Elucidation of Molecular Parameters Governing the Interactions and Properties of Brush Particles

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Abstract

Elucidation of the mutual influence of the composition and architecture of polymer canopies on the assembly and physical properties of particle brush-based materials holds the promise of advancing the understanding of the governing parameters controlling interactions in hybrid materials and the development of novel functional materials. In this thesis, how the brush molecular parameters govern the collective interactions and properties was investigated.

A number of precedent studies clarified the role of architecture (depending on chain length, particle size and particle size dispersity) on the interactions in brush particle assembly. Based on the previous reports, the present thesis further explored new parameters, the surface functionalization density and dispersity in chain length governing the mechanical or thermal properties. First, the elastic properties of three series of brush particle systems were investigated, differentiated by grafting density as dense, intermediate and sparse brush systems. Dense and intermediate systems displayed uniform microstructures; the degree of order increased with grafting density. For dense and intermediate brush particle systems, instrumented indentation analysis revealed an increase of the elastic modulus and hardness with the degree of polymerization of tethered chains. Furthermore, the effectiveness of ligands to enhance interactions increased with decreasing grafting density. The results were rationalized as a consequence of more pronounced brush interdigitation in the case of intermediate systems and the resulting increase of the dispersion interactions between ligands of adjacent particles. A reversed trend in modulus was observed in films of sparse brush particles that also featured the formation of string-like superstructures. Here, the elastic modulus and hardness were substantially increased for low molecular ligands and continuously decreased with increasing degree of polymerization of tethered chains along with a transition from string-like to uniform morphologies. Also, the molecular weight distribution of grafts was found to affect the structure formation and interparticle interactions. Wide-dispersed brush particles assembled into a less-ordered superstructure due to the less-regular brush thickness around a core. The wide-distributed molecular weight practically encouraged entanglement formation in the system by thinning the concentrated brush layer. Toughness of the dispersed brush particle films was enhanced by the increased entanglement density. Glass transition was turned out to be broadened as the molecular weights broke up.

In addition, phase behavior driven by interparticle brush interactions in binary brush particles was also studied via collaborative works. Specifically, two types of binary brush materials were explored: binary mixtures of homopolymer-tethered particles and diblock copolymer-tethered particles. In the binary mixture materials, a LCST-type pair of ligands was found to induce the reversible phase separation throughout a relevant thermal processing. Diblock copolymer brush, on the other hand, led the particulate colloids to phase separated assemblies depending on grafting density. Dense BCP brush particles formed concentric particle distribution while sparser BCP systems assembled into network structures in different levels subject to grafting density.

The systematic investigations that demonstrated the importance of molecular design of particle brush and the pioneering works that explored the controllability of assembly structure of heterogeneous particle brush system filled and widened the field of brush particle-based hybrid material. The results of this thesis identified the applicability and versatility of the building block materials with functionality and mechanical durability.

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1. Introduction

1.1. Nanoparticles

The advancement in understanding unique characteristics of nanoparticles and in nanotechnology rendering fabrication of precisely-controlled nanoparticles in size and composition have considerably expanded its application into a wide range of fields from medicine to light emitting devices using its mechanical, electronic, optical, and thermal properties.^{1,2} Nanoparticles are defined as particles of which the size is in the range of one nanometer to hundreds of nanometers. The remarkable characteristics of nanoparticles originate in confinement effects as well as their generally high surface-to-volume ratio.³

1.2. Nanoparticle assembly

Collective features of nanoparticle assembly in 2-dimensions or 3-dimensions resulted from their distinctive interaction leading particles not linked via covalent bond but ordered through interparticle forces such as van der Waals forces, hydrogen bonding, or dipole interactions in short-range^{4–7} and electrostatic forces in long-range⁶ have been extensively investigated in recent decades. The close adjacency and the interaction between particles in nanoparticle assembly results in changes in optical, magnetic, and electronic properties compared to those of bulk state as well as those of dilute state.⁵ As shown in Figure 1-1, nanoparticles arrays tend to form their densest packing due to the balance of the operated forces in both of 2-dimensional and 3-dimensional cases when an adequate mobility to reach equilibrium is guaranteed.^{7,8}



Figure 1-1 (a) Transmission electron micrograph of 2-dimensional Ag nanocrystals superlattice⁸ and (b) scanning electron micrograph of 3-dimensional superlattice of cuboctahedral Ag nanocrystals.⁷

The physical properties of nanoparticle materials with controlled size and shape have rendered inorganic nanoparticles and their assemblies a unique platform to facilitate technological breakthroughs. However, while a variety of viable techniques for the synthesis of individual nanoparticles with precise control of size and architecture have been established, the processing of nanoparticles into solid material assemblies for device integration remains challenging. A widely used approach for the fabrication of particle array structures relies upon the self-assembly of ligand-coated particles from particle dispersions by solution casting or controlled precipitation.^{9,10} Driven by the advance of synthetic techniques as well as the understanding of the physics underlying the organization of colloidal systems, the controlled assembly of particles into long-range ordered uniform or binary superlattice structures that mimic atomic crystal structures has become possible.^{11–14}

It is important to note that while the formation of complex and long-range ordered assembly structures has been demonstrated, major barriers remain in the scalable production of functional materials based on particle solids and their integration in devices (in the following the term 'particle solids' will be used to denote 2D and 3D particle assembly structures.) These challenges include: (1) the inherent fragility of particle solids that renders particle solids vulnerable to crack formation during the fabrication and processing of film structures.^{15–17} (2) The slow dynamics of

assembled particle solids that could result in the retardation of non-equilibrium structures and in impediment of the fabrication of desired structures.

1.3. Surface Modification of Nanoparticle with Polymer

The motivation of the projects is to understand the role of polymeric surfactants and their architecture on the interactions, structure formation and properties in particle solid structures. Throughout this research effort, it was demonstrated that the tethering of polymeric chains (with appropriate degree of polymerization and grafting density) provides a path towards colloidal materials capable of organizing into colloidal crystal-type superlattice structures that can be processed by facile fabrication methods such as spin-coating, extrusion or injection molding.^{11,12,18} The tunability of mechanical property from particle-like to polymer-like interactions suggests new opportunities to integrate particles into designated assembly structures in a facile manner.

To render nanoparticle assembly to carry mechanical toughness resistant to internal or external stress and to be dispersed in long-range ordered regime, grafting of polymeric chain molecules, 'ligands', onto the particle surface has been studied in a wide range of views, from synthetic techniques to effects of grafted polymer on integrated structure or mechanical/thermal properties.^{11,12,19–23} A term frequently used in this document, particle brush refers to polymer-grafted nanoparticle material. By controlling its architecture and composition of polymer ligands, the approach of particle brush exploits controllability of the interparticle interactions. Murray and co-workers used the variation of organic ligands and the size ratio of the particles in binary particle blends to demonstrate the feasibility of the formation of unique superlattice structures as shown in Fig. 1-2.²⁴



Figure 1-2 Range of binary superlattice structures that can be assembled by changing particle size ratio and ligands²⁴

Recent advances in surface-initiated controlled radical polymerization (SI-CRP) allowing precise control of the architecture of polymer chain grown from surfaces have further extended the range of possible ligand compositions to encompass polymer chains.¹¹ Not only the size and geometry of the particle core but also the degree of polymerization and grafting density of polymer ligands can vary properties of materials self-assembled from polymer-tethered particles.^{11,25} For the special case of densely polymer-tethered particle systems, it was shown that increasing the chain length of ligands gives rise to a transition from hard sphere-type to soft interactions and a

progressively more polymer-like response of particle assembly.²⁶ The architecture tailoring has leaded to offer intriguing chances to improve the properties of particle assemblies. For instance, polymer ligands were shown to increase the elastic modulus and toughness of colloidal crystal-type particle assemblies.^{13,27}

The initial use of surface-grafted polymers was the grafting of polymer chains from flat surfaces. SI-CRP techniques allow for the density of the surface-grafted chains to be controlled up to high densities, forming 'polymer brushes'. The grafting density of ligand chains (*i.e.* the number of grafted chains per surface area of nanoparticle) was known to be significantly influential in the conformation of tethered chains.²⁸ As presented in Figure 1-3a, the chains grafted from a flat surface tend to have a randomly coiled 'mushroom' conformation similar to free chains in solution in case that the spacing between initiators (black semicircles in the figure) of polymerization, D, is larger than the overall size of polymer, represented by $2R_g$ ($D > 2R_g$; where is the radius of gyration). When grafting density increases so that the spacing between initiators is smaller than the chain size ($D < R_g$), repulsive interactions among chains lead to a stretched 'brush' conformation (Figure 1-3b).



