smart alternative, Scheme I-15.90 First, star-like copolymers were synthesized by functionalizing β-cyclodextrin (CD) with ATRP initiators. Block-copolymers PS-b-PtBA-b-PS, including PtBA-b-PS, P4VP-b-PtBA-b-PS and were subsequently synthesized using SI-ATRP, and PtBA segments were later hydrolyzed to PAA. Here tBA denotes tert-butyl acrylate and 4VP denotes 4vinylpyridine, respectively. Inorganic precursors were then selectively added to P4VP and PAA, and transformed into metals using either the sol-gel method or calcination. Depending on the location of the PtBA block in the block copolymer, highly monodisperse metals NPs with various morphologies including solid, hollow,

and core-shell were synthesized. This competitive alternative to graft polymers from metal cores exhibits a more dispersed particle size.



Scheme I-15. Illustration of synthesizing monodisperse star-like copolymer from ATRP initiator functionalized β -cyclodextrin (21Br- β -CD initiator), and subsequent conversion to metal oxide nanoparticles via SI-ATRP, loading of precursors, and hydrolysis. Reproduced from reference 90 with permission from [Nature Publishing Group].

I.7. Thesis goal

The main objective of this thesis is to exploit the excellent control over the architecture, composition, and distribution of polymer grafts, facilitated by SI-ATRP (and other SI-RDRP techniques), and explore the opportunities to tailor the interaction, assembly, and properties of polymer-grafted particle (particle-brush) based materials. This capability for precise design of hybrid materials also gives rise to intriguing opportunities to provide novel scientific insights into the physics

of nanostructured hybrid materials in addition to development of novel functional materials that can be developed for specific applications.

Therefore, one of the main objectives of this thesis focuses on gaining a fundamental understanding of the SI-ATRP mechanism (Chapter II) and development of improved synthetic methodologies, including establishment of novel strategies for fast and clean polymerizations (Chapter III). For instance, conducting the SI-ATRP of MMA under high pressure, or high particle dilution, diminished chain termination reactions resulted in high molecular weight (MW) polymer, leading to the ability to form chains tethered to surfaces with MW > 10⁶. In addition, high temperature SI-ATRP facilitated a dramatic decrease in k_l/k_p^2 , which provides much faster reactions with less termination and better control providing another route to high MW polymers. This strategy is even applicable to S that is known to continuously generating new chains during SI-ATRP. Low *D* SiO₂-PS was observed after the extraction from untethered thermal self-initiated polymers from the final reaction product.

The second goal of the thesis is to further expand the range of applications for SI-ATRP products by synthesis of functional polymer/inorganic (hybrid) NCs with targeted properties. In particular, the synthesis of polymer grafted inorganic particles (also termed as particle-brushes) suitable for use as fillers in selected matrices with additional enthalpy interaction to aid filler dispersion (bi-component system, Chapter IV) and without matrix (1-component system, Chapter V) are

discussed. The optical, mechanical, and thermomechanical of these functional NCs and their potential applications will be discussed along the dissertation (Chapter VI – VIII).

I.8. References

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Chapter II

The Fundamental of Particle-brush Synthesis – Congestion Effect on Particles in SI-ATRP

Preface As reviewed in the prior chapter, there are many applications that incorporate nanofillers (NFs) into polymer based commercial products and a number of review articles that detailed the applications of inorganic/organic nanocomposites (NC)s. For example, the addition of sheet alumosilicates (such as montmorillonite) or nanotubes improve the mechanical performance of polymeric hosts (e.g., for automotive parts) and the addition of silica particles and colloids have been used to tailor the thermal expansion of polymeric substrates, the modulation of dielectric and transport properties for the design of optical materials, supercapacitors, or protective coatings. Even for the conceptually most "simple" particle-brush systems, i.e., spherical particles uniformly grafted with amorphous nonpolar polymers, the complex superposition of interactions and time/length-

^{*} Work in this chapter has been partially published in the following papers: Choi, J.; Hui, C. M.; Schmitt, M.; Pietrasik, J.; Margel, S.; Matyjazsewski, K.; Bockstaller, M. R., Effect of Polymer-Graft Modification on the Order Formation in Particle Assembly Structures. *Langmuir* **2013**, *29* (21), 6452-6459. Hui, C. M.; Pietrasik, J.; Schmitt, M.; Mahoney, C.; Choi, J.; Bockstaller, M. R.; Matyjaszewski, K., Surface-Initiated Polymerization as an Enabling Tool for Multifunctional (Nano-)Engineered Hybrid Materials. *Chemistry of Materials* **2014**, *26* (1), 745-762. Other works will be submitted to *Macromolecules*. Copyright © 2013 – 2014 American Chemical Society.

scales related to particle core and tethered chains could provide a rich and largely unexplored parameter space for the design of novel functional materials. Surfaceinitiated atom transfer radical polymerization (SI-ATRP) is the currently most used RDRP method in the synthesis of particle-brushes in literature. It presents intriguing opportunities for the development of innovative hybrid materials due to its applicability on substrates with unique and diverse topologies, and its versatility in the polymer engineering of different MW, composition, and architectures. However, the effects and challenges associated with introducing particles in SI-ATRP are still unclear and debated. Therefore, the first question that this chapter will answer is whether the same initiation and propagation kinetics that is observed in bulk ATRP copolymerization apply to SI-ATRP of various monomers on diverse surfaces with numerous surface curvatures. Another question that this chapter will answer is how surface-tethered polymer brush conformations are affected by surface curvature and polymer degree of polymerization. Both questions are important in the field since the former could affect the control of MW and MWD, while the latter could affect the polymer interaction with the surrounding media, which could dramatically change the properties of the desired nanocomposites. Hence, the effects and challenges associated with introducing particles in SI-ATRP by studying the congestion effect of particle initiators will be discussed in this chapter. First, the effects of surface congestion on initiation and propagation of various monomers on various surfaces (6 types of monomers, nanoparticles with 2 different sizes and nanotubes) polymerized by SI-ATRP are evaluated. It was demonstrated that the congestion effect limits the possible number of growing

chains, however both tethered polymers and untethered polymers generally share the same identities except when monomers are bulky and/or hydrophilic. This chapter also investigates the applicability of the Daoud-Cotton (DC) model to particle-brushes in solid state in order to predict the tethered polymer architecture that was expected to affect composites' properties (such as glass transition temperature and fracture toughness). The existence of both CPB and SDPB regimes in hybrid particle systems was confirmed by the electron microscopy of a library of particle-brush samples, and these results correlated quite well with the DC model. Therefore, the DC model will be implemented throughout the remaining portion of the dissertation to predict the conformation of tethered polymer brushed.

II.1. Introduction

Based on the literature articles published each year, ATRP is one of the most robust and utilized CRP methods.¹ ATRP was discovered in 1995 in our laboratories and has been applied commercially to produce a variety of specialty polymers since 2004. ATRP can polymerize a wide range of monomers, and provide well-defined polymeric materials with precisely controlled topology, composition, and functionality.² In addition, surface-initiated atom transfer radical polymerization (SI-ATRP) has become an indispensable tool for engineering the structure and properties of polymer/inorganic and polymer/organic interfaces.³ As has been previously discussed, one of the most studied systems is polymer grafting-from particle system. In this typical SI-ATRP system on particles,

tetherable ATRP initiators were first introduced at a specific initiator density onto the particles. From the functionalized particles, the polymers can directly grow from the surface of particles and produce high polymer grafting density with controlled MW and MWD.⁴ However, the effects of replacing small organic molecular initiators with nanometer sized multi-functional particle initiators on ATRP kinetics are still unclear and debated.

Nanoparticles have surface areas that encompasses from a couple hundreds to thousands m²/g, so it is expected that these newly introduced interfaces in ATRP could affect polymerization kinetics. In particular, since ATRP initiators were attached to the particle surfaces, the diffusions of catalysts (both low oxidation state activators and high oxidation state deactivators) and monomers to the initiator sites and chain ends could be limited by the existence of the particle surface. As mentioned in Chapter I, these effects are concluded with a term congestion effect (also termed as confinement effect). Previous reports show that the congestion effect can be affected by grafting density, grafted chain MW, solvent quality, and substrate surface curvature.⁵ That being said there are many possible limitation factors, the rate limiting steps and kinetics on surface polymerizations. Therefore, they may be different from those in bulk/solution polymerizations, resulting in different MWD between tethered and untethered polymer. Indeed, simulations have suggested that when the congestion increased, either through change of curvature or increase of grafting density, the MW and MWD could be affected.⁶

Understanding the congestion effect of SI-ATRP is important, since the difference in polymer composition, MW, and MWD can dramatically affect the structural and physicochemical properties of the formed NCs. Readers are referred to Chapters V and VII for more details about this matter. Comparing polymerization kinetics on surfaces versus contact solution is a direct method. This has been done by adding some untethered (sacrificial) initiators when grafting polymers from surfaces.⁷ The MW and MWD from these untethered polymer chains can then be used to compare with those of tethered polymer chains. Previous experimental results show that in some cases concurrent growth from the surface and in solution provides very similar polymers⁸ but in other cases MW of polymers formed by SI-ATRP are lower than in solution.^{5, 9} This could be due to the particular choice of monomers, filler nature, substrate surface curvatures, and other factors, such as tetherable initiators, catalysts, and reaction conditions. In the current study, the focus is on effect of monomer size and surface curvature. Therefore, in the first part of this chapter, ATRP of different monomers (including bulky and hydrophilic oligo(ethylene glycol) methyl ether methactylate, OEOMA) from various surfaces (including silica nanotubes that carry both concave and convex surfaces) and in contact solution will be presented. Their real number of growing chains (initiator density **x** initiation efficiencies) and propagation behaviors using SI-ATRP will be compared.

The congestion effect can also affect the conformation of surface-tethered polymer in which excluded volume interactions force tethered polymers to a more

stretched architecture. Previous research shows these conformations are intimately related to the materials properties.¹⁰ The conformation of surface-tethered polymers was first described by de Gennes and Alexander. These polymers were named as "polymer brushes" since the tethered polymers form a more extended conformation on a surface than the untethered free polymers in the contacting solution.¹¹ Polymer brushes, with a controlled molecular conformation have important attributes in the control of wetting, corrosion, and tribological characteristics of materials.¹¹⁻¹² In a typical flat surface system, the conformations of brushes are affected by the grafting density - the higher the graft density the greater the crowding between surrounding polymers. Thus, the polymer chains adopt a more stretched conformation due to higher steric hindrance. This behavior can be expressed by the relationship between the average chain distance (*D*) and the chain radius of gyration (*R*_G). That is, chains assume a relaxed conformation when $D/2R_G > 1$ while chains become more extended when $D/2R_G < 1.^{13}$

Interestingly, tethered brushes on a particle surface may comprise more than one type of brush conformation because *D* is a dynamic value of a particle system. As the brush extends farther away from the particle core, i.e. when the brush MW increases, the polymer chain can enjoy more freedom as the accessible volume in a sphere is proportional to the cube of sphere's radius. This special behavior is not observed for polymers tethered to a flat surface. It was first described by the Daoud–Cotton (DC) model, which characterized star polymer systems, and was recently expanded to the polymer-grafted particle (particle-

brush systems).¹⁴ Briefly, a particle with high grafting density experiences a stronger crowding effect near the core, in which $D/2R_G < 1$, which forces chains to be highly extended. This regime is called the concentrated polymer brush (CPB) regime. However, the farther away is the chain end from the core, the bigger the value of $D/2R_G$ and the less steric hindrance. This affects the conformation of the polymer brushes resulting in a more relaxed conformation. This regime is named the semi-diluted polymer brush (SDPB) regime.

To evaluate the brush regime of the respective particle-brush samples, a critical distance is introduced to determine the transition between the two brush regimes:

 $R_{\rm c} = R_0(\sigma^*)^{1/2}(\nu^*)^{-1}$

Equation II-1

here R_0 denotes the particle core radius, $\sigma^* = \sigma a^2$ the reduced grafting density, $v^* = v/(4\pi)^{1/2}$ is the reduced excluded volume parameter; σ is the grafting density and a is the length of a repeat unit.^{14b} Hence, particle-brushes are considered to be within the CPB regime if the total particle radius is less than the critical radius, i.e. $R = R_0 + h < R_c$, where $h = h_{CPB} + h_{SDPB}$ denotes the brush height, and otherwise within the SDPB regime. The distinct conformational regimes that are predicted on the basis of the DC model are illustrated in Figure II-1 for the case of a spherical particle-brush.



Figure II-1. Panel a: Illustration of a particle-brush system with a particle radius R_0 and grafting density σ exhibiting "concentrated polymer brush" (CPB) and "semidilute polymer brush" (SDPB) with stretched and relaxed chain conformation, respectively. The CPB \rightarrow SDPB transition occurs at the critical radius R_c . Panel b: Illustration of the predicted Equation II-1 change in scaling of the brush height with the grafted degree of polymerization of polymer brush (N_G) associated with the CPB \rightarrow SDPB transition.

However, the applicability of the DC model to particle-brushes in solid state has not been disclosed yet. Therefore, the scaling relationship between the particle surface-to-surface distance (d) and the surface-grafted degree of polymerization of the polymer brushes (N_G) will be later discussed, including the results from electron micrographs in the second part of this chapter. The chain-conformational regime (CPB or SDPB) of the particle-brush systems that will be investigated in this chapter is very important throughout the remaining portion of this dissertation.

This chapter investigates the effects and challenges associated with introducing particles in SI-ATRP by studying the congestion effect of particle initiators. First, the effects of surface congestion on initiation and propagation of various monomers on various surfaces (6 monomers, 2 different sized particles, and nanotubes) are evaluated. It is demonstrated that the congestion effect limits the possible number of growing chains. However, both tethered and untethered polymers generally share the same identities except when polymerizing bulky and/or hydrophilic monomers. This chapter also investigates the applicability of the DC model to particle-brushes in solid state, in order to predict tethered polymer conformation that is affected by the surface congestion effect. Predicting polymer brushes conformation is very important since these conformations are expected to affect composites' properties (such as glass transition temperature and fracture toughness). The existence of both CPB and SDPB regimes in hybrid particle systems was proven by electron microscopies of a library of particle-brush samples and complied quite well with the DC model. Therefore, this method will be applied to other chapters to predict the conformation of tethered polymer brushes.

The structure of this chapter is as follows: first, a detailed analysis of the real number of growing chains and propagation behavior of numerous monomers on various surfaces and in contact solution will be studied by kinetics. Their corresponded tethered and untethered polymer MW will be measured and compared using size exclusion chromatography (SEC). Next, a systematic

analysis of the scaling relationship between the particle surface-to-surface distance and the degree of polymerization of surface-grafted chains ($d \sim N_G^x$) will be determined by analysis of electron micrographs.

II.2. Experimental section

II.2.1. Materials

Styrene, acrylonitrile, and methyl methacrylate (S, AN, and MMA, Aldrich, 99%) were purified by passing through basic alumina columns before use. Di(ethylene glycol) methyl ether methacrylate (M(EO)₂MA) and poly(ethylene glycol) methyl ether methacrylate (MW = 475, OEOMA₄₇₅) (Aldrich) was slightly warmed before passing through basic alumina column. Copper (I) bromide was prepared by reduction of an aqueous solution of CuBr₂ with an aqueous (aq.) solution of ascorbic acid, and copper (I) chloride was prepared by reduction of CuCl₂ aq. solution using an aq. solution of sodium sulfite. Both copper (I) halides were then sequentially filtered, washed with methanol, dried and stored under vacuum before use. Silica nanoparticles (SiO₂), 30% solution in methyl isobutyl ketone (MIBK-ST, Nissan Chem. Corp. USA) with effective radius $R_{0,\text{TEM}} \cong 7.7 \pm$ 2.0 nm, 30% solution in isopropanol (IPA-ST-L, Nissan Chem, Corp. USA) with effective radius ($R_{0,\text{TEM}} = 29.6 \pm 6 \text{ nm}$), and 30% solution in isopropanol (IPA-ST-ZL, Nissan Chem. Corp. USA) with effective radius $R_{0,\text{TEM}} \cong 56.6 \pm 6.0 \text{ nm}$, and monodispersed silica powder (SIO2P050, Fiber Optic Center Inc.) with effective radius $R_{0,\text{TEM}} \cong 233.2 \pm 16.9$ nm were kindly donated by their supplier and used as received. α-bromoisobutyryl capped silica nanotubes (NT-Br) with pore diameter 15.5 ± 0.5 nm and BET surface area 351.36 m²/g (measured by nitrogen adsorption) were synthesized by Prof. Michal Kruk's laboratory in the College of Staten Island of the City University of New York. TEM images show this NT-Br sample has ca. 70 nm in length. 5-Hexen-1-ol (98%), α-bromoisobutyryl bromide (98%), triethoxysilane (95%), ethyl 2-bromoisobutyrate (EBiB, 98%), 4,4'-dinonyl-2,2'-bipyridine (dNbpy, 99%), *N*,*N*,*N'*,*N''*,*P* entamethyldiethylenetriamine (PMDETA, 99%), and anisole (99%) were purchased from Aldrich and used as received. Hydrofluoric acid (50 vol% HF) were purchased from Acros Organics and used as received. All other chemicals and solvents were supplied by Aldrich and Acros Organics.

II.2.2. Tethering the ATRP initiator 3-(chlorodimethylsilyl)propyl 2-bromo-2methylpropionate (CIPBrMP) onto particle surfaces

The procedures for the synthesis of the tetherable ATRP surface initiator 3-(chlorodimethylsilyl)propyl 2-bromo-2-methylpropionate (CIPBrMP) and the subsequent functionalization of the SiO₂, MIBK-ST and IPA-ST-L, were as performed according to previously described methods.¹⁵

II.2.3. Tethering the ATRP initiators 6-(triethoxysilyl)hexyl 2-bromo-2methylpropanoate (TES-HBMP) onto particle surfaces

5-Hexen-1-ol (**1**), α -bromoisobutyryl bromide (2-bromo-2-methylpropanoyl bromide, **2**), and triethoxysilane (TES) were used to synthesize a tetherable ATRP initiator; 6-(triethoxysilyl)hexyl 2-bromo-2-methylpropanoate (TES-HBMP, **4**) and

finally attached the initiator onto silica nanoparticles (IPA-ST-ZL was shown as an example) using a modification of a reported procedure, see Scheme II-1.¹⁶ The Br terminated ATRP initiator functionalized SiO₂ (SiO₂-Br) was washed with 99.5%+ ethanol followed by centrifugation. This procedure was repeated 10 times in order to wash away all initiators that were not attached to SiO₂-Br. 500 MHz ¹H NMR with 1024 scans showed no observable initiator residue remaining in the ethanol dispersion after these washing cycles., and then the solvent was exchanged to anisole. SIO2P050 was modified in the similar way.

II.2.4. Typical SI-ATRP example

In a typical SI-ATRP of S in a grafting polymerization from the surface of SiO₂-Br, 15.4 g of 6.5 wt% SiO₂-Br in anisole dispersion (1.0 g of SiO₂-Br with 90 μ mol Br/g) and 20.6 mL of S (180 mmol) were mixed with a stock solution containing 5 mg of CuBr₂ (22.5 μ mol), 51.7 μ L of PMDETA (247.5 μ mol), and 2.1 mL DMF (ca. 5.4 vol%) in a 100 mL Schlenk flask equipped with a rare earth magnetic stirring bar. The use of a rare earth magnetic stirring bar in the grafting reactions from SiO₂-Br is important, as it was noted that gelation of the reaction mixture occurred significantly earlier in the absence of a sufficient stirring, especially at high monomer conversion. The mixture was first stirred overnight then degassed by 4 cycles of freeze-pump-thaw. The flask was subsequently immersed in liquid nitrogen and purged with nitrogen when 32.3 mg of CuBr (225 μ mol) was added to the frozen reaction mixture. The flask was sealed, evacuated for 40 min, back-refilled with nitrogen 3 times, warmed to room temperature, and

finally immersed in an oil bath at 70 °C. The mixture was stirred at a suitably fast rate until the desired time had elapsed, the flask was then cooled while continuing stirring, and the reaction was terminated by adding oxygenated tetrahydrofuran (THF) to stop the reaction. The same reaction conditions were employed with various catalysts, at different temperatures and in the presence of other types of monomers, sacrificial initiators, and surfaces (i.e. 2 different sizes of particles and nanotubes). The final product suspended in THF was dialyzed against THF and methanol until the characteristic color of the copper (II) catalyst complexes disappeared.

II.2.5. Separation of polymer grafted particles and untethered polymers

In the polymerization of concurrently chain grafting from surface tethered initiators and untethered initiators, the samples were first dried after dialysis. The dried sample was redispersed in toluene then stirred for 24 h before centrifugation. The centrifugation was carried out gently until ca. 20 wt% of the sample in the centrifugation tube was collected. The absence of any untethered polymers in the centrifugation solid residue was later verified by TEM, and the residue was labeled as "particle-brushes". The remaining filtrate was kept in the centrifugation tube until the SiO₂ peak in the dynamic light scattering spectrum disappeared (DLS, 0.1 - 1 mg mL⁻¹ in toluene solution using a Malvern Zetasizer Nano ZS). The final filtrate was first passed through the 0.45 μm, 0.20 μm, and 0.10 (optional: depends on MW) μm polytetrafluoroethylene (PTFE) syringe filter, and labeled as "untethered

polymers". It was later confirmed by SEC measurement that there was no particle peak in these samples.

II.2.6. Characterization of polymer-grafted particles

SiO₂-polymer and SiO₂-Br were imaged with transmission electron microscopy (TEM) using a JEOL 2000 EX electron microscope operated at 200kV. Images were acquired using a Gatan Orius SC600 high-resolution camera. The size of the particles was determined by a statistical analysis of the TEM images using ImageJ software. The apparent initiator density of SiO₂-Br was determined by elemental analysis (bromine content), conducted by Midwest Microlab (IN). Monomer conversion during SI-ATRP was monitored by 500 MHz ¹H NMR (256 scans). The weight of the polymer brushes grafted from particles was measured by thermogravimetric analysis (TGA) using a Q50 TGA analyzer from TA Instruments (New Castle, DE) under nitrogen up to 850 °C.

Molecular weight (MW) and molecular weight distribution (MWD) were determined by size exclusion chromatography (SEC), using a Waters 515 pump and Waters 2414 differential refractometer using PSS columns (Styrogel 10⁵, 10³, 10² Å) in THF as an eluent (35 °C, flow rate of 1 mL min⁻¹), with toluene and diphenyl ether used as internal references. Linear polystyrene (PS) and poly(methyl methacrylate) (PMMA) standards were utilized for calibration. Samples were etched from particles and nanotubes with HF in a polypropylene vial for 20 h, neutralized with ammonium hydroxide, and dried with magnesium

sulfate before SEC injection. Neutralization process was conducted with caution under liquid nitrogen to dissipate heat.

II.2.7. Particle-brush film preparation

Approximately monolayer films of all particle-brush systems were prepared by spin-casting of dilute particle solutions (1–3 mg mL⁻¹ in toluene) on the poly(acrylic acid) (PAA) substrate and subsequent thermal annealing in a vacuum for 24 h at T = 120 °C. Equilibrium films were lift-off by water immersion and transferred onto Cu-grids.



Scheme II-1. Synthesis of polymer-grafted SiO₂ (SiO₂-polymer) by surfaceinitiated ATRP is a 3-steps process. SiO₂-PS was shown as an example. First, 5-hexen-1-ol (1), α -bromoisobutyryl bromide (2), and triethoxysilane (TES) were employed to synthesize a tetherable ATRP initiator, 6-(triethoxysilyl)hexyl 2-bromo-2-methylpropanoate (TES-HBMP, 4) via the intermediate 3. Second, TES-HBMP was attached to the surface of SiO₂ to form SiO₂-Br. Finally, SiO₂-PS was synthesized via SI-ATRP while TSI occurred concurrently to form untethered-PS.

II.3. Result and discussion

II.3.1. Particle-brush synthesis

Silica particles (SiO₂) were donated by Nissan Chemical Co. and Fibers Optic Inc. Nanotubes (NT) were synthesized and provided by Prof. Michal Kruk's laboratory (see material section for details). Both systems were synthesized using surface-initiated atom transfer radical polymerization (SI-ATRP).^{15, 17} In this technique, a low molecular initiator species (typically a 2-bromo-isobutyrate derivative) was first covalently bound to the substrate surface using a silanization coupling reaction. Readers are referred to "Materials" section for more details. Subsequently, the polymer is polymerized from the substrate surface. The SI-ATRP approach has shown in the past to facilitate precise control of N_{G} , molecular weight distribution (MWD), and grafting density of surface-grafted chains (σ) and thus provides an ideal means towards hybrid model systems for the study in this dissertation.¹⁸ A synthesis examples was outlined by Scheme II-1 followed by a modification of a previously reported procedure.¹⁶

II.3.2. Apparent initiator density

The particle size of IPA-ZT-L ($R_{0,\text{TEM}} \cong 56.6 \pm 6.0 \text{ nm}$) was determined from a statistical analysis using ImageJ software. The density of SiO₂ used for all calculations was 2.2 g/cm³. Specific surface area and therefore the amount of

initiators required to modify the surface was then calculated. The apparent initiator density 0.72% Br/g of SiO₂-Br was obtained by elemental analysis, which is equivalent to 0.09 mmol Br/g and ~1.94 initiator/nm². The apparent initiator density of other particle and nanotube samples were calculated accordingly.

II.3.3. General SI-ATRP reaction conditions

Table II-1 summarized the reaction conditions used in the synthesis of polystyrene-, poly(styrene-*r*-acrylonitrile)-, and poly(methyl methacrylate)-grafted silica nanoparticles (particle-brush sample IDs: SiO₂-PS, SiO₂-PSAN, and SiO₂-PMMA). The predominant method used for synthesizing these materials is the targeting a high MW (higher monomer volume). As previously discussed, this is effective at reducing particle collision probability and instant radical concentration, and so reliefs the inter-particle termination (see Chapter I for details). These reactions were carried out with either SI-activator regenerated electron transfer ATRP (SI-ARGET ATRP) or conventional SI-ATRP. SI-ARGET ATRP was employed to synthesize the high MW particle-brushes with very low copper concentration (30 ppm). This is because reducing agents in SI-ARGET ATRP are able to regenerate Cu(I) activators from Cu(II) deactivators (that are accumulated due to chain terminations) during the reaction. However, SI-ARGET ATRP generally gave rise to boarder MWDs in both the low MW region and in the polymerizations of higher $k_{\rm p}$ monomers. This is probably owing to the excessive use of ligand that forms more reactive (higher KATRP) catalyst complex in ARGET ATRP, which is used to compensate the competitive complexation of the low

amount of transition metal.¹⁹ Therefore, conventional SI-ATRP was selected to synthesize SiO₂-PMMA and low MW SiO₂-PS and SiO₂-PSAN. Halogen exchange was applied to further increase the initiation efficiency in the synthesis of SiO₂-PMMA.²⁰ This was done by using copper chloride catalyst complexes instead of the bromide analogs. This is because the value of the ATRP equilibrium constant (*K*_{ATRP}) for alkyl chloride-type of chain-end is 1 - 2 orders of magnitude lower than the alkyl bromides with the same structure. Therefore, C-Cl bond activation is slower, and thus the rate of propagation is decreased with respect to the rate of initiation (e.g. *K*_{ATRP}^{SiO2-PMMA-Cl} × *k*_P < *K*_{ATRP}^{SiO2-Br} × *k*). Finally, it was found that SiO₂-PS reaction condition listed in Table II-1 can be directly used in the syntheses of SiO₂-PSAN when 22 - 37.5 mol% of S was replaced with AN. However, the reaction rates are not identical as SiO₂-PS. The final AN composition in the PSAN brush is related but not equal to the molar ratio of AN fed in the beginning of the reaction. More information will be discussed in the later sections.

Table II-1. Example of SI-ATRP conditions used to synthesize SiO ₂ -PS,	SiO ₂ -
PSAN, and SiO ₂ -PMMA.	

Targeted Products ^{a,b}	[SiO ₂ -Br] ₀ :[St] ₀ :[AN] ₀	[CuBr] ₀ /[CuBr ₂] ₀	[bpy/PMDETA]0	[Me ₆ TREN] ₀ [Sn(EH) ₂] ₀
PSAN < 150	1:500:300	625 / 62.5 ppm	2 / 1 fold	-
PSAN (x to 3x) ^d	1: <mark>10x:6</mark> x	0 / 30 ppm	-	10 folds of Cu
PS < 150	1:500:0	625 / 62.5 ppm	2 / 1 fold	-
PS (x to 3x) ^d	1:16x:0	0 / 30 ppm	-	10 folds of Cu
Target DP ^{a,c}	[SiO ₂ -Br] ₀ :[PMMA] ₀	[CuCl] ₀ /[CuCl ₂] ₀	[dNbpy]₀	[Me ₆ TREN] ₀ [Sn(EH) ₂] ₀
PMMA (x - 3x) ^d	1:20x	1400 ppm/140 ppm	-	-

^a Functional silica (SiO₂-Br): R_0 : ~7.7 - 250 nm with rare earth stir bar;

^b 70 - 90 °C with anisole;

° 70 °C with DMF;

^d x is a variable that based on the targeted product.

^e bpy = 2,2'-bipyridine; dNbpy = 4,4'-dinonyl-2,2'-bipyridine; PMDETA = N,N,N',N'',N''-pentamethyldiethylenetriamine;Me₆TREN = tris(2-dimethylaminoethyl)amine; Sn(EH)₂ = tin(II) 2-ethylhexanoate.

II.3.4. Real number of growing chains

The number average MW (M_n) of tethered chains is related to but not always proportional to conversion times the apparent initiator density. This is because some of the surface-tethered initiating sites could be blocked by the neighboring polymers (congestion effect) or terminate with each other at the beginning of reaction, as shown in Scheme II-2. For this reason, the blocked initiating sites cannot initiate polymerization. The average σ over the whole polymerization was previously used to approximate the real number of growing chains and theoretical $M_{\rm h}$. The theoretical $M_{\rm h}$ calculated this way had very good agreement with the experiment $M_{\rm p}$.¹⁶ First, MMA (with less side reaction) was grafted from SiO₂-Br with the following molar ratio of reagents [MMA]₀ : [SiO₂-Br]₀ : [CuCl]₀ : [CuCl₂]₀ : [dNbpy] = 2000 : 1 : 2.5 : 0.25 : 2.75; SiO₂-Br in anisole dispersion = 6.5 wt%, DMF = 5.4 vol% of total reaction volume, T = 70 °C. Samples were taken at 10%, 20%, and 30% conversion, the $M_{\rm h}$ were measured by SEC after cleaving the tethered PMMA from particles, and the polymer/silica weight fractions were measured by TGA. Using the measured R_0 and the SiO₂/polymer weight fraction, the average σ in this reaction was calculated to be 0.63 initiators/nm², which is ca. 3 times less than the value of apparent initiator density. This average σ will be used to calculate theoretical M_n in later sections. The real number of growing chain of another particle sample and nanotube were calculated accordingly.





Since the real number of growing chain is much less than the apparent initiator density, it is expected that the surface congestion could also affect the polymerization behavior on surface. Monomer types and surface curvatures are the two parameters that will be discussed in the current study. First, the surface congestion effects of the standard grafting polymerizations and copolymerizations of diverse monomers, i.e. MMA, S, AN, and 2 ethylene oxide methyl methacrylate monomers: (M(EO)₂MA and M(EO)₄₋₅MA - also termed as OEOMA₄₇₅) will be disclosed. Second, homopolymerizations from substrates with diverse curvatures (SiO₂ of $R_{0,TEM} \cong 7.7$ and 56.6 nm, and NT) will be compared and discussed.

II.3.5. Standard grafting polymerization and copolymerization via conventional SI-ATRP

In a standard grafting from functionalized silica particles (SiO₂-Br, $R_{0,\text{TEM}} \cong$ 7.7 ± 2.0) using one of the broadly utilized ligands dNbpy for polymerization of MMA via conventional SI-ATRP (see Table II-1 for reaction condition, x = 120), the results matched those of solution polymerizations, generating linear semilogarithmic kinetic plots and linear evolution of MW with conversion, Figure II-2. Also, SiO₂-PSAN was compared with linear PSAN that synthesized from untethered initiator EBiB under under azeotropic conditions (60 mol % of S). Note that EBiB was employed here since it has similar structure as the tethered ATRP initiator, so similar reactivity is expected. The results suggested that the existence or absence of SiO₂ did not affect the polymer composition. Both reactions produced PSAN with 41 ± 4 mol%. The composition of the synthesized SiO₂-PSAN was desired to be miscible with PMMA owing to the attractive interaction (χ) parameter.²¹ Using this strategy, particle dispersion in PMMA could be improved, more details will be discussed in Chapter IV.



Figure II-2. a) Kinetics and b) MW evolution plots of standard grafting polymerization of SI-ATRP using the reaction condition provided in Table II-1.

II.3.6. Copolymerization of bulky and hydrophilic monomers

The polymerization and copolymerization of relatively small monomers (molar mass ~100 or less) revealed no apparent kinetic difference between SI and bulk polymerization. Thus, this section specifically targets the homopolymerization and copolymerization of relatively sterically bulky and hydrophilic monomers, i.e. di(ethylene glycol) methyl ether methacrylate (M(EO)2MA) and poly(ethylene glycol) methyl ether methacrylate (MW = 475, OEOMA₄₇₅). This was examined by studying the grafting of the monomers M(EO)₂MA and OEOMA₄₇₅ from SiO₂-Br $(R_{0,\text{TEM}} \cong 7.7 \pm 2.0, 1.44 \text{ initiators/nm}^2)$. M(EO)₂MA and OEOMA₄₇₅ impart their hydrophilicity and bulkiness from their overall length of ethylene glycol units incorporated into the monomer. The results were analyzed in time-dependent instead of conversion-dependent MW evolution plots since some reactions had conv. < 5% and or decreased in conversion over time, Figure II-3a. Note that these are the expected errors of NMR measurements. It was determined that M(EO)₂MA can polymerize from the surface of the SiO₂-Br but OEOMA₄₇₅ cannot be effectively grafted from the surface of the particle. The same observation was found in the copolymerization of both monomers and the conversion of OEOMA₄₇₅ was always approximately zero for copolymerizations. However, after a M(EO)₂MA segment had been grafted from the surface of the particle, the chains could be extended by polymerization of OEOMA₄₇₅, Figure II-3c. This ability to form block-copolymers was rationalized to be due to the increase of surface hydrophilicity and the increase of the average chain distance (*D*) when the brush extended farther away from the particle core (less congestion). This hypothesis is illustrated in Figure II-3 and readers are referred to the "Introduction" section for more details. Hence, block copolymers with PM(EO)₂MA as the first block and POEOMA₄₇₅ as the second block were successfully grafted from SiO₂-Br, and different ratio of the block copolymer segmented arms were prepared. It was also found that an appropriate ratio of M(EO)₂MA:OEOMA₄₇₅ ca. 1:2 by wt. can be grafted from the particles, and its hydrophilicity was suitable as stabilizers in xylene/water (50/50) Pickering emulsions with 0.005 wt%, and the emulsions were still stable after <1.5 years.



Figure II-3. a) Time-dependent MW evolution plot of $[SiO_2-Br]_0 : [M(EO)_2MA]_0 : [OEOMA_{475}]_0 : [CuBr]_0 : [CuBr_2]_0 : [HMTETA]_0 = 1 : x : y : 1 : 0.25 : 1.25, where x and y are listed in the plot represents the monomer ratio in homopolymerization and copolymerization. b) Illustration of grafting of OEOMA_{475} from SiO_2-Br. c) SEC traces of chain extension from SiO_2-PM(EO)_2MA (purple trace) with OEOMA_{475}. The green curve represents the SEC trace after chain extension.$

II.3.7. Concurrent polymerization on particle surfaces with diverse curvatures and in bulk

As the summary of the above section, congestion effects could be affected by the monomers' steric bulky and hydrophilicity. The next step in understanding the congestion effects on surfaces is to study the congestion effects determined by surface curvature. Simulations have suggested that congestion increased when the curvature decreased in concave surfaces or increased in convex surfaces. from this increase in congestion and the MW could be affected.⁶ Similar observation has been confirmed through experiments.^{5, 9} These studies also concluded that comparing polymerization kinetics on surfaces versus contact solution is a direct and reliable method. This has been done by adding some untethered (sacrificial) initiators when grafting polymers from surfaces. The tethered and untethered polymers were then separated by centrifugation and analyzed by SEC accordingly. Note that direct injection of inorganic substrate in SEC could be harmful to the SEC column so it is suggested to cleave the tethered polymers before injection. For example, tethered polymers can be cleaved from SiO₂ surface using hydrofluoric acid. The procedure was discussed in the Materials section. To determine the reliability of this method, concurrent grafting polymerization of MMA from SiO₂-Br ($R_{0,\text{TEM}} \cong 56.6 \pm 6.0$ nm, real number of growing chain ca. 0.63 chains/nm²) and initiation by ethyl 2-bromoisobutyrate (EBiB) was performed, using the reaction conditions in Table II-1 (molar ratio of initiator sites on SiO₂-Br : EBiB = 1 : 1). The molecular weights of cleaved tethered polymers and untethered polymers in bulk were very similar, Figure II-4. Same

behavior was observed also in the system with larger SiO₂-Br ($R_{0,TEM} \cong 233.2 \pm 16.9$ nm). These results agreed with the MW relationship that was previously reported in literature, as guided by the linear relationship in Figure II-4.⁷ Similar experiments were performed by grafting S from SiO₂-Br and the reaction was conducted at 90 °C, a statistically significant difference in final MW was observed when compared to S grafted to EBiB (detailed results are in Chapter VII). This difference was attributed to the side reaction of thermal self-initiation of S, which concurrently generated new chains in the contacting solution but did not affect the tethered chains. In a summary, the congestion effect is expected to have a minor impact on particle (convex) system.



Figure II-4. Relationship between M_n of cleaved tethered polymers and that of untethered polymers in SI-ATRP of MMA, using the reaction condition suggested by Table II-1. Two sizes of SiO₂-Br were tested - $R_{0,TEM} \cong 56.6 \pm$ 6.0 nm (data represented by empty square) and $R_{0,TEM} \cong 233.2 \pm 16.9$ nm (data

represented by solid circle). The straight line guided the suggested relationship by ref 7.

II.3.8. Concurrent polymerization on concave and convex surfaces

One could argue that the accessible volume in particle systems is very small so, the build up by the congestion effect for concvex surfaces is hard to observe. A previous work involving SI-ATRP grafting of PAN and polv(2-(dimethylamino)ethyl methacrylate) (PDMAEMA) from concave surfaces of cylindrical mesopores was reported.^{8a} The grafting process was optimized by varying the amount of Cu(II) species that act as deactivators. This optimization allowed for the growth of polymer layers with controlled thickness, which consisted of monodisperse polymer chains of controlled MW. However, a "tailing" was observed in the reported SEC graph and the origin of this phenomenon was unclear. The "tailing" may represent a population of polymer chains that grew on the external surface of particles of FDU-1. While the growth of polymer chains inside the pores was hindered (because of the limited accessible volume), the chains growing on the external surface had no such restriction. In other words, this may suggest polymerization kinetics behavior on both concave and outside concave surfaces are similar until pores were filled up. Intrigued by this idea, polymerization of n-butyl acrylate (BA) from functionalized silica nanotube (NT-Br, provided by Prof. Michal Kruk, see Materials section for more details) was performed. The choice of BA was due to the convenience of future AFM morphology measurement, the use of NT-Br was because it carried both concave

and convex surfaces. The results showed that the reaction kinetics changed when the grafting from reaction was continued past a certain point which was noticed by the decreased slope, Figure II-5a. A high MW shoulder appeared in the SEC curves, Figure II-5b, these could be attributed to the pores of NT-Br being filled with polymer, but active chain ends with access to the solution continued to grow on the exterior of the pore. More importantly, this special concurrent polymerization system on concave and convex surfaces suggested that the polymerization kinetics were not always affected by the congestion effect generated by the change of surface curvature, but could be affected by the particular choice of monomers (as mentioned in the last section), initiators, catalysts, and reaction conditions.



Figure II-5. a) Kinetic plot and b) SEC traces for grafting polymerization from NT-Br at different reaction times.

II.3.9. Congestion effect on surface-tethered polymer conformation

Since the congestion can affect the polymerization kinetics of bulky monomers, it could also affect the conformation of surface-tethered polymers
(polymer brushes), which are significantly more bulky in size. Previous research showed the conformations of polymer brushes were intimately related to the materials properties.¹⁰ Therefore, a strategy to predict the polymer conformation is very important. As mentioned in the introductory section, the conformation of polymer brushes can be evaluated on the basis of the DC model to describe the structural transitions in the suspension state. In particular, a critical distance $R_{\rm c}$ was postulated to predict the polymer conformation. The main two regimes are the CPB regime in which excluded volume interactions give rise to stretched chain conformations and the SDPB regime in which chains assume a relaxed chain conformation. However, the applicability of the DC model to particle-brushes in solid state has not been disclosed yet. Therefore, the scaling relationship between the particle's surface-to-surface distance (d) and $N_{\rm G}$ was investigated using TEM. Samples in this section were synthesized with the reaction conditions listed in Table II-1, and sample information is listed in Table II-2. In Table II-2, sample IDs R_0 SiO₂-PSN_G and R_0 SiO₂-PMMAN_G were used to represent the samples.

Approximately monolayer structures were prepared by dilute solution casting of particle-brush systems (c < 1 mg/mL in toluene) and subsequent thermal annealing for 1 h in vacuum at T = 120 °C to remove residual solvent. Figure II-6 depicts representative electron micrographs of the monolayer structures of polymer-grafted small and medium-sized particle-brush systems (panels a – d: $8SiO_2$ -PMMA*N*_G, *N*_G = 40 – 4000; panels e - h: $30SiO_2$ -PS*N*_G, *N*_G = 0 – 1800),

confirming both the uniformity of polymer graft modification and the expected trend of increasing d with increasing N_{G} .

sample ID	M _{n,GPC}	<i>M</i> _w / <i>M</i> _n	wt % SiO ₂	σ(chain/nm²)	<i>R</i> ₀ (nm)
8SiO ₂ -PMMA40	4 100	1.12	77.4	0.67	7.7
8SiO ₂ -PMMA150	15 400	1.14	24.6	0.63	7.7
8SiO ₂ -PMMA570	57 000	1.14	8.97	0.56	7.7
8SiO ₂ -PMMA4000	400 400	1.18	1.4	0.54	7.7
8SiO ₂ -PMMA16K*	1 608 400	1.28	0.7	0.25	7.7
8SiO ₂ -PS10	1 000	1.08	84.7	0.59	7.7
8SiO ₂ -PS150	15 600	1.21	23.8	0.61	7.7
8SiO ₂ -PS770	80 400	1.32	9.3	0.33	7.7
8SiO ₂ -PS1360	141 700	1.79	5.3	0.25	7.7
30SiO ₂ -PS100	10 400	1.19	71.8	0.67	29.6
30SiO ₂ -PS1000	104 000	1.42	20.3	0.53	29.6
30SiO ₂ -PS1800	187 000	1.67	12.4	0.46	29.6
60SiO ₂ -PS130	13 000	1.08	81.1	0.61	56.6
60SiO ₂ -PS400	41 000	1.12	38.8	0.61	56.6
60SiO ₂ -PS630	65 500	1.25	23.9	0.52	56.6
60SiO ₂ -PS2100	220 000	1.29	10.4	0.47	56.6

 Table II-2. Characteristics of particle-brush systems with polystyrene (PS)

 and poly(methyl methacrylate) (PMMA) brushes

Asterisk (*) indicates that high-pressure ATRP conditions were used for synthesis (see ref 22).



Figure II-6. Representative bright-field transmission electron micrographs depicting particle monolayers for different types of particle-brush systems (panel a–d: $8SiO_2$ -PMMAN_G; panels e–h: $30SiO_2$ -PSN_G) with grafting density $\sigma > 0.5 \text{ nm}^{-2}$: (a) $N_G = 40$, (b) $N_G = 150$, (c) $N_G = 570$, (d) $N_G = 4000$, (e) $N_G = 0$ (i.e., neat SiO₂), (f) $N_G = 100$, (g) $N_G = 1000$, and (h) $N_G = 1800$. Scale bars are 100 nm (panel a–d) and 200 nm (panels e–h).

In contrast to the small 8SiO₂-PMMA*N*_G, 8SiO₂-PS*N*_G and the medium-sized 30SiO₂-PS*N*_G particle-brush systems for which an appreciable size disparity can be discerned from electron micrographs, Figure II-7 reveals a rather uniform size distribution in case of the larger particle-brush system 60SiO₂-PS*N*_G. The difference in size disparity is significant in the context of the order formation in the respective particle-brush systems that will be discussed in Chapter V.



Figure II-7. Representative bright-field transmission electron micrographs depicting particle monolayers for large particle-brush systems ($R_{0,TEM} = 56.6 \pm 6$ nm) with grafting density $\sigma > 0.5$ nm⁻²: (a) $N_G = 130$, (b) $N_G = 400$, (c) $N_G = 630$, and (d) $N_G = 2100$. Scale bars are 200 nm.

To determine the chain-conformational regime (CPB or SDPB) of the particle-brush systems, the scaling relationship between the particle surface-to-surface distance and the degree of polymerization of surface-grafted chains $(d \sim N_G^x)$ was determined by analysis of electron micrographs similar to those shown in Figure II-6 and Figure II-7. The combined result depicts the observed scaling relation in terms of the reduced parameters d/R_c (the reduced particle size) and N_G/N_c (the reduced degree of polymerization), where R_c and N_c are the expected critical brush radius and the corresponding degree of polymerization at the CPB \rightarrow SDPB transition based on the DC-type scaling model described above (with $\sigma = 0.6$ nm⁻² and x = 0.8 it follows that $N_c \cong 250$, 1280, and 1850 for the particle system with R_0 ca. 8, 30, and 60 nm, respectively). As an example, the relationship *d* and N_G was plotted, Figure II-8. The plot reveals that all particle systems exhibit a change in the scaling exponent *x* from $x \cong 0.8$ to $x \cong 0.5$ with increasing of N_G , thus confirming the transition from stretched to relaxed chain

conformations. The transition between the scaling regimes is found to be in good agreement with the predicted CPB \rightarrow SDPB transition that is indicated as the borderline between the different colored regions. This confirms that the ability of the DC scaling model to capture structural transitions in particle-brush systems in the solid state within experimental uncertainty.



Figure II-8. Plots of inter-particle distance (*d*) vs. grafted degree of polymerization of polymer brushes (N_G) (left) with different silica diameters. The predicted transition agrees with the Daoud-Cotton Particle model. The critical transition N_c value is also as predicted, when the diameter of particle (R_0) increases, N_c also increases.

II.4. Conclusions

This chapter investigated the effects and challenges of SI-ATRP from particles. The congestion effect of particle initiators on the tethered polymer initiation efficiency, composition, MW, and polymer conformation in SI-ATRP were studied. The results showed that tethered and untethered polymers generally follow the same kinetics when growing from particles except when grafting bulky and/or hydrophilic monomers. However, the real number of growing chain is less than the initiator density probably due to the surface congestion. Also, polymerization from silica nanotube that carries 2 different surfaces with extremely different curvatures was performed. The results suggested that polymerization kinetic were slightly affected by surface curvature but more serious by other parameters, such as the particular choice of monomers. Finally, the applicability of DC model to capture structural transitions in the particle-brush systems in the solid state was tested. The results suggested that DC model can be used to estimate the transition between CPB and SDPB regimes within the experimental uncertainty.

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Chapter III

Particle-Brushes with High MW Grafts Synthesized by SI-ATRP

Preface As discussed in Chapter I, the creation of more robust commercial plastics by embedding fillers has drawn considerable attention in both academia and industry during the past two decades. However, nanometer-sized fillers tend to aggregate to minimize surface energy, resulting in loss or diminution of desired properties. Grafting polymer brushes from/onto fillers to improve the filler dispersion in the matrix has been demonstrated previously. Chapter II showed that ATRP could be applied to grafting polymers from fillers. Particle-brushes with controlled MW and high grafting density were obtained in SI-ATRP regardless of the surface congestion, except when sterically bulky and/or hydrophilic monomers were employed.

Therefore, polymers grafting *via* SI-ATRP have potential to aid filler dispersion by screening filler-filler interactions. This enhanced ability for dispersion

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was limited to the cases such that the degree of polymerization of tethered chains was higher than that of the matrix chains. Hence, high molecular weight SI-ATRP is desired. Yet, fillers usually have large surface areas and a high number of initiating sites, so interparticle termination reactions could produce a macroscopic gel. Prior works showed that low monomer conversion, slow polymerization, and the addition of sacrificial initiators could minimize termination. However, these approaches produce additional monomer/polymer waste and/or require additional purification. More importantly, these methods have the flaws of long reaction times and/or cannot achieve high MW.

In this chapter, particle-brushes with a silica core and grafted poly(methyl methacrylate) or poly(*n*-butyl methacrylate) chains (SiO₂-PMMA and SiO₂-PBMA) were prepared via activators generated by electron transfer for atom transfer radical polymerization (AGET ATRP) at room temperature under high pressure (i.e. 6 kbar). Due to the enhanced propagation rate coefficient (k_p) and the reduced termination rate coefficient (k_i) of the polymerization conducted under high pressure, the rate of polymerization was much faster compared with ATRP under ambient pressure, while preserving good control (i.e. D < 1.2). SiO₂-PMMA and SiO₂-PBMA with MW in excess of 1 million were obtained using this high pressure approach. High MW SiO₂-PMMA was also achieved at ambient pressure, but higher particle dilution and higher temperature were required under these conditions using SI-ATRP. Higher particle dilution can reduce the chance of particle collisions and radical concentration, which diminishes the interparticle

termination. Higher temperature also can enhance $k_{\rm p}/k_{\rm t}$ value. From this different methodology, particle-brushes with MW ca. 1 million were obtained without high pressure but a longer reaction time was required. Three different nanoparticle dilutions were tested by varying the monomer volume (increase target DP, \uparrow [M]₀/[I]₀). As expected, the higher dilution reaction was slower but yielded polymers with lower *D*. This could be attributed to the decrease of particle collision and the reduced radical concentration during polymerization. Therefore, the chance of the interparticle termination is further reduced. In the lowest dilution case, the reaction became viscous and the *D* started to increase when the MW reached 0.8 million. This could be rationalized by the decrease of deactivator diffusion rate in the SI-ATRP system, and the increase of radical concentration at high monomer conversion. This concept was expanded to styrene (S) polymerization, in which higher temperature (i.e. 150 °C) was required due to lower $k_{\rm p}/k_{\rm t}$ for S. However, thermal self-initiation of styrene (TSI of S) broadened the MWD at the elevated temperatures. Fortunately, particle-brushes can be separated from untethered polymers generated by TSI of S. PS with MW of up to 0.3 million was obtained. This polymerization of S under higher particle dilution and higher temperature polymerization can be much faster. However, it requires further optimization for higher MW polymers. The synthesized particle-brushes exhibited semi-diluted brush architecture as discussed in the prior chapter.

III.1. Introduction

Physical properties of nanocomposites, containing various nanometersized fillers, can be significantly affected by fillers' content, size, and dispersability/aggregation.¹ Bare fillers easily aggregate inside polymer matrixes and reduce the performance of the nanocomposites. Therefore, the surface of fillers should be modified to prevent such aggregation. One of the methods commonly used for surface modification relies on tethering a polymer layer to the fillers' surfaces. Various grafting techniques (grafting from and grafting onto) have been developed for this purpose.² Grafting from provides excellent control of the composition of the polymer chains and functionality as well as grafting density. Densely grafted chains efficiently prevent aggregation by screening the filler-filler interactions. If the molecular weight (MW) of tethered chains is higher than that of the matrix, hybrid particles disperse well and avoid depletion of mixing and aggregation.³

Reversible deactivation radical polymerizations (RDRPs) are powerful methods for the synthesis of materials with diverse polymer architectures, including hybrid materials.⁴ However, since RDRPs are radical based processes, they are always accompanied by irreversible radical termination reactions, which limit polymer MW. The preparation of hybrid materials by "grafting from" employs the chain growth from the fillers surface, which has been modified with hundreds to thousands of covalently attached initiators. One of the biggest challenges of this approach is the prevention of macroscopic gelation stemming from inter-filler

termination reactions. To minimize this effect, polymerizations are carried out under limited to low monomer conversion⁵ and/or low MW and/or performed in the presence of sacrificial initiator⁶. These strategies yield the generation of significant solvent and/or monomer waste streams or require the separation of hybrid fillers from the untethered polymers. The separation can be challenging, especially when small fillers are utilized. One alternative approach is to conduct polymerizations in miniemulsions. Although the microscopic cross-linking/gelation can still occur inside the single droplets, the macroscopic gelation can be avoided.^{2f}.

A more efficient solution is to directly reduce the dead chain fraction at the desired MW. This could be done by depressing the termination rate constant (k_t) and elevating the propagation rate constant (k_p).⁷ Therefore, understanding the mechanism of the propagation and termination pathways, and how to manipulate these parameters is the major task of the current chapter.

Free radicals are highly active species that react at very high rates. Thus, if one or more of the reacting species has a low diffusion rate, this step can become the rate-determining step and the reaction then becomes diffusion-controlled.⁸ For example, propagation involves the reaction of a chain radical with highly mobile monomers. The diffusion rate of monomer to chain end is usually much faster than propagation. Therefore, propagation is not typically diffusion controlled. In contrast, termination is a diffusion-controlled process. This is due to the involvement of an extremely fast chemical coupling reaction, while reduced

diffusion rate is due to the bulkiness of the polymer chains and increased viscosity. Thus, limiting polymer chain diffusion in radical polymerization by increasing medium viscosity can depress $k_{t.9}$ Increasing pressure can also increase k_p/k_t since the diffusion rate of monomer will increase and the diffusion rate of polymer will decrease.¹⁰ Thus, RDRPs performed under high pressure can occur at a relatively high rate of polymerization while retaining good control over polymer architecture without sacrificing MW or conversion.¹¹

Three diffusion processes are important in radical polymerization.⁸ Translation diffusion represents the movement of the center of mass of the chain through space to meet with another chain. Segmental diffusion describes the chain ends' movement via bond rotations and local reconfiguration. For instance, when two chains approach each other, termination does not occur immediately. It requires segmental diffusion that allows active chain ends come into close enough proximity to react. Finally, reaction diffusion identifies the process of an active chain end propagate via monomer addition in an essentially vitrified state. In a radical polymerization, translational diffusion determines the termination rate at low monomer conversion, since both segmental and reaction diffusion processes are rapid at this stage. At a high conversion, both segmental and translational diffusion are limited by the increased viscosity. Therefore, reaction diffusion becomes the rate-determining step.

In surface-initiated atom transfer radical polymerization (SI-ATRP) grafting from particles, there are two termination processes, the intra-particle termination and the interparticle termination. In the intra-particle termination process, chains are already held together on the same surface with high grafting density. Therefore, chain movements could be restricted by the surface and the surface congestion. A recent study suggested that direct bimolecular termination between active chain ends on the same surface can be difficult.¹² Readers are referred to Ch1 for more details. Interparticle termination process involves first the collision of two particles, and then pair(s) of active chain ends on these particles contact each other to terminate by coupling/disproportionation. Since particle-brushes are magnitudes bigger than chains, translational diffusion is more restricted when compared to in bulk polymerization. Therefore, increasing pressure could diminish interparticle termination and avoid macroscopic gelation by immobilizing particle translational diffusion.

Another alternative way to diminish interparticle termination is to use dilute particle concentrations at the beginning of the reaction and increase the reaction temperature. The idea is to reduce the particle concentration in the beginning of the reaction by increasing monomer volume. Thus, the particle collision probability and termination can be reduced. (Note that dilution of particles can also be fulfilled by adding solvents. However, adding solvent will also reduce monomer concentration, which further slows down propagation.) Reactions are faster when monomer conversion and MW increased. This is due to the increase of radical

concentration at high monomer conversion. It is also related to the reduction in termination reactions, which is expected from the increase in viscosity of the contacting polymerization medium. Although radical concentration was increased at the higher monomer conversion range, the high MW of the tethered polymers limited termination, since termination is diffusion controlled. Increasing temperature can also increase $k_{\rm p}/k_{\rm t}$, probably also attributed to the diffusion controlled termination process.⁹ However, one should be cautioned that transfer reactions and other reactions that have higher activation energy may dominate. For example, thermal self-initiation (TSI) of styrene continuously generates new radicals during the reaction *via* a bimolecular / trimolecular pathway and gives untethered polymers.¹³ Fortunately, particle-brushes can be separated from these untethered polymers.

In this chapter, two methodologies to achieve high MW grafting of polymer brushes from nano-sized silica particles (SiO₂) will be presented. The first method is performed under ambient temperature using high pressure SI-AGET (activators generated by electron transfer) ATRP with low concentration of Cu catalyst.^{4b, 4c, 14} In contrast, the second method is carried out under elevated temperature and high particle dilution but ambient pressure using traditional (non-AGET) SI-ATRP. Using the former method, SiO₂-PMMA and SiO₂-PBMA with brushes' MW > 1 million were obtained in a short reaction time. Using the latter method, SiO₂-PMMA with ~1 million MW polymer brushes were obtained even without high pressure but took a longer time. SiO₂-PS using the second method was also synthesized.

Although this reaction is 6 times faster than normal SI-ATRP, MW was lower than that of SiO₂-PMMA, only ca. 0.3 million. Also, separation of SiO₂-PS from untethered polymers that generated by TSI was required. Therefore, further reaction optimization is required for more robust and higher MW production.

III.2. Experimental section

III.2.1. Materials

Methyl methacrylate (MMA) (Aldrich, 99%), n-butyl methacrylate (BMA) (Aldrich, 99%), methyl acrylate (MA) (Aldrich, 99%), and styrene (S) were distilled to remove inhibitor prior polymerization. Tris(2-pyridylmethyl)amine (TPMA) was synthesized following the previously reported procedure.¹⁵ Anisole (Sigma-Aldrich, 99%), dimethylformamide (DMF) (Chempur, >99.7%), copper(II) bromide (Fluka, 99%), copper (II) chloride (Aldrich 99.995%), copper (I) chloride (Aldrich, ≥99.99%), 4,4'-dinonyl-2,2'-dipyridyl (dNbpy) (Aldrich, 97%), 1,1,4,7,10,10hexamethyltriethylenetetramine (HMTETA) (Aldrich, 97%). ethvl 2bromoisobutyrate (EBiB) (Acros, 98%), ascorbic acid (AsAc) (Aldrich, 99%), were used as received. Silica nanoparticles (SiO₂), 30% solution in methyl isobutyl ketone (MIBK-ST, Nissan Chem. Corp. USA) with effective radius $R_{0,\text{TEM}} \cong 7.7 \pm$ 2.0 nm, 30% solution in isopropanol (IPA-ST-ZL, Nissan Chem. Corp. USA) with effective radius $R_{0,\text{TEM}} \cong 56.6 \pm 6.0$ nm, and 30% solution in ethylene gycol (KE-E10, Nissan Chem. Corp. USA) with effective radius ($R_{0,\text{TEM}} = 60 \pm 4.6 \text{ nm}$) were kindly donated by their supplier and used as received. All other chemicals and solvents were purchased from Aldrich or Fisher Scientific and used as received.

III.2.2. General example of polymerization procedure: Synthesis of PMMA using conventional SI-ATRP from SiO₂-Br

The general synthetic procedure and the corresponded reaction condition of PMMA using conventional SI-ATRP were discussed in Chapter II in details.

III.2.3. General example of polymerization procedure: Synthesis of PMMA using SI-AGET ATRP from SiO2-Br

Synthetic conditions: [MMA]₀ / [SiO₂-Br]₀ / [CuBr₂]₀ / [TPMA]₀ / [AsAc]₀ = 10,000/1/2/25/25 in anisole (48 vol%) and DMF (8 vol%), at 22 °C, 6 kar. TPMA (36.3 mg, 0.125 mmol), 10M solution of CuBr₂ in DMF (1mL, 0.010 mmol), solution of SiO₂-g-Br in anisole (0.5 mL of solution of 19.6 mg/10mL, 0.005 mmol Br), anisole (4.9 mL) and MMA (5.4 mL, 47 mmol) were placed in 25-mL Schlenk flask equipped with a magnetic stir bar. The flask was sealed, and the resulting solution was subjected to three freeze-pump-thaw cycles. AsAc (19 mg, 0.11 mmol) was weighted in Teflon ampoule (ca. 10 mL) which was placed in glass tube connected to Schlenk line. The sealed tube was evacuated and filled with argon three times. The tube was open and the reaction mixture (ca. 10 ml) was transferred into the Teflon ampoule via syringe in a stream of dry argon. Finally, the ampoule was sealed under argon atmosphere and placed in a high-pressure chamber. The pressure was increased to 6 kbar at 25 °C, and the reaction mixture was kept under these conditions for the desired time. After decompression, the samples were exposed to air, dissolved in THF (1 - 3 L) to form a solution, which was filtered through a pad of neutral alumina. The solution was then added dropwise to hexane (ca. 7 L). Precipitated material was filtered, washed with hexane and dried under high vacuum. Molecular weight distribution of attached polymer was analyzed after cleavage from SiO₂.

III.2.4. General Procedure for Cleavage of Polymer Brushes from Nanoparticles

SiO₂-polymer samples were cleaved with hydrofluoric acid (HF) before injection to SEC. A 49% HF(aq.) solution (1 mL) was added to 1 mL particle solution in tetrahydrafuran (THF) (~ 10 mg/mL), and the reaction was allowed to stir at room temperature overnight. An ammonium hydroxide solution (28.0-30.0% NH₃ basis) was very slowly added into the mixture in ice bath or with caution in liquid nitrogen bath, until the pH value was above 8. The cleaved polymer was recovered by evaporating the THF phase in air.

III.2.5. Synthesis of PMMA using ATRP from SiO₂-Br

Synthetic conditions: Table III-1, Entry 1. SiO₂-*g*-Br (0.3643 g, 0.186 mmol Br), CuCl₂ (0.0125 g, 0.093 mmol), dNbpy (0.2280 g, 0.558 mmol), DMF (0.4 mL), anisole (2 mL) and MMA (10 mL, 93 mmol) were added to a 25-mL Schlenk flask equipped with a magnetic stir bar. The flask was sealed, and the resulting solution was subjected to three freeze-pump-thaw cycles. After equilibration at room temperature, CuCl (0.0184 g, 0.186 mmol) was added to the solution under nitrogen flow and the flask was placed in preheated oil bath at 40°C. After a predetermined time, the flask was removed from the oil bath and opened to expose

the catalyst to air. The polymerization solution was diluted with THF, passed through neutral alumina and the polymer was isolated by precipitation into methanol.

Table III-1.	Experimental	conditions	and	properties	of	PMMA	brushes
prepared by	ATRP from 8Si	O2-Br.					

Entry	MMA/ SiO ₂ -Br	cata	alyst	ligand	
1	500/1	1	0.5	3	40 ºC
		CuCl	CuCl ₂	dNbpy	<i>M</i> _n =3,800
					Đ =1.13
2	500/1	1	0.43	2.8	60 ºC
		CuCl	CuCl ₂	dNbpy	<i>M</i> _n =15,000
					Đ =1.20
3	2,000/1	1	0.25	1.25	70 ºC
		CuBr	CuBr ₂	НМТЕТА	<i>M</i> _n =56,000
					Đ =1.16
4	20,000/1	10	-	20	70 ºC
		CuCl		dNbpy	<i>M</i> _n =410,000
					Đ =1.20

SiO₂-Br: ~2 Br/nm², Entry 1-2: anisole 20 vol%, DMF 4 vol%, Entry 3: DMF 4 vol%, Entry 4: bulk

III.2.6. Preparation of SiO₂-PMMA-b-PMA Grafted Chains using ATRP

0.10 g SiO₂-PMMA was dissolved in 16.8 mL DMSO in a 25 mL Schlenk flask. Then MA (4.2 mL, 0.047 mol), CuBr₂ (0.026 mg, 0.12 µmol) and Me₆TREN (2.5 µL, 9.4 µmol) were added. After three freeze-pump-thaw cycles, the flask was filled with nitrogen, the mixture was immersed in liquid nitrogen, and then 0.6 mg Cu(0) powder (~75 µm) (9.32 µmol) was quickly added. The flask was sealed with a glass stopper, evacuated, and back-filled with nitrogen four times. After melting the reaction mixture, the sealed flask was placed in an oil bath thermostated at 25

°C. After 124.0 h, the polymerization was stopped by opening the flask and exposing the catalyst complex in the solution to air. The final sample was diluted with tetrahydrofuran, precipitated in methanol, yielding white solid (M_n SEC cleaved = 2 350 000; $M_w/M_n = 1.18$).

III.2.7. Characterization

Monomer conversions were determined from the concentration of the unreacted monomer in the samples periodically removed from the reactions using a Finnigan TraceGC ultra gas chromatograph, equipped with a capillary column (Supelcowax-10, 30 m \times 0.25 mm \times 0.25 µm, Supelco). Anisole was used as internal standard for calculation of monomer conversions. Apparent molecular weight and molecular weight distribution were measured using SEC (Waters Microstyragel columns (guard, 10², 10³, and 10⁵ Å), THF eluent at 35 °C, flow rate = 1.00 mL/min). The detectors consisted of a differential refractometer (Waters 410, $\lambda = 930$ nm) and a multiangle laser light scattering (MALLS) detector (Wyatt Technology DAWN EOS, 30 mW, λ = 690nm). The apparent molecular weights were determined with a calibration based on poly(methyl methacrylate) (PMMA) standards using SECWin software from Polymer Standards Service. Absolute molecular weights were determined with the *dn/dc* values of 0.059 using Wyatt ASTRA software. Elemental analysis was conducted to determine ATRP initiator amount on modified silica nanoparticles (SiO₂-Br). Thermogravimetric analysis (TGA) experiments were performed with grafted particle samples placed in aluminum pans, using a Polymer Laboratories TG1000 instrument operating in the

20-580 °C temperature range, under nitrogen, at a heating rate of 20 °C/min. Thin (approximately monolayer) films of all nanoparticle systems were prepared by casting of dilute particle solutions (c = 3 mg/mL in toluene) on poly(acrylic acid) (PAA) substrate and subsequent thermal annealing in vacuum for 24h at T = 120 °C. Equilibrated films were lift-off by water immersion and transferred onto Cugrids. The particle film morphology was imaged by transmission electron microscopy (TEM) using a JEOL FX2000 electron microscope.

III.3. Result and discussion

III.3.1. Synthesis of SiO₂-Br

Functionalized silica particles $8SiO_2$ -Br ($R_{0,TEM} \cong 7.7 \pm 2.0$ nm) and $60SiO_2$ -Br ($R_{0,TEM} \cong 56.6 \pm 6.0$ nm) were prepared by reacting respectively 1-(chlorodimethylsilyl)propyl 2-bromoisobutyrate^{5a} or 2-bromoisobutyryloxyhexyltriethoxysilane ^{6a} with the silanol groups on the SiO₂ surface. On the basis of elemental analysis, $8SiO_2$ -Br had average ~2600 initiating sites (~ 2 Br/nm²), whereas $60SiO_2$ -Br had 10^5 sites (also ~ 2 Br/nm²). Lower initiator density (~600 initiating sites (0.5 Br/nm²) per each $8SiO_2$ -Br) was obtained when chlorotrimethylsilane was used in a mixture with 1-(chlorodimethylsilyl)propyl 2bromoisobutyrate to block some silanol groups and reduce initiator density. The measurement of the real number of growing chain was discussed in Chapter II.

III.3.2. High pressure SI-AGET ATRP

The choice of AGET ATRP with low concentration of copper was dictated by plausible lower solubility of the catalyst under high-pressure and higher robustness of the system, a simplified set up, when CuBr₂ complex in the presence of reducing agent was used at the initial stages of the polymerization. The reactions were carried out in closed vessels, without stirring, for a specified time and terminated by exposing the reaction mixture to air. Several polymerizations were carried out at 6 kbars pressure using the following reaction conditions: [MMA]₀/[-Br]₀/[CuBr₂]₀/[TPMA]₀/[AsAc]₀ = 10,000/1/2/25/25 in anisole (46 vol%) and DMF (8 vol%) at 22 °C, where TPMA is tris(2-pyridylmethyl)amine (ligand), AsAc is ascorbic acid (reducing agent) and DMF is dimethylformamide (Entries 2-3, Table III-2).