Figure 1-3 Conformation of polymer chains (a) tethered on a flat surface with low grafting density, (b) tethered on a flat surface with high grafting density, (c) from the Daoud-Cotton model predicting star polymers to have three unique regimes: *i*) core, *ii*) unswollen, and *iii*) swollen, (d) of the modified Daoud-Cotton model predicting particle brushes to have two unique regimes: *i*) the concentrated polymer brush regime and *ii*) the semi-dilute polymer brush regime. (reproduced from references ²⁵ for (a) and (b), and ^{29,30} for (c) and (d))

The established SI-CRP techniques motivated an interest in adopting a curved surface such as spherical nanoparticles. The Daoud-Cotton (DC) model (Figure 1-3c)²⁹ that predicted that the scaling of star-polymer size with chain length varies with the distance from the surface radially, expressed by three conformational regimes, was used to predict conformation of the particle brush by Ohno *et al.*³⁰ Grafting density plays a key role in the chain conformation as in the polymer brushes on a flat surface. To be specific, the DC model introduces three distinct conformational regimes in star polymers and accounts for the radial variation of the segment density, $\rho(r)$: *i*) constant value (the core), *ii*) $\rho(r) \simeq r^{-1}$ (the unswollen regime) *iii*) $\rho(r) \simeq r^{-4/3}$ (the swollen

regime).²⁹ For particle brush, Ohno *et al.* derived the expected crossover radius where a conformational transition occurs to be:

$$R_c = R_0 \sigma^{*\frac{1}{2}} v^{*-1}$$
 Equation 1-1
$$\sigma^* = \sigma_s a^2, v^* = v (4\pi)^{-\frac{1}{2}}$$

Where R_0 is the core radius, σ^* is the dimensionless surface grafting density (*a* is the repeat unit length of grafted polymer), and v^* is the reduced excluded volume parameter of repeat units. If the polymer-grafted particle has a sufficiently high grafting density as shown in Figure 1-3d, *i*) the inner hollow with higher density shows a stretched chain regime due to steric repulsion (concentrated polymer brush, CPB) while *ii*) the outer hollow with lower density of polymer chain indicates a relaxed chain regime (semi-dilute polymer brush, SDPB). This conformational transition occurs at the crossover radius, R_c and is obviously observed when the surface graft density and degree of polymerization are high. Early work by Choi *et al.* has demonstrated the transition in geometry of polymer-grafted silica nanoparticles by analyzing interparticle distance as a function of chain length.¹³

1.4. The Effect of Chain Architecture on Mechanical Property

Mechanical properties of particle brush assemblies have attracted attentions because the motivation of introducing polymers to hard particle assemblies was to improve the mechanical frailness of unfunctionalized particle assemblies. For example, Choi *et al.*^{13,18,22} pioneered the effect of polymer modification on interaction and structure formation in particle brush assembly structures. The authors used SI-ATRP to prepare a series of PS-/PMMA-tethered silica particles. All particles in the study were densely grafted, *i.e.* grafting density was fixed to dense system.

Nanoindentation was utilized to examine mechanical properties of the films. The structure of dense brush particles revealed highly ordered crystal-type structures. An extended study on densely tethered brush particles by Schmitt *et al.*²⁷ clarified the effect of brush architectures on processability of particle brush films and failure behavior. As presented in Figure 1-4, Young's modulus and hardness transitioned from particle-like to polymer-like as grafts became long. Flexibility of photonic films and processing by injection molding were also demonstrated. Hansoge *et al.*³¹ predicted Young's modulus and toughness in brush particle assemblies with many parameters such as degree of polymerization, graft density, ligand-particle interaction and aspect ratio of the particle using a latest simulation method. They observed an decrease in modulus and an enhancement of toughness when chains become longer in sparsely grafted particle films. The result also suggests that very dense functionalization is not suitable for applications that need robust and tough materials.



Figure 1-4 Young's modulus (filled symbols) and hardness (open symbols) as a function of degree of polymerization of surface-grafted chains. Dashed lines represent the reference values for high molecular weight polystyrene ($M_n = 300\ 000\ g/mol$). With increasing N the values approach the corresponding value of the high molecular weight reference polymer

Furthermore, fine controllability of grafted-chain length via advanced synthesis technology of easy removal and reintroduction of chain agent enables synthesis of bimodal brushes, *i.e.*, nanoparticles tethered with two distinct monodisperse chain populations.^{14,32} In recent years, the bimodal brush materials have attracted attention because it turned out that particle brushes with short chain length present restrained mechanical characteristics such as brittle fracture mechanisms as observed in particle solids and that an analog with long chain length lack in performance due to the high ratio of polymers to nanoparticles.¹¹ To exhibit high performance of the nanoparticle assembly, inorganic fraction in particle brush is needed to be larger than that achieved in past studies on dense and monodisperse materials. The bimodal brush is expected to take both advantages of the outstanding performance of particle solids and the mechanical durability of unimodal particle brushes by effective inter-ligand entanglements with long chains and decreasing inorganic fraction with short chains simultaneously.



1.5. Limitation of Past Works

Figure 1-5 Nanoparticle loading in dense, intermediate and sparse brush particles as a function of degree of polymerization.

Previous studies by Choi *et al.*²² and Schmitt *et al.*²⁷ attempted to investigate the influence of some architectural parameters such as particle size, graft length on the collective properties of particle brush materials. These advancements were related mostly to densely grafted brush particles. Unfortunately, in the limit of dense functionalization, high particle loading is sacrificed. However, considerable containing of inorganic nanoparticles in functional materials is necessary for high performance. For example, for 16 nm silica particles densely-tethered with moderately long PS chains (N = 500, $\sigma_s = 0.5$ nm⁻²), the inorganic fraction corresponds to approximately 5 vol%. The relation between grafting density and inorganic ratio is shown in Figure 1-5. Thus, the present thesis aims to understand the implications of reduction of brush contents (by decreasing graft density and increasing brush molecular weight dispersity) and consequent brush interactions.

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2. Objectives and Hypotheses

A number of investigations, for example, recent work by Choi *et al.* or Schmitt *et al.*, have demonstrated that the mechanical characteristics of particle solids can be improved through polymer graft modification. While these results point to potential new opportunities for the fabrication, processing and application of particle assembly structures, these previous studies were also limited by a small inorganic fraction. The latter is a consequence of the 'dense graft architecture' that was applied in these previous systems as indicated in Chapter 1.

The objective of the research documented in this thesis was to elucidate the interrelation between graft polymer architecture and interactions, and in particular to understand the effect of grafting density and molecular weight distribution of tethered chains on the mechanical properties of particle brush solids. The ultimate goal of this thesis is thus to establish the knowledgebase for enabling the optimization of particle brush synthesis. In particular, the realization of particle brush systems that are capable of forming (short-range) ordered yet plastic array structures that are amenable to polymer-like forming techniques could facilitate a transformative material platform for the high-throughput fabrication of nanocomposite structures that combine thermodynamic stability with optimized microstructure to maximize properties. The following questions were addressed in this thesis:

1. What is the implication of chain length dispersity on structure formation and mechanical properties of mono- and multilayer particle films?

2. What is the 'optimum' chain grafting density to maximize fracture resistance in the limit of high inorganic content?

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The principal hypothesis of this work is that interactions in particle brush assembly structures are dominated by dispersion interactions between tethered chains. It is hypothesized that these interactions will increase with increasing degree of interdigitation of tethered chains. This can be accomplished by either reducing the density of tethered chains (*i.e.* more sparse brush architectures) or by increasing the degree of dispersity of tethered chains.

2.1. Outline of Thesis

In this thesis, interactions in brush-based particulate films were elaborated with regard to brush conformation resulting from architectural parameters. We mostly focus on the interdigitations and entanglements formed in relaxed brushes based on Daoud-Cotton model to interpret results. Chapter 3 will provide details regarding experimental methodologies that can help successive researchers to understand the fundamentals of experimental instruments and to practically exploit the tools for managing time effectively as well as making the best use. Chapter 4 and 5 will cover main parts of the thesis: the effect of grafting density and chain dispersity on the interactions and the consequential properties respectively. Chapter 6 explores the assembly behavior in heterogeneous brush particles using ligand interactions. Chapter 7 will summarize all results covered in the previous chapters and will provide some suggestions for future works in the field.

3. Experimental Methods

In this chapter, experimental details which help other researchers such as who follow this study. Specific values or set-up relevant to measurements are given in each chapter to fulfill respective purposes.

3.1. Materials

To process particle brush materials, organic solvents were used. In case of PMMA brush materials, toluene was used to dissolve because of well-matched solubility parameters and refractive indices. However, when both PS- and PMMA-brushes are investigated in a study, tetrahydrofuran (THF) was preferred since the solubility parameter is neutral to the two polymers. The use of neutral solvent prevent a system from unintended phase separation by solvent effect. Dimethyl phthalate was preferred for a plasticizer due to the high boiling point (284 °C) that enables thermal treatment for a long time and the chemical stability.

3.2. Thick Film Preparation

For mechanical characterizations such as nanoindentation and tensile test, thick films (> 100 μ m) were used. Brush particles were processed in thick toluene solution (~ 30 mg/mL) prior to thick film casting. A solution was cast in a customized PTFE mold for 1–2 days in a ventilated system. Slow evaporation of solvent results in a uniform film in a nearly equilibrium state. Thus, a double capping with a PTFE film and an aluminum foil was applied with some small holes for respiration to close the system and quench solvent evaporation.

3.3. Thin Film Preparation

Structure of particle brush was studied with thin films using transmission electron microscopy. Dilute solutions (~ 1 mg/mL) were directly cast on carbon-coated copper grid, or cast on poly(acrylic acid) (PAA) substrates by spin-coating (and following water-immersion + lift-off). Direct casting on C-coated grids was used for its facile processing, while spin-coating on PAA substrate renders more uniform (and thin if a high rpm was applied) thickness and enables to observe crack formation which usually occurs during lift-off using tweezers. In case of heterogeneous materials such as block copolymer brush materials and binary blend of homopolymer brush particles, staining using RuO₄ was performed in the atmosphere for 8 mins. RuO₄ is known to selectively stain (darken) the styrene domain.¹

3.4. Transmission Electron Microscopy (TEM)

Thin particulate film morphology and craze formation were studied using TEM with a JEOL EX2000 electron microscope operated at 200 kV. Approximately monolayered particle brush films (< 100 nm) were obtained according *via* 3.3. preparation. In case that a film involves heterogeneous polymer components, RuO₄ staining was carried out as described in 3.3. Depending on film thickness, the optimum staining duration varies. In many cases, staining for 8 min operates very well for the monolayered films. But, if it was overstained 6 min staining was performed. 10 min staining also works if understained. Overstained brush particle films led to contrast levels with a broken balance (too dark styrene domains) that made a difficult image analysis. Images with amplitude and phase contrast were obtained at × 4,000, × 10,000, × 20,000, × 40,000 and × 80,000 magnifications by a Gatan Orius SC600 high resolution camera. Data was saved in the 'dm3' format in order to be processed and analyzed without scale bars using Matlab or ImageJ.

3.5. Image Analysis

A quantitative analysis on TEM micrographs following a systematic processing was conducted using Matlab. The sequence for the analysis is shading correction – blurring – dilation – erosion – particle recognition – tessellation (but the sequence can be optimized for the best matching with

raw data).² Bandpass filter was applied to correct shading. As next steps, the combination of dilation and erosion was exploited to separate merged (neighboring) domains. Gaussian blurring is necessary to reduce detail for better recognition. Given that unstained TEM images provide two distinct contrast levels (dark (silica particles) and bright (polymer brush)), each domain was mapped by binarization. In case of heterogeneous systems (block copolymer brush particle or binary blend of distinct brush particles), thresholding on a stained film (by RuO₄) was carried out in two levels. The effective domain of each particle was recognized *via* Voronoi tessellation using centroid information. In addition, the area fraction of each domain was calculated to demonstrate correspondence with molecular parameters.

3.6. Tensile Test

Thick films cast from the PTFE mold were mechanically characterized using TA instruments RSA-G2 solids analyzer. Dimension of a film was measured ahead of a measurement; thickness was measured as an average from three measurements at different locations. To get rid of thinning effect from grips when screws were too tight, screws were tightened moderately, but sufficiently to avoid slipping. Using tweezers is the only way to treat self-standing films, but it highly needs a caution against unintended deformation and breaking. Tensile force was applied at strain rate of 0.001 mm/s from strain-free state. Data was analyzed using Matlab script (see attached in Appendix). Young's modulus (E) was obtained from the maximum gradient of stress-strain curve at the beginning stage (0–10 s). Toughness (U_T) was calculated by integrating area under stress-strain curve before fracture. Systematic error in modulus and toughness was calculated by measuring reference homopolymer films prepared in the same way and applied to all results.

3.7. Nanoindentation

MTS nanoindenter XP with vibration-resistant system characterized mechanical responses (Young's modulus and hardness) from thick films by indentation. Film thickness prepared following 3.2. was greater than 100 μ m. The thickness is far above a minimum limit (= 1000% of indentation depth) where substrate starts to influence mechanical response. Indents of 500 nm depth were made, so that 5 μ m is the limit. Films were fixed to silicon substrate using Krazy glue. The Berkovich indenter of which the shape is tetrahedral was used as this type of indenter has been most widely used for composite materials.^{3,4} Poisson's ratio of a material was calculated based on composition using Voigt model for composite materials⁵:

$$\nu = \nu_{org} \varphi_{org} + \nu_{SiO_2} \varphi_{SiO_2}$$
 Equation 3-1

where, v_i is the Poisson's ratio of component *i* and ϕ_i is the volume fraction of component *i*.



Figure 3-1 Schematic illustration of load-displacement curve

Measurements were recorded at indentation rate 5 nm/s. Variation of the indentation rate in the range 1–25 nm/s was used to confirm the absence of viscoelastic contributions to the response of films.⁶ This is important because our analysis of instrumented indentation results rests on the assumption of samples undergoing elastic-plastic deformation only. Indentation depths of 500 nm were chosen to ensure meaningful sampling of interactions (the test volume 20 μ m³ corresponds to > 1,000 brush particles) and to eliminate the substrate effect. The elastic modulus was evaluated from load-displacement curves using the Oliver-Pharr method that has been shown to yield results with satisfying accuracy for glassy polymeric materials.⁷ Films were imaged (using AFM) after indentation to ensure the absence of excessive pile-up in the indent region. According to the surface topology pile-up was insignificant allowing assumptions underlying Oliver-Pharr method. 25 locations (9 locations in case of a large number of specimens) were indented with 500 nm depth limit, 5 nm/s displacement rate, 0.05 nm/s allowable drift rate and 10 seconds constant loading

time before unloading for each sample. The standard deviation of the measurements was calculated as experimental error.

According to Oliver and Pharr, Young's modulus (E) can be measured as follows.

$$S = \beta \frac{2}{\sqrt{\pi}} E_{\text{eff}} \sqrt{A}$$
 Equation 3-2

where *S* is the gradient of load-displacement data when unloading, β is a correction factor (1.03 was used for Berkovich indenter calculated by finite element model), E_{eff} is the effective elastic modulus without consideration of indenter's effect and *A* is the projected area of an indent. Considering the indenter's mechanical property, one could calculate *E*:

$$\frac{1}{E_{\text{eff}}} = \frac{1 - \nu^2}{E} + \frac{1 - \nu_{\text{ind}}^2}{E_{\text{ind}}}$$
Equation 3-3

where, v_{ind} is the Poisson's ratio of indenter and E_{ind} is the Young's modulus of indenter. Hardness can be computed directly from the measurement:

$$H = \frac{P_{\text{max}}}{A}$$
 Equation 3-4

where P_{max} is the maximum load.

The instrument and method have been very well defined and established throughout decades. However, one should be aware of many assumptions made and correction factors applied. The most difference from tensile test is the effect of voids or defects. When pressing, void space disappear and does not alleviate modulus.

3.8. Atomic Force Microscopy (AFM)

The residual indentations from nanoindentation or phase map of binary brush particle films were visualized using AFM on an NT-MDT SolverNEXT system in semi-contact mode with silicon cantilevers (300 kHz resonance frequency, 40 N m⁻¹ force constant) of small tip radius (< 10 nm). Samples were imaged in height and phase imaging modes. Raw data were analyzed using Gwyddion, a freeware for SPM data processing. Interpretation of AFM results always require a good understanding of interfacial interactions between the substrates and materials. The thickness of films can also be measured using AFM by measuring height image on scratched-off film using a razor.

3.9. Differential Scanning Calorimetry (DSC)

Thermal characterization such as glass transition behavior was performed using a DSC-Q20 (TA Instruments) with 4 repeating cycles of heating and cooling across a temperature range of interest. Aluminum pan and lid held specimen during measurement because of the thermal stability. To get rid of instable hysteresis during first cycle, last three heating cycles were analyzed to evaluate glass transition behavior. Data analysis was performed using TA Universal Analysis. Glass transition temperature (T_g) was determined as inflection point, and breadth of glass transition was characterized by the difference between onset and offset points (defined as intersections of tangents at each stage).

To obtain reliable data, the combination of zeroing with empty aluminum pans and calibration with an indium standard was performed in advance of a series of measurements. Some unexpected thermal transitions were observed without the adjustment.

3.10. Thermogravimetric Analysis (TGA)

TGA using TA Instruments 2950 or TA Instruments Q50 was used to measure the composition in the hybrids. Platinum pan was user due to its stable characteristic even at very high temperatures. Before taring the pan, it was cleaned with acetone, ethanol and water to remove any residual materials. Some unexpected shoulders in data were observed when this procedure was missing. The data were analyzed with TA Universal Analysis. The heating procedure involved four steps: (1) jump to 120 °C; (2) hold at 120 °C for 10 min; (3) ramp up at a rate of 20 °C/min to 800 °C; (4) hold for 2 min. The reason holding temperature at 120 °C is to remove probable residue of solvent. The TGA plots were normalized to the total weight after holding at 120 °C.

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4. The Effect of Grafting Density on Mechanical Properties and Cohesive Interactions in Brush Particle Films

This part was submitted to Macromolecules.

4.1. Background

Recent advances in the field of surface-initiated reversible deactivation radical polymerization (SI-RDRP) enable the grafting of polymeric chains to the surface of nanoparticles with controlled grafting density, molecular weight, dispersity and composition.^{1–6} The resulting brush (or 'hairy') particles have been pursued as building blocks for the fabrication of 'one-component hybrid materials' that are formed via the assembly of brush particles in the absence of an additional matrix polymer.⁷⁻¹² Interest in one-component hybrids is motivated by microstructural features that give rise to novel property characteristics.^{13,14} Mean-field theory, computer simulations, and experiments have revealed that 'steric confinement' in sufficiently dense brush materials gives rise to a transition of chain conformation from more stretched (in the vicinity of the surface) to more relaxed at sufficiently high degree of polymerization or low grafting density or particle size.⁷⁻ 9,11,15-21 Because physical properties of polymers are sensitive to orientation, this presents the prospect of realizing novel functionalities in brush particle hybrids by deliberate control of the orientation of tethered chains. For example, increasing chain orientation in dense brush systems has been argued to raise thermal transport, to reduce dielectric breakdown, or to result in novel phonon transport characteristics of brush particle hybrids.²²⁻²⁴ More relaxed (coiled) chain conformations were shown to promote chain entanglement, thus giving rise to polymer-like deformation properties and formability.⁷⁻⁹ This was used to enable the fabrication of 'moldable colloidal crystals' as well as transparent high refractive index glasses or low-modulus hybrid elastomers that might find use in soft robotics.^{8,12,25–27} As brush particles are assembled into films

(these will be denoted 'particle solids' in the following), the constraints arising from the packing into ordered structures have been shown to induce further chain perturbation that has been harnessed, for example, for the fabrication of mesoporous membranes.²⁸

4.1.1 Interactions in Sparse Brush Particles

As the density of tethered chains is reduced to values of about 0.05 nm⁻² (the so-called 'sparse' grafting regime), distinctive differences in the assembly behavior of brush particles – such as the formation of anisotropic sheet and string structures – was observed.^{20,29–33} The polarization of particle interactions was related to the segregation of tethered chains into the galley regions between particle strings. This breaking of symmetry is thought to minimize free energy by enabling more relaxed chain conformations and more effective particle core interactions.^{29–33}