 Table III-2. Experimental conditions and properties of polymers prepared by

 AGET ATRP from SiO₂-Br under high pressure at ambient temperature.

Entry	Monomer	DP_{target}	Initiator	Pressure (kbar)	Time (h)	M _{n,SEC}	Ð	σ (chain/nm²)
1ª	MMA	10,000	8SiO ₂ -Br	10 ⁻³	48	62,000	7.98	-
2ª	MMA	10,000	8SiO ₂ -Br	6	7	1,610,000	1.28	0.32
3ª	MMA	10,000	8SiO ₂ -Br	6	8	1,300,000	1.13	0.14
4ª	MMA	100,000	8SiO ₂ -Br	6	18	1,100,00	1.40	0.05
5ª*	MMA	100,000	60SiO ₂ -Br	6	4	27,000,000	1.17	0.14
6ª	BMA	10,000	8SiO ₂ -Br	6	4	2,300,000	1.16	0.04
7 ^b	MA	400,000	8SiO ₂ -Br	10 ⁻³	125	2,350,000	1.18	-

^a M / -Br / CuBr₂ / TPMA / AsAc = DP_{target} / 1 / 2 / 25 / 25; T=22 °C, in anisole (48 vol%) and DMF (8 vol%); ^b MA/-PMMA-Br/Cu(0)/CuBr₂/Me₆TREN = 400,000/--/80/1/81, 25 °C, MI-Entry 2; ^c $M_{n, \text{ theo}}$ =([M]₀/[-Br]₀) × conversion. Entry 1,2,4,5,6,7 – SiO₂-Br ~ 2 Br/nm², entry 3 - SiO₂-Br ~ 0.5 Br/nm². *analyzed by MALLS.

Figure III-1 presents the evolution of MWD with the reaction time for an AGET ATRP of methyl methacrylate (MMA) initiated from $8SiO_2$ -Br (conditions as in Entry 2, Table III-2). The polymers were detached from SiO_2 surface by dissolving SiO_2 with HF, and analyzed by SEC. The entire molecular weight distribution (MWD) moved smoothly towards higher MW, demonstrating good control over polymerization. On the contrary, when the polymerization was carried out under the same conditions but under ambient temperature and normal pressure, no control over the polymerization was obtained (Entry 1, Table III-2). Note that the currently employed AGET condition can rapidly increase Cu(I) and so radical concentration. Therefore, the condition is suitable for high pressure or high temperature with depressed k_i , but not for ambient pressure conditions.



Figure III-1. Evolution of molecular weight distribution during polymerization for AGET ATRP of MMA under high pressure. Experimental conditions:

MMA/-Br/CuBr₂/TPMA/AsAc=10,000/1/2/25/25; T=22 °C, in anisole (48 vol%) with DMF (8 vol%), P=6 kbar. Polymers were analyzed by SEC after etching SiO₂ with HF.

Thermogravimetric analyses of precipitated polymers show very high content of organic fraction (92-99.4%). The grafting densities of polymer chains were calculated based on the known MW and the amount of polymer from thermogravimetric analysis. The highest grafting density of 0.32 chain/nm², suggests that brushes can be considered as "semi-diluted density" brushes, Entry 2, Table III-1. Grafting efficiency 16% was calculated from the ratio σ/σ_0 where σ_0 is the number of initiating sites and σ is the number of the tethered chains per nm², respectively. Such low grafting efficiency could be the consequence of relatively fast growth of polymer chains with low catalyst concentration and resulting steric hindrances in surface initiated polymerizations.¹⁶ The initiation efficiency increased to 27% when the SiO₂-Br with a lower content of attached initiator was used, ~600 initiating sites on 8SiO₂-Br (~ 0.5 Br/nm²), Entry 3, Table III-2.

Additional experiments were performed in order to determine the effect of targeted degree of polymerization (DP_{target}, [M]₀/[I]₀), size of SiO₂ and type of monomer on the polymerization of methacrylates via AGET ATRP. Table III-2 lists the results from these experiments. Our previous high pressure AGET ATRP of linear polymers showed a decrease of the polymerization rate with increasing DP_{target}, while maintaining the good control over molecular weight distribution.^{11b} The same effect was observed for multifunctional initiators (Entry 4). However,

grafting density was significantly reduced, i.e. 0.05 chain/nm² (2.5% initiation efficiency) when compared to the reaction with DP_{target} =10,000. This could be rationalized with the decrease of catalyst concentration. Entry 5 illustrates the effect of the size of SiO₂-Br on polymerization of MMA. $60SiO_2$ -Br was employed as initiator in this case. Each functionalized $60SiO_2$ -Br had ~10⁵ initiating sites on the surface which corresponds to~ 2 Br/nm², similar to that of 8SiO₂-Br. Molecular weight of the PMMA brushes was significantly higher and, according to SEC analysis, exceeded exclusion limit of the SEC columns (MALLS indicated a value in the range of M_w=27,000,000). Based on the absolute molecular weight obtained from MALLS, initiation efficiency could be slightly higher for $60SiO_2$ -Br in comparison to $8SiO_2$ -Br ones (7%, 0.14 chain/nm²). Entry 6 in Table III-1 shows the results of the polymerization of BMA also proceeded with good control.

III.3.3. High particle dilution by conventional SI-ATRP

The preliminary results (Table III-1, Entry 4) show that SiO₂-PMMA with brushes of 0.4 million MW can be obtained under ambient pressure. In this experiment, halogen exchange was introduced to increase the initiation efficiency. This was done by using CuCl catalyst instead of its Br analogs. Readers are referred to Chapter II for more details. The reason for such high MW at ambient pressure is probably due to the use of a higher temperature of 70 °C instead of ambient temperature. This is because the energy of activation of propagation is larger than that of termination, so increasing the reaction temperature can increase k_p/k_t .⁹ However, this reaction became highly viscous after the MW increased above 0.4 million. The reaction was stopped, since the \mathcal{D} began to increase dramatically at this stage. This increase in \mathcal{D} could be attributed to the decrease of deactivator diffusion,¹⁷ especially since the polymer congestion was high on surface. This could be also rationalized by the increase of radical concentration at high monomer conversion. Based on the results in Table III-1, Entry 4, other reaction conditions were explored, as shown in Table III-3. The effect of deactivator concentration was tested by varying the amount of deactivator, Table III-3, Entry 1. Interestingly, the added deactivator did not only improve the \mathcal{D} in the beginning of reaction, but it did delay the jump in \mathcal{D} until MW ~1 million. Polymerization kinetics and MW/ \mathcal{D} evolution plots were created to study this particular reaction in detail, Figure III-2.

Linear kinetics and MW evolution were observed in the beginning of the reaction. Polymerization rate and \mathcal{D} dramatically increased at 30% conv. One explanation is the increase of radical concentration at high monomer conversion. However, the rate increase occurred at the same time when the reactions viscosity increased. In conventional ATRP, there was no added supplemental thermal-initiator to generate new radicals in the polymerization (except S self-initiation). Therefore, both the polymerization rate and \mathcal{D} rises could be attributed to the increase of reaction viscosity. The increase of reaction rate could also be rationalized to the decrease of deactivator diffusion to particle surfaces at high MW regime.

Entry	Initiators	DP _{target}	Time (h)	Conv. (%)	M _{n,SEC}	M _w /M _n
1	SiO ₂ -Br	20,000	48	48.3	940,000	1.29
2	SiO ₂ -Br	60,000	58	20.1	987,000	1.22
3	SiO ₂ -Br	80,000	70	13.2	1,050,000	1.23
4	EBiB	80,000	21	< 5	150,000	1.53

Table III-3. Experimental conditions and properties of polymers prepared by high particle dilution and high temperature MMA SI-ATRP from SiO₂-Br.

All reactions were performed in DMF (5 vol%); SiO₂-Br ($R_{0,TEM} \cong 7.7$ nm) ~ 0.30 mmol Br/g ~ 0.88 Br/nm². Possible number of growing chains is the average σ at different conversion ~ 0.58 chains/nm². EBiB stands for ethyl 2-bromoisobutyrate, which is a structurally similar untethered initiators.

The preliminary results (Table III-1, Entry 4) show that SiO2-PMMA with brushes of 0.4 million MW can be obtained under ambient pressure. In this experiment, halogen exchange was introduced to increase the initiation efficiency. This was done by using CuCl catalyst instead of its Br analogs. Readers are referred to Chapter II for more details. The reason for such high MW at ambient pressure is probably due to the use of a higher temperature of 70 °^C instead of ambient temperature. This is because the energy of activation of propagation is larger than that of termination, so increasing the reaction temperature can increase *kp/kt.*⁹ However, this reaction became highly viscous after the MW increased above 0.4 million. The reaction was stopped, since the *D* began to increase dramatically at this stage. This increase in *D* could be attributed to the decrease of deactivator diffusion,¹⁷ especially since the polymer congestion was high on

surface. This could be also rationalized by the increase of radical concentration at high monomer conversion. Based on the results in Table III-1, Entry 4, other reaction conditions were explored, as shown in Table III-3. The effect of deactivator concentration was tested by varying the amount of deactivator, Table III-3, Entry 1. Interestingly, the added deactivator did not only improve the \mathcal{D} in the beginning of reaction, but it did delay the jump in \mathcal{D} until MW ~1 million. Polymerization kinetics and MW/ \mathcal{D} evolution plots were created to study this particular reaction in detail, Figure III-2.

Linear kinetics and MW evolution were observed in the beginning of the reaction. Polymerization rate and D dramatically increased at 30% conv. One explanation is the increase of radical concentration at high monomer conversion. However, the rate increase occurred at the same time when the reactions viscosity increased. In conventional ATRP, there was no added supplemental thermal-initiator to generate new radicals in the polymerization (except S self-initiation). Therefore, both the polymerization rate and D rises could be attributed to the increase of reaction viscosity. The increase of reaction rate could also be rationalized to the decrease of deactivator diffusion to particle surfaces at high MW regime.

Table III-3

Table III-3 Entry 2 and 3, are reactions with higher target DP (reactions that were further diluted by addition of monomer). These three reactions with different nanoparticle dilutions were compared with each other. All reactions were stopped
at the same MW to compare their reaction rates and MWD controls. As expected, the higher dilution reactions were slower and yielded polymers with lower *Đ*. This could be attributed to the decrease in particle collisions and the reduced radical concentration during polymerization. Therefore, the probability of the interparticle termination was significantly reduced.

Entry 4 shared the same reaction condition with Entry 3, but initiators were replaced with structurally similar untethered ethyl 2-bromoisobutyrate (EBiB). Surprisingly, MWD of Entry 4 became broad at ca. 5% monomer conversion. Longer polymerization further increased *Đ*. This could be attributed to the different dispersion behavior of tethered polymers and untethered polymers.



Figure III-2. a) Kinetics and b) MW and *D* evolution plots of SI-ATRP reactions of Table III-3, Entry 1.

Scheme III-1 depicts the diffusion behavior of tethered polymers grafted from particles and untethered polymers in bulk. Note that the polymers attached to

the particles are much farther away from each other than homogeneously distributed untethered polymers. Also, since larger objects are controlled by translational diffusion, the rate of interparticle termination was expected to be lower than inter-homopolymers termination. Moreover, the probability of intra-particle termination between chains on the same surface was found low according to the discussion in Chapter I. These together created a new concept to produce high MW PMMA, facilitated by grafting polymers from surfaces, diluting particles concentration and increasing of temperature. The hypothesis is the following: first, particles were highly diluted at the beginning of the reaction and sufficiently depressed the interparticle termination. Therefore, only limited interparticle termination could occur even when "classical" $k_{\rm t}$ should be very high at low viscosity and conversion. At high conversion, k dramatically decreased due to the substantial increase of reaction viscosity, so termination was also limited. Also, deactivator diffusion could be limited and radical concentration are high, thus both polymerization rate and *D* increased.



Scheme III-1. Scheme compares the diffusion behaviors of tethered polymers grafted from particles with untethered polymers in bulk. Illustration

shows that particles are much farther away from each other than homogeneously distributed untethered polymers.

III.3.4. Concept of high temperature and high particle dilution styrene SI-ATRP

The idea of high dilution was expanded to styrene (S) polymerization. Preliminary results at 70 °C revealed that polymerization could not reach 0.1 million MW at reaction time in days. Therefore, the reaction temperature was increased to 150 °C. Table III-4**Error! Not a valid bookmark self-reference.** lists typical k_p , k_t and calculated k_l/k_p^2 values of S at various temperatures. The k_l/k_p^2 value is a parameter that affects the dead chain fraction (DCF) in a radical polymerization process, Equation III-1.⁷ As a consequence, the ratio of DCF at 150 °C. In other words, a reaction targeting the same MW at 150 °C has 110 times less terminated chains as compared to a reaction at 50 °C while holding the rest of the reaction conditions constant.

Table III-4. List of typical k_p and k_t values of S radical polymerization at various temperatures.

$k_{\rm p}/k_{\rm t}$ of S varied by Temp.								
Т	Approximate <i>k</i> p	Approximate <i>k</i> t	~ k t/ k p ²	DCF				
°C	L.mol ⁻¹ s ⁻¹	L.mol ⁻¹ s ⁻¹		Ratio				
50	220	7 x 10 ⁷	1450	110				
100	1200	14 x 10 ⁷	97.2	7.4				
150	4000	21 x 10 ⁷	13.1	1				

However, one should be cautioned that transfer reactions and other side reactions which have higher activation energies may dominate at higher temperatures.⁹ In S radical polymerization, thermal self-initiation (TSI) of styrene is an unavoidable process at high temperatures. TSI of S continuously generates new radicals during the reaction *via* a bimolecular / trimolecular pathway and gives untethered polymers.¹³ Fortunately, studies have shown that SiO₂-PS can be separated from untethered polystyrene generated by TSI of S, Scheme III-2.^{13, 18}

DCF = 2
$$[\ln(1-p)]^2$$
 DP_T $\frac{1}{t} \frac{1}{[M]_0} \frac{k_t}{k_p^2}$

Equation III-1. Equation shows the dependence of dead chain fraction on monomer conversion (p), target DP (DP_T), initial monomer concentration ([M]₀), and rate coefficients of termination (k) and of propagation (k_{p}).



Scheme III-2. Scheme depicts that TSI effect can concomitantly generate new chains during S SI-ATRP from SiO₂. However, these new chains could also be removed by centrifugation.

A reaction was carried out to demonstrate the ability of this process. A solvent with high b.p > 150 °C, good miscibility with S monomers, and good solubility of high MW PS is desired. Solvent miscibility with S is important, as bad solubility with high MW PS could cause PS precipitation. Ethylene carbonate fits all these requirements and was employed in a trial reaction. The reaction condition was: $[SiO_2-Br^*]_0$: $[S]_0$: $[CuBr]_0$: $[CuBr2]_0$: $[PMDETA]_0 = 1 : 30,000 : 20 : 5 : 25;$ and the flask was equipped with a rare-earth magnet stir bar @ 150 °C in 66 vol% ethylene carbonate. (*SiO₂-Br: apparent initiator density = 0.090 mmol Br/g or 1.9 initiators/nm² with $R_{0,TEM} \cong 56.6$ nm, density of growing chain = 0.029 mmol Br/g or 0.63 chain/nm².) Note that larger particles ($R_{0,TEM} \cong 56.6$ nm instead of $\cong 7.7$ nm) were employed in this section, since larger particles are easier to be removed from untethered polystyrene.

Polymerization kinetics and MW/D evolution plots are shown in Figure III-3. A slightly curved kinetic plot was observed under both reaction conditions. A similar phenomenon in SI-reversible addition-fragmentation chain transfer (SI-RAFT) polymerization was previously reported.¹⁸ The kinetic plot is curved because TSI of S generates more radicals at the beginning of the reaction, since TSI is dependent on monomer concentration to a second or a third power.¹⁹ Values of theoretical $M_{\rm h}$ ($M_{\rm h,theo}$) was calculated using the real number of growing chains (graft density), instead of the apparent initiator density. Experimental $M_{\rm h}$ ($M_{\rm h,exp}$) clearly deviated from $M_{\rm h,theo}$. This observation agrees with the TSI mechanism

since TSI continuously generates new polymer chains of lower MW which results in a gradual reduction of $M_{n,exp}$ and a boarder MWD.

Finally, SiO₂-PS and untethered polymers were separated and injected to SEC, Figure III-4. Readers are referred to the experimental section in Chapter II for precise procedures. The trace of untethered polymers is boarder and has lower MW compared with tethered polymers. Also, this trace has a tail at the low MW region, which could be the fractions of both low MW polymers and dead chains. This phenomenon suggested the participation of TSI.²⁰ New radicals generated by TSI can grow new chains with low MW or get terminated due to the short lifetime of radicals. In another cases, SEC traces of untethered polymers and tethered polymers overlapped with each other.¹⁸ The lack of high MW fraction of untethered polymers at ca. 300,000 in the current work was probably attributed to the catalyst diffusion behavior. Since the congestion is high on surfaces as mentioned in Chapter II, the polar copper catalyst complex diffusion into the non-polar polymer layer to reach chain-end at high polymer MW could be problematic. Thus, the radical concentration might be higher on the surface resulting in faster propagation and longer tethered polymers. Note that this polymerization was to showcase the ability of this process and the possibility to separate SiO₂-PS from unterthered polystyrene. Therefore, lower MW PS compared with PMMA grafts of up to 0.3 million was obtained. This polymerization of S requires further optimization for synthesis of higher MW polymers.



Figure III-3. a) Kinetics and b) MW and \mathcal{P} evolution plots of SI-ATRP with the following condition: $[SiO_2-Br]_0$: $[S]_0$: $[CuBr]_0$: $[CuBr2]_0$: $[PMDETA]_0 = 1$: 30,000 : 20 : 5 : 25; with rare-earth magnetic stir bar @ 130 and 150 °C in 66 vol% ethylene carbonate.



Figure III-4. Size exclusion chromatographic traces for the tethered (solid curve) and untethered (broken curve) polymers at 7.5 h of polymerization of

styrene (S) in $[SiO_2-Br]_0$: $[S]_0$: $[CuBr]_0$: $[CuBr2]_0$: $[PMDETA]_0 = 1 : 30,000 : 20 : 5 : 25$; with rare-earth magnetic stir bar @ 130 and 150 °C in 66 vol% ethylene carbonate.

III.3.5. Chain extension experiment

Chain extension experiment can be used to confirm chain end functionality. For example, the PMMA chain ends preserved their activity during polymerization under high pressure (SiO₂-PMMA, Entry 2, Table III-2) since they were successfully extended with poly(methyl acrylate) (MA), Entry 7, Table III-1. SEC traces moved towards higher molecular weight region confirming that polymer brushes prepared under high pressure AGET ATRP can be used for the block copolymers synthesis, Figure III-5.



Figure III-5. Evolution of molecular weight distribution during polymerization for AGET ATRP of MA from SiO₂-g-PMMA-Br under high pressure.

Experimental conditions: MA/-PMMA-Br/Cu(0)/CuBr₂/Me₆TREN = 400,000/1/80/1/81; T=25 °C, in anisole (48 vol%) with DMF (8 vol%), P=6 kbar. Polymers were analyzed by SEC after etching SiO₂ with HF.

III.3.6. Morphology analyses

The hybrid of SiO₂-PMMA with M_{n} = 1,610,000 prepared under 6 kbar from 8SiO₂-Br (Entry 2 Table III-2) was analyzed by transmission electron microscopy (TEM). The TEM of thin films prepared from the bulk particles are shown in Figure III-6a. One can notice a uniform distribution of SiO₂ in PMMA matrix. Hybrid with the polymer brush grafted polymerization degree ($N_{\rm G}$) = 16,000 was compared with hybrids containing PMMA brushes with smaller $N_G = 4064$; 560; 150; 38, synthesized by ATRP under normal pressure (synthetic conditions in Experimental Part, Table III-1). The average particle surface-to-surface distance (d) was calculated and plotted as function of N_G in Figure III-6. Applying DC model discussed in Chapter II, the resulting scaling ratio $d \sim N_{\rm G}^{0.52}$ for polymer brushes with high MW indicates the brushes above certain N_G switch from concentrated brush regime to the semi-diluted brush regime (scaling law $d \sim N_G^{0.80}$). This result is as expected since the previous calculated N_c for 8SiO₂-Br is only 250. The detailed studies on properties of these systems and their dependence on particle curvature, graft density, and $N_{\rm G}$ and will be discussed in Chapter V.



Figure III-6. Representative bright field transmission electron micrographs of SiO₂-PMMA particle monolayers. Panel a: Grafted degree of polymerization of polymer brush N_G = 16000, σ = 0.32 chain/nm². Panel b: N_G = 4064, σ = 0.55 chain/nm². Panel c: N_G = 150, σ = 0.62 chain/nm². Panel d: N_G = 560, σ = 0.72 chain/nm². Panel e:. N_G = 38; density of surface-grafted chains σ = 0.6 chain/nm². Panel f: Plot of average particle surface-to-surface distance *d* for various particle samples as determined from panel a-e. Scaling $d \sim N_G^{0.80}$ indicates the concentrated brush regime, the reduced scaling $d \sim N_G^{0.52}$ indicates transition to semidiluted brush regime for large degree of polymerization (N_G > 560). Scale bar is 200 nm.

III.4. Conclusion

In a summary, two methodologies to achieve high MW grafting of polymer brushes from nano-sized silica particles were discussed. The first method was performed under ambient temperature using high pressure SI-AGET ATRP with low concentration of Cu catalyst. In contrast, the second method was carried out under elevated temperatures and high particle dilution but ambient pressure using traditional SI-ATRP. The idea of both methods was to suppress interparticle termination. Since termination is controlled by translational diffusion in a particlebrush system, high pressure, or high temperature and high dilution were effective in suppressing termination. Using the high pressure approach, SiO₂-PMMA and SiO_2 -PBMA with brushes' MW > 1 million were obtained. The main advantage of this method is fast reactions, but it requires special facilities to increase pressure. Using the latter method, SiO₂-PMMA with ~1 million MW polymer brushes were obtained even without high pressure. However, the reaction time was much longer. Finally, SiO₂-PS using the second method was also synthesized. The reaction was extremely slow at 70 °C due to low $k_{\rm p}/k_{\rm t}$ S values. While increasing the temperature to 150 °C allowed the reaction to reach high MW in 12 h, low MW polymers and dead chains generated by TSI of S could contaminate the systems. Fortunately, particles brushes could be extracted from the homopolymer impurities. After purification, MW of SiO₂-PS of ca. 0.3 million was obtained, at 150 °C. Further optimization of this method is required for SiO_2 -PS of > 0.3 million MW and faster reaction time. Finally, the synthesized particle-brushes exhibited semi-diluted brush architecture as predicted in the prior chapter.

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Chapter IV

Strategies for the Synthesis of Thermoplastic Polymer NC Materials with a High Fraction of Inorganic Filling

Preface The fundamental understandings of SI-ATRP were examined in the previous two chapters. The utilities of the synthesized particle-brush materials are explored starting from this chapter here on in. As discussed in Chapter I, the creation of more robust commercial plastics by embedding fillers has drawn considerable attention in both academia and industry for over two decades. However, fillers tend to aggregate to minimize surface energy, resulting in loss or diminution of desired properties. Grafting polymer brushes from fillers has successfully aided the filler dispersion in a matrix when the degree of polymerization (DP) of tethered chains exceeded the matrix chains. Synthesizing

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particle-brushes with ultra-high MW was demonstrated in Chapter II. However, high MW of grafts decreases filler loading and the corresponding desired properties. Consequently, a new strategy one that can aid particle dispersion with shorter grafted brushes is desired. In this chapter, the governing parameters controlling the miscibility of particle additives within polymeric host media were analyzed for the particular case of SiO_2 fillers embedded within a poly(methyl methacrylate) (PMMA) matrix. For athermal polymer-graft modification of particles, corresponding to the same chemical composition of grafted and matrix polymer, compatibility is a sensitive function of the DP of grafted and host polymer chains, as well as the particle radius. In agreement with theoretical predictions, uniform particle dispersion is observed if the DP of grafted chains is comparable to (or exceeds) the corresponding value of the polymer matrix. The resulting restriction to the high DP limits the accessible inorganic fraction that is attainable in athermal particle/polymer blends. In contrast, favorable enthalpic interactions between grafted polymer chains and the polymeric host, as realized in the case of poly(styrene-r-acrylonitrile)-grafted SiO₂ (SiO₂-PSAN) embedded within PMMA matrix, facilitated thermodynamically stable and uniform particle dispersion across the entire compositional range, even in the limit of large particle size, short grafted chains, and high molecular matrix chains. The synthesis of thermoplastic composite materials with inorganic fraction exceeding 50 vol % by combining quantitative optical limiting within the UV frequency range and polymer-like mechanical properties will be discussed.

IV.1. Introduction

Nanofillers (NFs) additives (both organic and inorganic) are ubiquitously being used to augment the physicochemical properties of polymer materials while retaining their advantageous processability and thus broaden the range of technological applications of polymer materials.¹ Examples include the addition of sheet silica particles (such as montmorillonite) or nanotubes to improve the mechanical performance of polymeric hosts (e.g., for automotive parts), and the addition of silica particles and colloids to tailor the thermal expansion of polymeric substrates (e.g., for chip packaging), or the modulation of dielectric and transport properties for the design of optical materials, supercapacitors, or protective coatings.^{1b, 2} The interest in NF additives derives from the possibility to achieve a desired property enhancement at low concentrations of added NFs while maintaining other auxiliary properties such as optical transparency and processability—although it should be mentioned that whether the benefit of NFs can be realized depends heavily on the ability to control the particle dispersion. The role of microstructure on the properties of polymer nanocomposites has been widely reviewed in literature, and often (in case of isotropic fillers) uniform particle dispersion is viewed as the most favorable morphology to achieve maximum property enhancement (except for percolated structures that can be favorable when conductive pathways are desired).^{1b, 2e}

The intimate relation between dispersion morphology and properties of nanocomposites (or its aptitude toward physical aging if nonequilibrium conditions are set by the fabrication process) has fueled research to elucidate the governing parameters that control the mixing of particle additives in polymeric media. A common approach to facilitate miscibility of NFs within a polymer matrix is by means of grafting polymeric ligands that are chemically identical to the host polymer. The thermodynamics of mixing in these athermal polymer-grafted particle (in the following called "particle-brush") dispersions is determined by the subtle interplay of entropic effects that render polymer-grafted SiO₂ (particle-brush) miscibility a sensitive function of the architecture of the particle-brush and the DP of the matrix chains (the term "architecture" is used to describe the "geometrical" characteristics of the particle-brush, i.e., surface curvature, density, and DP of surface-grafted chains).³ The interplay between various parameters is generally complex, and although significant progress in the understanding of the physics of particle-brush dispersions has been made, several challenges exist, for example, in the area of computational modeling of the phase behavior of particle-brush dispersions. The objective of this contribution is to present a systematic experimental evaluation of the governing parameters that control the dispersion of particle-brush model systems within polymeric media using a new material system in which precise control of polymer brush architecture and composition is achieved by means of surface-initiated atom-transfer radical polymerization (SI-ATRP).⁴ By variation of the polymer-graft composition to facilitate both athermal and favorable interaction, this method allows to contrast the role of entropic and enthalpic

contributions and to establish criteria for the synthesis of thermoplastic polymer nanocomposites with high inorganic concentration. It is hoped that the presented results will provide a reference for comparison with theoretical simulations but also stimulate new design strategies for the synthesis of novel functional nanocomposite (NC) materials.

The structure of the paper is as follows: First, a brief review of prior studies on particle–brush/polymer dispersions is provided to establish the context for the interpretation of our results. Subsequently, the miscibility characteristics of a series of athermal particle-brush model systems with systematically varied architecture will be discussed, and the limitations of the athermal compatibilization approach toward technologically relevant hybrid materials will be highlighted. Finally, favorable interactions between particle–brushes and the polymeric embedding medium that provide an efficient means to "override" unfavorable entropic contributions will be discussed. A system that utilizes the entropic interaction to facilitate nanocomposites in which the inorganic constituent assumes the role of the majority component will be presented.

Before proceeding, a brief review of particle–polymer compatibility studies is in order. Here, only a selections of works will be considered that are deemed to be of particular relevance for the present work—for a more comprehensive summary of the literature in this field, the reader is referred to recent review articles by Green and Ganesan.⁵

IV.2. Background

Because chemical interactions between inorganic and polymeric media cannot easily be controlled (and in most instances will be unfavorable toward mixing), most of the research on the stabilization of particle/polymer dispersions has focused on athermal polymer/particle-brush blends. A typical example is presented by particle-brush fillers in which the particle has surface-modifications containing a polymer that is chemically equivalent to the polymeric matrix. Here it is assumed that the grafting is *dense*, that is, $\sigma^{-1} < N_G a^2$ where σ denotes the grafting density, a the length of a repeat, and $N_{\rm G}$ the grafted DP of polymer brush. Since in such a system (to a first approximation) there is no change in net interactions upon particle addition, the free enthalpy of mixing is determined by entropic contributions only. Three major sources for entropic contributions have been distinguished in the literature. The first contribution is associated with the randomization of particles' center-of-mass positions during mixing that result in increased configurational entropy of the system—this contribution will generally favor mixing. However, because of the small number of degrees of freedom (DoF) associated with particle fillers that are significantly larger than the polymer repeat (as is the case for most technologically relevant systems), contributions resulting from configurational entropy changes typically make only a negligible contribution to the overall free energy of mixing (this is in contrast to small molecular mixtures where configurational entropy is often dominant).⁶ A second contribution is associated with the effect of particle fillers that reduce the number of chain

conformational DoF of the polymeric host due to the excluded volume presented by the particle filler.⁶⁻⁷ The decrease of chain conformational entropy counteracts mixing and results in depletion-like attraction (and phase separation) of embedded particles. A third contribution to the entropy of mixing relates to the possibility of matrix chains to interpenetrate the "shell" of grafted polymer chains (in the case of particle–brush fillers). The penetration of the brush by matrix chains raises the entropy of the mixed as compared to the phase-separated state and thus provides a driving force toward mixing of particle-brush and host polymer.⁸ An important basis for the evaluation of the thermodynamic stability of athermal particlebrush/polymer dispersions has therefore been the theoretical analysis of the parameters that control the interaction of planar polymer brushes in contact with chemically identical polymer (melt) chains.⁹ In the case of planar polymer brushes, two major regimes are distinguished corresponding to the interpenetration or expulsion of the matrix chains within the brush (the so-called "wet" and "dry" brush regimes) depending on whether the DP of surface-grafted chains (N_G) exceeds or is lesser than the DP of the matrix chains ($N_{\rm M}$), respectively. Extensions to the original model for planar brushes to curved surfaces (corresponding to, for example, colloidal systems) have suggested that the condition for brush interpenetration (i.e., the wet brush regime) broadly follows the trends observed for planar systems with $N_{\rm G} > \alpha N_{\rm M}$, where $\alpha < 1$ is a parameter of the order of unity that accounts for the decrease of chain crowding with increasing surface curvature.^{8, 10} Experimental and theoretical studies have broadly confirmed this prediction.¹¹ It should be noted that the physical origin of the "autophobic dewetting"

of particle-brushes that is observed when particle-brushes are embedded within a high molecular matrix (i.e., $N_G < \alpha N_M$) remains a subject of debate. For example, recent simulation studies by Meng et al. suggest that multiparticle effects are responsible for particle aggregation.¹²

A comment should be made regarding the applicability of the above arguments in discerning the compatibility of particle–brush/polymer blends. In particular, the emphasis of entropic contributions (i.e., the neglect of particle-brush–matrix interactions) is expected to be appropriate only for densely grafted brushes. This is because in sparse brush systems the interaction between matrix chains and the particle surface can have a relevant (and often unknown) contribution to the overall thermodynamic driving force for mixing. Further complications are expected to arise due to the compositional heterogeneity of polymer-grafted particles that is expected to be intrinsically higher for sparsely grafted systems.¹³ The compatibility of sparsely grafted particle-brushes to polymer hosts is therefore more system dependent and less amenable to generalizable arguments.

From the above discussion it follows that compatibility in athermal particlebrush dispersions can be expected only if $N_G \ge N_M$. The restriction severely limits the attainable inorganic fraction in athermal miscible composites because—for values of N_M corresponding to those of technologically relevant thermoplastics the majority of the volume of particle-brush is polymeric due to high molecular

surface-grafted chains. A solution to this challenge is provided by tailoring the surface chemistry such as to facilitate favorable interactions between the graft and matrix chains.¹⁴ In this case, the (negative) enthalpy of mixing per particle-brush due to graft–matrix interactions can be estimated to be $\Delta H_{\text{mix}} \approx (k_{\text{B}}T)n_{\text{G}}\xi N_{\text{G}}\chi_{\text{GM}}$ where n_G denotes the number of grafted chains of a particle-brush, χ_{GM} is the Flory–Huggins parameter describing the interactions between graft and matrix chains, $k_{\rm B}$ is the Boltzmann constant, and ξ is the "graft penetration" parameter that measures the probability of contacts between a grafted chain and the matrix (ξ is generally expected to depend on χ_{GM} , N_G , N_M , and σ ; see ref 10).¹⁰ Since the enthalpy of mixing will generally dominate entropic contributions, compatibility of the particle/polymer composite is expected even for entropically unfavorable conditions. The main objective of the present contribution is to demonstrate the dominating influence of enthalpic interactions on the morphology of polymermatrix nanocomposites and to illuminate its role in facilitating high inorganic content composite materials. Scheme IV-1 illustrates the relevant parameters that determine the stability of polymer NC materials.



Scheme IV-1. Illustration of the relevant geometrical and molecular parameters governing the dispersion of particle-brushes in polymer embedding materials (see text for more details).