4.1.2 Mechanical Properties in Particle Brush Films

To understand the effect of brush architecture on material performance, research has focused on the thermomechanical and relaxation behavior of brush particle hybrids. With regard to mechanical properties of solid brush particle films, two quantities were of particular interest, *i.e.* the elastic (Young's) modulus and the fracture toughness.^{34–36} The former is related to short-range interactions between constituents (and thus gives information about the relevant bonding interactions) while the latter gives insight into dissipative pathways within materials during fracture. Elasticity of particle brush solids was evaluated using a variety of techniques such as micro- and nanoindentation, uniaxial extension, buckling as well as non-contact Brillouin scattering.^{7,8,20,24,29,37–41} Indentation experiments by Podsiadlo *et al.* (on films assembled from low molecular surfactant-coated semiconductor nanocrystals) were the first to suggest the elastic response of particle solids to be determined by dispersion interactions between tethered ligands.³⁷

ligands.^{7,8,20,41,42} These studies further revealed a toughening transition above a threshold molecular weight of polymeric tethers that was attributed to the onset of entanglement of tethered chains and the associated increase in ductility of particle brush hybrids. Experiments, theory and simulations correlated this brittle-ductile transition to the more relaxed (coiled) chain conformations that are favored for sufficiently large degree of polymerization.^{7,16,18,19,43} In sparse grafted systems, mechanical analysis (using wrinkling and shear tests) have revealed a significant enhancement of elastic moduli.^{20,29} This was interpreted to be a consequence of the organization of sparse brush particles into anisotropic string-like superstructures. Recent BLS experiments and simulations suggested that this 'strengthening effect' is caused by the concentration of polymer segments within 'interstitial spaces' between particle strings and the associated increase of the contribution of core-core interactions to the elastic modulus.^{16,40}

4.1.3 Motivations and Goals

Collectively, previous research illustrates the relevance of brush architecture on the properties of particle brush-based materials. A requisite for translating these results into opportunities for material design is the better understanding of the mutual influence of the various relevant characteristics of polymer canopies on performance. For example, while modulus and toughness have been shown to increase with molecular weight of polymeric tethers, the associated reduction of inorganic content limits the practical use of the one-component hybrid approach for material design.^{7–9,42} A concurrent reduction of the grafting density could alleviate this problem. This raises intriguing questions: Is there an optimum graft density to enhance mechanical properties of particle brush materials? Can isotropic microstructures be retained in the limit of low grafting densities (which might be preferable for applications)? What is the role of graft composition (monomodal vs. multimodal) and chain dispersity (narrow vs. wide) on the interactions in brush particle

materials? This contribution presents a systematic evaluation of the effect of grafting density on the structure and elastic properties of narrow-dispersed and monomodal brush particle systems; the role of graft molecular weight distribution will be explored in a subsequent paper. Six series of particle brush model systems representing the dense, intermediate and sparse grafting regimes, respectively, were evaluated. In principle, the distinct grafting regimes could be distinguished on the basis of the conformation of tethered chains that is predicted, for example, via the Daoud-Cotton (DC) model.^{44–47} The latter ascribes a 'critical' radius $r_c = r_0 \sigma_s^{1/2} / v$, where σ_s denotes the grafting density, r_0 the particle radius, and v the excluded volume parameter, to indicate the transition between two conformational regimes. Segmental crowding in the limit of $r < r_c$ is predicted to induce stretched chain conformations (the concentrated polymer brush regime, CPB) whereas relaxed conformations are expected for a brush particle diameter $r > r_c$ (the semi-dilute polymer brush regime, SDPB). Conceptually, one might then distinguish dense, intermediate and sparse grafting regimes, as those corresponding to $r_0 < r_c$, $r_0 \sim r_c$, and $r_0 > r_c$, respectively. However, in the literature, the sparse grafting regime has been identified on an empirical basis as the regime in which grafting density is low enough to drive the formation of string-like superstructures.³⁰ The latter not only depends on the characteristics of tethered chains but also on geometrical features such as particle size or uniformity.^{19,29} For this reason, in the following, a more 'ad hoc' definition of grafting regimes will be adopted that is based on the underlying initiator density and the observed behavior of brush particle assemblies. The material system consists of silica particles with radius $r_0 = 7.9 \pm 2.2$ nm tethered with polystyrene (PS) and poly(methyl methacrylate) (PMMA). Both polymers are glassy at room temperature for all tested molecular weights. This is a requisite for the purpose of the present study as it simplifies the analysis of elastic properties and avoids convoluting influences of morphological features (such as crystallization) on structureproperty relations. Dense, intermediate and sparse regimes are defined as grafting density in the range of 1, 0.3 and 0.05 nm⁻² (the numbers correspond to the respective density of initiator sites, see below). While this definition is, by nature, specific for the present material system, the conclusions are consistent with reported findings in the literature on diverse brush particle compositions.^{8,20} We thus expect this classification to be useful as a basis for the more general categorization of brush particle systems. For brush particles with dense and intermediate grafting density, we find the effectiveness of ligands to enhance interactions (measured in terms of Young's modulus as a function of volume fraction of polymer repeat units) to increase with decreasing grafting density. This is interpreted as a consequence of increased brush interdigitation which raises interactions between ligands of adjacent particles. In this regime, the elastic modulus increases with the degree of polymerization of tethered chains, a trend that is captured by a model that attributes the effective brush particle interactions to the dispersion forces between segments of interdigitated chains. In contrast, the opposite trend in modulus is observed in films of sparse brush particles that feature the formation of string-like superstructures. Our results point to subtle relationships between brush architecture, interactions, and properties of brush particle films that could benefit material design and hence merit further investigation.

4.2. Experimental Methods

4.2.1 Synthesis

Materials

Monomers (styrene (S, 99%, Aldrich) and methyl methacrylate (MMA, 99%, Aldrich)) were purified by passing through a column filled with basic alumina to remove the inhibitor. Tris(2dimethylaminoethyl)amine (Me₆TREN, 99%, Alfa), 4,4'-dinonyl-2,2'-bipyridyne (dNbpy, 97%, Aldrich), anisole (99%, Aldrich), tetrahydrofuran (THF, 99%, VWR), methanol (99%, VWR), hexane (99%, VWR), acetone (99%, VWR), N,N-dimethylformamide (DMF, 99%, VWR), 2bromoisobutyryl bromide (2BiB, Aldrich, 98%), triethylamine (TEA, Aldrich, 99.5%), copper(II) bromide (CuBr₂, 99%, Aldrich), copper(II) chloride (CuCl₂, 99%, Aldrich), copper(I) chloride (CuCl, 97%, Sigma-Aldrich), tin(II) 2-ethylhexanoate (Sn(EH)₂, 95%, Aldrich), hexane (Fluka), 48% hydrofluoric acid aqueous solution (HF, >99.99%, Aldrich), ammonium hydroxide aqueous solution (NH₄OH, 28.0-30.0%, Fisher), anhydrous magnesium sulfate (MgSO₄, Fisher), hexamethyldisilazane (HMDZ, Aldrich, 99%) were used as received unless otherwise stated. Copper (I) bromide (CuBr, 98%, Acros), was washed with glacial acetic acid to remove any soluble oxidized species, filtered, washed twice with anhydrous ethyl ether, dried and kept in vacuum. Silica nanoparticles (SiO₂) 30 wt% dispersion in methyl isobutyl ketone (MIBK-ST), with effective radius 7.9 \pm 2.2 nm, measured by transmission electron microscopy (TEM), were donated by Nissan Chemical America Corp. The surface initiator densities are moderated with a dummy initiator chlorotrimethylsilane (99%, Aldrich).

Synthesis of tetherable initiator, 3-(Chlorodimethylsilyl)propyl 2-bromoisobutyrate (BiBSiCl)

18.6 mL (273 mmol) of allyl alcohol and 38.1 mL (273 mmol) of TEA were dissolved in 100 mL of dry THF in a round bottom flask and cooled down to 0 °C in an ice bath. 27.0 (218 mmol) mL of 2BiB was diluted with 50 mL of dry THF. The 2BiB solution was added dropwise to the reaction solution over 30 min while the reaction was stirred in the ice bath. The reaction mixture was then stirred at room temperature overnight. The resulting suspension was filtered and the residue washed with THF. The filtrate was diluted with 200 mL of ethyl ether and washed three times with deionized (DI) water, once with saturated NaHCO₃ solution and once with brine. The organic solution was dried over anhydrous Na₂SO₄. Upon removal of solvents in vacuo, allyl 2-bromoisobutyrate was obtained as a slightly yellow liquid. 1 H NMR (300 MHz, CDCl₃) δ: 5.94

(dt, J = 17.3, 10.5, 5.6 Hz, 1H), 5.39 (dq, J = 17.3, 1.5 Hz, 1H), 5.27 (dq, J = 10.5, 1.5 Hz, 1H), 4.67 (dt, J = 5.5, 1.4 Hz, 2H), 1.95 (s, 6H) ppm.

30.0 g (145 mmol) of allyl 2-bromoisobutyrate and 94.4 mL (869 mmol) of chlorodimethylsilane were mixed in a round bottom flask sealed with a rubber septum. The flask was placed in an ice bath and dry nitrogen was bubbled through the solution for 10 min. 1.2 mL of Karstedt's catalyst solution was added dropwise to the purged solution then the reaction solution was stirred for two days after returning to room temperature. Conversion was monitored by 1 H NMR. Unreacted silane was removed by rotary evaporation. The platinum catalyst was precipitated when the crude product was cooled down to -18 °C, and was removed via filtration through a 450 nm PTFE syringe filter. The product was obtained as a yellow liquid. 1 H NMR (300 MHz, CDCl₃) δ : 4.18 (t, J = 6.7 Hz, 2H), 1.94 (s, 6H), 1.86-1.78 (m, 2H), 0.93-0.83 (m, 2H), 0.44 (s, 6H) ppm

Surface modification of silica NPs

Dry nitrogen was bubbled through 10 mL of a dispersion of the silica particles (in MIBK-ST) for 5 min then 1.5 mL of a mixture of initiator and dummy initiator solutions was slowly injected into the dispersion. The reaction was stirred at 60 °C for 24 h then the flask was cooled down to room temperature and 1.1 mL (5.4 mmol) of HMDZ was slowly injected to the reaction. The pale brown dispersion was stirred at 35 °C for another 12 h. The modified nanoparticles were dialyzed against methanol three times and acetone twice.

SI-ATRP of PS-grafted silica NPs

Surface-modified NPs (SiO₂-Br), monomers (styrene, methyl methacrylate), solvents (anisole, DMF), CuBr₂, and Me₆TREN were mixed thoroughly in a sealed Schlenk flask. Meanwhile, a stock solution of $Sn(EH)_2$ in anisole was prepared. Both mixtures were degassed by nitrogen purging, then the $Sn(EH)_2$ solution was injected into the Schlenk flask to activate the catalyst

complex and the flask was immediately put into an oil bath. For a detailed procedure, we followed the reference.⁴ Characteristics of the polymer were monitored by gravimetric analysis and SEC, respectively.

4.2.2 Size Exclusion Chromatography (SEC)

Number-average molecular weights (M_n) and molecular weight distributions (MWDs) were determined by SEC. The SEC was conducted with a Waters 515 pump and Waters 410 differential refractometer using PSS columns (Styrogel 105, 103, 102 Å) in THF as an eluent at 35 °C and at a flow rate of 1 mL min⁻¹. Linear PS and PMMA standards were used for calibration.

4.2.3 Thermogravimetric Analysis (TGA)

TGA with TA Instruments 2950 was used to measure the fraction of SiO₂ in the hybrids. The data were analyzed with TA Universal Analysis. The heating procedure involved four steps: (1) jump to 120 °C; (2) hold at 120 °C for 10 min; (3) ramp up at a rate of 20 °C/min to 800 °C; (4) hold for 2 min. The TGA plots were normalized to the total weight after holding at 120 °C.

4.2.4 Transmission Electron Microscopy (TEM)

Approximately monolayer films of all particle brush systems were prepared by drop-casting of dilute colloidal solutions (~ 1 mg/mL in THF) on a carbon-supported copper grid. The particulate film morphology and craze formation were studied using TEM with a JEOL EX2000 electron microscope operated at 200 kV. Images with amplitude and phase contrast were obtained by a Gatan Orius SC600 high resolution camera.

4.2.5 Nanoindentation

Relatively thick films (> 20 μ m) were prepared from concentrated solutions (~ 20 mg/mL) using PTFE molds. Elastic modulus and indentation hardness of films were characterized using an MTS

nanoindenter XP with a Berkovich indenter of which the shape is tetrahedral. Displacement was under control to no more than 10% of the particulate film thickness to exclude any effect from substrates. Poisson's ratio of a material was calculated based on composition using Voigt model for composite materials.³⁵ Details are shown in supporting information. At least nine locations were indented with 500 nm depth limit, 5 nm/s displacement rate, 0.05 nm/s allowable drift rate and 10 seconds constant loading time before unloading for each sample. The standard deviation of the measurements was calculated as experimental error.

4.2.6 Atomic Force Microscopy (AFM)

The residual indentations from nanoindentation were visualized using AFM on an NT-MDT SolverNEXT system in semi-contact mode with silicon cantilevers (300 kHz resonance frequency, 40 N m^{-1} force constant) of small tip radius (< 10 nm). Samples were imaged in height and phase imaging modes to observe the indented surface.

4.2.7 Image Analysis

Micrographs were analyzed using the combination of ImageJ and MATLAB. Particle-to-particle distance was manually measured with ImageJ, while Voronoi tessellation analysis was carried out by programming with MATLAB. See details in Appendix (supporting information).

4.3. **Results and Discussion**

A library of silica particle ($r_0 = 7.9 \pm 2.2$ nm) brush materials with systematically controlled degree of polymerization (*N*) of grafted polystyrene (PS) and poly(methyl methacrylate) (PMMA) chains as well as surface grafting density (σ_s) was synthesized *via* surface-initiated atom transfer radical polymerization (SI-ATRP) using established protocols^{1,3,5,48,49}. The classification of brush particles into dense, intermediate, and sparse (sample ID: SiO₂-*d/i/s*-(S or MMA)*N*) is based on the respective composition of active and inactive sites of partially passivated silica particles as illustrated in Figure 4-1.



Figure 4-1 Synthesis and categorization of dense (*d*), intermediate (*i*), and sparse (*s*) brush particles. Control of grafting density is facilitated by silanization with distinct ratio between active initiator (*X*, black circle; 3-(chlorodimethylsilyl)propyl 2-bromoisobutyrate, BiBSiCl) and inactive (*Y*, gray circle; chlorotrimethylsilane) sites.

A summary of the relevant characteristics of PS- and PMMA-brush particle systems is presented in Table 4-1 and 4-2. Where possible, the results will be complemented with those of PMMA brush particles (~ 0.4 chains/nm²) that were synthesized as part of a previous study (and hence present an independent reference) to strengthen the generalizability of the presented results. The compositional characteristics for these particles are tabulated in Table S4-1; data relating to these materials in figures is marked with asterisks.

Sample ID	N	$M_{ m w}/M_{ m n}$	$f_{ m org}$	ф _{org}	σ₅ (nm ⁻²)
SiO ₂ - <i>d</i> -S120	120	1.17	0.75	0.86	0.78
SiO ₂ -d-S136	136	1.11	0.78	0.88	0.85
SiO ₂ -d-S204	204	1.10	0.83	0.91	0.74
SiO ₂ - <i>d</i> -S212	212	1.14	0.83	0.91	0.72
SiO ₂ - <i>d</i> -S226	226	1.11	0.84	0.92	0.74
SiO ₂ -d-S231	231	1.20	0.82	0.90	0.62
SiO ₂ -d-S231(2)	231	1.14	0.85	0.92	0.78
SiO ₂ - <i>d</i> -S355	355	1.10	0.87	0.94	0.61
SiO₂- <i>d</i> -S365	365	1.15	0.89	0.94	0.71
SiO ₂ -d-S365(2)	365	1.18	0.87	0.93	0.58
SiO ₂ -d-S400	400	1.22	0.88	0.94	0.61
SiO ₂ -d-S432	432	1.47	0.91	0.96	0.75
SiO ₂ -d-S549	549	1.25	0.89	0.94	0.46
SiO ₂ -d-S638	638	1.36	0.91	0.95	0.50
SiO ₂ - <i>d</i> -S762	762	1.35	0.92	0.96	0.49
SiO ₂ -d-S829	829	1.72	0.94	0.97	0.60
SiO2-d-S841	841	1.18	0.93	0.96	0.48
SiO ₂ -d-S890	890	1.25	0.93	0.96	0.45
SiO ₂ -d-S1087	1087	1.28	0.92	0.96	0.33
SiO ₂ -d-S1777	1777	1.19	0.91	0.96	0.19
SiO ₂ -d-S1800	1800	1.42	0.93	0.96	0.22
SiO ₂ - <i>i</i> -S221	221	1.09	0.55	0.72	0.17
SiO ₂ - <i>i</i> -S255	255	1.11	0.49	0.66	0.12
SiO ₂ - <i>i</i> -S313	313	1.15	0.59	0.75	0.15
SiO ₂ - <i>i</i> -S328	328	1.14	0.62	0.77	0.16
SiO ₂ - <i>i</i> -S440	440	1.15	0.63	0.78	0.12
SiO ₂ - <i>i</i> -S758	758	1.10	0.71	0.84	0.10
SiO ₂ - <i>i</i> -S1103	1103	1.24	0.72	0.84	0.07
SiO ₂ -s-S432	432	1.21	0.31	0.48	0.03
SiO ₂ -s-S600	600	1.29	0.42	0.60	0.04
SiO ₂ - <i>s</i> -S954	954	1.33	0.45	0.63	0.03
SiO ₂ -s-S1576	1576	1.47	0.55	0.72	0.03

Table 4-1 Molecular characteristics of polystyrene tethered SiO_2 -d/i/s-SN brush particles.

Variables represent the degree of polymerization of graft, N; dispersity index, M_w/M_n ; weight fraction of polymer, f_{org} ; volume fraction of polymer, ϕ_{org} ; surface grafting density, σ_s .

Sample ID	N	$M_{ m w}/M_{ m n}$	$f_{ m org}$	ф _{org}	σ₅ (nm ⁻²)
SiO2-d-MMA188	188	1.21	0.80	0.88	0.71
SiO ₂ -d-MMA213	213	1.18	0.82	0.90	0.69
SiO ₂ - <i>d</i> -MMA250	250	1.25	0.84	0.91	0.69
SiO ₂ -d-MMA382	382	1.15	0.90	0.95	0.79
SiO ₂ -d-MMA405	405	1.18	0.89	0.94	0.68
SiO ₂ -d-MMA445	445	1.16	0.91	0.95	0.76
SiO ₂ -d-MMA460	460	1.18	0.92	0.96	0.80
SiO₂- <i>d</i> -MMA777	777	1.15	0.95	0.97	0.78
SiO ₂ - <i>i</i> -MMA206	206	1.35	0.49	0.65	0.16
SiO ₂ - <i>i</i> -MMA379	379	1.22	0.70	0.82	0.20
SiO ₂ - <i>i</i> -MMA563	563	1.13	0.74	0.84	0.17
SiO ₂ - <i>i</i> -MMA637	637	1.25	0.78	0.87	0.19
SiO ₂ - <i>i</i> -MMA732	732	1.13	0.83	0.90	0.22
SiO ₂ - <i>i</i> -MMA752	752	1.24	0.83	0.90	0.21
SiO ₂ -s-MMA232	232	1.23	0.23	0.36	0.04
SiO ₂ -s-MMA365	365	1.15	0.32	0.47	0.04
SiO ₂ -s-MMA401	401	1.17	0.38	0.54	0.05
SiO ₂ -s-MMA477	477	1.13	0.42	0.58	0.05
SiO ₂ -s-MMA798	798	1.07	0.53	0.68	0.05
SiO ₂ -s-MMA993	993	1.11	0.62	0.75	0.05
SiO ₂ -s-MMA1067	1067	1.25	0.65	0.78	0.06
SiO ₂ - <i>s</i> -MMA1147	1147	1.27	0.64	0.78	0.05
SiO ₂ - <i>s</i> -MMA1410	1410	1.11	0.70	0.82	0.05

Table 4-2 Molecular characteristics of poly(methyl methacrylate) tethered SiO_2 -d/i/s-MMAN brush particles.

Variables represent the degree of polymerization of graft, N; dispersity index, M_w/M_n ; weight fraction of polymer, f_{org} ; volume fraction of polymer, ϕ_{org} ; surface grafting density, σ_s .