IV.3. Experimental section

IV.3.1. Homopolymers

Polystyrene (PS, relative molecular weight measured by SEC M_n = 100 000, molecular weight dispersity index D = 1.02) and poly(methyl methacrylate) (PMMA, relative molecular weight measured by GPC M_n = 93 000 and 960 000 with molecular weight dispersity index D = 1.01 and 1.03, respectively) were obtained from Polymer Source and used without further purification.

IV.3.2. Particle-brush synthesis

SiO₂ were obtained from Nissan Chemicals. Methyl methacrylate (MMA), styrene (S), and acrylonitrile (AN) monomers were obtained from Aldrich and purified by passing through a column filled with alumina. The synthesis of PMMA

and PS-grafted particle-brush (SiO₂-PMMA and SiO₂-PS) systems was performed using surface-initiated atom-transfer radical polymerization (SI-ATRP) as described previously and in Chapter II.¹⁵ For the synthesis of poly(styrene-*r*-acrylonitrile) SiO₂-PSAN a Schlenk flask was charged with 0.40 g of initiator-modified silica nanoparticles (0.477 mmol Br/g silica; 0.19 mmol of ATRP initiator sites) and anisole (12.1 mL). The mixture was stirred for 24 h until a clear homogeneous mixture was formed. Styrene (4.5 mL, 39.7 mmol), AN (1.5 mL, 23.3 mmol), and PMDETA ligand (7.7 µL, 0.04 mmol) were added to the flask. The composition was chosen to result in a final molar composition of the random copolymer of S:AN = 3:1. Purification of product followed Chapter II and previously published methods on SI-ATRP.¹⁵

IV.3.3. Morphological analysis

Particle–brush/polymer composite films were prepared by film casting from a toluene solution after blending appropriate amounts of polymer and particle– brush systems in toluene to result in 5% (w/v) solutions of the respective target composition. Films were thermally annealed for 7 days at T = 125 °C and subsequently sectioned using a Leica Ultracut microtome at T = -120 °C. The morphology of particle distributions was subsequently determined by electron imaging of microsectioned films. Imaging was performed by transmission electron microscopy (TEM) using a JEOL EX2000 electron microscope operated at 200 kV.

IV.3.4. Small-angle x-ray scattering (saxs)

SAXS was performed using a Rigaku S-Max3000 with a 2D multiwire detector. Data were acquired at room temperature under vacuum. Twodimensional SAXS patterns were azimuthally integrated to obtain plots of scattered intensity vs modulus of momentum transfer vector, $q = (4\pi/\lambda) \sin \theta$, where θ is half the scattering angle and $\lambda = 1.54$ Å (Cu K α). Data were background corrected by subtraction of the data obtained from corresponding pristine polymer films.

IV.4. Results and discussion

IV.4.1. Particle-brush information

The system in our study consists of two distinct SiO₂ systems with particle core radius (determined through transmission electron microscopy, TEM), $R_{0,\text{TEM}} =$ 7.7 ± 2 nm and $R_{0,\text{TEM}} =$ 56.6 ± 6 nm, respectively, that were modified with polystyrene (PS), poly(methyl methacrylate) (PMMA), and poly(styrene-*r*-acrylonitrile) (PSAN, molar composition S:AN = 3:1). Both SiO₂ nanoparticles were obtained from Nissan Chemicals and functionalized using surface-initiated atom transfer radical polymerization (SI-ATRP) as described above. Readers are referred to Chapter II for more details. Particle systems with the following graft characteristics are the subject of the present study: PMMA-grafted small particle systems ($R_{0,\text{TEM}} = 7.7 \pm 2$ nm) with $\sigma \cong 0.5-0.7$ nm⁻², $N_G \cong 40-4000$ (sample ID: 8SiO₂-PMMA N_G); PS-grafted small particle systems ($R_{0,\text{TEM}} = 7.7 \pm 2$ nm) with $\sigma \cong 0.5-0.8$ nm⁻², $N_G = 10-2200$ in case of PS grafts (sample ID: 8SiO₂-PS N_G); PSAN-grafted small particle systems ($R_{0,\text{TEM}} = 7.7 \pm 2$ nm) with $\sigma \cong 0.6-0.7$ nm⁻²

², $N_{\rm G} = 10-600$ (sample ID: 8SiO₂-PSAN $N_{\rm G}$); PS-grafted large particle systems ($R_{0,\text{TEM}} = 56.6 \pm 6 \text{ nm}$) with $\sigma \cong 0.5-0.7 \text{ nm}^{-2}$ and $N_{\rm G} = 130-2000$ (sample ID: 60SiO₂-PS $N_{\rm G}$) as well as PSAN-grafted large particle systems ($R_{0,\text{TEM}} = 56.6 \pm 6 \text{ nm}$) with $\sigma \cong 0.6 \text{ nm}^{-2}$ and $N_{\rm G} = 100-610$ (sample ID: 60SiO₂-PSAN $N_{\rm G}$). The characteristics of all particle-brush systems are summarized in Table IV-1.

Sample ID	<i>R</i> ₀/nm	<i>M</i> _n	M _w	N _G	σ/nm ^{−2}
8SiO ₂ -PSAN17	7.7 ± 2	1 450	1 700	17	0.63
8SiO ₂ -PSAN600	7.7 ± 2	52 000	72 500	600	0.67
8SiO ₂ -PMMA40	7.7 ± 2	4 000	4500	40	0.60
8SiO ₂ -PMMA150	7.7 ± 2	15 000	17 100	150	0.62
8SiO ₂ -PMMA570	7.7 ± 2	57 000	64 600	570	0.70
8SiO ₂ -PMMA4060	7.7 ± 2	406 000	479 000	4060	0.50
8SiO ₂ -PS100	7.7 ± 2	10 400	11 200	100	0.61
8SiO ₂ -PS370	7.7 ± 2	40 000	44 000	370	0.59
8SiO ₂ -PS520	7.7 ± 2	54 080	60 600	520	0.57
8SiO ₂ -PS2200	7.7 ± 2	230 000	300 000	2200	0.57
60SiO ₂ -PSAN190	56.6 ± 6	16 000	20 000	190	0.61
60SiO ₂ -PSAN290	56.6 ± 6	24 000	30 000	290	0.61
60SiO ₂ -PSAN450	56.6 ± 6	41 000	53 000	450	0.61
60SiO ₂ -PS130	56.6 ± 6	13 500	14 000	130	0.61
60SiO ₂ -PS400	56.6 ± 6	41 000	45 900	400	0.61
60SiO ₂ -PS610	56.6 ± 6	63 400	81 800	610	0.55
60SiO ₂ -PS2100	56.6 ± 6	220 000	280 000	2100	0.47

Table IV-1. Summary of particle-brush systems and molecular parameters.

IV.4.2. Analysis of filler/matrix compatibility

To evaluate the effect of particle-brush architecture on the compatibility of particle-brushes in polymeric media, films of 2 wt % inorganic content in PS ($N_{M,PS} = 961$, for SiO₂-PS series) and PMMA ($N_{M,PMMA} = 929$ and 9588 for SiO₂-PSAN and SiO₂-PMMA series) were prepared by casting from toluene solution and subsequent thermal annealing at T = 125 °C for 7 days. The blended microstructure was determined by transmission electron microscopy. Blend compositions were considered miscible if no significant formation of particle aggregates could be observed and if the average particle–particle distance (as determined from electron micrographs) was of the order of the estimated particle distance for a random particle distribution, i.e., $\langle D \rangle \approx (V/n_P)^{1/3}$, where n_P/V is the number density of particle fillers (in select cases miscibility was independently evaluated by SAXS analysis; see discussion below).

IV.4.3. Athermal filler/matrix hybrid blending system

Figure IV-1 depicts representative electron micrographs for the athermal PMMA/8SiO₂-PMMA series revealing particle aggregation in case of short chain grafts (8SiO₂-PMMA40, Figure IV-1a) and dispersed morphologies in the cases of higher N_{G} -grafted systems 8SiO₂-PMMA150 (Figure IV-1b) and 8SiO₂-PMMA570 (Figure IV-1c). Similar results were observed for PS-grafted small particle fillers (PS/8SiO₂-PS series) in which case aggregation was observed in case of N_{G} = 100 and random dispersion in case of N_{G} = 370, 520, and 2200 (results not shown here).



Figure IV-1. Representative bright field transmission electron micrographs depicting the microstructure of aggregated (a) and compatible (b, c) athermal particle-brush dispersions in PMMA ($N_{M,PMMA} = 929$). Particle concentration is 2 wt %, and particle radius is $R_0 = 7.7 \pm 2$ nm. Panel a: 8SiO₂-PMMA40; panel b: 8SiO₂-PMMA150; and panel c: 8SiO₂-PMMA570. Scale bars are 100 nm, and insets depict structure of the respective neat particle systems (image width is 400 nm). Improved compatibility is observed for increasing N_{G} .

The improved dispersion of particle-brushes with increasing $N_{\rm G}$ of grafted chains approximately follows the predicted trend based on the wet/dry brush model first proposed by Leibler.¹⁰ It is interesting to note that particle dispersion is observed for $N_{\rm G} < N_{\rm M}$; in particular, compatibility of the small particle series (R_0 = 7.7 nm) for $N_{\rm G}$: $N_{\rm M}$ = 150:910 in case of PMMA and 370:960 for PS (no data points were available in the range 100 < $N_{\rm G}$ < 370 for the PS system) was observed. This confirms previous theoretical predictions about the relaxation of the wet brush condition in case of particle-brush systems due to the reduced chain crowding across the curved particle surfaces.^{8, 9b, 9c} Figure IV-2 depicts the results for the large particle-brush system (PS/60SiO₂-PS series). Similarly to the small particle homologues, phase separation is observed in case of $N_{\rm G}$ = 130 << $N_{\rm M}$ (Figure

IV-2a) while for $N_{\rm G}$ = 610 $\leq N_{\rm M}$ (Figure IV-2b) and 2200 > $N_{\rm M}$ (not shown here) uniform particle dispersion is observed (the insets in Figure IV-2a,b represent micrographs of the respective pristine particle-brush systems).¹⁶



Figure IV-2. Representative bright field transmission electron micrographs depicting the microstructure of aggregated (a) and compatible (b, c) athermal particle-brush dispersions in PS ($N_{M,PS} = 961$). Particle concentration is 2 wt %, and particle radius is $R_0 = 56.6 \pm 6$ nm. Panel a: $60SiO_2$ -PS110; panel b: $60SiO_2$ -PS630. Scale bars are 500 nm, and insets depict structure of the respective neat particle systems. Improved compatibility is observed for increasing N_G . Note that the required N_G to facilitate particle compatibility exceeds the one of small particle fillers.

In agreement with predictions, our results demonstrate that with increasing particle core size the threshold DP of surface-grafted chains to facilitate compatibilization increases ($N_{\rm G}$ = 150 for R_0 = 7.7 ± 2 nm and $N_{\rm G}$ = 610 for R_0 = 56.6 ± 6 nm). We interpret the increased efficacy of polymer grafts to facilitate
compatibilization in the case of smaller particles as a consequence of the decrease of chain crowding (due to the increased surface curvature) and the associated relaxation of chain conformation that supports entanglement and wetting by matrix chains.¹⁷

IV.4.4. Thermal filler/matrix hybrid blending system

It is important to note that although the above results demonstrate the feasibility of polymer-graft modification to facilitate the dispersion of particle additives, the "athermal particle-brush" route cannot be considered a viable strategy for the synthesis of nanocomposites with high inorganic content. This is because the required grafting of chains with sufficient DP to facilitate mixing imparts a constraint to the attainable inorganic content that can be achieved in athermal blended compositions. In particular, the upper limit for the attainable inorganic content is determined by the volume fraction inorganic per particle-brush. The latter can be estimated, for example, for the 8SiO₂-PMMA150 particle-brush system to $\Psi_{inorg} \approx 0.15$. As elaborated above, the challenge of restricted inorganic content can be resolved by tailoring the chemical composition of the grafted chains such that it facilitates favorable interactions with the matrix chains. This is realized in the two composite systems PMMA/8SiO₂-PSAN and PMMA/60SiO₂-PSAN, where PMMA and PSAN represent a miscible blends system with $\chi_{MMA/SAN} \approx -0.15$ at T = 25 °C (we note that the favorable interaction is specific to a narrow compositional range of PSAN around S:AN = 3:1 and that the PMMA/PSAN system has a lower critical solution temperature of $T_{LCST} \approx 180$ °C).¹⁸ Figure

IV-3a,b depicts representative electron micrographs revealing the dispersion of both 8SiO₂-PSAN17 (a) and 8SiO₂-PSAN600 (b) in PMMA ($N_{M,PMMA} = 929$).



Figure IV-3. Characterization of miscible particle-brush dispersions with favorable interactions (particle concentration is 5 wt % and particle radius is $R_0 = 7.7 \pm 2$ nm). Panel a: representative bright field TEM image depicting the microstructure of PMMA/8SiO₂-PSAN17; panel b: representative bright field TEM image depicting the microstructure of PMMA/8SiO₂-PSAN600. Scale bars in (a) and (b) are 100 nm. Note that compatibility is observed in (a) despite of $N_{\rm G} \ll N_{\rm M}$ (see text for more details). Insets depict structure of the respective neat particle systems. Panel c: Guinier presentation of normalized SAXS data measured before (black) and after (red) thermal annealing of the 5 wt % PMMA/8SiO₂-PSAN17 system. The existence of a linear region with similar slope confirms that particle size (and hence dispersion morphology) remains unchanged during thermal annealing. The particle radius of gyration can be estimated from the slope of the linear region to $R_{g} \cong 6$ nm, thus confirming single particle dispersion. The dotted line indicates the q-value corresponding to maximum intensity $I(q_{max})$. Inset shows scattering data across experimental *q*-range (arrow indicates beamstop position).

The dispersion of 8SiO₂-PSAN17 (with $N_G \ge N_M$) is significant because it confirms that even in case of short-chain grafted brushes the enthalpy associated

with favorable interactions dominates over unfavorable entropic contributions. All PMMA/SiO₂-PSAN blend systems were found to exhibit miscibility across the entire compositional range. To independently verify the thermodynamic stability of the particle filler dispersion in the case of the 8SiO₂-PSAN17/PMMA composite, small-angle X-ray scattering (SAXS) analysis was performed during thermal annealing of a 5 wt % reference system. This concentration was chosen as a compromise between two requirements: First, to facilitate adequate scattering strength of the sample and, second, to ensure that the particle concentration is sufficiently dilute such that the scattering of individual particle fillers can be analyzed. Figure IV-3c presents the Guinier plot (log I(q) vs q^2) of the scattering data obtained from samples before (black) and after (red) thermal annealing. The linear trend with nearly equivalent slope confirms that particle size (and hence dispersion morphology) is retained after thermal annealing, thus providing further evidence for the stability of the particle-brush/polymer dispersion that is facilitated by PSAN-graft modification. The presence of favorable interactions is furthermore confirmed by the effect of particle addition on the glass transition temperature T_{g} of the composite systems which was found to increase with inorganic content as revealed in Figure IV-4.¹⁹ We have attributed the more pronounced increase of T_g in case of smaller particle fillers (8SiO₂-PSAN/PMMA system, see red square symbols in Figure IV-4) to the larger surface-to-volume ratio which allows for more efficient interactions at equal inorganic content. It is noted that in case of PMMAgrafted particle fillers no distinctive trend of the glass transition temperature was

observed (i.e., T_g was found to remain approximately constant this is the trend then within the experimental certainty; results not shown here).^{5a, 20}



Figure IV-4. Effect of addition of PSAN-grafted particles on glass transition temperature T_g of composite (T_g° = 105.5 °C is the glass transition temperature of the neat PMMA matrix). Both 8SiO₂-PSAN and 60SiO₂-PSAN systems are found to raise T_g , indicating favorable interactions and miscibility of both composite systems—the increase in T_g is more pronounced for smaller particle fillers consistent with the increased surface-to-volume ratio of small particle systems.

IV.4.5. Dispersion characteristics comparison of thermal and athermal blending systems

Figure IV-5 summarizes the dispersion characteristics for all particle-brush systems reported inTable IV-1. The figure confirms that the trend for athermal particle-brush composites approximately follows the predicted trend for dry/wet brush behavior; however, the miscibility criterion for planar brushes ($N_G > N_M$) is increasingly relaxed with increasing surface curvature (i.e., decreasing particle size). Therefore, although both particle-brush systems are found to behave qualitatively similar, (athermal) polymer grafting is found to be more effective for smaller particle fillers.



Figure IV-5. Compatibility maps of small ($R_0 = 7.7 \pm 2$ nm) and large ($R_0 = 56.6 \pm 6$ nm) SiO₂ particle/polymer blend systems (evaluated for a particle concentration of 2% w/v and $N_{M,PS} = 961$ and $N_{M,PMMA} = 929$, respectively). For athermal blends the miscibility condition is approximately described by $N_G = \alpha N_M$, where α is a compatibility parameter of the order unity (α decreases with decreasing particle size). Universal miscibility is observed for favorably interaction particle/polymer composite materials ($\chi_{GM} < 0$).

IV.4.6. Novel polymer-filled inorganic hybrid (volume fraction of inorganic > 50 vol%)

Note that Figure IV-5 also illustrates the effect of favorable interactions to "override" unfavorable entropic contributions and to facilitate universal miscibility of particle fillers. Because of the dominating influence of enthalpic interactions at even small degrees of polymerization of surface-grafted chains (as in the case of the 8SiO₂-PSAN17 system), very high inorganic filling fractions can be obtained based on favorably interacting polymer/particle-brush blends. This is demonstrated in Figure IV-6 that depicts electron micrographs of a PMMA/8SiO₂-PSAN17 composite film with a particle-brush content of 71 vol % within a high molecular PMMA matrix with DP *N*_{M,PMMA} = 9588. Note that in this case the silica volume fraction is $\P_{SiO2} \approx 0.52$, and thus is the majority component and is constituted by the inorganic phase (thus rendering the composite effectively a "polymer-filled inorganic").



Figure IV-6. Panel a: transmission electron an optical micrographs of PMMA/8SiO₂-PSAN17 composite film with a particle-brush volume fraction

of 72% (corresponding to inorganic volume filling fraction $\Psi_{SiO2} \approx 0.52$) and a DP of the matrix of $N_{M,PMMA} = 9588$. The micrograph reveals uniform particle distribution. Scale bar is 100 nm. Inset shows illustration of entangled network structure of high molecular chains in particulate matrix. Panel b: micrograph of crack formed during early state of fracture upon deformation at T = 23 °C. The formation of "particulate fibrils" that connect the fracture surface is observed. The formation of fibrils indicates the formation of entanglements between the high molecular weight matrix chains. Scale bar is 50 nm. Panel c: image of $\Psi_{SiO2} \approx 0.52$ NC sample before tensile deformation. Panel d: picture of sample after strain application of 200% at T = 70 °C. Whitening occurs due to scattering of surface cracks that form during deformation.

Figure IV-6a reveals that particles are uniformly distributed throughout the matrix (individual particle positions are difficult to discern because the image projection in conjunction with the high particle density blurs particle boundaries). Interestingly, the dispersion of the particle-brushes within a high molecular weight matrix ($N_{M,PMMA} = 9588$) imparts remarkable polymer-like mechanical properties on the composite. For example, analysis of the relative fracture toughness (normalized to the fracture toughness of the matrix polymer K_{IC}^{0}) using nanoindentation revealed $K_{IC}/K_{IC}^{0} \approx 0.6$. In contrast, the application of a PMMA matrix with $N_{M,PMMA} = 929$ did yield very brittle samples ($K_{IC}/K_{IC}^{0} \approx 0.01$) that were difficult to process and analyze (results not shown here). We interpret the remarkably high fracture toughness (for a mostly particulate material) to be a consequence of chain entanglement between the high molecular matrix chains that—despite the overall small volume fraction of matrix component $\Psi_{PMMA} \approx$

0.29-are expected to pervade a large volume that can be estimated as $R_e^3 \approx N_{PMMA}^{3/2} a_{PMMA}^3 \approx 10^5 \text{ nm}^3 \text{ per chain, where } a_{PMMA} \text{ denotes the length of}$ one MMA repeat unit and Re the polymer chain end-to-end distance (for ideal conditions).²¹ The situation might be compared to those of viscoelastic dilute solutions of high molecular polymers (known, for example, as Boger liquids) in which entanglements give rise to elasticity of the solution even at very small polymer concentration.²² Indeed, as demonstrated in Figure IV-5. Compatibility maps of small ($R0 = 7.7 \pm 2$ nm) and large ($R0 = 56.6 \pm 6$ nm) SiO2 particle/polymer blend systems (evaluated for a particle concentration of 2% w/v and NM_{.PS} = 961 and NM_{.PMMA} = 929, respectively). For athermal blends the miscibility condition is approximately described by NG = α NM, where α is a compatibility parameter of the order unity (α decreases with decreasing particle size). Universal miscibility is observed for favorably interaction particle/polymer composite materials (χ GM < 0).b, the analysis of fracture cracks that form during the deformation of the $\Psi_{SiO2} \approx 0.52$ system reveals the formation of "particulate" fibrils" that span the crack surface similar to craze formation during fracture of amorphous polymers (such as PMMA). Since craze formation is known to result as a consequence of chain entanglement in polymeric materials, we propose that the fibrils that are observed in the $\P_{SiO2} \approx 0.52$ system are caused by the entanglement of matrix chains that effectively act as "tie chains" between particle fillers (see the inset of Figure IV-6a).²³ The polymer-like thermoplastic properties of the $\Psi_{SiO2} \approx 0.52$ system are also illustrated in Figure IV-5c,d that demonstrate the ductility (fracture strain is $\varepsilon_F > 2$) of specimen during tensile deformation at 70

°C. Note that the inorganic content imparts remarkable optical properties to the polymer composite as illustrated in Figure IV-7 for the example of a film of 500 μ m thickness.



Figure IV-7. UV absorption spectrum of free-standing film of PMMA/8SiO₂-PSAN17 ($^{\phi}$ _{SiO2} \approx 0.52) system (red) and PMMA reference (black) revealing near-quantitative limiting of UV radiation in the wavelength range 250 < λ < 290 nm by composite film. Film thickness is 500 µm. Inset shows UV/vis absorption spectra of free-standing films NC (red) and PMMA reference (black) revealing high transparency ($T \approx 0.8$) of NC film across the visible wavelength range.

Figure IV-7 demonstrates the near-quantitative limiting of UV radiation in the wavelength range 250 < λ < 290 nm—a consequence of the high inorganic content. Remarkably, the high limiting efficiency in the UV range is realized while maintaining a high degree of optical transparency. UV/vis absorption spectroscopy (as depicted in the inset of Figure IV-7) reveals $T \approx 0.8$ (for film thickness t = 500 µm) in the visible wavelength range despite the high particulate content. We interpret the high optical transparency as a consequence of both the low optical heterogeneity (that results from the high inorganic filler content in conjunction with the uniform particle distribution) as well as the specific contribution of refractive indices of core, shell, and matrix in the PMMA/8SiO₂-PSAN17 system. A more detailed discussion of the optical properties of PMMA/SiO₂-PSAN NC systems will be presented in a forthcoming publication.

IV.5. Conclusions

The effect of polymer-graft modification on compatibility of particle fillers within polymeric embedding media was analyzed. In athermal blends corresponding to graft and matrix polymer having identical chemical composition compatibility is observed when the DP of the grafted chains is similar to, or exceeds the DP of the matrix polymer. The observed experimental trend generally supports a previously postulated compatibility criterion for miscible athermal particlebrush/polymer dispersions that can be formulated as $N_{\rm G} = \alpha N_{\rm M}$, where α is an efficiency parameter that is equal to unity for planar brushes and decreases with grafting density). particle size (for constant However, an enthalpic compatibilization that is facilitated by favorable interactions between the graft and matrix chains was found to facilitate particle compatibilization even for entropically unfavorable conditions - such as $N_{\rm G} \ll N_{\rm M}$ and $R_0 \gg R_{\rm e}$. This strategy provides a viable procedure for the preparation of thermodynamically stable particlebrush/polymer blend systems with high inorganic loading and polymer-like

mechanical properties. The enthalpic compatibilization approach is therefore relevant for the design of new thermoplastic NC materials in which enhanced functionality results as a consequence of increased inorganic content in combination with stability against physical aging.

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Chapter V

Particle-brush Materials – From Engineered Colloids to 'Quasi'-One Component Systems

Preface The objective of the current chapter is to illustrate the potential of hybrid *particle-brush*es as a platform for developing novel functional bulk materials. As discussed in Chapter I, the miscibility of solid particles with a host polymer matrix is one of the major challenges in the plastics industry. Usually, this problem is resolved by grafting polymer brushes from/to the particle surface that are longer than the targeted matrix chains, which can be achieved using the method mentioned in Chapter III. However, this approach limits the filler loading if the material requires a high MW grafted chain.

As explained in Chapter IV, the concept of exploiting a favorable enthalpic interaction between the tethered brush and matrix was introduced. The enthalpic

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interaction assisted filler dispersion allows the synthesis of a thermally and mechanically stable film with filler loading over 50 vol%. However, this concept is not broadly applicable as the number of miscible copolymer blends is very limited. This limitation stimulated an innovative idea that directly led to examination of the properties of self-assembled *particle-brush*es, which could eliminate the need for a separate polymer matrix. Since there is no matrix, the unfavorable entropy of mixing between the interfaces of the filler and matrix does not exist. As a result, this new material revealed 'zero-aggregation'.

Due to the limitation of sample size, the mechanical characteristics of these materials were monitored by nanoindentation. It was found that the elastic modulus, hardness, and toughness all increased when the grafted degree of polymerization of the polymer brushes (N_G) increased while grafting from particles of the same size (R_0) and at the same grafting density (σ). Scaling models suggested only toughness was architecturally dependent, since the toughness had a sharp transition, at the transition between the concentrated polymer brush regime (CPB) and semi-diluted polymer brush regime (SDPB), while both the modulus and hardness did not share the same behavior. This was as expected, since only toughness is related to the ability of a material to exhibit crazing. The experimental results revealed that the degree of polymerization in the SDPB (N_{SDPB}) had to exceed double the degree of polymerization of entanglement (N_e) of the particular choice of monomer units in the polymer brush in order to form crazes and generate polymer-like toughness. In other words, *particle-brush* solids

with longer polymer grafts are tougher. However, as the *N*_{SDPB} increased beyond a threshold value, a reduction of the structural regularity was observed that was rationalized with the increased volume occupied by relaxed polymer segments. The capacity of polymer grafts to control order and toughness in bulk *particle-brush* assembly structures was therefore interpreted on the basis of a mean-field scaling model, and "design criteria" were developed to help guide the future synthesis of colloidal systems that will be capable of forming mechanically robust yet ordered assembly structures.

V.1. Introduction

Traditional polymer/inorganic composite materials are formed by embedding inorganic particles into a polymeric matrix. Such materials retain not only the chemical advantages of the polymer matrix but also they inherit thermal, mechanical, and optical properties from the additive particles.¹ However, the properties of classical composite materials can be significantly decreased by the phase separation of particles from polymer matrix, e.g. by agglomeration, resulting in the loss of transparency and mechanical robustness.²

Recent advances in self-assembly of polystyrene star polymers to generate well-organized honeycomb morphology suggests the possibility of self-assembling *particle-brush* materials without blending with a matrix, providing the possibility of aggregation-free filler/polymer materials.³ However casting a film, consisting only of particles, generates a material that is easy to crack, if there is no additional

forces to join the particles together.⁴ Therefore, the formation of an ordered particle array, providing tough *particle-brush*es, relies on brush-brush interactions. It is well established that fracture in entangled amorphous polymers involves microscopic flow processes that lead to the formation of crazes, thereby providing a key mechanism for energy dissipation during fracture.⁵ However, the formation of crazes is a fingerprint of the presence of inter-chain entanglements in glassy polymers and is therefore dependent on the polymer brush conformation. Consequently, some background information on polymer brush conformation and the parameters that can control polymer brush conformation is recommended before proceeding with this chapter and readers are referred to the introduction section in Chapter II.

Briefly, the structure of *particle-brush* materials can be evaluated on the basis of a scaling model that was first derived by Daoud and Cotton (DC) to describe the structural transitions in topologically related star polymers that was recently extended to *particle-brush* systems.⁶ According to the DC model, the structure of *particle-brush*es can be divided into two regimes: the concentrated *particle-brush* (CPB) regime in which excluded volume interactions give rise to stretched chain conformations and the semi-dilute *particle-brush* (SDPB) regime in which chains assume a relaxed chain conformation. Due to the very different chain conformation between CPB and SDPB regimes, it is expected that the mechanical properties of the formed *particle-brush* solids will change dramatically during the transition. A simple method to predict this transition by extending the

DC model to *particle-brush* systems was created.⁷ In particular, a critical distance R_c was postulated to separate the CPB from the SDPB brush regime.^{7a} Thus, for a total particle size $R_0 + h < R_c$ *particle-brush*es are assumed to be in the CPB regime (with $h \approx N^x$, and 1 > x > 3/5) whereas for $R_0 + h > R_c$ the SDPB regime is expected (with $h \approx N^y$; and y = 3/5 in good solvents). By adopting the Daoud–Cotton treatment, the critical distance is

$$R_{\rm c} = R_0(\sigma^*)^{1/2}(v^*)^{-1}$$

Equation V-1

Where $\sigma^* = \sigma a^2$ is the reduced grafting density, *a* is the length of a repeat, and $v^* = v/(4\pi)^{1/2}$ is the effective excluded volume parameter.^{7a}

The effects of polymer graft modification on the deformation characteristics and the order formation of particle solids are evaluated in this chapter. It is demonstrated that polymeric ligands (with appropriate N_G and σ) grafted to the particle surface can facilitate the assembly of nanoparticles into mechanically robust and ordered solid structures with polymer-like elastic and fracture characteristics when an appropriate values for N_G , R_0 , and σ were chosen. The emergence of polymer-like mechanical characteristics during *particle-brush* assembly is rationalized as the result of chain entanglements between surfacegrafted chains of an appropriate architecture, generally with high N_G . However a disordering of particle array structure may occur when the N_G within the SDPB regime exceeds the free volume between particles and starts to force particle separation. From the observed transitions of the mechanical properties and

particle ordering, a general 'design criteria' can be derived that facilitates the extension of the approach to diverse particle compositions.

The structure of this chapter is as follows: first, a detailed analysis of the mechanical characteristics (elastic modulus and fracture toughness) of particle assemblies measured using nano-indentation will be presented for particle systems with systematically varied architecture of surface-grafted chains in order to establish the relevant structural parameters that control deformation in polymergrafted particle solids. Electron microscopy analysis of crack formation in films of mono-, and multilayers of particles will be used to determine the microscopic origin for the transition from 'hard-sphere-like' to 'polymer-like' mechanical response in polymer-grafted particle solids. Second, a systematic analysis of order formation in 2D particle assemblies will be presented as a function of the $N_{\rm G}$, with constant σ , to establish the relevant structural parameters that control order formation in polymer-grafted particle solids. Finally, the results will be interpreted on the basis of a scaling model that captures the major experimental trends and provides design criteria for the synthesis of polymer-grafted particle systems that will be capable of forming both ordered and robust particle solid structures.

V.2. Experimental section

V.2.1. Particle synthesis

Silica nanoparticles (SiO₂), 30% solution in methyl isobutyl ketone (MIBK-ST, Nissan Chem. Corp. USA) with effective radius $R_{0,\text{TEM}} \cong 7.7 \pm 2.0$ nm, 30%

solution in isopropanol (IPA-ST-L, Nissan Chem. Corp. USA) with effective radius ($R_{0,\text{TEM}} = 29.6 \pm 6 \text{ nm}$), and 30% solution in isopropanol (IPA-ST-ZL, Nissan Chem. Corp. USA) with effective radius $R_{0,\text{TEM}} \cong 56.6 \pm 6.0$ nm, and monodispersed silica powder (SIO2P050, Fiber Optic Center Inc.) with effective radius $R_{0,\text{TEM}} \cong 233.2 \pm 16.9$ nm were kindly donated by their supplier and used as ATRP initiator 1-(chlorodimethylsilyl)propyl-2-bromoisobutyrate received. synthesized (**1**, Figure V-1) was using а previously reported procedure.⁸ Styrene (Aldrich, 99%) and methyl methacrylate (MMA) were purified by passing through a basic alumina column. Copper(I) bromide (Aldrich, 98+%) and copper(I) chloride (Aldrich, 99+%) were purified by washing sequentially with acetic acid and diethyl ether, filtering and drying, and were stored under nitrogen before use. 4,4'-Dinonyl-2,2'-bipyridine (dNbpy, Aldrich, 99%), anisole (Aldrich, 99%), *N*,*N*,*N*',*N*'',*N*''-pentamethyldiethylenetriamine (PMDETA) (Aldrich, 99%), and hydrofluoric acid (50 vol% HF, Acros) were used as received. All other chemicals and solvents were obtained from Aldrich and Acros Organics.

V.2.2. Tethering the ATRP initiator on the surface of the particles

The procedures for the synthesis of the tetherable ATRP initiators and subsequence surface modification followed the prior works and the procedures in Chapter II.⁸⁻⁹

V.2.3. Example of growing tethered polymer chains from particles using SI-ATRP

Short chain PS-grafted silica nanoparticles (8SiO₂-PS10) were prepared by charging a Schlenk flask with 1.48 g initiator-modified silica nanoparticles (SiO₂-Br, 0.353 mmol Br per g silica; 0.524 mmol ATRP initiator sites, product 1) and anisole (12.0 mL). The mixture was stirred for 24 h forming a clear suspension. Styrene (6.0 mL, 52.4 homogeneous mmol) and PMDETA ligand (21.9 µL, 0.105 mmol) were added to the flask. After three freezepump-thaw cycles, the mixture was immersed in liquid nitrogen and 15.0 mg (0.105 mmol) of CuBr was added, while the flask was filled with nitrogen gas. The flask was sealed with a glass stopper, evacuated and back-filled with nitrogen, five times. The reaction mixture was warmed to room temperature then the sealed flask was placed in an oil bath heated to 90 °C. The polymerization was stopped by exposing the catalyst to the air after 5 h of reaction time. The product was precipitated by adding the reaction mixture to methanol and the solid was filtered and washed withmethanol prior to drying in a vacuum oven at 60 °C. All other samples with N_G < 1500 were prepared using similar synthetic procedures. The 8SiO₂-PMMA4000 nanocomposite (NC) was prepared in a similar way, however, in order to achieve a better control at a higher molecular region, the less active CuCl/dNbpy catalyst/ligand complex was used instead of the CuBr/PMDETA system, and the ratio of reagents was [8SiO₂–Br]₀ : [MMA]₀ : [CuCl]₀ : [dNbpy]₀ = 1 : 20 000 : 10 : 20. Ultra-high molecular weight polymer/SiO₂ hybrid (8SiO₂-PMMA 16k) was polymerized via activators generated by electron transfer for atom transfer radical polymerization (AGET-ATRP) under high pressure to enhance the

propagation rate constant and reduce the termination rate constant for very high molecular weight. The details of the high pressure procedure are described in Chapter III.¹⁰

Polystyrene with (number-average) molecular weight $M_n = 52~000$ (dispersity index $M_w/M_n = 1.02$) and $M_n = 300~000~(M_w/M_n, D = 1.2)$ was obtained from Polymer Source and used as received. Toluene solvent was obtained from Aldrich and used without further purification. Table V-1 presents a summary of the composition of the *particle-brush* system used in the present study. MW and D of surface-grafted chains were determined by size exclusion chromatography (SEC) after etching the silica in the composites with HF. The SEC was conducted with a Waters 515 pump, a Waters 410 differential refractometer (λ = 930 nm) and a Wyatt Technology DAWN EOS multiangle laser light scattering (MALLS) detector (30 mW, λ = 690 nm) using Waters Microstyragel columns (guard, 10², 10³, and 10⁵ Å) in THF as an eluent (35 °C, flow rate of 1 mL min⁻¹). The apparent MWs were determined with a calibration based on linear PS and PMMA standards using GPCWin software from Polymer Standards Service. Absolute MW were determined with the measured d*n*/*dc* values using Wyatt ASTRA software.

V.2.4. Film preparation and analysis

Approximately monolayer films of all *particle-brush* systems were prepared by spin-casting of dilute particle solutions $(1 - 3 \text{ mg mL}^{-1} \text{ in toluene})$ on the poly(acrylic acid) (PAA) substrate and subsequent thermal annealing in a vacuum for 24 h at T = 120 °C. Equilibrium films were lift-off by water immersion and transferred onto Cu-grids. Thick films for nanoindentation were prepared by drop casting of particle solutions with high concentration (10–20 mg mL⁻¹) on the silicon substrate. The spatial distribution of particles was analyzed using ImageJ software.

V.2.5. Nanoindentation

Mechanical properties such as elastic modulus, hardness, and fracture toughness were measured by nanoindentation experiments using an MTS Nanoindenter XP with a Berkovich tip under displacement control to not more than ~ 10% of the nanocrystal film thickness. For PS reference samples, experiments were performed at varied load rates $(1 - 25 \text{ nm s}^{-1})$ in order to exclude load rate dependence of the results. Experimental data of *particle-brush* samples were obtained from at least 20 indentations per sample from which the experimental error was determined by the standard deviation of the measurements. The displacement rate during the indentation was 5 nm s⁻¹ to a maximum load, followed by a constant load indentation for 20 seconds. In order to analyze the residual impression formed by indentation, the fracture surfaces were scanned in a tapping mode using an atomic force microscope (AFM, NT-MDT Explorer) with a silicon cantilever (5.1 N m⁻¹ force constant) with sharpened pyramidal tip.

V.2.6. Electron microscopy

Both the particle film morphology and its craze formation were imaged by transmission electron microscopy (TEM) using a JEOL EX2000 electron microscope operated at 200 kV. Imaging was taken by amplitude and phase contrast, and images were acquired using a Gatan Orius SC600 high-resolution camera.

V.2.7. Dynamic light scattering

Hydrodynamic radii of SiO₂-PS *particle-brush*es in toluene solution ($c \cong 1$ mg mL⁻¹) were determined by dynamic light scattering (DLS) analysis using a Malvern Zetasizer Nano ZS. Hydrodynamic radii are reported as number averaged values.

V.3. Result and discussion

V.3.1. Particle-brush synthesis

The system in the current study consists of polystyrene (PS) and poly(methyl methacrylate) (PMMA) grafted silica particles with systematically varied polymer graft architecture. Particle systems were synthesized using surface-initiated atom transfer radical polymerization (SI-ATRP).^{8-9, 11} For more details about the synthesis, readers are referred to Chapter II. The SI-ATRP approach has shown in the past to facilitate precise control of the degree of polymerization, molecular weight distribution, and grafting density of surface-grafted chains and thus provides an ideal means towards *particle-brush* model systems for systematic structure–property correlations.¹² The modification process is schematically illustrated in Figure V-1.

There are three PS and PMMA grafted silica particle systems with distinct particle core radius (determined through transmission electron microscopy, TEM), i.e., $R_0 = 7.7 \pm 2$ nm, $R_0 = 29.6 \pm 6$ nm, and $R_0 = 56.6 \pm 6$ nm. Particle-brush systems with the following graft characteristics are the subject of the present study:

PMMA-grafted small particle systems ($R_0 = 7.7 \pm 2$ nm) with $\rho_s \equiv 0.5-0.7$ nm⁻² and $N_G \equiv 40-16000$ (sample ID: 8SiO₂-PMMAN_G); PS-grafted small particle systems ($R_0 = 7.7 \pm 2$ nm) with $\rho_s \equiv 0.5-0.8$ nm⁻² and $N_G = 10-1360$ in case of PS grafts (sample ID: 8SiO₂-PSN_G); PS-grafted medium-sized particle systems ($R_0 = 29.6 \pm 6$ nm) with $\rho_s \equiv 0.5-0.7$ nm⁻² and $N_G = 100-1800$ (sample ID: 30SiO₂-PSN_G); and PS-grafted large particle systems ($R_0 = 56.6 \pm 6$ nm) with $\rho_s \equiv 0.5-0.6$ nm⁻² and $N_G = 130-2100$ (sample ID: 60SiO₂-PSN_G). Here, ρ_s denotes the grafting density on the particle surface and N_G the degree of polymerization of surface-grafted chains. The characteristics of *particle-brush* systems are summarized in Table V-1.



Figure V-1. Illustration of the synthetic procedure for graft modification of silica particles by SI-ATRP (illustration is for the example of PS-graft modification). The conditions correspond to (i) chlorodimethylsilane (Me₂SiCIH), Pt(0), CH₂Cl₂, 25 °C; (ii) MIBK, 60 °C, 24 h; and (iii) styrene or methyl methacrylate, CuBr/PMDETA or CuCl/dNbpy, 70 or 90 °C, precipitation in CH₃OH.

As discussed in Chapter II, the dependence of the particle surface-tosurface distance *d* on the grafted degree of polymerization of polymer brushes can be determined from electron imaging of the particle monolayers in order to evaluate the brush regime of the respective particle samples. Sample sets with R_0 = 7.7 were shown as examples in the study. Figure V-2 depicts electron micrographs of the respective particle monolayer (panels a–d: PS-grafted particles and panels e–h: PMMA-grafted particles) revealing two scaling regimes, *i.e.* $d \approx N_G^{0.8}$ and $d \approx N_G^{0.52}$, respectively, thus confirming the predicted scaling relation in CPB and SDPB regimes.

The transition between the CPB and SDPB regimes is observed at $N_{crit} \cong 250$ in good agreement with the prediction based on Equation V-1 that is indicated by the colored regimes in Figure V-2 (in estimating N_{crit} from Equation V-1 equal chain persistence was assumed for PMMA and PS). Note that the scaling within the SDPB regime is close to the expected scaling for polymer melts thus confirming the relaxed conformation of chain segments within the SDPB regime that is a prerequisite for chain entanglement (see discussion below).¹³

sample ID	M _{n,GPC}	<i>M</i> _w / <i>M</i> _n	wt % SiO ₂	σ(chain/nm²)	<i>R</i> ₀ (nm)
8SiO ₂ -PMMA40	4 100	1.12	77.4	0.67	7.7
8SiO ₂ -PMMA150	15 400	1.14	24.6	0.63	7.7
8SiO ₂ -PMMA570	57 000	1.14	8.97	0.56	7.7
8SiO ₂ -PMMA4000	400 400	1.18	1.4	0.54	7.7
8SiO ₂ -PMMA16K*	1 608 400	1.28	0.7	0.25	7.7
8SiO ₂ -PS10	1 000	1.08	84.7	0.59	7.7
8SiO ₂ -PS150	15 600	1.21	23.8	0.61	7.7
8SiO ₂ -PS770	80 400	1.32	9.3	0.33	7.7
8SiO ₂ -PS1360	141 700	1.79	5.3	0.25	7.7
30SiO ₂ -PS100	10 400	1.19	71.8	0.67	29.6
30SiO ₂ -PS1000	104 000	1.42	20.3	0.53	29.6
30SiO ₂ -PS1800	187 000	1.67	12.4	0.46	29.6
60SiO ₂ -PS130	13 000	1.08	81.1	0.61	56.6
60SiO ₂ -PS400	41 000	1.12	38.8	0.61	56.6
60SiO ₂ -PS630	65 500	1.25	23.9	0.52	56.6
60SiO ₂ -PS2100	220 000	1.29	10.4	0.47	56.6

Asterisk (*) indicates that high-pressure ATRP conditions were used for synthesis (see reference 10).



Figure V-2 Electron micrographs depicting particle monolayers of PSgrafted silica (panels a-d) and PMMA-grafted silica (panels e-h) with grafting density $\rho_s > 0.5$ chain nm⁻². The figures correspond to various degrees of polymerization of surface-grafted chains, *i.e.* for $8SiO_2$ -PSN_G: (a) $N_G = 10$, (b) $N_G = 150$, (c) $N_G = 770$, and (d) $N_G = 1360$; for $8SiO_2$ -PMMAN_G: (e) $N_G = 40$, (f) $N_G = 150$, (g) $N_G = 570$, and (h) $N_G = 4000$, respectively. Scale bar is 100 nm. Panel (i) depicts the dependence of the particle surface-tosurface distance d and brush height $R_{\rm H} - R_0$ on the degree of polymerization N_G of surface-grafted chains. Filled circles (8SiO₂-PSN_G) and open circles (8SiO₂-PMMAN) represent d determined byTEM of particle monolayers shown in panels a-h; blue squares (8SiO₂-PSN) and open circles (8SiO₂-PSN determined from reference 9) represent $R_{\rm H} - R_0$ determined by DLS in toluene solution. The particle surface-to-surface distance and the brush height found scale with the degree are to of polymerizationas $d \approx N^{0.8}$ and $(R_{\rm H} - R_0)$ ≈ *N*_G^{0.98} (CPB) regime) and $d \approx N_G^{0.52}$ and $(R_H - R_0) \approx N_G^{0.58}$ (SDPB regime), respectively. The good agreement between the predicted and experimentally observed CPB \rightarrow SDPB transition at $N_{crit} \cong 250$ based on both TEM and DLS analysis supports the applicability of the Daoud–Cotton model to describe structural transitions of *particle-brush*es in the solid state.

V.3.2. Nanoindentation

The mechanical characteristics (elastic modulus, hardness, and fracture toughness) of *particle-brush* solids were evaluated by nanoindentation of drop cast thick films of *particle-brush* systems (film thickness is approximately 50 µm) on the silicon substrate. In nanoindentation the mechanical characteristics of a material are inferred from the analysis of the load-displacement curves associated with the elastic recovery of material subsequent to indentation with а а nanoscopic diamond-based tip-indenter of defined geometry (a trigonal pyramid in the case of the most commonly used Berkovich indenter).¹⁴ Nanoindentation has become a widely used technique to study the micromechanical properties of thin film materials and although the results are not directly comparable to bulk measurements (such as tensile stress-strain tests) the technique has been shown to correctly reproduce trends of mechanical properties for a wide range of materials.15

Nanoindentation for all *particle-brush* samples was performed at a rate of 5 nm s⁻¹ up to a maximum load corresponding to 10% relative indentation depth of the film. The surface morphology of the *particle-brush* film assemblies was observed using atomic force microscopy (AFM) in tapping mode before and after nanoindentation. Figure V-3a depicts an AFM image of sample 8SiO₂-PS770 confirming the short-ranged ordered arrangement of *particle-brush*es within the film (similar to the structure revealed in the electron micrograph shown in Figure V-2c) as well as a uniform surface topology with a root-mean-squared

roughness of 2.06 nm over a size of $5 \times 5 \ \mu m^2$. Note that the lateral dimension of the indents is approximately 5 μm (see the inset of Figure V-3a) and thus the indenter samples over a large number of particles during the indent formation. This is a critical prerequisite for the result to reflect the collective properties of *particle-brush* films.



Figure V-3. Panel a: Atomic force microscope (AFM) image of a surface of a sample $8SiO_2$ -PS770 thin film depicting a short-ranged ordered packing arrangement of the particles. Scale bar is 500 nm. The inset shows the residual impression of an indentation made at a maximum displacement of 500 nm. Scale bar is 1 µm. Panel b: Load–displacement curves obtained by indentation for $8SiO_2$ -PS*N*_G thick films, exhibiting a systematic increase of slope with the degree of polymerization.

V.3.3. Mechanical characteristics measured by nanoindentation

Representative load-displacement curves for all PS-grafted particle systems are shown in Figure V-3b revealing a pronounced dependence of indent

formation on the architecture of the *particle-brush*. In particular the slope of the load–displacement curves is found to increase with the degree of polymerization of surface-grafted chains up to values that are comparable to the reference PS sample ($M_{n,GPC}$ = 300 000). Mechanical characteristics such as hardness and elastic modulus can be deduced from the slope of the elastic recovery of the film after indentation as described in the literature.¹⁴⁻¹⁵

Figure V-4 depicts the average elastic modulus E (hardness H) determined from load–displacement curves (Figure V-3b) for both the PS- and PMMA-modified particle-brush systems, revealing the continuous increase of the modulus and hardness of the particle film assemblies from about 1.5 GPa (0.1 GPa) for short polymer grafts (8SiO₂-PS10) to about 4.5 GPa (0.2 GPa)—close to the value of the respective reference linear homopolymer-for long polymer grafts (8SiO₂-PMMA4000). Note that modulus and hardness are found to level off beyond a threshold molecular weight that is less than the CPB \rightarrow SDPB transition for both *particle-brush* series. This observation can be interpreted as a consequence of the elastic modulus (and hardness) of polymer-grafted particle assemblies being primarily determined by weak dispersion interactions between the surface-grafted chains.¹⁶ Since the latter do not depend on chain entanglement but rather on the molecular polarizability, the stiffness is expected to level off once the molecular volume exceeds the maximum effective interaction volume that depends on the coherence length of induced dipolar moments and thus on the chemical nature of the polymer. Similar observations were reported previously, for example, by




Figure V-4. Elastic modulus *E* (filled symbols) and hardness *H* (open symbols) as a function of the degree of polymerization of polymer grafts measured by nanoindentation of the *particle-brush* film assemblies. Solid and dotted lines denote the measured *E* and *H* for both linear PS ($M_{n,GPC}$ = 300 000) and linear PMMA ($M_{n,GPC}$ = 996 000), respectively. The error bars represent standard deviations determined by averaging at least 20 indentations per sample. Colored regions indicate CPB (red) and SDPB (yellow) regimes, respectively.

A more pronounced effect of entanglement and thus of chain length of surface-grafted chains is expected for the toughness of the *particle-brush* solids *K*_{ic}.

The latter can be determined from the analysis of the dimensions of cracks that form along the indenter-tip regions during the indentation process as illustrated in Figure V-5 for the case of the reference sample PS ($M_{n,GPC} = 52\ 000$).



Figure V-5. Illustration of process used to determine the toughness of *particle-brush* solids from nanoindentation experiments. Panel a: Threedimensional AFM image (8 × 10 μ m²) of the residual impression by nanoindentation on a PS film ($M_{n,GPC} = 52\,000$) revealing crack formation. Panel b: Schematic of a crack created with a Berkovich tip where a total crack length *c* is measured from the center of contact to end of crack at the sample surface, *t* is the distance from the center of the indenter to the corner, and *l* is the length of the cracks that emanate from the corners. From the measured crack dimensions the sample toughness can be determined using Equation V-2 (see text for more details).

Figure V-5a depicts a 3D-AFM image (tapping mode) of the residual impression after nanoindentation under displacement control (indentation depth equals 500 nm) that was used to measure the crack length *I* and the center-to-corner distance *t* of the indent (see Figure V-5b). The fracture toughness was then

determined from the measurements of the radial crack length on the film surface with the following equation:¹⁴

$$K_{IC} = 1.076 x_v (\frac{t}{l})^{\frac{1}{2}} (\frac{E}{H})^{\frac{2}{3}} \frac{P_{\text{max}}}{c^{\frac{3}{2}}}$$

Equation V-2

Here *c* is the total length of the cracks, P_{max} is the maximum load, and $x_v = 0.015$ is an empirical constant.¹⁴ Using Equation V-2 the toughness K_{lc} of *particle-brush* solids was evaluated for 20 distinct indents per sample.

Figure V-6 depicts the experimental fracture toughness K_{lc} (normalized with respect to the reference values K_{lc}° of high molecular weight PS and PMMA reference samples, with $M_{n,PS}$ = 300 000 and $M_{n,PMMA}$ = 996 000) as a function of the degree of polymerization of surface-grafted chains for both *particle-brush* series.

For both polymer graft series the figure reveals the increase of toughness by about an order of magnitude as the degree of polymerization increases beyond the CPB \rightarrow SDPB transition; the toughness eventually levels off at values close to those of the high *M* reference homopolymers (*i.e.*, $K_{lc}/K_{lc}^{\circ} \cong 1$ for high *N* grafts). In the limit of short polymer ligands (*i.e.* 8SiO₂-PS10 and 8SiO₂-PMMA40) the *particle-brush* systems exhibit small values of fracture toughness (<40 KPa m^{1/2}), similar to those reported previously for small molecular ligandcoated nanocrystal superlattice structures.¹⁸ Macroscopic films in this range of fracture toughness are found to be fragile and sensitive to minor stresses that can arise, for example, during solvent evaporation.



Figure V-6. Dependence of normalized fracture toughness K_{lc}/K_{lc}° on the degree of polymerization ofpolymer grafts in the CPB and SDPB regimes. K_{lc}° denotes the measured toughness of linear polymeranalogues with high molecular weight (*i.e.*, PS with $M_{n,GPC}$ = 300 000 and PMMA with $M_{n,GPC}$ = 996 000). The inset shows a plot of the experimental toughness of 8SiO₂-PS770 (filled circles) and linear PS with $M_{n,GPC}$ = 52 000 and 300 000 (open circles) in comparison to toughness values for PS reported in the literature.¹⁹ To allow for equal scale the literature data were normalized with respect to the limiting value at high molecular weights.

In contrast to the trends observed for the elastic modulus and hardness, the fracture toughness significantly increases the degree as of polymerization increases beyond the CPB \rightarrow SDPB transition (note that in terms of absolute values the toughness of PMMA-grafted brushes was found to exceed those of PS-grafted systems by approximately 20% in agreement with expectations based on the characteristic properties of the respective homopolymers). This can be rationalized as a consequence of the existence of chain entanglements that are expected to form in the limit of high N_G of surface-grafted chains. Based on the CPB/SDPB model entanglement formation is expected once the degree of polymerization of surface-grafted chains is large enough such that the segment length in the relaxed SDPB regime exceeds about twice the critical segment length for entanglement formation, *i.e.* $N_{\text{SDPB}} \ge$ 2*N*_e.^{5a} It is well established in entangled that fracture amorphous polymers involves microscopic flow processes that lead to the formation of crazes that provide a key mechanism for energy dissipation during fracture.⁵ Note that the formation of crazes is a fingerprint of the presence of entanglements in glassy polymers and is not expected unless the polymer's degree of polymerization exceeds about twice the threshold value for entanglement formation (see discussion below).^{5a}

V.3.4. Tough matrix-free filler material

Interestingly, the toughness of *particle-brush* solids in the SDPB regime is found to significantly exceed the toughness that would be expected for

corresponding homopolymers with equal molecular weight as the surface-grafted chains. This is illustrated in the inset of Figure V-6 that compares the measured toughness of PS-grafted particle-brushes with literature values for PS homopolymers (data from reference 19). While adopted both PS homopolymer systems that were evaluated in the present study confirm the reported trend of $K_{\rm lc}(M)$ the toughness of 8SiO₂-PS770 is found to exceed the expected toughness by almost one order of magnitude. The increased toughness of *particle-brush* solids was rationalized as a consequence of the connectivity of grafted chains with the particle center that imposes (topological) constraints on the deformation of the entanglement network. Since each particle core is connected to $n = 4\pi R_0^2 \rho_s \cong 10^3$ polymer grafts the effective number of entanglements per particle-brush should be of the order of 10³ increased as compared to one individual grafted chain. Similar to high molecular weight homopolymers the increase of connectivity between the constituents should result in the stabilization of crazes that increase the resistance of the system against crack propagation.

The presence of entanglements (and thus their contribution to energy absorption by means of craze formation) can be evaluated by characterization of the microstructural changes associated with the fracture process (*i.e.* the analysis of crack formation at the early stages of the fracture process). To test for craze formation in *particle-brush* solids, films were prepared by spin casting of *particle-brush* solutions on the water soluble substrate (such as poly(acrylic acid)) and subsequently lifted off and analyzed by TEM (the film thickness was controlled by

adjustment of particle concentration; thick films were pre-stressed prior to analysis). Figure V-7 depicts electron micrographs of films after lift-off for PS- (Figure V-7a and b) and PMMA- (Figure V-7c and d) grafted particles revealing distinct modes of fracture in *particle-brush* thin films depending on the architecture of the grafted chains.



Figure V-7. Deformation characteristics of PS- and PMMA-grafted *particle-brush* assemblies revealing craze formation in particle solids in the SDPB regime. Panel a: Electron micrograph revealing hard-sphere type crack formation in $8SiO_2$ -PS10 ($N_G = 10$) thin films. The inset shows multiple crack formation. Panel b: Typical craze formation in the thick film of $8SiO_2$ -PS770 ($N_G = 770$). The formation of fibrils is observed in the monolayer of $8SiO_2$ -PS770 that "bridge" particle cores across the fracture surface (inset). Panel c: Crack propagation in the thick film of $8SiO_2$ -PMMA40 exhibiting brittle fracture. The inset shows magnification. Panel d: Electron micrograph revealing the formation of craze in the thin film of $8SiO_2$ -PMMA570. The inset shows localized shear necking of fibrils connecting particle cores that arise from plastic flow. Scale bar is 300 nm (main figure) and 200 nm (inset), respectively.

Whereas for short chain-grafted *particle-brush* solids the formation of sharp cracks is observed (Figure V-7a and c) that is typical for brittle fracture, the micrographs of SDPB systems (Figure V-7b and d) reveal the formation of crazes

that bridge the surface of propagating cracks. The observed transition from particle-like to polymer-like fracture characteristic is accompanied by a change from brittle behavior (with multiple crack formation during the film drying process) to flexible *particle-brush* solid structures that can be peeled-off from surfaces without undergoing fracture (see also reference 20).

V.3.5. Fragile-crazing transition

Since chain entanglement is a critical prerequisite for craze formation to occur, the micrographs shown in Figure V-7b and d suggest that for a total degree of polymerization $N_{\rm G}$ the polymer segment length in the relaxed SDPB regime of the respective particle-brush systems (8SiO₂-PS770 in Figure V-7b and 8SiO₂-PMMA570 in Figure V-7d) exceeds about twice the critical entanglement limit, *i.e.* $N_{\text{SDPB}} \ge 2N_{\text{e}}$. The condition for entanglement formation provides a basis for the prediction of the minimum degree of polymerization that is required to facilitate craze formation in *particle-brush* solids. Following the extended Daoud-Cotton model the relative segment length of the grafted polymer chains that are with associated the regimes be estimated via two can $R_{\rm c} = R_0 + a N_{\rm GCPB} x$ (where x is the scaling parameter in the CPB regime, see Figure V-2i) and $N_{SDPB} = N_G - N_{CPB}$, respectively. Polymer-like mechanical properties of *particle-brush* solids can be expected if the length of the relaxed segments of the grafted chains exceeds about twice the critical segment length for entanglement (*i.e.* $N_{SDPB} \ge 2N_{e}$)—this situation is illustrated in Figure V-8a. Thus

according to the CPB/SDPB model the minimum degree of polymerization to facilitate chain entanglement should be approximately determined by

 $N_{\rm min} = 2N_{\rm e} + [a^{-1}(R_{\rm c} - R_0)]^{1/x}$

Equation V-3



Figure V-8. Panel a: Illustration of the transition in the deformation characteristics of *particle-brush* solids. Craze formation (and thus increased resistance to fracture of the particle solid) is expected if the segment length in the SDPB regime exceeds the threshold segment length for entanglement formation. Panel b: Predicted dependence of the threshold degree of polymerization to facilitate entanglement formation of grafted chains on the particle core size calculated using Equation V-3 assuming a grafting density $\sigma = 0.5$ chains nm⁻² (the inset shows theoretical prediction for various grafting densities σ). The curves are expected to approximately delineate the transition from fragile particle-like to polymer-like fracture. Circles and squares represent PS- and PMMA-grafted *particle-brush* systems, respectively. Colored regions correspond to predicted mechanical response of the *particle-brush* system.

Figure V-8b depicts the calculated trend for the minimum degree of polymerization to facilitate chain entanglement in *particle-brush* solids as a function of both particle radius and grafting density (inset in Figure V-8b).

As expected, the minimum degree of polymerization is found to increase with both particle size and grafting density. The good agreement between predicted and experimentally determined transitions in mechanical properties illustrates that the Daoud–Cotton scaling model, despite being based on rather oversimplifying assumptions, should provide a useful practical guideline for the synthesis of *particle-brushes* with 'engineered' polymer-like mechanical properties. The increased toughness that is observed in *particle-brush* solids (as compared to homopolymers equal to the surface-grafted chains) should also render particlebrushes an intriguing platform for facilitating novel quasi-one-component NC materials in which advantageous mechanical properties are paired with the increased control of the microstructural characteristics and thus properties of the NC. This concept is illustrated in Figure V-9 that contrasts the microstructure (Figure V-9a and b) and mechanical characteristics (Figure V-9c) of a 'quasi-onecomponent' particle-brush-based NC (8SiO₂-PS770) with those of a 'classical' NC consisting of a binary polymer/particle blend of 8SiO₂-PS150 dispersed in PS ($M_{n,GPC} = 52\,000$) with near identical composition (*i.e.* approximately 10 wt%) SiO₂).



Figure V-9. Comparison of structure and mechanical properties of *particle*-NC brush based quasi-one-component with binary particle/homopolymers composite. Panel a: TEM of a 'quasi one-component' NC composed of the particle-brush system 8SiO₂-PS770 revealing shortranged ordered arrangement. Panel b: TEM of binary NC (composed of a blend of the particle-brush system $8SiO_2$ -PS150 and linear PS with $M_{n,GPC}$ = 52 000) exhibiting randomized particle dispersion. Scale bar is 100 nm. Panel c: Toughness (filled symbols) and elastic modulus (open symbols) of guasione-component (circles) and binary (stars) nanocomposites with near identical filling fraction of inorganic component (10% w/v silica). Significantly increased toughness is observed in the case of the particlebrush NC.

Comparison of the micrographs shown in Figure V-9 reveals that the molecular connectivity between the particle and polymer components in *particle-brush* systems facilitates the formation of short-ranged ordered structures with regular particle spacing (Figure V-9a) whereas a random particle dispersion is observed in the case of the binary NC system (Figure V-9b).

V.3.6. Ordered particle array structures

The ability of the particle system to organize, under appropriate conditions. into long-range ordered array structures in which new properties can arise due to coupling and interaction between the particles within the array is an important feature of colloidal particles. Retaining this capability in *particle-brush* solids is therefore a desirable goal. The uniformity of the packing structure of *particle-brush* monolayers was evaluated by analysis of the distribution of Voronoi cell areas of particle monolayers (conditioned by thermal annealing at T = 120 °C for 48 h). In a first step, electron micrographs of particle monolayers are subjected to thresholding and Voronoi tessellation (using MATLAB).²¹ The analysis of the structural uniformity of the particle monolayer then becomes equivalent to the statistical characterization of the dimensions of Voronoi polygons. In case of perfect regularity of the particle assembly (in this case the Voronoi cell would be equivalent to the Wigner-Seitz cell of the 2D crystal structure of the particle monolayer) the Voronoi cells would be identical and the distribution of cell areas would be a delta function $\delta(x - \langle V \rangle)$, where $\langle V \rangle$ denotes the (average) Voronoi cell size—as the structural regularity decreases, the variance of the Voronoi cell areas increases. Voronoi cell analysis has been widely used to characterize the structure of liquids as well as solids with predominant short-range order (such as the particle-brush monolayers) where it has been shown to provide more accurate information than alternative techniques such as the analysis of pair distribution functions or Fourier transform methods.²² The analysis follows earlier work by Montoro and Abascal, who demonstrated that the width of the distribution of

Voronoi cell areas provides a quantitative descriptor of the structural regularity of liquids and solids.²² Thus, in order to quantitatively assess the effect of *particle-brush* architecture on the order formation in particle monolayers, the distribution of cell areas for all particle systems was fitted with a Gaussian function, and the order parameter was introduced as (1– fwhm), where fwhm denotes the full width at half-maximum of the areal distribution that is normalized with respect to $\langle V \rangle$.²³ Figure V-10 illustrates the process of evaluating fwhm for the example of a monolayer of the sample 8SiO₂-PMMA570 and 30SiO₂-PS1800.



Figure V-10. Voronoi tessellation of the *particle-brush* monolayers corresponding to 8SiO₂-PMMA570 (panel a) and 30SiO₂-PS1800 (panel b) where dots represent a center of particle cores. Inset shows a relative frequency of Voronoi cell areas fitted by a Gaussian distribution.

V.3.7. Parameters that affect the regularity of *particle-brush*

The effect of brush architecture on the regularity of *particle-brush* monolayers is shown in Figure V-11, which depicts the order parameter for all *particle-brush* systems. With increasing $N_{\rm G}$ the regularity is found to increase up

to a maximum value and to subsequently decrease (for the $30SiO_2$ -PSN_G series only the initial increase is observed; see discussion below). For both small particle systems ($8SiO_2$ -PSN_G and $8SiO_2$ -PMMAN_G) the transition from increasing to decreasing regularity (indicated by arrows in Figure V-11) is observed at a similar threshold degree of polymerization that equals about twice the critical degree of polymerization for the CPB \rightarrow SDPB transition (indicated as the borderline between the distinct colored regions in Figure V-11). For the large particle system, ($60SiO_2$ -PSN_G) the trend of the order parameter suggests the transition from increasing to decreasing regularity is observed around the CPB \rightarrow SDPB transition.



Figure V-11. Dependence of the order parameter (1 – fwhm) determined from the full width at half-maximum of a Gaussian fit to the areal frequency distribution on the normalized degree of polymerization. Arrows indicates

the maximum order parameter for the respective *particle-brush* system (squares: $8SiO_2$ -PS- N_G and $8SiO_2$ -PMMA-N; circles: $30SiO_2$ -PS- N_G ; and triangles: $60SiO_2$ -PS- N_G). Lines are introduced to guide the eye.

The proximity of the degree of polymerization to attain maximum structural regularity (i.e., maximum order parameter) to the CPB \rightarrow SDPB transition suggests that the distinct chain conformations associated with both regimes play an important role in determining order formation in *particle-brush* assemblies presumably via their implication on *particle-brush* interactions. In previous experimental studies on the effect of chain conformation (i.e., particle-brush regime) on the interaction between particle-brushes in solution, it was shown that interactions between *particle-brush*es in the CPB regime are approximately of hard-sphere type, thus indicating that chain crowding and the associated excluded volume interactions between surface-grafted chains result in strong repulsive interactions between *particle-brush*es.²⁴ In contrast, more polymer-like interactions were observed in solutions of *particle-brushes* in the SDPB regime as indicated by significant chain interpenetration at the brush overlap concentration.²⁴ The prominent influence of polymer chain conformation on the interaction between particle-brushes is also supported by recent theoretical studies. For example, Genz et al. demonstrated that densely grafted polymer chains act to increase the effective hard-sphere radius of particles.²⁵ Simulation studies of *particle-brush* systems by Lin and Gast using self-consistent field theory have revealed that the strong repulsive interactions in densely grafted particlebrush systems arise from excluded volume interactions and the entropic penalty

associated with the overlap of crowded surface-grafted chains.²⁶ Thus, particles with a dense layer of surface-grafted chains (i.e., *particle-brushes* within the CPB regime) are expected to show steep repulsive potentials similar to hard spheres with an effective radius equal to the sum of particle radius and brush height. On the basis of these prior experimental and theoretical studies, it is possible that the structure formation in *particle-brush* assemblies can be (approximately) interpreted by decoupling of the respective contributions of segments in the CPB and SDPB regime. Therefore, the formation of ordered hexagonal particle arrays was attributed to the presence of repulsive (hard-sphere-type) interactions that are exclusively due to segments in the CPB regime. Thus, for as long as the degree of polymerization of surface-grafted chains remains within the CPB regime, essentially hard-sphere-type ordering of *particle-brush*es is expected. Counteracting to order formation is the polydisperse nature of the commercial particle systems used in the present study.²⁷ The grafting of uniform polymer chains (in the CPB regime) to the particle surface reduces the effective size disparity of the particle-brush system due to the associated increase in total particle size. To quantify the effect of graft architecture on the size disparity of particle-brushes, the effective particle-brush size dispersity (SD) can be defined as SD = $\sigma/(2R_0 + d)$, where σ is the standard deviation of the particle core diameter and d the particle surface-to-surface distance (or twice the brush height) that is determined from electron micrographs of *particle-brush* monolayers. Figure V-12 depicts the dependence of SD on the degree of polymerization revealing a continuous decrease of SD from about 17% for short polymer grafts ($N_G \approx 40$) to

less than 5% for long polymer grafts ($N_G \ge 1000$) in the case of 8SiO₂-PS N_G and 8SiO₂-PMMA N_G .