4.3.1 Structure Formation of Brush Particle Films Depending on Grafting Density

The structure of particle brush materials was characterized using transmission electron microscopy (TEM). Figure 4-2 (and Fig. S4-1) display representative TEM images of PS (PMMA) brush materials in the respective grafting regime. Brush particles in the dense and intermediate grafting regimes display uniform microstructures while sparse systems display the formation of string-like superstructures. To determine whether uniform or string-like structures are present, image analysis was performed on electron micrographs on particle monolayers (after vacuum annealing at T = 130 °C, 24 hours) to determine the distance between adjacent particles. Structures were considered

'uniform' if distance distributions were monomodal; in this case the average distance was denoted d. In contrast, structures were considered 'string-like' if a bimodal distribution of particle distances was observed (Fig. S4-3 depicts an example of the analysis for the images shown in Fig. 4-2 a, 4-2 b and 4-2 c). For dense and intermediate grafting densities, Voronoi cell analysis revealed that the degree of ordering (measured in terms of the variance of Voronoi cell area, see insets of Fig. 4-2 a and 4-2 b and similar Fig. S4-1 for PMMA systems) in particle brush films decreases with grafting density. Following to procedures established in the literature, a measure for the 'degree of order' was defined as 1-FWHM where FWHM is the full-width at half-maximum of the distribution of Voronoi cell areas, normalized by the average cell area.⁴² Figure 4-2 d displays 1-FWHM of PS-brush systems clearly revealing the trend towards a higher degree of structural order in films of dense brush systems (note that results are only shown for samples for which unambiguous analysis of electron micrographs could be performed). This is attributed to the more hard-sphere-type interaction potential in dense brush particle systems that support the formation of more ordered structures.^{2,42,47,50-53}



Figure 4-2 Representative bright field transmission electron micrographs for (a) dense (SiO₂-*d*-S365), (b) intermediate (SiO₂-*i*-S328) and (c) sparse (SiO₂-*s*-S432) PS-brush systems with similar degrees of polymerization. Also shown are schematic illustrations of the corresponding microstructures. The characteristic distance *d* is defined as inter-particle distance in dense and intermediate systems and as inter-string distance in sparse system. The area distributions of Voronoi cell from the dense and the intermediate materials are shown as insets in (a) and (b). All scale bars are 50 nm (20 nm in insets). (d) Comparison of 1-FWHM for monolayer particle brush films of dense (red circles) and intermediate (green squares) systems. Larger values indicate higher degree of order (for the case of a close packing of spheres in a plane, a reference value of '1' is expected). For dense and intermediate brush systems an average degree of order $\langle 1-FWHM \rangle_{dense} = 0.422$ and $\langle 1-FWHM \rangle_{interm.} = 0.325$ is observed (indicated by red solid and green dashed lines respectively).

In agreement with literature reports, sparsely grafted systems were found to form string-like superstructures (the conclusion of string *vs.* sheet structures was based on imaging microsectioned bulk materials, not shown here).^{17,19,29,31,54,55} Hence, while dense and intermediate brush particle assemblies were described by one characteristic distance *d*, sparse systems were characterized by two distances that will in the following be denoted *d* (representing the inter-string particle distance) and *d'* (representing the intra-string particle distance). The inter-string distance was considered as the analog to *d* in dense/intermediate systems since it identifies the spacing between particles separated by polymeric ligands. The average number of particles per string of SiO₂-*s*-S432 determined from Figure 4-2c was approximately 23. The structure formation of sparse systems will be discussed in more detail in a later part of this paper.

To discern the effect of grafting density on the conformation of tethered chains, the characteristic distance d was analyzed by electron imaging. Figure 4-3 displays the dependence of interparticle distance on N for brush particles in the various grafting regimes. Dense brush systems (red symbols) reveal two distinct regimes with scaling exponents 0.8 and 0.5 thus indicating a transition from oriented to random chain conformation with increasing degree of polymerization. This supports previous findings on dense brush particle systems that were analyzed using TEM and scattering analysis.^{8,42,53,56,57} The transition between the two regimes occurs at a similar degree of

polymerization ($N_{crit} \approx 300$) for PS and PMMA brush particles. This finding is attributed to the similar grafting density and comparable persistence length of both polymers.⁴⁵ In contrast, intermediate brush systems (green symbols) as well as the inter-string distance in the case of sparse brush particles (blue symbols) exhibit $N^{0.5}$ scaling for all (tested) values of N. This is consistent with the expectation that a reduction of chain crowding across the particle surface affords more relaxed chain conformations. For the case of sparse brush particle systems, we note that the $N^{0.5}$ scaling supports prior reports that attributed the formation of string structures in part to the increase of chain conformational entropy that is associated with the segregation of polymer chains to the galley regions between particle strings.^{20,29,31} We also note that no effect of N on the intra-string distance d' was observed; however, the average 'length' of strings decreased with increasing N (this aspect will be further discussed below).



Figure 4-3 Dependence of the characteristic distance d (dense & intermediate: inter-particle distance, sparse: inter-string distance) on the degree of polymerization of PS (a) or PMMA (b) for all systems (red: dense, green: intermediate and blue: sparse system). The trend lines indicate corresponding brush regimes: CPB (dotted) and SDPB (dashed). Data points with asterisks indicate additional (intermediate dense) PMMA brush particles.

4.3.2 Mechanical Properties Depending on Grafting Density

The elastic modulus (*E*) and hardness (*H*) of 20–60 µm thick brush particle films were measured using nanoindentation after thermal annealing in vacuum (T = 130 °C, 24 hours). Representative load-displacement curves and images of residual indents are shown in Figure S4-4. Measurements were recorded at displacement rate 5 nm/s. Variation of the indentation rate in the range 1–25 nm/s was used to confirm the absence of viscoelastic contributions to the response of films.⁷ This is important because our analysis of instrumented indentation results rests on the assumption of

samples undergoing elastic-plastic deformation only. Indentation depths of 500 nm were chosen to ensure meaningful sampling of interactions (the test volume 20 μ m³ corresponds to > 1,000 brush particles). The elastic modulus was evaluated from load-displacement curves using the Oliver-Pharr method that has been shown to yield results with satisfying accuracy for glassy polymeric materials.⁵⁸ Films were imaged (using AFM) after indentation to ensure the absence of excessive pile-up in the indent region. For each sample, more than nine independent measurements were evaluated. Figure 4-4 depicts the resulting trends of *E* and *H* along with the respective standard deviations. In discussing the results, we will focus on the elastic modulus since it directly relates to constituent interactions in materials. However, because 'hardness' is a quantity that is directly determined from indentation measurements (as opposed to the elastic modulus, which is indirectly inferred from load-displacement curves), hardness values are shown in support. The common trend of *E* and *H* that is seen for all systems in Figure 4-4 supports the validity of the analysis.

The elastic moduli (and hardness) of bare and initiator-tethered silica particle films were measured as a reference. The elastic modulus of initiated-tethered reference systems was determined to be 1.8 GPa (black symbols in Fig. 4-4), regardless of the ratio of active initiator to inactive sites. We note that the total modification density (active and inactive sites) was identical for d/i/s – brush systems (~ 1 nm⁻²); only the ratio of active and inactive surface groups changed accordingly for the different systems. This value was markedly less than the value for pristine silica particles that was found to be 5.5 GPa (not shown here). This result confirmed a previous report on the effect of organic ligand coatings on silica particle interactions and was rationalized as a consequence of the weaker cohesive interactions upon replacement of polar hydroxy-group functionalities with nonpolar low-molecular ligands (trichlorosilane or initiator) that interact predominantly through

dispersion interactions.^{37,59,60} The result thus further supported the assumption that brush particle interactions are dominated by ligand-ligand rather than core-core interactions. Increasing the degree of polymerization of tethered chains was found to exert two distinct effects, depending on the grafting density. For brush systems with dense and intermediate grafting density (Figs. 4-4a– d) the elastic modulus (and hardness) continuously increased and eventually leveled off at values similar to the respective bulk homopolymer reference ($E_{PS} = 3.9$ GPa and $E_{PMMA} = 3.8$ GPa) which are indicated as dotted lines in Figure 4-4. We rationalized the threshold degree of polymerization for leveling-off as being related to a correlation length beyond which dispersion interactions become independent of chain length (an analogous argument applies to the molecular weight dependence of the elastic modulus of amorphous polymers in general³⁴).



Figure 4-4 Young's modulus (*E*, left *y*-axes, filled symbols) and hardness (*H*, right *y*-axes, open symbols) of PS-grafted (left column) and PMMA-grafted (right column) particle films in the (a, b) dense, (c, d) intermediate and (e, f) sparse systems measured by nanoindentation. Fitted lines from the data are exhibited as dotted (for *H*) and dashed (for *E*) lines with the same colors. The black and navy dashed lines indicate the elastic modulus and hardness ($E_{PS} = 3.9$ GPa, $E_{PMMA} = 3.8$ GPa, $H_{PS} = 0.16$ GPa, $H_{PMMA} = 0.14$ GPa) of bulk homopolymer reference systems with degree of polymerization $N_{PS} = 500$ and $N_{PMMA} = 1200$. The data points at N = 1 (black symbols) correspond to initiator-tethered nanoparticle films. Axis labels and titles in the intervening spaces are removed for convenience.

4.3.3 Effectiveness of Interparticle Ligand Interactions

In stark contrast to dense and intermediate systems, sparse brush particle films displayed an opposite behavior (Fig. 4-4e and 4-4f). Here, the elastic modulus assumed a maximum value for

the smallest *N* tested (6.3 GPa for PS with N = 432 and 6.9 GPa for PMMA with N = 232) and subsequently decreased with increasing degree of polymerization. This trend was rationalized as a consequence of the anisotropic assembly structures in sparse brush particle films (see below).

To evaluate the role of graft architecture on the elastic modulus in dense and intermediate brush particle systems, Figure 4-5 depicts the dependence of *E* on the organic volume fraction ϕ_{org} for the case of PS brush particles. Interestingly, the elastic modulus of intermediate brush systems increased at a distinctively lower threshold volume fraction of polymer component. Conversely, at equal volume fraction of organic component, the elastic modulus of intermediate brush systems systematically exceeded the modulus of dense analogs. For example, sample SiO₂-*i*-S1103 (indicated by the green arrow in Fig. 4-5) exhibited a modulus of *E* = 4.2 GPa while the dense analog, SiO₂-*d*-S120 (indicated by the red arrow in Fig. 4-5) only displayed *E* = 2.1 GPa. The data thus revealed polymer repeat units to be more effective in raising brush interactions in the case of intermediate brush architectures.



Figure 4-5 (a) Young's moduli of the dense (red squares) and intermediate (green circles) PSgrafted particle films as a function of the volume fraction of the polymer with trend lines. The black dashed line indicates the elastic modulus of bulk homopolymer reference ($E_{PS} = 3.9$ GPa). Arrows indicate systems with comparable composition (green: SiO₂-*i*-S1103, red: SiO₂-*d*-S120) that were chosen for crack formation analysis. Panel (b) and (c) illustrate chain structures of intermediate (b) and dense (c) systems. Panel (d) and (e) show TEM micrographs of SiO₂-*i*-S1103 and SiO₂-*d*-S120. The inset in panel (d) is a magnified micrograph showing craze formation. Scale bars are 200 nm (100 nm in inset).

To rationalize this observation, we proposed that the relevant component of the total cohesive

interactions with regard to the measured elastic modulus in instrumented indentation analysis - at

least in the case of dense and intermediate systems - is the dispersion interaction between ligands

of adjacent particles. The latter should be sensitive to the interdigitation of brush layers between adjacent particles. We note that because of the pronounced distance dependence of dispersion interactions ($U(r) \sim r^{-6}$, where r is the distance between two molecules) 'side-on' orientation of ligands should contribute substantially more to the net bonding interactions as compared to 'endon' alignment.⁶¹ The reduced elastic modulus of dense brush systems could thus be interpreted as a consequence of the reduction of cohesive interactions in non-interdigitating brush particle assemblies. This situation is schematically depicted in Figures 4-5 b and 4-5 c. Indirect evidence for the reduced interdigitation in dense brush particle solids is provided in Figures 4-5 d and 4-5 e that depict TEM images of cracks formed in approximately monolayer films of intermediate (SiO₂*i*-S1103, Fig. 4-5 d) and dense (SiO₂-*d*-S120, Fig. 4-5 e) brush particle systems with near equal organic content. Craze formation that was observed in sample SiO₂-*i*-S1103 provided evidence for the interdigitation of chains while the smooth surface of cracks in the dense SiO₂-d-S120 system was indicative of brittle fracture (and hence the absence of significant chain entanglement). We note that the effect of graft architecture is expected to be reduced once the degree of polymerization is large enough to support sufficient brush interdigitation in dense systems – a trend that is indeed consistent with the data shown in Figure 4-5 a.

4.3.4 Estimation of Cohesive Interactions in Particle Brushes

To further support the interpretation of the effect of graft architecture, an analytical model was used to estimate the role of brush interpenetration on the cohesive energy density and effective elastic modulus of brush particle films. Only van der Waals interactions between nanoparticle cores and London dispersion interactions between ligands were considered; the system was assumed to consist of silica nanoparticles with uniform radius $r_0 = 7.9$ nm grafted with uniform PS chains of degree of polymerization N (*i.e.* particle and polymer molecular weight dispersity is neglected). Van der Waals and ligand dispersion interactions in brush particle films were calculated on the basis of pairwise interaction models published in the literature.^{62,63} Comparison between ligand-ligand and core-core interactions (see Fig. S4-5) revealed that the latter is negligible if the distance between particle cores exceeds about one nanometer, which is small compared to the experimental value of particle spacings for any of the (intermediate or dense) brush systems that were the subject of the present study (see Fig. 4-3). Hence, in the following, the contribution of core-core interactions to the cohesive interactions in dense and intermediate brush particle materials was neglected. Our approach consisted of two steps: First, the *inter*particle cohesive energy density (*IPCED*) was calculated that accounts (only) for the dispersion interactions contributed by chain segments that participate in interdigitation between adjacent brush particles (*i.e.* the interaction between ligands that are aligned end-on is neglected, see Fig. 4-6 a and 4-6 b). The dispersion interaction between two side-on oriented ligands was determined from Eq. 1 that was first provided by Salem *et al.* and later confirmed by numerous studies.

$$U_l(L) = -C_{\rm PS} \frac{3\pi L}{8\lambda^2 x^5}$$
 Equation 4-1

where $C_{PS} \sim 7.1 \times 10^{-79} \text{ J} \cdot \text{m}^6$ is the interaction constant for PS, *L* is the length of overlap between two parallel (*i.e.* side-on aligned) chain segments, λ is the length of the monomer (~ 0.25 nm), and *x* is the intermolecular spacing between chains (~ 0.4 nm).^{63–66} Note that we focused on the cohesive energy density contributed by interdigitating chain segments because it was expected to be the primary origin for the elastic forces resisting the perturbation of particle positions. In a second step, the effective elastic modulus was derived on the basis of the *IPCED* and compared with the experimental data.

The *inter*particle cohesive energy density was calculated as the sum of all dispersion interactions between interpenetrated ligands per material volume. To calculate IPCED, a cubic close-packed (face-centered cubic; fcc) microstructure of brush particle films was assumed.^{2,37,45,51,67} The assumption of a lattice structure simplifies the estimation of the cohesive energy density because it reduces the relevant volume element to the respective Wigner-Seitz (WS) cell of the structure (for example, a rhombic-dodecahedron in the case of fcc). Cubic close-packed structures have indeed been observed in films of dense brush particles and were rationalized as consequence of hard-sphere-type interactions between dense brush particles.^{24,47,50} For brush systems with intermediate graft density (or dense systems with sufficiently high degree of polymerization of polymer tethers) the assumption of close packing is an approximation. However, since the errors associated with non-close packing were estimated to be within 15% of the result, fcc packing was assumed for all brush particle systems. Since the volume associated with each WS cell $V_{\rm WS}(d) = (2r_0 + d)^3/\sqrt{2}$ is determined by the distance d between particle cores (d was known from TEM analysis, Fig. 4-3) and since the volume fraction of organic component was known from TGA characterization, the cohesive energy density of brush particle films could be estimated by summation of ligand dispersion interactions across each WS cell and subsequent normalization by the cell volume. To estimate the number of polymer repeat units contributing to the IPCED (i.e. the number of polymer repeat units that are part of interdigitating segments), the assumption was made that only segments in the semi-dilute brush region (SDPB) participate in interdigitation. This restriction is motivated by prior reports demonstrating dense brush layers to allow for only limited overlap of polymer canopies both in the solution^{45,64} and solid state^{7,8,29,50}. For the dense brush particle series (SiO₂-d-SN), the CPB-SDPB transition was determined by

evaluating the experimental scaling behavior $d \sim N^x$ (with x = 0.8 in the CPB and x = 0.5 in the SDPB regime, see Fig. 4-3). Following to this process, the *IPCED* could be expressed as

$$IPCED = U_{l}(L)\frac{\lambda}{L}\rho_{S}\left[\frac{\sqrt{2}}{2}(2r_{0} + BN^{0.5})^{3} - \frac{4}{3}\pi(r_{0} + \frac{A}{2}N_{c}^{0.8})^{3}\right]$$
Equation 4-2
$$/\left[\frac{\sqrt{2}}{2}(2r_{0} + BN^{0.5})^{3}\right]$$

where A and B are constants experimentally determined from Figure 4-3 a (A = 0.335 nm, B = 0.907 nm), $L = N_{\text{SDPB}} \lambda$ is the length of side-on overlap among chains in the SDPB regime and $\rho_{\text{S}} = 6.07 \times 10^{27} \text{ m}^{-3}$ is the number density of the repeat units (which was assumed to be independent of chain orientation). For brush systems with intermediate grafting density the length of chain segments participating in interdigitation was assumed to be equal to the contour length of tethered chains. The resulting trend of *IPCED* for dense and intermediate brush particle systems is shown in Figure 4-6.



Figure 4-6 Illustrations of (a) end-on arrangement of densely tethered ligands, and (b) side-on arrangement of interdigitated tethered ligands. Panel (c) shows a scheme of the Wigner-Seitz (WS) cell of particle brush (blue inner shell: CPB; red outer shell: SDPB). Panel (d) depicts a plot of the interparticle cohesive energy density (*IPCED*) in dense and intermediate brush particles as functions of degree of polymerization along with the corresponding values of elastic modulus (see text for more detail). Inset shows *IPCED* as function of organic volume fraction.

Since for materials undergoing only elastic-plastic deformation the stored elastic energy upon deformation is directly related to the corresponding change in cohesive energy density (*CED*), the elastic modulus of brush particle films could be determined from the calculated *IPCED*. Specifically, Willbourn *et al.* demonstrated the empirical relation $E \approx 8.04$ *CED* to apply to a wide range of polymers.⁶⁵ The resulting prediction of Young's moduli is depicted in Figure 4-6. Note that the predicted trend of E_{ICPED} confirmed the initial increase and following level-off with increasing degree of polymerization. Discrepancies from the experimental result (more rapid increase of modulus in intermediate system and increase of modulus in dense system arising from

 N_{crit}) might be attributable to the contribution of *inter*particle interaction between CPB-regime ligands to the total cohesive interaction, which is not considered in the calculation. Interestingly, despite the approximations made by the model, the resulting absolute values of the Young's modulus are captured within a factor of about two.