Figure V-12. Dependence of the effective size dispersity for $8SiO_2$ -PMMA-N_G particle-brush system, given by the ratio of the standard deviation of the core particle size to the particle size, on the degree of polymerization. The images show the electron micrographs of the individual particle-brush system depicting an increase of the brush thickness with degree of polymerization. Inset depicts corresponding relationship for the $30SiO_2$ -PS-N_G particle-brush system.

In agreement with expectations, Figure V-12 confirms that the decrease of SD is more pronounced in the CPB regime due to the stretched conformation of grafted chains ($d \sim N_G^{0.8}$) as compared to the SDPB regime ($d \sim N_G^{0.5}$). Since it has been shown that the propensity of hard-sphere systems to form ordered array

structures decreases with increasing particle size disparity, The initial increase of the order parameter was rationalized with increasing N_G (see Figure V-11) as a consequence of the alleviating effect of polymer graft modification on the size disparity of the respective particle system.²⁸ Note that Figure V-11 also reveals a qualitatively similar trend for the order parameter (i.e., the order parameter initially increases with N_G) in the case of the larger particle system ($60SiO_2$ -PS N_G) despite the significantly reduced particle size disparity. This indicates that the alleviating effect on size disparity that is associated with polymer graft modification is not the only cause for the observed increase of the order parameter but rather that the presence of polymer grafts (in the CPB regime) has more complex implications on the interaction between *particle-brush*es that favor order formation. It is hypothesized that the presence of polymer grafts provides a more mobile environment that facilitates short-range particle motion during the film annealing stage that increases the coarsening kinetics of the particle array structure.

Eventually, as N_G exceeds a threshold value, the order parameter (1 – fwhm) is found to decrease—Figure V-11 reveals that the threshold value is independent of the graft chemistry and about twice the degree of polymerization N_c that marks the CPB \rightarrow SDPB transition in the case of the small particle systems (8SiO₂-PSN_G and 8SiO₂-PMMAN_G), whereas the transition is observed closer to the CPB \rightarrow SDPB transition in the case of the large *particle-brush* system (60SiO₂-PSN_G). To semiquantitatively capture the decrease in order parameter, it was assumed that segments within the SDPB regime do not

contribute repulsive interactions and therefore predominantly act to "dilute" the particle array structure. Although the latter assumption is rather simplifying, it was noted that the neglect of contributions of SDPB segments to the "hard-sphere-type" interactions between particle-brushes is supported by the scaling coefficient $x \sim 0.5$ as well as the mechanical properties of particle array structures that confirm interpenetration and entanglement of segments in the SDPB regime (see also reference 29). Within the particle array the relaxed segments are then expected to occupy the void space between effective hard spheres (constituted of inorganic core and CPB shell) in order to reduce the amount of high-energy polymer/air interfacial area.³⁰ Support for this assumption is also provided by recent numerical simulations by Bozorqui et al., who demonstrated that surfacetethered chains in arrays formed by sparse *particle-brush*es (in which all segments) assume relaxed chain conformations) fill in the interstitial space in the particle lattice structure.³¹ As the volume of relaxed chain segments exceeds the available void space, the close-packed regular structure cannot longer be maintained, and a decrease of the order parameter is expected. Figure V-13 illustrates the proposed mechanism for the transition between regimes with increasing and decreasing order parameter.



Figure V-13. (a) Illustration of the proposed architecture of two-phase *particle-brush*es depicting the stretched-to-coil transition of chain conformations. (b) The close-packed hexagonal order formed by the dense brush inner region (i.e., $R_0 + h_{CPB}$) where the interstitial regions that are filled by coiled chain segments in the SDPB regime have been highlighted in blue. (c) Schematic presentation of the expected trend of order parameter depending on degree of polymerization (red, see text for more details).

V.3.8. Maximum degree of polymerization for particle order formation

Following to the above argument, the critical degree of polymerization to result in the decrease of structural regularity of particle arrays can thus be estimated by the condition that the volume fraction of segments in the SDPB regime exceeds the available void space,

i.e. $\phi_{\text{SDPB}} = C(4\pi)R_0 / a^{3>} \phi_{\text{void}} \sim 0.26$

Equation V-4

where a close-packed arrangement of monodisperse particles has been assumed and *C* is a constant (of the order unity) that accounts for the number of particles per unit cell volume. Evaluation of this condition as a function of particle core size, grafting density, and degree of polymerization of surface-grafted chains allows the construction of a "structure map" for the expected order formation characteristics of *particle-brush* systems as illustrated in Figure V-14.



Figure V-14. Threshold degree of polymerization for the "order-to-disorder" type transition as a function of particle core size R_0 at grafting density $\sigma = 0.5 \text{ nm}^{-2}$ calculated on the basis of Equation V-4 (inset: corresponding predictions for various grafting density σ). The curves are expected to approximately delineate the transition from ordered to disordered arrangement. Green and yellow symbols denote increasing and decreasing order parameter with increasing degree of polymerization of surface-grafted chains for the respective particle system (squares: 8SiO₂-PS-*N*_G and 8SiO₂-PMMA-*N*_G; circles: 30SiO₂-PS-*N*_G; and triangles: 60SiO₂-PS-*N*_G).

The transition criterion defined by Equation V-4—despite of the simplifying assumptions underlying its derivation—quantitatively captures the threshold degree of polymerization (shown as point symbols in Figure V-14) for all *particle-brush* systems within the experimental uncertainty. It is noted that the above interpretation is consistent with the observed shift of the "order–disorder transition" to smaller N_G/N_c (i.e., closer to the CPB \rightarrow SDPB transition) in the case of the large particle system. This is because N_c increases with particle size, and thus a given change of N_G/N_c represents a larger net change in the total number of segments in the SDPB regime for larger particle diameter.

On the basis of Equation V-4 *particle-brush*es are expected to form ordered structures analogous to hard sphere systems if $N_G < N_{max}$. Although the above arguments can only be considered to provide (at best) a semi-quantitative guideline to predict and interpret the characteristics of *particle-brush* materials there is an interesting hypothesis that follows from the above discussion. In particular, Equation V-3 and Equation V-4 suggests *particle-brush* systems to be capable of forming both ordered and tough array structures if the degree of polymerization of tethered chains is within the range $N_{min} < N_G < N_{max}$, where N_{min} is the minimum DP to achieve toughening as discussed above. This condition is illustrated in the highlighted region of Figure V-15a, that depicts the predicted trend lines representing Equation V-3 and Equation V-4 calculated for a grafting density $\sigma = 0.5$ nm⁻². The predicted combination of structural and mechanical properties is substantiated by the analysis of PS-grafted silica particles with $R_0 \cong 56.6$ nm, $\sigma =$

0.5 nm⁻² and N_G = 2200 (60SiO₂-PS2200). Figure V-15b illustrates the formation of flexible and free-standing 'photonic' films fabricated by rapid solution casting. Figure 5c and 5d reveal the origin of the optical and mechanical properties of the 60SiO₂-PS2200 solid film. In particular Figure V-15c depicts a TEM image of a bilayer film of 60SiO₂-PS2200 revealing a high degree of regularity of the *particlebrush* solid that is consistent with the observed uniform optical iridescence. The formation of crazes during the deformation of 60SiO₂-PS2200 films (see Figure V-15d) confirm the presence of polymer-like chain entanglement that also rationalizes the films' mechanical flexibility, see inset of Figure V-15b. The fortuitous combination of structure formation and mechanical properties could render *particle-brush*es, with appropriate architecture, interesting candidates for the synthesis of photonic inks and paints.



Figure V-15. . Panel a: Plot of N_{min} and N_{max} as function of particle size for $\sigma \cong 0.5 \text{ nm}^{-2}$ according to Equation V-3 and Equation V-4 in the text. Highlighted in yellow is the predicted range of *particle-brush* architectures that combine craze formation (and hence increased toughness) with the capability of forming long-range ordered *particle-brush* arrays. Panel b: Image of thick film ($t \sim 0.5 \text{ mm}$) of PS-grafted SiO₂ particles ($R_0 \cong 56.9 \text{ nm}$, $\sigma \cong 0.5 \text{ nm}^{-2}$, N_G = 2200) revealing strong iridescence. Inset shows flexural stability of film during bending. Panel c: Transmission electron micrograph (TEM) of particle bilayer revealing regular superstructure. Particles in bottom-layer form

hexagonal array, particles in top-layer are centered on interstitials of bottomlayer. The observed structure is commensurate with cubic or hexagonal close packing in the solid state. Panel d: TEM of particle monolayer upon deformation revealing multiple craze formation during fracture.

V.4. Conclusion

In this chapter, the existence of both concentrated polymer brush (CPB) and semi-diluted polymer brush (SDPB) regimes in hybrid particle systems was proven by examining the relation between the brush height (h) and the number of repeating units in the polymer graft (N_G). The method suggested in Chapter II was used, which provided a scaling coefficient of $x \sim 0.8$ in the CPB and $x \sim 0.5$ in the SDPB regime. The effect of polymer conformation as the chains transitioned through the CPB and SDPB regimes was evaluated for polystyrene and poly(methyl methacrylate) (PS and PMMA) grafted silica particle systems using nanoindentation. A significant increase in film toughness was observed for films in which the brushes were in the SDPB regime. The increase in film toughness concurred with the formation of crazes during fracture of the particle-brush material and was clearly observed by TEM. The formation of crazes is a direct confirmation of the presence of chain entanglements in the SDPB *particle-brush* regime which provides a microscopic polymer-like interaction generating high fracture toughness. Therefore, in order to provide high fracture toughness the $N_{\rm G}$ has to be sufficiently high such that the chains enter the SDPB regime. However, a disordering of particle array may occur when the $N_{\rm G}$ at SDPB regime exceeds the free volume between particles and starts to force particles apart from each other.

Both "fragile-crazing" and "order–disorder" transitions were then evaluated using a mean-field scaling model that interprets the structure of the polymer brush as being constituted of two distinct conformational regimes, stretched and relaxed. The model provides "design criteria" for the synthesis of *particle-brush* systems that are capable of forming tough and ordered self-assembled structures that could be harnessed, for example, for the synthesis of novel multifunctional materials including mechanically robust colloidal crystal structures. These materials have potential utility for the synthesis of photonic inks and paints.

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Chapter VI

Thermal Properties of Particle-brush Materials: Effect of Polymer Graft Architecture on the Glass Transition Temperature in Polymer-Grafted Colloidal Systems

Preface The previous chapter introduced a new class of hybrid nanocomposites, specifically particle-brush materials that did not require an additional blending step with polymer matrix to form a stable cohesive material. This occurred when the grafted polymer brushes were long enough that the polymer-grafted particles were interconnected via brush-brush entanglement interactions. In other words, the interface between bushes on different particles constituted the matrix of the particle-brush material. Therefore, the polymer brush conformation was expected to contribute to the material's properties. Indeed, in the last chapter, different mechanical properties were observed based solely on the conformation of the grafted polymer chains. In order to expand the understanding of the effect of the

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brush conformation and brush particle interfaces on the properties of particle-brush materials, the glass transition temperatures of polymer-grafted particle systems with various brush conformations were analyzed. This chapter discusses the particular case of densely grafted polystyrene (PS)-grafted silica colloids. The glass transition temperature of the surface grafted polymer chains increased as compared to linear chain polymers of equivalent degree of polymerization (DP). The difference in the glass transition temperature between polymer-grafted particle systems and their respective linear polymer analogs increased with decreasing grafted DP of polymer brushes ($N_{\rm G}$) and leveled off at similar plateau values for particle-brushes of distinct particle core sizes. This trend toward increased glass transition temperature was interpreted to be the consequence of the increased steric hindrance resulting from densely grafted polymer chains close to the particle The increase in glass transition temperature was shown to be surface. approximately consistent with the chain conformational regimes that are predicted on the basis of a Daoud-Cotton type scaling model, which was descripted in Chapter II, III, and V.

VI.1. Introduction

Solid particle assembly structures (in the following denoted as 'particle solids') play an important role for the integration of nanomaterials into a wide range of device architectures with applications ranging from sensor to photovoltaic technologies.¹ A widely used approach for the fabrication of particle solid

structures relies upon the self-assembly of ligand-coated particles from particle dispersions. A major barrier for the scalable production of self-assembled particle array structures arises due to the weak and short-ranged particle interactions that promote the formation of cracks and limit the processing and integration of particle solid structures.² The development of techniques to increase the cohesive interactions within particle assembly structures without the need of extensive post-processing of particle films is thus an important prerequisite for broadening the range of applications of nanoparticle solids.

Opportunities to address the challenge of fragility in particle solids are presented by consideration of the role of surfactants on the mechanical properties of particle solids. In the last chapter, polymer-modified particles – in the limit of high grafted degree of polymerization of polymer brush $N_{\rm G}$ – were shown to be capable of forming flexible film structures with elastic properties similar to the corresponding graft-polymer as well as order-of-magnitude increase of fracture toughness.³ The increase of film stability has been related to conformational transitions within the grafted polymer chains that are expected to assume more stretched conformations in the vicinity of the particle surface and more relaxed conformations with increasing $N_{\rm G}$ of surface grafted chains. In particular, the mechanical transition between brittle and tough behavior was consistent with the predicted chain conformational transitions on the basis of a scaling model originally introduced by Daoud and Cotton to describe the structural transitions in Star-polymers.⁴ Following to the Daoud-Cotton approach that was discussed in Chapter
II, particle-brushes are categorized depending on the polymer grafting density and N_G into two regimes, *i.e.* the concentrated particle-brush regime (CPB) in which excluded volume interactions give rise to more stretched chain conformations and the semidilute particle-brush regime (SDPB) in which chains assume more relaxed conformations.⁵ Fukuda and coworkers introduced critical а distance $R_c = R_0(\sigma^*)^{1/2}(v^*)^{-1}$ (with R_0 denoting the particle core radius, $\sigma^* = \sigma a^2$ the reduced grafting density, a the length of a repeat unit and $v^* = v/(4\pi)^{1/2}$ the effective excluded volume parameter) to determine the transition between the two conformational regimes.⁵ Particles are considered to be within the CPB regime if the total particle radius (*i.e.* the sum of the core radius and the height of polymer graft layer) does not exceed R_c and to be within the SDPB regime otherwise. The relevant geometrical characteristics of the Daoud-Cotton particle-brush model are illustrated in Figure VI-1.



Figure VI-1. Illustration of relevant geometrical parameters of particle-brush system according to the Daoud-Cotton model. A transition from stretched ($h_{CPB} \sim N^{0.8}$) to relaxed ($h_{SDPB} \sim N^{0.5}$) chain conformations is expected at $R_c = R_0 + h_{CPB}$ (see text for more details).

The Daoud-Cotton model is based upon the assumption of negligible excluded volume interactions and is expected to become increasingly inaccurate with increasing packing density of polymer chains across the surface. Recent numerical simulations have demonstrated the limitations of the Daoud-Cotton approach to accurately predict the details of chain packing within the CPB regime.⁶ However, despite of these shortcomings, the scaling model has been widely shown to adequately describe experimental observations related to structural transitions in particle-brush systems both in the liquid and solid state.^{3b, 6-7} The purpose of the present chapter is to establish the effect of particle-brush architecture on the thermal properties of particle solids. Here, it is demonstrated that the glass

transition temperature (T_g) associated with grafted polymer chains in particle-brush solids increases when compared to the respective linear polymer reference system (T_g^0). The difference in glass transition temperature $\Delta T_g = T_g - T_g^0$ is shown to exhibit a step-function type decrease as the N_G exceeds a threshold value that is consistent with the predicted CPB \rightarrow SDPB transition based on the Daoud-Cotton model. The increase of ΔT_g within the CPB regime is interpreted as a consequence of increased excluded volume interactions as compared to the SDPB regime that reduce the chains' conformational entropy and counteract the relaxation of surface-grafted chains. The results therefore provide new insights into the implications of chain conformational transitions on the physical properties of particle-brush materials and the applicability of the Daoud-Cotton model to capture relevant structural transitions.

VI.2. Experimental Part

VI.2.1. Polystyrene Reference Polymers

Polystyrene of different molecular weights were obtained from Polymer Source and used without further purification.

VI.2.2. Particle-Brush Synthesis

Readers are referred to Chapter II for more details. Briefly, particle systems were obtained from Nissan Chemicals. Styrene (S) was obtained from Aldrich and purified by passing through a column filled with alumina. The synthesis of PS-grafted particle-brush systems was performed using surface-initiated atom-

transfer radical polymerization (SI-ATRP) as described in the previous chapter and elsewhere.⁸ Purification of products also followed previously published methods on SI-ATRP.⁸ Table VI-1 presents a summary of the composition of the particle-brush system used in the present study.

Sample ID	R _{o,TEM} (nm)	M _n	M _w	N _G	σ (nm ⁻²)	N _c	
8SiO ₂ -PS100	7.7 ± 4.0	10 400	11 200	100	0.61	250	
8SiO ₂ -PS370	7.7 ± 4.0	40 000	44 000	370	0.59	250	
8SiO ₂ -PS520	7.7 ± 4.0	54 100	60 600	520	0.57	250	
8SiO ₂ -PS2200	7.7 ± 4.0	230 000	300 000	2200	0.57	250	
30SiO ₂ -PS130	29.6±8.5	14 000	16 700	130	0.62	550	
30SiO ₂ -PS350	29.6±8.5	36 400	43 000	350	0.57	550	
30SiO ₂ -PS550	29.6±8.5	57 000	69 000	550	0.52	550	
30SiO ₂ -PS1900	29.6±8.5	198 000	255 000	1900	0.48	550	
60SiO ₂ -PS130	56.6±6.0	13 000	14 000	130	0.61	1200	
60SiO ₂ -PS400	56.6±6.0	41 000	45 900	400	0.61	1200	
60SiO ₂ -PS610	56.6±6.0	63 400	81 800	610	0.55	1200	
60SiO ₂ -PS2100	56.6±6.0	220 000	280 000	2100	0.47	1200	

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rable	VI-I.	Particle-	-brusn :	systems	used in	the	bresent study	.

VI.2.3. Thermal Analysis

Differential scanning calorimetry (DSC) measurements were performed using a DSC-Q20 (TA Instruments). Measurements were performed at heating and cooling rate of 10 °C/min. Measurements of the glass transition temperature were performed during third cooling cycle.

VI.2.4. Morphological Analysis

Particle-brush thin films were prepared by film casting from toluene solution (concentration 1% w/v). Films were thermally annealed for 1 day at T = 125 °C in vacuum. The morphology of particle distributions was subsequently determined by electron imaging. Imaging was performed by transmission electron microscopy (TEM) using a JEOL EX2000 electron microscope operated at 200 kV.

VI.3. Results and Discussion

VI.3.1. Particle-brush and untethered polymer samples

The system in this study consists of three distinct silica particle (SiO₂) systems with particle core radius (determined by TEM) $R_0 = 7.7 \pm 4$ nm, $R_0 = 29.6 \pm 8.5$ nm, and $R_0 = 56.6 \pm 6$ nm, respectively. All particle systems were obtained from Nissan Chemicals and functionalized using surface-initiated atom transfer radical polymerization (SI-ATRP) as described in the section 'Experimental Part'. Particle systems with the following graft characteristics are the subject of the present study: PS-grafted small particle systems ($R_0 = 7.7 \pm 4$ nm) with $\sigma \approx 0.5-0.8$ nm⁻², $N_G = 10-2200$ (sample ID: 8SiO₂-

SN_G); PS-grafted medium-sized particle systems ($R_0 = 29.6 \pm 8.5$ nm) with $\sigma \approx 0.5-0.7$ nm⁻², $N_G = 130-1900$ (sample ID: $30SiO_2-SN_G$); and PS-grafted large particle systems ($R_0 = 56.6 \pm 6$ nm) with $\sigma \approx 0.5-0.7$ nm⁻² and $N_G = 130-2000$, (sample ID: $60SiO_2-SN_G$). Here, σ denotes the grafting density on the particle surface. The characteristics of all particle-brush systems are summarized in Table VI-1.

To evaluate the effect of brush architecture on the glass transition temperature of surface-grafted chains, the T_g of equilibrated particle-brush solids was compared to the corresponding value (T_g^0) in linear PS reference polymer systems. Five different PS reference systems were chosen with respective DP of N_{PS} = 101, 380, 600, 960, 2000 close to the particle-brush systems (sample ID: PS- N_{PS}); the conditions for film preparation were analogous to those of particle-brush solids. The characteristics of all reference PS systems are summarized in

Table VI-2.

Sample ID	<i>M</i> _n	M _w	Ð	N _{PS}	T _g (°C)
PS-101	10 500	11 400	1.09	101	94.0
PS-380	40 000	42 000	1.05	380	95.5
PS-600	62 000	64 400	1.04	600	98.5
PS-960	97 000	100 000	1.06	960	105.0
PS-2000	208 000	227 000	1.09	2000	105.5

Table VI-2. Reference linear polystyrenes used in the present study.

Figure VI-2 depicts representative transmission electron micrographs of the $60SiO_2$ -SN_G particle series revealing a uniform composition of particle-brush systems. Note that from the scaling of the particle surface-to-surface distance (*d*) with N_G, the critical DP N_c for the CPB \rightarrow SDPB transition can be estimated to N_c ≈ 250 (8SiO₂-N_Gseries), 550 (30SiO₂-N_G series), and 1200 (60SiO₂-N_G series) according to the study in Chapter II.



Figure VI-2. Transmission electron micrographs depicting monolayer assembly structures of $60SiO_2$ - N_G particle-brush series. Within the range of particle-brush systems N_G = 130, 370, and 610 the interparticle distance is found to scale with the DP of surface-grafted chains as $d \sim N_G^{0.8}$ confirming stretched polymer chain conformations (CPB regime). Scale bar is 200 nm.

VI.3.2. Effect of polymer brush conformation on glass transition temperature

The glass transition temperatures T_g of the 'polymer graft phase' in all particle-brush materials were determined using differential scanning calorimetry (DSC) and compared to those of linear chain polymers with approximately equal DP as the grafted polymer chains. Figure VI-3a depicts representative heat flow

curves (cooling cycle) for PS and particle-brush systems. The effect of particlebrush architecture on the T_g of the graft polymer chains was then evaluated by analysis of the difference to the respective linear PS reference system with comparable DP, *i.e.* by analysis of $\Delta T_g = T_g - T_g^0$. Figure VI-3b depicts the trend of ΔT_g for all particle-brush systems as a function of the particle-brush inorganic content (that is inversely related to the N_G).



Figure VI-3. Thermal analysis of particle-brush systems. Panel a: Representative heat flow curves (cooling cycle) of particle-brush systems and corresponding polystyrene reference polymer. The glass transition is found to increase in case of particle-brush materials. Panel b: Summary plot of the change in glass transition temperatures ΔT_g of particle-brush and reference polystyrene systems. ΔT_g is found to increase to plateau value ($\Delta T_g \approx 12$ °C) with increasing inorganic fraction (decreasing N_G) for 8SiO₂- N_G and 30SiO₂- N_G particle-brush series.

The figure reveals that for all particle-brush systems ΔT_g increases as compared to the linear reference polymers (this is in agreement with recent simulations and experimental results for related material systems such as

'molecular brushes').⁹ Several important observations can be made: First, within each particle-brush series ΔT_g increases with increasing fraction of inorganic component, *i.e.* with decreasing N_G . Second, for all three particle-brush series ΔT_g is largest in the limit of small N_G and shows a sudden decrease at some threshold inorganic content – the threshold inorganic concentration increases with particle core diameter. Third, in the limit of small N_G (or high inorganic content) ΔT_g is found to converge to a similar plateau value ($\Delta T_g \approx 12$ °C) for the 8SiO₂- N_G and 30SiO₂- N_G series while the plateau value for the 60SiO₂- N_G particle-brush series is found to be significantly smaller ($\Delta T_g \approx 6$ °C).

It is interpreted that the observed trends of ΔT_g as a consequence of the constraints on the chain conformational entropy that are implied by the particlebrush architecture. Since the softening temperature T_g in general is associated with the activation of dynamic processes, it is expected that T_g increases with decreasing conformational entropy of surface-bound chains. Thus the coupling of one chain end to the particle-brush surface as well as the existence of stretched polymer segmental regimes (as illustrated by the CPB regime in which the chain end-to-end distance is found to scale as $R_e \sim N^{0.8}$, see references 6 and 19 are expected to result in the increase of the glass transition temperature. Note that under the condition of equal grafting density, the reduction of chain conformational degrees of freedom should – in the limit of small N_G (or within the CPB regime) – be comparable for small and large particle-brush systems and thus (under ideal conditions) a similar increase of ΔT_g should be observed (for small N_G) irrespective of particle core size. This conclusion is indeed supported by the data as indicated by the similar plateau values of ΔT_g for the 8SiO₂-N_G and 30SiO₂-N_G particle-brush series. Qualitatively similar trends are observed in the case of the large (60SiO₂- $N_{\rm G}$) particle-brush series albeit the plateau value is observed to be reduced as compared to the former systems. It is interpreted that the reduction of the plateau value in case of the $60SiO_2$ -N_G particle-brush series as a consequence of the higher $N_{\rm G}$ that could give rise to a plasticization effect (albeit other parameters relating to the particle-brush architecture could play a role). A general comment should be regarding the methodology to determine ΔT_g that gives rise to minor uncertainty in the absolute values of ΔT_{g} . In particular, the graft polymer and the respective linear homologues were synthesized by different techniques, i.e. ATRP and anionic polymerization, respectively. The different synthetic routes could give rise to differences in the polymers' tacticity and thus minor differences in the glass temperature of brush and linear reference polymers could be expected. While this uncertainty cannot be excluded or quantified with the available material systems it is expected that the effect of tacticity on the samples softening temperature to be small compared to the observed ΔT_{g} .

The arguments presented above suggest that the trend of ΔT_g should sensitively depend on the CPB or SDPB nature of the particle system. This is indeed observed in Figure VI-4 that presents a plot of the ΔT_g as a function of the normalized N_G (in units of the critical DP for the CPB \rightarrow SDPB transition, N_c). The figure reveals that the decrease of ΔT_g for all particle-brush systems approximately

coincides with the CPB \rightarrow SDPB transition that is predicted by the Daoud-Cotton model, *i.e.* $N_c \approx N_G$.



Figure VI-4. Difference in glass transition temperature ΔT_g as function of N_G/N_c for all particle-brush systems. The uniform decrease of ΔT_g at $N_G/N_c \approx 1$ indicates relevance of steric constraints and chain crowding on the observed increase in glass transition temperature. See text for more details.

The common trend among the different particle-brush systems in Figure VI-4 confirms the close relation between chain conformational constraints and the glass transition in particle-brush materials. The figure also suggests that – despite of the oversimplifying assumptions underlying the scaling approach – the Daoud-Cotton particle-brush model does capture experimental trends within the experimental certainty (although an increasing deviation between the change of ΔT_g and the predicted conformational transitions is observed with increasing

particle size). This is in agreement with the last chapter about the effect of polymergraft modification on the mechanical properties of particle-brush solids that found the formation of chain entanglements in particle-brush solids to be closely related to the CPB \rightarrow SDPB transition predicted by the Daoud-Cotton model. It should be noted that besides the specific deficiencies of the model itself other experimental parameters, such as the size disparity of inorganic particle cores, are expected to contribute to the trend in glass transition temperatures. More experimental data will be needed to draw assertive conclusions about the applicability and limitations of the scaling model in describing the thermal properties of particle-brush materials (for alternative interpretations on the effect of inorganic interfaces on the chain dynamics of polymer films that reader is referred to references 22 and 23).¹⁰

VI.4. Conclusion

The current study shows that the glass transition temperature of particlebrush materials sensitively depends on the architecture of particle-brush systems. In general, the grafting of polymers to the particle surface is found to raise the polymers' glass transition temperature, the relative increase (with respect to the corresponding linear polymer of equal DP) is found to increase with decreasing N_{G} . The increase in T_{g} is interpreted as a consequence of the reduced conformational entropy of surface-bound chains that results from chain crowding as well as a reduced number of chain ends. The results suggest that in the limit of small degrees of polymerization the difference in T_{g} between bound and free chains converges to a limiting value that is only weakly dependent on particle size. A

pronounced reduction of ΔT_g is observed with increasing N_G , the reduction is particularly pronounced at a threshold DP that coincides approximately with the CPB \rightarrow SDPB transition as predicted by the Daoud-Cotton model. The results thus underline the relationship between architecture and the physical properties of particle-brush materials that will support the design of novel 'quasi-one-component' nanocomposite materials in which improved control of the physical properties is achieved by the tailored molecular engineering of the particle-brush constituent systems.

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VI.6. References

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Chapter VII

Effect of Thermal Self-Initiation on the Synthesis, Composition and Properties of Particle-Brush Materials

Preface Chapter V discussed the use of surface-initiated atom transfer radical polymerization (SI-ATRP) to synthesize polymer-tethered particles (particle-brushes) and self-assemble particle-brushes into hybrid materials with well-defined microstructure, morphology and enhanced mechanical properties or optical transparency, as compared to binary particle/polymer nanocomposite materials. However, side reactions – such as the thermal self-initiation (TSI) of some monomers, such as styrene, during the polymerization – can result in the formation of varying amounts of homopolystyrene, in addition to particle-brushes. The presence of homopolystyrene impurity can be generally undesirable because it reduces the predictability of properties and impedes the interpretation of structure-property relations in particle-brush materials. This chapter presents a systematic evaluation of the formation of TSI homopolystyrene and its implications on the properties of polystyrene-tethered silica based particle-brush materials.

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Kinetic and molecular weight studies reveal that the fraction of untethered chains generated by TSI sensitively depends on reaction conditions and increases with the degree of polymerization of surface-tethered chains. The presence of homopolystyrene results in a decrease of the softening temperature but also in an increase of ductility and toughness of particle-brush solids. Structural analysis of particle-brush assemblies admixed with small particle tracer inclusions suggest that the increase in ductility is related to the preferential segregation of the polystyrene impurity within the corner regions of the Wigner Seitz cell of the particle-brush array structure.

VII.1. Introduction

The grafting of polymeric chains to and from the surface of nano- or colloidal particles has attracted interest both from the perspective of controlling the interactions between particles and their assembly behavior and also as a means of developing novel multifunctional composite materials.¹ Examples include the assembly of polymer-tethered particles (here called 'particle-brushes') into one-component hybrid materials with enhanced optical transparency and mechanical properties, as compared to their binary particle-in-polymer matrix analogs,² or the controlled organization of particle fillers in polymeric embedding media.³ Recent computer simulations furthermore suggest the existence of a hierarchy of 'microdomain-type' morphologies depending on the composition of particle-brush materials.⁴ To harness the opportunities afforded by particle-brush based materials,

the synthesis has to offer precise control over the architecture of surface-tethered chains.

Surface initiated reversible deactivation radical polymerization (SI-RDRPs, also termed as SI-controlled radical polymerizations) have recently received particular attention in the synthesis of particle-brush materials due to their ability to establish a dynamic equilibrium between a small number of propagating radicals and a large number of dormant species thereby providing the ability to produce much better-defined hybrid materials compared to conventional radical polymerization approaches.⁵ SI-atom transfer radical polymerization (SI-ATRP) is an excellent tool for the preparation of polymers with well-controlled chain-end functionality, degree of polymerization (N) and graft density (σ) grafted from particle surfaces, and has been successfully used to prepare various organic/inorganic hybrid materials.⁶ Importantly, many ATRP reagents are currently commercially available, including tetherable initiators.⁷ ATRP tolerates some impurities and is applicable to a wide range of monomers with various functional groups, also in aqueous media.⁷⁻⁸ However, in SI-ATRP (as well as for other RDRP reactions) side-reactions, such as radical termination or thermal selfinitiation (TSI) can occur that can alter the physicochemical properties of particlebrush materials. TSI, typical for styrene-based systems, presents a challenge since the formation of homopolystyrene impurity can complicate the interpretation of structure-property relations in particle-brush materials as well as preparation of particle-brush materials with predictable properties.⁹ In this article, we analyze the

influence of homopolystyrene formed by TSI on mechanical properties of particlebrush materials. ATRP initiators were covalently tethered to silica particles (radius $R_0 \equiv 56.6 \pm 6.0$ nm) and used to prepare polystyrene (PS). PS was chosen due to the glassy character of PS (that supports the analysis of mechanical properties by nanoindentation). The rate of TSI was controlled by carrying out SI-ATRP at 2 different temperatures with 2 different ligands and monitoring the TSI effect on polymerization kinetics and molecular weight (MW) evolution. The amount of untethered polystyrene (un-tPS) generated by TSI was quantified by the combination of centrifugation, filtration, SEC, and TGA. Finally, the effect of TSI on the particle-brush properties was evaluated using DSC and nanoindentation. The results suggest that an appropriate amount of un-tPS resulted in an improvement of the mechanical properties of the particle-brush system due to an enhancement of the entanglement density on the Wigner-Seitz cell. TEM images were additionally implemented in order to support this hypothesis.

VII.2. Experimental

VII.2.1. Materials

Styrene and methyl methacrylate (S and MMA, Aldrich, 99%) were purified by passing through basic alumina columns before use. Copper (I) bromide was prepared by reduction of an aqueous solution of CuBr₂ with an aqueous (aq.) solution of ascorbic acid, and copper (I) chloride was prepared by reduction of CuCl₂ aq. solution using an aq. solution of sodium sulfite. Both copper (I) halides were then sequentially filtered, washed with methanol, dried and stored under

vacuum before use. Silica nanoparticles (SiO₂), 30% solution in isopropanol (IPA-ST-ZL), effective radius measured by TEM, $R_0 \cong 56.6 \pm 6.0$ nm, were donated by Nissan Chemical Corp. and used as received. 5-Hexen-1-ol (98%), α -bromoisobutyryl bromide (98%), triethoxysilane (95%), ethyl 2-bromoisobutyrate (EBiB, 98%), 4,4'-dinonyl-2,2'-bipyridine (dNbpy, 99%), *N*,*N*,*N'*,*N''*-pentamethyldiethylenetriamine (PMDETA, 99%), and anisole (99%) were purchased from Aldrich and used as received. Hydrofluoric acid (50 vol% HF) were purchased from Acros Organics and used as received. All other chemicals and solvents were supplied by Aldrich and Acros Organics.

VII.2.2. Tethering ATRP initiators on particle surfaces

5-Hexen-1-ol (**1**), α-bromoisobutyryl bromide (2-bromo-2-methylpropanoyl bromide, **2**), and triethoxysilane (TES) were used to synthesize a tetherable ATRP initiator; 6-(triethoxysilyl)hexyl 2-bromo-2-methylpropanoate (TES-HBMP, **4**) and finally attached the initiator onto IPA-ST-ZL using a modification of a reported procedure, see Scheme VII-1.¹⁰ The Br terminated ATRP initiator functionalized SiO₂ (SiO₂-Br) was washed with 99.5%+ ethanol followed by centrifugation. This procedure was repeated 10 times in order to wash away all initiators that were not attached to SiO₂-Br. 500 MHz ¹H NMR with 1024 scans showed no observable initiator residue remaining in the ethanol dispersion after these washing cycles, and then the solvent was exchanged to anisole.

VII.2.3. Typical SI-ATRP of S

In a typical SI-ATRP of S in a grafting polymerization from the surface of SiO₂-Br, 15.4 g of 6.5 wt% SiO₂-Br in anisole dispersion (1.0 g of SiO₂-Br with 90 µmol Br/g) and 20.6 mL of S (180 mmol) were mixed with a stock solution containing 5 mg of CuBr₂ (22.5 μ mol), 51.7 μ L of PMDETA (247.5 μ mol), and 2.1 mL DMF (ca. 5.4 vol%) in a 100 mL Schlenk flask equipped with a rare earth magnetic stirring bar. The use of a rare earth magnetic stirring bar in the grafting reactions from SiO₂-Br is important, as it was noted that glassy state of the reaction mixture occurred significantly earlier in the absence of a sufficient stirring, especially at high monomer conversion. The mixture was first stirred overnight then degassed by 4 cycles of freeze-pump-thaw. The flask was subsequently immersed in liquid nitrogen and purged with nitrogen when 32.3 mg of CuBr (225) µmol) was added to the frozen reaction mixture. The flask was sealed, evacuated for 40 min, back-refilled with nitrogen 3 times, warmed to room temperature, and finally immersed in an oil bath at 70 °C. The mixture was stirred at a suitably fast rate until the desired time had elapsed, the flask was then cooled while continuing stirring, and the reaction was terminated by adding oxygenated tetrahydrofuran (THF) to stop the reaction. The same reaction conditions were employed with various catalysts, at different temperatures and in the presence of other types of monomers. The final product suspended in THF was dialyzed against THF and methanol until the characteristic color of the copper (II) catalyst disappeared. The remained solid was labeled as "polystyrene grafted silica particles + untethered polystyrene (SiO₂-PS + un-tPS)" and dried in vacuum at 25 °C for 48 h before further characterization.



Scheme VII-1. Synthesis of polystyrene-grafted SiO₂ (SiO₂-PS) by surfaceinitiated ATRP is a 3-steps process. First, 5-hexen-1-ol (1), α bromoisobutyryl bromide (2), and triethoxysilane (TES) were employed to synthesize a tetherable ATRP initiator, 6-(triethoxysilyl)hexyl 2-bromo-2methylpropanoate (TES-HBMP, 4) via the intermediate 3. Second, TES-HBMP was attached to the surface of SiO₂ to form SiO₂-Br. Finally, SiO₂-PS was synthesized via SI-ATRP while TSI occurred concurrently to form untethered-PS.

VII.2.4. Characterization

VII.2.5. Separation of SiO₂-PS and un-tPS

The dried sample (SiO₂-PS + un-tPS) was redispersed in toluene, sonicated for 1 h, then stirred for 24 h before centrifugation. The centrifugation was carried out gently until ca. 10 - 20 wt% of the sample in the centrifugation tube was collected. The absence of any un-tPS in the centrifugation solid residue was later verified by TEM, and the residue was labeled as "SiO₂-PS". The remaining filtrate was kept in the centrifugation tube until the SiO₂ peak in the dynamic light scattering spectrum disappeared (DLS, 0.1 - 1 mg mL⁻¹ in toluene solution using a Malvern Zetasizer Nano ZS). The final filtrate was first passed through the 0.45 μ m, 0.20 μ m, and 0.10 μ m polytetrafluoroethylene (PTFE) syringe filter, and labeled as un-tPS. It was later confirmed by SEC measurement that there was no particle peak in these samples.

VII.2.6. Characterization of polymer-grafted particles before and after un-tPS removal

SiO₂-PS and SiO₂-Br were imaged with transmission electron microscopy (TEM) using a JEOL 2000 EX electron microscope operated at 200kV. Images were acquired using a Gatan Orius SC600 high-resolution camera. The size of the particles was determined by a statistical analysis of the TEM images using ImageJ software. The apparent initiator density of SiO₂-Br was determined by elemental analysis (bromine content), conducted by Midwest Microlab (IN). Monomer conversion during SI-ATRP was monitored by 500 MHz ¹H NMR (256 scans). The weight of the polymer brushes grafted from particles was measured by thermogravimetric analysis (TGA) using a Q50 TGA analyzer from TA Instruments (New Castle, DE) under nitrogen up to 850 °C.

MW and MW distribution (MWD) were determined by size exclusion chromatography (SEC), using a Waters 515 pump and Waters 2414 differential refractometer using PSS columns (Styrogel 10⁵, 10³, 10² Å) in THF as an eluent

(35 °C, flow rate of 1 mL min⁻¹), with toluene and diphenyl ether used as internal references. Linear polystyrene (PS) and poly(methyl methacrylate) (PMMA) standards were utilized for calibration. Samples were etched from particles with HF in a polypropylene vial for 20 h, neutralized with ammonium hydroxide, and dried with magnesium sulfate before SEC injection. Neutralization process was conducted with caution under liquid nitrogen to dissipate heat. The glass transition temperatures (T_g) of nanocomposites were determined by DSC-Q-20. Each sample was heated from 60 to 180 °C at a rate of 10 °C/min. T_g was determined as the temperature corresponding to half the complete change in heat capacity, calculated as the peak maximum in the first derivative of heat flow. All of the above characterizations were repeated after the separation of SiO₂-PS and un-tPS.

VII.2.7. Particle-brush film preparation and nanoindentation

Two linear PS samples ($M_n = 52\ 000$, D = 1.02 and $M_n = 300\ 000$, D = 1.2) were obtained from Polymer Source and used as reference for the nanoindentation experiments. Thick films for nanoindentation were prepared by drop-casting particle solutions at high concentration ($15 - 20\ \text{mg}\ \text{mL}^{-1}$) on the silicon substrate. The spatial distribution of particles was analyzed using ImageJ software. Mechanical properties such as elastic modulus and fracture toughness were measured by nanoindentation experiments using an MTS Nanoindenter XP with a Berkovich tip under displacement control of not more than ~10% of the nanocrystal film thickness. For PS reference samples experiments were performed at varied load rates ($1 - 25\ \text{nm}\ \text{s}^{-1}$) in order to exclude load rate dependence of the results. Experimental data of particle-brush samples were obtained from at least 20 indentations per sample and the experimental error was determined by the standard deviation of the measurements. The displacement rate during the indentation was 5 nm s⁻¹ to a maximum load, followed by a constant load indentation for 20 seconds. In order to examine the residual impression formed by indentation, the fracture surfaces were scanned in a tapping mode using an atomic force microscope (AFM, NT-MDT Explorer) with a silicon cantilever (5.1 N m⁻¹ force constant) with sharpened pyramidal tip.

VII.3. Results and discussion

In our previous study on a 'quasi' one-component system, PS (a glassy polymer with a reasonable entanglement limit) grafted SiO₂ was selected.¹¹ Polymerization of styrene (S) is always accompanied by a certain degree of thermal self-initiation (TSI) that spontaneously generates radicals during the polymerization process.⁹ Although TSI can be reduced at lower polymerization temperatures and using more active catalyst complexes (by decreasing the time of polymerization), generation of untethered polymers is unavoidable and centrifugation could be used to remove these "impurities". However, centrifugation is time-consuming and limits the processability of the system. Therefore, the effect of TSI on the mechanical properties of particle-brush system was studied. First, the synthesis of SiO₂-Br particles, apparent initiator density, and the number of growing chains are discussed. Second, the effect of S TSI on the SI-ATRP kinetics at 2 different temperatures and with 2 different ligands was analyzed. The amount

of untethered PS (un-tPS) generated by TSI was quantified using the combination of centrifugation, filtration, SEC, and TGA. Finally, the effect of TSI on the particlebrush properties that was characterized using DSC, nanoindentation, and TEM will be presented.

VII.3.1. Functionalization of silica nanoparticles

The particle size of IPA-ZT-L ($R_0 \cong 56.6 \pm 6.0$ nm) was determined from a statistical analysis using ImageJ software. The density of SiO₂ used for all calculations was 2.2 g/cm³. Specific surface area and therefore the amount of initiators required to modify the surface was then calculated. Scheme VII-1 outlines the synthetic route of SiO₂-Br followed by a modification of a previously reported procedure.¹⁰ The apparent initiator density 0.72% Br/g of SiO₂-Br was obtained by elemental analysis, which is equivalent to 0.09 mmol Br/g and ~1.94 initiator/nm².

VII.3.2. Number of growing chains

The number of growing chain was calculated using the exact procedure used in Chapter II.

VII.3.3. TSI effect on polymerization kinetics of S via SI-ATRP

TSI of S proceeding by radical mechanism has been known for more than a half of century.¹² Therefore, TSI of S has been used to initiate polymerization and surface grafting.¹³ The new radicals formed by TSI constantly form new polymer chains and therefore may alter the polymerization kinetics, *N*, σ , as well

as modify the particle-brush structure. In this section, the influence of TSI on the polymerization kinetics affected by TSI of S was first examined.

Previously, it was demonstrated that conducting a SI-ATRP at lower temperature with a more active Cu(I) catalyst complex provides PS with lower dispersity (*D*) in SI-ATRP.⁹ Since contribution of TSI is both temperature and time dependent, both lower temperature and faster polymerization decrease the contribution of TSI. Here, the kinetics of SI-ATRP conducted with Cu catalysts formed with dNbpy at 90 °C and PMDETA ligands at 70 °C were compared, due to similar K_{ATRP} and k_{deact} of S ATRP.¹⁴ Figure VII-1a presents the polymerization kinetics of these two reactions. SI-ATRP using Cu/dNbpy at 90 °C is slightly faster than with Cu/PMDETA at 70 °C due to higher $k_{\rm p}$ and the more pronounced TSI. A slightly curved kinetic plot was observed under both reaction conditions. A similar phenomenon in SI-reversible addition-fragmentation chain transfer (SI-RAFT) polymerization was previously observed.¹⁵ The kinetic plot is curved because TSI generates more radicals at the beginning of the reaction, since TSI is dependent on monomer concentration to a second or a third power.¹⁶ The MW evolution plot is presented in Figure VII-1b. Value of theoretical $M_{\rm h}$ ($M_{\rm n,theo}$) was calculated using the real number of growing chains (average graft density obtained from MMA SI-ATRP), instead of the apparent initiator density. Experiment M_n ($M_{n,exp}$) in both reactions clearly deviated from $M_{n,\text{theo}}$ but less in the case of PMDETA at 70 °C. These observations agree with the TSI mechanism since TSI continuously generates new polymer chains of lower MW which results in a gradual reduction

of $M_{n,exp}$. A better agreement is observed between $M_{n,exp}$ and $M_{n,theo}$ in a polymerization conducted with Cu/PMDETA at 70 °C, since a lower temperature and a faster reaction rate (using more reactive PMDETA as ligand) results in fewer radicals generated by TSI. Finally, higher D in the dNbpy at 90 °C reaction was observed, as shown in Figure VII-1a. This is attributed to TSI instead of termination, since k_p/k_t values should be higher at higher temperatures, resulting in less termination at a given conversion.¹⁷



Figure VII-1. a) Kinetics and b) MW and \mathcal{P} evolution plots of SI-ATRP with the following molar ratios [S]₀: [SiO₂-Br*]₀: [CuBr]₀: [CuBr₂]₀: [PMDETA/dNbpy]= 2000 : 1 : 2.5 : 0.25 : 2.75/5.5; DMF = 5.4 vol% and anisole = 40 vol%, temp = 70 or 90 °C, rpm = 1000 – 1500 rpm. *SiO₂-Br: apparent initiator density = 0.090 mmol Br/g or 1.9 initiators/nm² with $R_0 \cong 56.6$ nm, density of growing chain = 0.029 mmol Br/g or 0.63 chain/nm².

VII.3.4. Measurement of N and σ

Control over *N* and σ of tethered chains are the key parameters to form tough and well-ordered particle-brush materials.¹⁸ However, due to the participation of TSI, the *N* and σ measured directly by SEC and TGA without separation of SiO₂ are the

average values of tPS grafted from SiO₂ and the un-tPS, generated by TSI. Therefore, quantification and evaluation of un-tPS chains is necessary. Previously, un-tPS in S SI-ATRP was quantified by SEC of the entire reaction mixture.⁹ However, SEC analysis of systems containing particles can damage the SEC columns, especially for larger particles. Therefore, centrifugation method was developed, consisting of HF etching, and filtration before injection on the SEC column, as shown in WXYZ. The mixture of SiO₂-PS and un-tPS were first separated by centrifugation. For analysis purpose, only small weight fraction of SiO₂-PS was needed for SEC and TGA measurements. In addition, un-tPS was obtained by filtering the remainder with syringe filters after dilution with THF. Four samples collected at different reaction times in the 90 °C dNbpy reaction were selected as examples, and the results are summarized in

Table VII-1 (SampleID: (R_0)SiO₂-PS(N)). The successful extraction of untPs was verified by DLS and SEC as the particle peak disappeared. Successful extraction of pure SiO₂-PS were confirmed by TEM, as shown in Figure VII-2. The un-tPS before removal were located not only around particles but also segregate into the corner regions of the Wigner-Seitz cell (WSC). This specific morphology should influence the particle-brush properties, as discussed in the next section.

After successful separation of SiO₂-PS from un-tPS, the SiO₂ in SiO₂-PS was etched with HF to provide samples of the tPS. The *N* of both tPS and un-tPS were then measured by SEC. In addition, σ of polymer-grafted particles with or without un-tPS were then calculated by TGA before and after SiO₂-PS separation.

Table VII-1 shows the calculated *N* and σ . In samples with *N* < 1000, the σ and *N* do not differ much after the separation process. However, the σ and *N values* before and after the separation process were dissimilar in the sample 60SiO₂-PS1950. This is attributed to the fact that 60SiO₂-PS1950 had higher *N* which also required longer reaction time. Both parameters directly increased the fraction of un-tPS generated by TSI in the final sample and enhanced the effect on σ and *N*. The weight fractions of each component, including (*f*_{SiO2}, *f*_{iPS}, and *f*_{un-tPS}), were calculated using TGA data and Equation VII-1. In Equation VII-1, TGA "loss" and "residue" represent the weight loss and remaining weight fraction directly obtained from the corresponded TGA spectrums, respectively. The "before" and "after" numbers indicate the TGA measurements before and after the separation process. The calculated weight fractions of each component are listed in

Table VII-1. The results agree with the above discussion, since longer reaction times generate more un-tPS, and the higher *N* increases the weight fraction of un-tPS.



Scheme VII-2. Scheme of methodology used to determine *N* and σ of grafted (tPS) and unattached chains (un-tPS).



Figure VII-2. TEMs of 60SiO₂-PS650 before (up: a & b) and after (down: c & d) purification of TSI polymer, scale bars are a) 200, b) 100, c) 500, d) 100 nm.

Equation VII-1:

 $f_{polymer} = f_{un-tPS} + f_{tPS} = f_{TGA:loss,before}$ $f_{SiO2NP} = 100 - f_{TGA:loss,before} = f_{TGA:residue,before}$ $f_{tPS} = f_{SiO2NP} \times \frac{f_{TGA:loss,after}}{f_{TGA:residue,after}}$ where f_i denotes the weight fraction of component *i*.

Table VII-1. Sample characterizations of "SiO₂-PS + un-tPS" before and after the separation of SiO₂-PS and un-tPS, R_0 of the SiO₂-Br = 56.6 ± 6.0 nm.

Sample Name	Before separation			After separation			Calculation		
(<i>R</i> ₀)SiO₂-PS <i>(N</i>)	N	TGA lost (f _{TGA-loss,before})	σ / nm ²	N	TGA lost (f _{TGA-loss,after})	σ / nm ²	f _{un-tPs} by TSI	f _{tPS}	fsio2np
60SiO₂-PS150	150	0.324	0.67	149	0.324	0.68	0.0	0.324	0.676
60SiO₂-PS400	392	0.563	0.67	403	0.555	0.64	0.018	0.546	0.437
60SiO₂-PS650	637	0.684	0.69	653	0.667	0.63	0.051	0.633	0.316
60SiO₂-PS1950	1632	0.877	0.81	1950	0.840	0.55	0.231	0.646	0.123

Table footnote: *N* and σ are the apparent number average degree of polymerizations and grafting densities of samples before and after the separation process. TGA weight% loss was directly obtained from the correspondence TGA spectra. The calculation of the weight fractions of different components, including un-tPS, t-PS and silica were calculated using Equation VII-1.
VII.3.5. Effect of Thermal Self-Initiation on Thermo-Mechanical Properties of Particle-brush Materials

To evaluate the effect of TSI on the thermo-mechanical properties of particle-brush materials, the glass transition temperature, elastic modulus, and toughness of all systems were evaluated before and after purification. Figure 5 depicts the trend of glass transition temperatures (T_g) determined by differential scanning calorimetry (DSC). The figure reveals an increase of the glass transition with increasing degree of polymerization of surface-tethered chains and a leveling off at $T_g \sim 107.5$ °C for N > 500. While glass transition temperatures are similar (within the experimental certainty) for purified and unpurified systems, T_g at N = 1950 was only slightly higher than at N = 650. This is consistent with the elevated fraction of thermally initiated chains (see

Table VII-1) for high *N* tethered chains that are expected to lower the glass transition temperature of the blend system. Steric confinement may limit the mobility of tethered chains and hence increases T_{g} as compared to the untethered polymer.¹⁹



Figure VII-3. Glass transition temperatures of (R_0)SiO₂-PS(N) listed in Table I-1 before and after the separation process.



Figure VII-4. a) Elastic modules and b) the normalized toughness of (R₀)SiO₂-PS(N)

samples listed in

Table VII-1 before and after the separation process. The dashed line in Figure VII-4a indicates the elastic modulus of linear PS standard of M_n 300,000.

To assess the effect of homopolymer on the mechanical properties of particle-brush materials the elastic modulus and toughness of particle-brush films (thickness $t \sim 100 \ \mu m$) was evaluated by nanoindentation. This technique was used instead of more conventional dynamic mechanical testing due to its ability to measure small sample volumes. Experimental design and procedures were analogous to previously published reports with more details on the characterization of the mechanical characteristics of particle-brush solids by nanoindentation.¹¹ A Berkovitch indenter with 40 μ m width and an indentation depth of 10 μ m was used to guarantee averaging over statistically significant volumes and to avoid artifacts due to the inhomogeneous structure of individual brush particles. To ensure reproducibility of results, experiments on selected particle-brush systems were performed at different load rates (ranging from 1 - 25 nm s⁻¹). No rate dependence was observed in the specified range; reported data present results obtained at 5 nm s⁻¹. Figure VII-4a depicts the elastic modulus of particle-brush systems before and after purification of homopolymer impurity. For both purified and unpurified systems the Young's modulus increases with increasing degree of polymerization of surface grafted chains and levels off at N > 500 to a value of $E \sim 4$ GPa that is approximately equal to the reference linear PS. It should be mentioned that this value exceeds (somewhat) literature values for linear PS that are typically quoted around E = 3.0 - 3.6 GPa. We attribute this minor deviation to the fundamental differences in probing the mechanical properties by indentation (indirect method) and bulk mechanical deformation (direct method) experiments, respectively. The former has been reported to induce minor systematic errors in the absolute values inferred from indentation.²⁰ The observed trend of E(N) resembles results of particle-brush systems with smaller silica particle size ($R_0 = 7.7 \pm 4.0$ nm). It indicates that the resistance to elastic deformation in particle-brush solids is primarily due to dispersion interactions between the tethered polymer chains.¹¹ Figure VII-4a reveals a more dramatic increase of Young's modulus for unpurified system compare with purified systems. The difference becomes more pronounced with increasing *N* of tethered chains. This is probably due to the extra interaction volume between particle-brushes created by the addition of TSI PS. Since the fraction of homopolymer formed by TSI increases with *N*, this effect should be most pronounced in the higher *N* regime – as it is indeed observed.¹⁹

Since the lowering of T_g should increase the molecular mobility (and hence ductility) of particle-brush materials, the presence of self-initiated homopolymer is expected to raise the toughness of particle-brush solids. This is revealed in Figure 6b that depicts the normalized toughness *K*_{IC}/*K*_{IC}⁰ (normalized with respect to the value of a molar mass 300 kg/mol linear PS reference polymer) for the distinct particle-brush solids. The figure reveals that toughness of the particle-brush materials in the unpurified system increased much more dramatically than in the purified system - due to the increased fraction of free homopolymer at higher *N*. However, the fundamental trend, the pronounced increase of the toughness of particle-brush materials at some threshold value of *N*, is similar for both purified and unpurified systems. In previous reports, this increase was attributed to the formation of entanglements between tethered chains. These results strongly

support the prior conclusions and confirm that the pronounced toughening with increasing degree of polymerization of surface-tethered chains cannot be solely attributed to the presence of self-initiated homopolymer impurity.

To better understand the mechanism by which impurities interfere with the structure formation in particle-brush solids, the structure of 2D thin film mixed particle-brush films in which the homopolymer was replaced with small PStethered silica particle additives ($R_0 = 7.7 \pm 4.0$ nm, N = 2000, SampleID: 8SiO₂-PS2000) was analyzed using electron imaging.¹⁸ Small SiO₂-PS fillers were chosen to approximately match the interactions of homopolymer impurities while providing a higher mass density core that facilitates identification during electron imaging. Figure VII-5 depicts an electron micrograph of the dispersion morphology of a mixed binary 60SiO₂-PS1950/8SiO₂-PS2000 particle-brush solid with 25 wt% content of small silica particle-brush fillers. The figure reveals the preferential segregation of the small particle filler within the corner regions of the Wigner-Seitz cell (WSC) of the regular array formed by 60SiO₂-PS1950 brush particles. The trend to segregate within the corner region of the WSC confirms previous reports on a similar observation for blends of smaller gold/silica brush particles. We rationalize the segregation of 8SiO₂-PS2000 within the WSC corner regions as a consequence of the non-uniform conformation of tethered polymer chains that are more stretched within the WSC corner regions (due to the systems tendency to fill interstitial space and avoid the formation of unfavorable polymer/air interfaces). The process is schematically depicted in Figure VII-5a.



Figure VII-5. Microstructure of particle-brush blend systems. Panel a: Illustration of the corner positions of the Wigner Seitz cell (red) within a hexagonal array of brush particles (gray) and depiction of polymer chain conformations in pristine particle-brush array. Polymer chains are stretched within corner regions (see text for more detail). Panel b: Electron micrograph revealing microstructure of mixed 60SiO₂-PS1950/8SiO₂-PS2000 particlebrush system. Small particles preferentially locate within corner region of Wigner Seitz cell.

We hypothesize that a similar 'concentration of filler' within the WSC corner regions occurs for homopolymer filler (albeit it cannot be visualized) and hence the increase of modulus and toughness should be attributed to the additional polymer/polymer and polymer/particle-brush interactions across the 'filled' interstitial regions. Of course, the above argument is only valid for impurity levels that are commensurate with the available interstitial volume (approximately 26% for a close packed hard-sphere-type assembly) and additional considerations (such as the role of homopolymer/particle-brush phase separation) will apply at higher impurity levels.²¹

VII.4. Conclusion

The influence of the thermal-self initiation of styrene on the SI-ATRP polymerization kinetics and particle-brush properties was investigated. Slightly curved kinetic plots were observed under both PMDETA@70 °C and dNbpy@90 °C reactions due to TSI of S. The influence of TSI was more pronounced at higher temperature and with less reactive catalysts. The combination of conventional separation and characterization methods including NMR, SEC, centrifugation, filtration, TGA, and TEM were used to quantify the amount of untethered polystyrene generated by TSI in samples synthesized by SI-ATRP. The presence of untethered polystyrene was also confirmed by TEM images before and after the separation process due to the change of inter-particle distance. The amount of untethered polystyrene was as much as 23 wt% calculated by TGA measurements before and after separating polymer-grafted particles and untethered chains. The presence of these thermally initiated homopolymer impurities enhances both the elastic modulus and toughness of particle-brush solids. The increased stability is attributed to the additional interactions imparted by homopolymer that is preferentially segregated within the corner regions of the Wigner-Seitz cell of the particle-brush array. However, while the presence of homopolymer can alter mechanical properties (by about 10% at a maximum homopolymer content of 23 wt% the fundamental trend of the behavior of particle-brush solids is unchanged after separation of the impurity. The presented results therefore support previous conclusions concerning the nature of interactions between tethered chains in particle-brush solids that were observed for unpurified materials.

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Chapter VIII

Particle-brush Solids as Templates for the Synthesis of Materials with Interconected Polymeric and Carbon Network Structure

Preface In prior chapters the uses of silica nanoparticles (SiO₂) for the synthesis of mechanically robust materials by conducting a grafting-from synthesis were explored. In this final chapter, the utility of SiO₂ as templates for nano-engineering the structure and properties of functional materials, including preparation of nanoporous polymers, and their related carbon materials is further reconnoitered. The nanoporous polymers can incorporate many structural features, such as controllable pore shape and size, tunable pore surface chemistry, well-developed porosity, high surface area, good conductivity, and low bulk density. Therefore, the materials could find utility in many fields including adsorption, catalysis,

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separations, medicine, environmental, and energy-related applications. Particlebrush hybrid materials can also serve as templates for the preparation of novel nanostructured carbons, in which the inorganic materials are employed as structural templates and the grafted polymeric materials serve as the nanocarbon precursor. For example, grafting of polyacrylonitrile (PAN) from convex and concave SiO₂ was previously demonstrated by our group. The SiO₂ were used as the sacrificial phase allowing, after graphitization, the preparation of well-defined nanostructured carbons. However, the synthesis of nanoporous carbons from other carbon precursor polymers prepared by ATRP had not yet been demonstrated, owing to polymers' thermal instability. This chapter reports new strategies to replacing PAN with carbonyl cross-linked polystyrene (PS) and poly(styrene-r-acrylonitrile) (PSAN) random copolymers. The results show that both the carbonyl cross-linked PS and the PSAN copolymers can be successfully converted to nanocarbons as a consequence of the external carbonyl crosslinking of PS and internal AN self-crosslinking, respectively.

VIII.1. Introduction

Nanoporous polymer and carbon materials can incorporate many structural advances, such as controllable pore shape and size, tunable pore surface chemistry, well-developed porosity, high surface area, good conductivity (for carbon materials), and low bulk density.¹ Therefore, they find utility in many fields including adsorption, separation, energy, environment, catalysis, and medicine.¹⁻² One of the most common and effective routes to prepare nanoporous carbon

materials are template methods, including hard template and soft template methods. The hard template method often uses thermally stable inorganic materials, such as silica nanoparticles (SiO_2) or ordered mesoporous silica SBA-15, while the soft template method usually employs thermally decomposable block copolymers to provide the tools for the formation of various types of nanopores.³ However, there are some drawbacks with both approaches. For example, the hard template method often involves incomplete filling of the pores and formation of a nonporous carbon as a result of deposition of carbon precursors on the external surface of the hard template.^{3h} On the other hand, the soft counterpart usually deals with the high cost of some sacrificial soft templates.⁴ Previously, novel strategies for the preparation of nanoporous carbons, based on atom transfer radical polymerization (ATRP)⁵ of acrylonitrile (AN)^{5b, 6} from initiation sites chemically bonded to hard templates including silica nanoparticles, ordered mesoporous silicas SBA-15 and FDU-1, and silica gel have been successfully developed.⁷ This approach provided a uniform filling of the template with polyacrylonitrile (PAN) and minimized the formation of non-templated PAN, thus mitigating the formation of non-templated carbon.

However, the carbon source used in the above mentioned ATRP-related nanoporous carbons synthetic strategies were still limited to PAN⁸ because of the thermal instability of many polymers, thus leading to some obvious disadvantages, e.g., quite low microporosity in the frameworks. One possible solution is to

crosslink the formed polymer network to enhance its thermal stabilization before carbonization. Recently, new nanomaterials with microporous crosslinked PS nanoparticles as the network unit were successfully developed.⁹ The formation of carbonyl (–CO–) crosslinking bridge between PS chains was demonstrated and created the unique network-type microporosity, and guaranteed the inheritability of the nanostructure during carbonization because the bridge simultaneously provides both a high crosslinking density and a proper amount of oxygen atoms.⁹ Alternatively, introduction of self-crosslinkable AN unit in PS chains to form random poly(styrene-co-acrylonitrile) (PSAN) copolymers was also found useful in nanocarbon preparation and imparted a microporous nature to the carbon framework.^{7b, 10}

Therefore, the synthesis of two new types of nano-network-structured polymer and carbon materials based upon particle-brushes synthesized by SI-ATRP and subsequent intra-/inter-particle carbonyl-crosslinking of the PS chains or self-crossllinkable PSAN chains were demonstrated. The overall synthetic procedure is illustrated in Scheme VIII-1. This study presents several significant advantages: First of all, the unique aspect of the as-prepared materials lies in the design and construction of the new core-shell nanosphere network unit. The final nano-network structure contains three types of nanopores, including an intraparticle crosslinking-induced network-type microporous shell, a silica-templating spherical mesoporous core, and an inter-particle crosslinking-induced meso-/macroporous network. Secondly, the unique well-defined core-shell nanostructure

could provide the nano-materials with some smart advanced performances such as highly selective adsorption and release property, with which the targeted small molecules in a mixture of molecules with different sizes could go across the microporous shell and then storage in the mesoporous core, followed by release after removing the mixtures outside. Thirdly, this new synthetic approach greatly promotes application of ATRP in nanoporous materials.



Scheme VIII-1. Preparation process of novel nanoporous polymer and carbon materials.

VIII.2. Experimental section

VIII.2.1. Materials

Styrene (S) (Aldrich, 99%) and acrylonitrile (AN) (Acros, 99%) were purified by passing through a column filled with alumina. The procedure for the synthesis of 1-(chlorodimethylsilyl)propyl 2-bromoisobutyrate and the subsequent functionalization of the silica nanoparticles (30 % wt. silica in methyl isobutyl ketone, ~ 18 nm diameter based on DLS and ~14 nm according to TEM images, Nissan Chemical) followed Chapter II and the previously described methods.¹¹ The Br content of the as-prepared functionalized silica (SiO₂-Br) was measured to be 0.353 mmol/g. Tris(2-(dimethylamino)ethyl)amine (Me6TREN) was synthesized following previously reported procedure.¹² Copper(I) bromide (Aldrich, 98+ %) was purified by washing sequentially with acetic acid and diethyl ether, filtration and drying, and was stored under nitrogen before use. Copper(II) bromide (Aldrich, 99.999%), 4,4'-dinonyl-2,2'-bipyridine (dNbpy; Aldrich, 99%), hydrofluoric acid (50 vol % HF, Acros), anhydrous aluminum chloride (Aldrich, 99.99%), carbon tetrachloride (anhydrous, Aldrich, 99.5%) were used as received.

VIII.2.2. Preparation of SiO₂-grafted-polystyrene (SiO₂-PS)

SiO₂-PS was synthesized according to the following recipe: S/SiO₂-Br/CuBr/CuBr₂/dNbpy = 1000/1/4/0.4/8.8 (molar ratio). A Schlenk flask was charged with SiO₂-Br, CuBr₂, dNbpy and S. After four freeze-pump-thaw cycles, the flask was filled with N₂, and then while the mixture was immersed in liquid nitrogen, CuBr was quickly added, and the flask was sealed with a glass stopper and evacuated for 30 min. After being filled with N₂, the sealed flask was transferred into thermostated oil bath at 90 °C. The reaction was stopped by opening the flask and exposing the catalyst to air after 20.5 h. The formed products were isolated and purified by precipitation into an excess of methanol and recovered by filtration.

VIII.2.3. Preparation of SiO₂-grafted-poly(styrene-co-acrylonitrile) (SiO₂-PSAN)

Synthesis of SiO₂-PSAN is similar but with a different ligand A Schlenk flask was charged with 0.50 g of initiator-modified silica nanoparticles (0.53 mmol Br/g silica; 0.27 mmol ATRP initiator sites) and anisole (16.8 mL). The mixture was stirred until a homogeneous solution was formed. Styrene (6.1 mL, 53.6 mmol), acrylonitrile (2.3 mL, 34.8 mmol) and Me6TREN ligand (62.7 µL, 0.27 mmol) were added to the flask. After three freeze-pump-thaw cycles, the flask was filled with nitrogen, then while the mixture was immersed in liquid nitrogen, 38.7 mg (0.27 mmol) of CuBr was added. The above molar ratio was S/AN/SiO2-Br/CuBr/Me6TREN = 200: 130: 1: 1: 1 in anisole (2 vol equiv of monomers). The flask was sealed with a glass stopper, evacuated, and back-filled four times with nitrogen. After melting the reaction mixture and warming to the room temperature, the initial sample was taken and the sealed flask was placed in thermostated oil bath at 70 °C. The polymerization was stopped after 53.2 h by opening the flask and exposing the catalyst to air. The product was precipitated twice into methanol, and at dried at vacuum oven to remove the solvent.

VIII.2.4. Preparation of nanoporous polymer from SiO₂-PS

SiO₂-PS (1.25 g) was dissolved in chloroform (125 ml) and then transferred to a Petri dish. The chloroform was evaporated over 1 day at room temperature, and then the resultant film was scraped out of the dish, resulting in isolation of broken SiO₂-PS films. The PS chains tethered to the SiO₂ particles were crosslinked by the Friedel–Crafts (F-C) reaction with anhydrous aluminum chloride (AlCl₃) as catalyst, and carbon tetrachloride (CCl₄) as crosslinker and solvent. 5.00 g AlCl₃ and 100 ml CCl₄ was mixed together and then heated at 75 °C for 1 h with magnetic stirring in a three-neck flask fitted with a condenser. 0.9400 g of the isolated SiO₂-PS film fragments were added to the above mixture. The resultant mixture was heated at 75 °C for 20 h under stirring. 100 ml 1M HCl was added slowly to the resulting mixture and heating at 75 °C was continued for a further 1 h under stirring. The product was filtered off, washed with acetone, 1M hydrochloric acid and pure water, and then dried. The resultant SiO₂/crosslinked PS composite was etched with HF, thus obtaining a nanoporous polymer. Another sample of the SiO₂/crosslinked PS composite was carbonized by heating to 800 °C in presence of 150 ml/min of N2 flow with a heating rate of 2 °C/min for 3 h. The as-obtained carbon/silica composite was etched with HF, thus forming a nanoporous carbon.

VIII.2.5. Preparation of nanoporous polymer from SiO₂-PSAN

The as-prepared SiO₂-PSAN powder sample was preoxidized at 280 °C for 6 h under airflow (150 ml/min) with a heating rate of 20 °C/min, and then was carbonized at 700 °C for 2 h in N₂ flow (150 ml/min) with a heating rate of 5 °C/min. Next, the carbon/silica composite was etched by HF solution, resulting in nanoporous carbon sample.

VIII.2.6. Characterization

Elemental analysis was conducted by Midwest Microlab (Indianapolis, IN) to determine the ATRP initiator amount on modified silica nanoparticles and

polymer weight ratio after polymerization. The PSAN polymer chains were cleaved from SiO₂-PSAN and SiO₂-PS nanoparticles using HF and then analyzed by a size exclusion chromatography (SEC) system conducted with a Waters 515 pump and Waters 2414 differential refractometer using PSS columns (Styrogel 105, 103, 102) A) in THF as an eluent (35 °C, flow rate of 1 mL/min). Linear polystyrene standards were used for calibration. The chain grafting density was calculated from the total polymer mass determined as the total organic mass obtained by elemental analysis, using the average molecular weight determined by SEC and assuming spherical shape of silica particles with diameter = ~ 20 nm and density = 2.07 g/cm³. The hydrodynamic diameter distributions of bare SiO₂ nanoparticles, SiO₂-PS, and SiO₂-PSAN hairy nanoparticles were measured by using a Malvern dynamic light scattering instrument. The concentration was 30 mg/1mL and 1mg/1mL THF for bare silica and hybrid particles, respectively. The nanostructure of the samples was investigated by a Hitachi H-7100 transmission electron microscope, a FEI Tecnai F20 transmission electron microscope, a Malvern dynamic light scattering instrument, and a Micromeritics ASAP 2010 analyzer at 77K. Nitrogen adsorptiondesorption isotherms were obtained with an ASAP2010 (Micromeritics Corp.) instrument at -196 °C. The samples were degassed at 200 °C prior to measurement. Raman spectrum was recorded in the wave number range 800-2000 cm⁻¹ using a Renishaw inVia Raman microscope. Subsequently, the spectrum was studied by a suitable curve fitting technique using a Lorentzian Fit Multi-peaks analysis tool from Origin 8 software.

VIII.3. Result and discussion

VIII.3.1. Synthesis of PS and PSAN particle-brush

The diameter of the bare SiO₂ was measured by DLS analysis to be ~ 18 nm, Figure VIII-1A, but ~ 14 nm according to the TEM image shown in Figure VIII-2A. Note that the hydrophilic state of nanoparticles could increase the diameter in suspension, thus leading to a slightly higher value from DLS compared to that from TEM.^{9b} These nanoparticles were functionalized by reaction with 1- (chlorodimethylsilyl)propyl 2-bromoisobutyrate to introduce Br-containing surface ATRP initiation sites.¹³ According to Figure VIII-1A and Figure VIII-2B, the resultant SI-ATRP initiator functionalized SiO₂-Br nanoparticles has almost the same diameter as the parent SiO₂, indicating that the functionalization treatment basically did not change the particle size. Subsequently, the SI-ATRP grafting of polystyrene and polyacrylonitrile onto the SiO₂-Br particle was carried out (see experimentl section).

The purified PS-grafted SiO₂ (SiO₂-PS) powder was dissolved in tetrahydrofuran (THF) at a concentration of 1 mg/ml, and had a narrow and unimodal size distribution with a maximum at 51 nm, according to DLS, Figure VIII-1A. PS was cleaved from the nanoparticles by etching with hydrofluoric acid (HF), and characterized by SEC. The cleaved PS had a narrow, unimodal peak with molecular weight M_n = 23,200 and M_w/M_n = 1.12, indicating an efficient SI-ATRP. The PS content of the SiO₂-PS nano-particles was measured to be 64 wt%

by thermogravimetric analysis, giving grafting density of approximately 0.22 or 0.28 chain/nm² based on the SiO₂ diameter of 14 nm (TEM) or 18 nm (DLS), respectively. Similarly, the as-prepared SiO₂-PSAN were dissolved in THF, 1 mg/mL, and had a narrow and unimodal size distribution with hydrodynamic diameter of 59 nm by DLS (Figure VIII-1B). PSAN was cleaved from the nanoparticles by etching SiO₂ with hydrofluoric acid (HF) and analyzed by GPC. The cleaved PSAN also had a narrow, unimodal molecular weight distribution ($M_w/M_n = 1.26$), with molecular weight $M_n = 21\,600$, indicating a controlled surface-initiated ATRP. The S/AN molar ratio, the polymer content, and the grafting density in the hybrids were about 3/2, 64 wt %, and 0.12 chain/nm², respectively.



Figure VIII-1. DLS size distributions for (A) SiO₂, SiO₂-Br, and SiO₂-PS, and (B) SiO₂ and SiO₂-PSAN.

VIII.3.2. Synthesis of nanoporous polymer from SiO₂-PS

The as-prepared SiO₂-PS nano-particles were cast into a film by evaporating a chloroform solution of SiO₂-PS at a concentration of 10 mg/ml to

dryness in petri dishes at room temperature. Figure VIII-2C shows the TEM image of the scratched SiO₂-PS films. The SiO₂-PS nanoparticles in the films retain a well-defined spherical shape with average size of about 18 nm, and aggregated with each other in various directions. Such aggregation facilitates the inter-particle crosslinking during the subsequent Friedel-Crafts (F-C) reaction. The F-C crosslinking was achieved by placing the SiO₂-PS films into a heated mixture of anhydrous aluminum chloride and carbon tetrachloride (CCl₄) and continuing heating for 20 h at 75 °C under stirring. The PS chains in the SiO₂-PS nanoparticles would undergo an intra-particle crosslinking process by formation of -CCl2crosslinking bridges between the benzene rings while swelling in the presence of CCl₄. This procedure subdivided the original solid PS shell into numerous micropores because of the formation of network structure. The –CCl₂– crosslinking bridges were subsequently hydrolyzed in the presence of water into the -COcrosslinking bridges,^{9, 14} which are essential for efficient carbonization of the PS framework and inheritability of the nanostructure during carbonization.⁹ The presence of the resultant micropores was confirmed by an adsorption uptake at low relative pressure in the N₂ adsorption-desorption isotherm.¹⁵ According to the pore size distribution (PSD) curve by density functional theory (DFT) in Figure VIII-3A, the size of the micropores is concentrated at 1.3 nm. During the crosslinking reaction, the swelled PS chains on the periphery of the shell of the inter-aggregated nanoparticles in the films would interpenetrate and then be joined with each other by inter-particle crosslinking under stirring, eventually leading to the formation of a 3D nanonetwork structure, Figure VIII-2D. Such a nano-network

contains lots of mesopores and macropores as a consequence of the combination of compact and loose crosslinked-aggregation of nanoparticles, respectively. The PSD curve, shown in Figure VIII-3A, indicates that the size of these meso-/macropores throughout the 3D network for the as-obtained SiO₂/crosslinked PS composite ranged from 2 to 170 nm with a maximum at 27 nm.

The SiO₂ core of the network unit can be removed to form a spherical mesopore, after treating the SiO₂/crosslinked PS composite with HF, resulting in a totally new targeted network unit. As shown in TEM images of the as-prepared nanoporous polymer, in Figure VIII-2E and F, the network units were well-defined hollow nanospheres, ~18 nm diameter, with a mesoporous core and microporous shell. They were interconnected with each other in various directions to form a unique 3D meso-/ macroporous network structure. A high magnification TEM image, Figure VIII-2G, confirms that the micropores were in the network of the crosslinked shell, and were interconnected with each other, and with the mesoporous core, as well as the meso-/ macroporous inter-particle network. Such perfect pore interconnectivity is essential to allow full use of these hierarchical nanopores in the final nano-structured materials.¹⁶ Furthermore, by comparing the PSD curves of the samples before and after etching, Figure VIII-3A vs B, the highest peak at 9 nm can be ascribed to the SiO₂-templating mesoporous core, with the intra-particle network micropores and the inter-particle network meso-/macropores concentrated at 1.5 and 25 nm, respectively. Note that this diameter

value of the SiO₂-templating mesoporous core using DFT is slightly lower than that of SiO₂ nanoparticle based on TEM image in Figure VIII-2A, most likely due to their different characterization mechanism. By applying Brunauer–Emmett–Teller (BET) theory to the N₂ adsorption-desorption isotherm, the BET surface area of the nanoporous polymer was calculated to be 417 m²g⁻¹; and t-plot method demonstrates that its micropore surface area and external, i.e., meso- and macropore, surface area are 143 and 274 m²g⁻¹, respectively.



Figure VIII-2. TEM images of (A) SiO₂, (B) SiO₂-Br, (C) SiO₂-PS, (D) SiO₂/crosslinked PS composite, (E,G, I) nanoporous polymer, and (F, H, J) nanoporous carbon.



Figure VIII-3. DFT pore size distributions of (A) SiO₂/crosslinked PS composite, (B) nanoporous polymer, and (C) nanoporous carbon.

VIII.3.3. Converting crosslinked SiO₂-PS composite to nanocarbon

The targeted nanoporous carbon was achieved by carbonization of the SiO₂/crosslinked PS composite over 3h at 800 °C followed by etching the resulting SiO₂/carbon composite. Comparison of TEM images of samples before and after carbonization, Figure VIII-2 E-G *vs* H-J, clearly demonstrates that the carbonyl-crosslinked polystyrene shells retained stability during carbonization, thus leading to the formation of a carbon network unit with a mesoporous core and a microporous shell structure. However, just like during the formation of most porous carbon materials, the initial network framework underwent a certain level of

framework shrinkage during the transformation from polymer to carbon because of the loss of many non-carbon elements and carbon-containing compounds during pyrolysis.^{9a, 17} This led to a decrease in the size of inter-particle network nanopores from the original 25 nm to 13 nm, see the comparison of Figure VIII-3B and C. Moreover, this burn-off led to the formation of numerous new micropores of 0.6 nm in the carbon framework, Figure VIII-3C, which increased the number of micropores, judging from a higher N₂ uptake at low relative pressure. However, the original intra-network micropores of 1.4 nm and the SiO₂-templated mesopores of 9 nm were retained after carbonization, Figure VIII-3C. The BET surface area of the as-prepared nanoporous carbon was calculated to be 525 m²g⁻¹, with 48 % attributable to the presence of micropores and 52% to meso-/macropores.

VIII.3.4. Converting SiO₂-PSAN composite to nanocarbon

To obtain the nanoporous carbon, the polymer powder sample was preoxidized at 280 °C in an air flow and then carbonized at 700 °C in a N₂ flow, followed by removal of the hard template SiO₂ nanoparticle by HF. The AN units from the grafted PSAN chains underwent a intra/interchain cross-linking reaction with the help of air during the preoxidation treatment, thus forming a continuous cross-linked polymer phase. This facilitated the successful framework transformation from polymer to carbon during carbonization, confirmed by comparison of the TEM images shown in Figure VIII-4B, C and D. The TEM analysis also demonstrated that the continuous phase shrank because of partial burnoff of the PSAN during preoxidation and carbonization, whose final yield was

measured to be 25 wt %. The diameter of the resulting spherical mesopores in the as-prepared nanoporous carbon was very close to that of SiO₂ nanoparticles (~10 nm), indicating these nanoparticles efficiently played the template role. The obtained carbon wall was around 5 nm in thickness, obviously smaller than the corresponding polymer wall.



Figure VIII-4. TEM images of (A) SiO₂ nanoparticle, (B) SiO₂-PSAN powder, and (C, D) nanoporous carbon.

The pore structure of the nanoporous carbon was quantitatively analyzed by measurement of N₂ adsorption. The carbon sample showed type IV isotherms with a distinct hysteresis loop at relative pressure $P/P_0 = 0.4-0.9$, indicating the characteristics of a mesopore structure (Figure VIII-5A)¹⁸, which was attributed to the SiO₂-templated spherical mesopores. The diameter of the mesopores, with a narrow size distribution, was calculated to be 14 nm by density functional theory (DFT) (Figure VIII-5 B). Note that this diameter value is slightly different from that based from TEM image, most likely due to different characterization procedures. Meanwhile, as shown in Figure VIII-5A, the amount of N₂ adsorption increased very sharply at low relative pressure, indicating the existence of numerous micropores. This can be ascribed to the burnoff of thermally decomposable S units, as well as noncarbon elements and carbon-containing compounds in the above cross-linked polymer framework from AN units during preoxidation and carbonization.^{4, 10c} The sizes of the micropores are mainly centered at 0.5 and 1.4 nm according to the DFT calculation.



Figure VIII-5. (A) N_2 adsorption-desorption isotherm and (B) DFT pore size distribution of nanoporous carbon.

Brunauer–Emmett–Teller (BET) calculation showed that the nanoporous carbon had a BET surface area (S_{BET}) of 348 m² g⁻¹. The *t*-plot method demonstrated that the micropore surface area (S_{mic}) and external (i.e., mesopore) surface area (S_{mes}) were 113 and 235 m² g⁻¹, respectively. The ratios of micropore (P_{mic}) and mesopore (P_{mes}) to the total surface area were calculated to be 32% and 68%, respectively, according to the following equations: $P_{mic} = (S_{mic}/S_{BET}) \times 100\%$ and $P_{mes} = 100\% - P_{mic}$. This means that the resulting carbon wall was highly

microporous mainly due to the use of PSAN with high burnoff as carbon source. Its total pore volume (V_{total}) was measured to be 0.65 cm³ g⁻¹ according to the adsorption amount at $P/P_0 = 0.99$.

The graphitic crystallite structure of nanoporous carbon was investigated by means of Raman spectroscopy. The Raman spectrum with a Lorentzian Fit Multipeaks analysis showed that nanoporous carbon had three bands around 1600, 1539, and 1345 cm⁻¹ (Figure VIII-6). The band around 1600 cm⁻¹ is known as the G (graphitic) mode and is attributed to "in-plane" zone-center atomic vibrations of large graphite crystallites.¹⁹ The band around 1530 cm⁻¹, denoted as A (amorphous) mode, was associated with amorphous sp²-bonded forms of carbon arising from interstitial defects of nanoporous carbon.²⁰ The band around 1345 cm⁻¹, often called as D (disordered) mode, is attributed to the phonons near the Brillouin zone boundary active in small crystallites or on the boundaries of larger crystallites.²¹ Furthermore, the microcrystalline planar crystal size L_a of nanoporous carbon can be calculated to be 1.4 nm using the empirical formula found by Tuinstra and Koeing ($L_a = 4.35 I_G / I_D$ (nm), where I_G and I_D are the integrated intensities of the G and D modes, respectively),²² which indicated that the nanoporous carbon revealed a low graphitization degree.



Figure VIII-6. Raman spectrum of nanoporous carbon.

VIII.4. Conclusion

In conclusion, novel nano-network-structured polymers and functional porous carbon materials were successfully designed and constructed based upon the combination of SI-ATRP of styrene or styrene/acrylonitrile, followed by postpolymerization carbonyl-crosslinking of the tethered PS chains and the selfcrosslinking of PSAN chains respectively. These procedures allowed formation or development of various types of nanoporous structures, including creation of intraparticle crosslinking-induced microporous shell with a silica-templated mesoporous core, and an inter-particle crosslinking-induced meso-/macroporous network. In the future, the nanostructure of this type of nanoporous carbon formed by tailoring the composition and structure of the particle-brush, including molecular weight, S/AN ratio, grafting density, polymer/silica ratio, and SiO₂ particle size will be examined and optimized for targeted applications. This type of nanoporous carbon material could find utility in a number of specific applications, such as supercapacitor electrodes, catalyst supports for fuel cell membranes, adsorbents, nanomaterial templates, and so on.

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VIII.6. References

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Chapter IX

Postscript

IX.1. Summary

The development of organic/inorganic (hybrid) nanocomposites (NCs) that initially found their utility during ancient times is an exciting, useful, and ever expanding area of research. Hybrid NCs combine the properties of both organic and inorganic materials to generate the desired properties that have targeted applications. However, the natural immiscibility between organic and inorganic materials generally produces weak interfacial interactions, and results in the diminution of the expected properties of the resulting composite material. Therefore, considerable research effort has been expended to overcome this important limitation by changing the nature of the surface of the inorganic nanofillers (NFs). Surface-initiated atom transfer radical polymerization (SI-ATRP) is among the most studied methods targeting surface modification, due to its capability to polymerize a wide-range of monomers using commercially available reagents under mild reaction conditions. Therefore, hybrid NCs prepared by SI-ATRP have created materials suitable for many potential applications in a variety of areas, including catalysis, coatings, electronics, chromatography and pharmaceutics. However, prior to the studies reported in this thesis, the surface congestion effect that affects the surface polymerization kinetics, and the unavoidable radical termination reactions that limit the MW of polymers tethered on surfaces in SI-ATRP were still unclear and debated. For this reason, the objectives of this thesis were to study the fundamental influence of surfaces on the polymerization kinetics of SI-ATRP, and to develop new methodologies that are simple and more efficient for the preparation of well-defined hybrid NCs.

MW control is crucial in the NC syntheses, since MW can dramatically change the desired properties of NCs. For example, MW can affect filler isotropicity in polymer matrix host, as mentioned in Chapter I. Moreover, other parameters such as grafting densities on surfaces are traditionally calculated using the MW of untethered polymers. Therefore, understanding and quantifying the surface congestion effect is significant in SI-ATRP. In order to find out the polymerization kinetic differences with or without the influence of surfaces, concurrent polymerization of methyl methacrylate (MMA) from both tethered initiators on silica nanoparticles (SiO₂) and untethered initiators in contacting media were carried out. The results revealed a similar polymerization rate for both, indicating that the polymerization rate is not significantly affected by nanoparticles. However, much slower polymerization was observed when polymerizing a sterically bulky and hydrophilic monomer, oligo(ethylene glycol) methacrylate (MW = 475, OEGMA475) from SiO₂ with a high initiator density. The results showed that the polymerization

of OEGMA₄₇₅ was not efficient unless a less sterically hindered polymer block was first grafted prior to the OEGMA₄₇₅ chain extension polymerization. Additional results showed that when polymerizing a monomer that was neither sterically bulky nor hydrophilic, polymerization kinetics was the same on both concave and convex surfaces. Consequences in chapter II therefore suggested that surface congestion effect on SI-ATRP polymerization kinetics is condition dependence. Surface congestion also affected the conformation of surface-tethered polymers. These polymers were called brushes due to their more extended conformation on surface induced by surface congestion. The relation between the grafted degree of polymerization ($N_{\rm G}$) and conformations of brushes were examined by the Dauod-Cotton mode (DC). This study concluded that $N_{\rm G}$ could affect the polymer conformation divided into 2 regimes, a more stretched regime (concentrated polymer brush regime, CPB) and a more relaxed regime (semi-diluted polymer brush regime, SDPB). The DC model was useful in estimating the transition between CPB and SDPB regimes within the experimental uncertainty.

Another major challenge in SI-ATRP was the unavoidable inter/intra particle termination. Although, previous report showed intra particle termination effect was minor and the fraction of terminated chains could be dramatically reduced by the reversible deactivation mechanism in SI-ATRP, one has to take into account the fact that a mere 0.1% of interparticle termination reactions in a hybrid system with 1000 growing polymer chains is enough to form a gel. This interparticle termination limits the properties and the processability of the formed NCs. It also influences the

reaction conditions that can be applied to NF surface modification reactions. One solution was to increase the value of the propagation to termination rate coefficient ratio (k_p/k_t) by increasing pressure in SI-ATRP. Under high pressure, k_p increases but k_t decreases. This is because the bimolecular termination step is diffusioncontrolled, which involves the coupling of two chain ends. Therefore, high-pressure approach is capable to form PMMA and PBMA with $M_{\rm h}$ in the range of 10⁶. This breakthrough technique, however, requires special equipment. Thus, an alternative method using high particle dilution and high temperature strategy was developed. High particle dilution was achieved by increasing reaction volume, which reduced both particle collision probability and radical concentration. Therefore, this approach successfully depressed interparticle termination, even when k_t was high at low monomer conversions. On the other hand, termination at higher monomer conversions was self-limited due to the gradual increase in viscosity, which limits the translational diffusion of particle-brushes. Therefore, even without high-pressure, PMMA with M_n of ca. 10⁶ was prepared. Particle dilution strategy however cannot be directly applied to low k_p monomers such as S unless higher temperatures are used. High temperature increased both $k_{\rm P}$ and $k_{\rm t}$ of S, which is different from the high pressure method. However, termination has much lower activation energy than propagation. Therefore, at higher temperature, the values of k_t/k_p^2 , directly proportional to the dead chain end fraction (DCF). For example, the DCF of S polymerization is 110 times lower at 150 °C compared with 50 °C. This means there is 110 times less dead chains at 150 °C when targeting the same MW under the same reaction conditions and rate. Yet, PS polymerization

is accompanied with thermal self-initiation (TSI) of S, which constantly generates radicals during polymerization, giving new and shorter untethered polymer chains. Therefore, SiO₂ was used as a shelter for polymers that are not generated by TSI, and later separated from TSI untethered polymer impurities. The results showed that the M_n of brushes on SiO₂ was higher than that of the untethered polymer impurities. Hence, PS with $M_n \sim 0.3 \times 10^6$ on SiO₂ was confirmed by SEC after the detachment of PS from SiO₂. The breakthrough of using higher temperature for S SI-ATRP was because TSI of S was generated in the contact solution, and did not affect the escorted polymer brushes on SiO₂.

High MW SiO₂-PMMA, SiO₂-PBMA and SiO₂-PS mentioned above are good candidates to synthesize NCs with good particle dispersion, since traditional NC preparation requires tethered polymers longer than their polymer host matrixes. However, the drawback of using high MW particle-brushes is relatively low inorganic loading. This was solved by the novel strategies discussed in Chapter IV and Chapter V. In Chapter IV, the governing parameters controlling the miscibility of NFs within polymeric host media were analyzed for the particular case of particle-brushes embedded within a PMMA matrix. An additional enthalpic component due to favorable interactions between the graft and matrix chains was able to aid particle dispersion. An example by grafting poly(styrene-*r*-acrylonitrile) PSAN brushes from SiO₂ showed very good NF compatibilization with a host PMMA matrix. This occurred even when the entropically unfavorable conditions persisted, such as with 500 times shorter graft compare with the matrix chains.

Therefore, this strategy overcomes the previously postulated compatibility criterion for miscible athermal particle-brush/polymer dispersions – that is grafted brushes have to be longer than matrix chains to create filler dispersion. The SiO₂-PSAN created mechanically and thermally stable films with SiO₂ volume fraction exceed 50 vol%. This "polymer filled inorganic" materials provided quantitative optical limiting within the UV frequency range and polymer-like mechanical properties.

Another innovative way to avoid filler aggregation in polymer matrix is to eliminate the polymer matrix. However, there are only weak Van der Waals interactions between NFs. Therefore, film casting of NFs solely formed easily cracked materials (with extremely low toughness). Hence, transition from 'hardsphere-like' to 'polymer-like' mechanical characteristics of particle solids is desired. Inherited from star polymers, self-assembly of particle-brushes by interparticlebrush entanglement enabled the production of a processable self-assembled film of hybrid NCs. They do not require blending of the particle-brushes with a matrix. The interpenetrating brush chains provided uniform NF dispersion in a monolayer film with zero aggregation. Since the material was constructed upon brushes entanglement, the conformation of polymer brushes was expected to influence the structural and mechanical properties of the materials. The elastic modulus, indentation hardness, and fracture toughness of this innovative material were examined by nanoindentation due to the need of only small sample volumes. All these properties were found dependent on the $N_{\rm G}$. When the polymer brushes were long enough, they transformed from the CPB to the SDPB. When the degree of polymerization at SDPB exceeded twice that of the entanglement limit of homopolymer, the materials were significantly toughened. The boundary of this transition was predicted by a mean field theory extended from the DC model. Although long polymer brushes are the key of mechanical robust materials, it can also reduce the filler's array ordering. By controlling the polymer brush length, grafting density and particle size, a tough film with well-ordered filler material was synthesized. This tough material also showed colorful reflection that provides potential applications in protective coating without the addition of pigments.

Chapter VI, VII, and VIII further disclosed the properties and applications of this matrix-free NC. Chapter VI presented the investigation of the glass transition temperature (T_g) dependence on polymer brush conformation. The T_g of particle-brush materials was sensitively dependent on the conformation of particle-brush systems. The grafting of polymers to the particle surface generally increased the polymers' T_g and was dependent on N_G . The relative increase of T_g (with respect to the corresponding linear polymer of equal MW, ΔT_g) increased with decreasing of N_G . The increase in T_g was interpreted as a consequence of the reduced conformational entropy of surface-bound chains, which was caused by chain crowding at the CPB. A pronounced reduction of ΔT_g was observed at the threshold N_G value that coincides approximately with the CPB \rightarrow SDPB transition as predicted by the DC model. The results thus underline the relationship between brushes' conformations and the physical properties of particle-brush materials.

Therefore, improved control of the physical properties was achieved by tailoring molecular engineering of the particle-brush constituent systems.

Since polymer brush conformation is the key to control particle-brushes properties. However, side reactions in the synthetic system of particle-brushes could deteriorate the brushes conformation. This potential lack in control could lead to diminishing their corresponded material properties. Thermal self-initiation (TSI) of S is an example of a side reaction in the synthesis of SiO₂-S at high temperatures, which simultaneously generates new chains and radicals during polymerization. The participation of TSI of S in SI-ATRP was proved by the polymerization kinetic studies at various temperatures using different ligands. Also, the amount of untethered polystyrene generated by TSI in samples synthesized by SI-ATRP was quantified by the combination of conventional separation and characterization methods including NMR, SEC, centrifugation, filtration, TGA, and TEM. The amount of untethered polystyrene was as high as 23 wt% calculated by TGA measurements before and after separating particle-brushes and untethered chains. The fundamental trend of the mechanical behavior of particle-brush solids was unchanged even with the TSI impurities. Instead, these thermally initiated homopolymer impurities enhanced both the elastic modulus and toughness of particle brush solids. The increased stability was attributed to the additional interactions imparted by homopolymer that was preferentially segregated within the corner regions of the Wigner-Seitz cell of the particle brush array. The presented results thus provide an additional parameter for the new design of particle-brushes.

Finally, the utility of particle-brushes was expanded to the synthesis of nanocarbons. Combination of SI-ATRP of styrene or styrene/acrylonitrile, followed by post-polymerization of carbonyl-crosslinking of the tethered PS chains or the self-crosslinking of PSAN chains, carbon materials were successfully designed and constructed. These procedures allowed formation and development of various types of nanoporous structures, including the creation of intra-particle crosslinking-induced microporous shell with a silica-templated mesoporous core, and an interparticle crosslinking-induced meso-/macroporous network. This type of nanoporous carbon material could find utility in a number of specific applications. Such applications include creating supercapacitor electrodes, catalyst supports for fuel cell membranes, adsorbents, nanomaterial templates, etc.

IX.2. Future Outlook

In summary, this dissertation targeted some major challenges in SI-ATRP and provided means to synthesize new and innovative NCs. On the basis of these studies, further developments could grant SI-ATRP a better position in the hybrid NC industry. In connection with the surface congestion effect, polymerization kinetics of brushes could be affected by several reaction conditions, as well as the monomer size. However, the detailed effects of catalysts, temperature, solvents,

and or the combination of all were not addressed here. Therefore, further research in this field is needed.

With regard to the MW limitation in SI-ATRP, high pressure, high particle dilution, and high temperature were all effective methods to increase k_0/k_t . This was due to the limited translational diffusion of particle-brushes as compared to monomers. However, the limitation of MW is still within the range of 1 - 2 million MW, and requires hours of reaction. High MW chains can transfer load more effectively by strengthening intermolecular interactions, and shorter reaction time can increase the production efficiency. Therefore, further increase of MW and shorter reaction time are needed. Pressure is the main parameter and reducing diffusion is a major problem in the high pressure activator generated by electron transfer (AGET) ATRP. Therefore, experiments at different pressures using various reducing agents are very important. Initiator density on particles is another parameter that determines the dilution level of particles. Higher grafting density gives higher monomer volume under the same target DP $([M]_0 / [I]_0)$. Therefore, reactions using particles with higher initiator density has lower particle to monomer volume ratio, and lower particle collision probability. Thus, growing polymers from high initiator density SiO₂ could further increase the MW limitation of this strategy. Optimizing the temperature is the key of high temperature S SI-ATRP, since both TSI and k_p/k_t compete with each other. While k_p/k_t can reduce the dead chain fraction, TSI can reduce the average MW, broaden MWD, and lower the yield of particle-brushes. Therefore, elevating S SI-ATRP temperature could generate the

conditions of the highest MW with the lowest TSI impurities. The separation of SiO₂-PS from TSI impurities is challenging and time-consuming. Potentially, this could be resolved by replacing SiO₂ with magnetic particles coated with silica, so particle-brush can be extracted in a faster and easier manner. It would also be interesting to combine the above 3 methodologies together. Thus, k_p can dramatically increase, while k_t cannot due to the diffusion limitation of particle-brushes. In addition, increasing temperature in a high pressure SI-AGET ATRP experiment may also improve the diffusion of reducing agent, further improves brushes MWD. However, one should be cautioned of the influence of the diffusion rate of other reactants such as ATRP catalysts.

The most desired use of SI-ATRP in industrial applications is to modify NFs to enhance the interfacial stability between fillers and matrix. PSAN/PMMA miscible blend demonstrated throughout this dissertation provides one possibility to attain this objective, yet there are not many known miscible blends. Thus, additional interactions such as introducing supplemental complementary functionalities (e.g. hydrogen bonding and ionic forces), which can improve filler miscibility in commercially available resins, is an attractive research direction.

Another interesting newly developed methodology is self-assembled particle-brush materials that do not require blending with a host matrix. The materials have the potential use in a one-step coating of a substrate or annealing or as freestanding reinforced films. However, only PS and PMMA particle-brushes were studied so far and examination of other homo- and block-copolymers could bring comparable or better results. For example, one can self-assemble PMMA-b-PBA particle-brushes. Therefore, the outer PMMA block can form entanglements while the soft PBA block can dissipate energy owing to its low T_{g} . Last but not least, the self-assembled superstructures also can act as photonic crystal material that form camouflage color without the necessity of pigment loading. This is because of their refractive index alterations between the NF and matrix phases. The color can further be adjusted by changing the arrangement of the particles' array, adjusting the inter-filler distances, or coupling with other NF that could induce color changes. Such adjustments could be brought upon the incorporation of resonance plasmon, fluorescence, and reflection effects of NFs, to produce even wider color selections. The arrangement of particle-brush building blocks could be adjusted by breaking the symmetry of interactions between individual particle-brushes. For example, one can use non-spherical shape or polar inorganic particles to achieve non-isotropic steric interactions. Structuring polymer graft layers by inducing MWD changes and introducing a secondary organization process (e.g. magnetic field) are other strategies to tune particle arrangement.

An intermediate material that has polymer matrix < 26 vol% was synthesized and investigated. The polymer matrix employed in this particular system was just the untethered polymer impurities produced by TSI of S simultaneously during S SI-ATRP. Results showed that these impurities enhanced materials' modulus and toughness owing to their segregation in the Wigner–Seitz cell of particle-brushes. This enhanced the brushes' entanglement density. Therefore, adding artificial impurities with different shapes and nature could further enhance materials properties. For example, it is interesting to add small amount of PSAN untethered polymers in PMMA particle-brush assembly to enhance the interaction between particle-brushes, or to blend particles with different sizes with or without special interaction to see how particles arrange. Finally, incorporation of small fractions of functional block-copolymers to induce filler arrangement in the final composite structure may also open up a new route to future material production.

A new platform to synthesize nanocarbons that are made from SiO₂-PS and SiO₂-PSAN using SiO₂ as a template was successfully created. Targeted properties of these template nanocarbons are related to the sizes and shapes of the nanoparticle templates, the length of the grafted polymers, and the nature of the homopolymer and copolymers. Therefore, the listed parameters are great tools to produce new porous materials with different pore sizes, surface areas, and morphologies to facilitate different applications.

Except those specific possibilities mentioned above, research in SI-ATRP should continue but can be generally improved. Studying the kinetics of SI-ATRP on surfaces is still time-consuming, due to the need to cleave the polymer brushes from the inorganic surfaces for analysis of the polymer chains. Therefore, synthesis of cleavable initiators such as incorporation of UV-etchable nitrobenzene

group that can be cleaved, or using an in-situ monitoring system, such as quartz crystal microbalance, could potentially help accelerate the related studies. Another limiting parameter of particle-brushes is chain-end functionality, which is important when particle-brushes are going to be used in catalysis or for drug delivery. Forming branching structure by adding inimers during the polymerization reaction can increase the concentration of chain-end functionalities. However, the reactivity ratio of the double bond and the initiating sites on the inimers has to be designed properly, such that inimers could graft from particles instead of keep growing untethered polymers in the contacting solution. Alternative, clicking multifunctional oligomers onto brushes' chain ends could also increase particle-brushes' chain end functionalities. These ideas are built on the basis of the low DCF, facilitated by SI-ATRP.