4.3.5 Structure and Interactions in Sparse Brush Particles

In contrast to dense and intermediate bush particle systems, sparse analogs displayed a systematic decrease of the elastic modulus with increasing degree of polymerization of polymeric tethers, eventually levelling out at values of *E* corresponding to the reference homopolymer (see Fig. 4-4). We attribute this opposing trend to the characteristic difference in microstructure in sparse brush particle films, specifically the formation of string-like aggregate structures. As discussed above, van der Waals interactions between particle cores increase when particles are in close proximity (less than about 0.5 nm). This is also confirmed by recent molecular dynamics simulation by Midya et al. that have shown core interactions to dominate other interactions in sparse brush particle architectures.⁴⁰ Qualitatively, the increased core-core interactions raise the *IPCED* of sparse brush materials and hence raise the elastic modulus. In fact, the mechanical properties of sparse brush particle hybrid materials might be better described by effective medium models for anisotropic filler shapes, such as the Cox short fiber model.⁶⁸ However, more quantitative information about the interactions within string aggregate structures would be required to test the applicability of effective medium models. Interestingly, the number of particles within aggregates (*i.e.* the string length) in SiO₂-s-SN systems decreases with increasing degree of polymerization. The corresponding reduction of core-core contacts rationalizes the observed decrease of E with increasing N that is observed in SiO_2 -s-SN systems. This situation is illustrated in Figure 4-7.



Figure 4-7 Structural transition in sparsely grafted particle films. The number of particles per string as a function of the degree of polymerization in PMMA analog (top) and PS analog (bottom) is plotted in a. Schematic illustrations of string formation in sparse brush particles when brushes are short (b) and long (c) are shown. Panel d and e show corresponding electron micrographs for short (d: SiO₂-*s*-S432) and a long tethered chains (e: SiO₂-*s*-S1576). Scale bars are 30 nm.

The above discussion centered on the interpretation of the elastic modulus of particle brush films.

This was motivated by the direct relation between the cohesive energy density and the elastic modulus that enables the interpretation of modulus changes on the basis of the interactions between constituents. However, as explained above, the determination of elastic moduli from instrumented indentation experiments is subject to assumptions about parameters such as Poisson's ratio that are difficult to determine experimentally. A more directly accessible – but less readily interpretable

quantity is the material's hardness that directly follows from the peak loading during indentation.
 Figure 4-8 displays an Ashby chart correlating the elastic modulus and hardness for all tested brush materials.



Figure 4-8 Indentation hardness (H) vs Young's modulus (E) plots of PS materials (a) and PMMA materials (b) (red: dense, green: intermediate, blue: sparse, black: initiator-tethered nanoparticles; symbols are matched up with the corresponding system). Trends are highlighted in yellow.

The linear trend in the E-H plots that is observed in the figure reveals that both quantities were correlated and hence obeyed similar structure-property relations. This suggests that hardness measurements might provide a versatile alternative to evaluate structure and interactions in brush particle solids. Figure 4-8 also might find use as 'design guideline' for the synthesis of particle brush materials with desired properties. For high modulus and hardness, brush systems with reduced grafting density are clearly preferable, depending on the constraints on the targeted microstructure.

4.4. Conclusion

In this work, three series of brush particle systems were investigated, differentiated by grafting density as dense (~ 1 nm^{-2}), intermediate (~ 0.3 nm^{-2}) and sparse (~ 0.05 nm^{-2}) brush systems. The density of tethered polymer chains exerted a pronounced effect on both structure and elastic modulus of films assembled from brush particles. Dense and intermediate systems displayed uniform microstructures while sparse systems formed string-like superstructures. For dense and intermediate systems, the elastic modulus – measured through instrumented indentation analysis – increased with increasing degree of polymerization of tethered chains. At a given volume fraction of organic component, the increase was found to be more pronounced for lower graft densities. This trend indicated that the restoring forces resisting elastic deformation are due to dispersion interactions between segments of interdigitated chains of adjacent brush particles. A reverse trend was observed in case of materials that were assembled from sparse brush particles. Here, Young's modulus continuously decreased with increasing degree of polymerization geree of polymerization of tethered chains – a trend that correlated with a decreasing number of particles per string.

We expect our results to be relevant in the context of mutual property optimization in particle brush-based hybrid materials. For example, if maximum reinforcement is to be achieved at high inorganic fractions and the formation of particle strings is to be avoided (such as in applications that require high dielectric breakdown strength) then our results suggest that brush particles with intermediate grafting density can be advantageous. Open questions that warrant further investigation include the better understanding of the mechanism of reinforcement in case of sparse particle brush assemblies. While the argument of increased contributions of core-core interactions is compelling, it is not clear why particle solids assembled from sparse initiator-capped particles (*i.e.* in the absence of any polymer) do not show a similar enhancement We hypothesize that the lower modulus in the case of initiator-capped particles might be, in part, caused by void spaces in the microstructure that are not present in the case of polymer tethered systems but this remains an issue to be clarified. A second question relates to the role experimental methodology. Complementary techniques such as Brillouin scattering (which probes the propagation of acoustic waves and hence gives information on both the bulk and the elastic modulus) could provide additional insight into the relevant modes of interaction in particle brush systems. An interesting question also concerns the role of chain length dispersity which was not considered in the present study. In particular, the deliberate control of the fraction of long to short chains could provide additional means to concurrently improve the modulus and fracture toughness of brush particle solids while maintaining high inorganic content in the hybrid material.

4.5. References

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5. The Effect of Chain Molecular Weight Dispersity on Mechanical and Thermal Properties

This part is in preparation to submit to Macromolecules.

5.1. Background

Colloidal nanoparticles without any coating have been considered fragile because predominant interaction is short-ranged, namely, van der Waals interactions.^{1–3} The surface modification of nanoparticles by means of tethering molecules, 'ligands', has been widely investigated to stabilize colloidal nanoparticles and to manipulate the interactions in the particulate system.^{1,2,4–9} Ligand-coated particles self-assemble into 2D or 3D structures through a balance between attractive and repulsive interactions in short- and long-range.^{4,10–13} Longer ligands (*i.e.*, polymer grafts) render mechanical durability to integrated hard spheres by strong ligand-ligand interactions resulting from entanglements.^{1,11–14} Brush (or 'hairy') particles refer to particulate materials tethered by polymeric chains on surface with chemical bonding. The hybrid constituter has demonstrated an applicability for a building block for the matrix-free uniform solids.^{15,16}

When it comes to grafting chains from a curved surface, *e.g.*, spherical particles, Ohno *et al.*¹⁷ successfully describe the conformation of grafted chains based on Daoud-Cotton model¹⁸ accounting for the size of a star-polymer as functions of the number of arms and the degree of polymerization of grafts. Similar to the Daoud-Cotton model, sufficiently long brushes grafted on spherical surfaces are expected to exhibit two distinct conformational regimes radially from the particle surface.¹⁷ Conformation in the inner shell indicates a stretched geometry because of the steric hindrance between adjacent ligands, so it is called the concentrated polymer brush (CPB). The outer shell where polymeric ligands form a relaxed and entangled structure is known as the semi-dilute polymer brush (SDPB) since the expanded spacing between neighboring chains in this

regime reduces the repulsive steric interactions. The critical radius (r_c) and the critical degree of polymerization (N_c) indicate where a CPB-to-SDPB transition arises and relate to grafting density and particle size:

$$N_{\rm c} \sim \frac{\sigma_{\rm s}}{r_0}$$
 Equation 5-1

where, σ_s is the surface grafting density (chains/nm²) and r_0 is the radius of nanoparticles.¹⁹ Experimental demonstration of the modified Daoud-Cotton model has been conducted in many works.^{11,17,20-24} In most of the studies, the brush height h has been scaled to validate the Daoud-Cotton model as a function of the degree of polymerization N and a parameter x, $h \sim N^x$. In this scaling, a high x value indicates a more stretched chain conformation. The scaling parameter x characterized by varying experiments such as transmission electron microscope (TEM),^{11,12,20} dynamic light scattering (DLS)^{12,17,23}, small angle neutron scattering (SANS)^{21,24} and atomic force microscope (AFM)²² is 0.8 - 0.98 in CPB and 0.5 - 0.6 in SDPB. The results commonly confirm that there is a conformational transition from stretched to relaxed regime in particle brush materials. 2D or 3D structure of particle brush assembly is sensitive to composition, grafting density, degree of polymerization, molecular weight distribution of tethered chains and particle size.^{5,11,12,25–31} For example, a recent study²⁵ by Kravchenko and Potemkin on 2D and 3D self-assembly of particle brush using molecular dynamics simulation predicted a gradational evolution in the structure: sheet - string - dispersion with increasing N or σ_s , or decreasing interactions between cores. The prediction of the anisotropic morphology (other than dispersion) was verified experimentally.^{32–37} The anisotropy in structure is driven by the inter-core interactions and the steric repulsion by surface modification. Inter-particle spacing decreases when the particles are sparsely grafted or when the grafted chains are short. In a system that consists of nonpolar particles, short-ranged van

der Waals forces are dominant and approximately proportional to r^{-6} , where *r* is the inter-particle distance.³⁸ Hence, the strong interactions by shortened spacing lead to the increase in the coordination number and following 1D-2D-3D agglomerations.

5.1.1 Mechanical Properties in Particle Brush Assembly

Mechanical properties of particle brush assemblies have attracted attention because the motivation of introducing polymers to hard particle assemblies seeks to improve the mechanical embrittlement of unfunctionalized particle assemblies. Choi et al.^{12,20,39}, for example, pioneered the effect of polymer modification on interaction and structure formation in particle brush assembly structures. The authors used SI-ATRP to prepare a series of PS-/PMMA-tethered silica particles. All particles in the study were densely grafted. Nanoindentation was used to examine mechanical properties of the films and revealed that colloidal brush particles was able to be tough if long polymer chains were densely tethered. The structure of dense brush particles revealed highly ordered close-packed structures. An extended study on densely tethered brush particles by Schmitt et al.¹¹ systematically clarified the effects of particle size, chain length and chain composition on modulus and toughness. Flexibility of the photonic films and facile processing as used in a material processing widely used in polymer industry were also demonstrated. In Chapter 4, the role of grafting density was also covered. Sparse brush particles assembled into string-like structure and exhibited mechanical properties following an effective medium model as a function of composition. Results of dense and intermediate brush regimes indicated that the significant increase of interdigitation encouraged by reduced grafting system leaded to more effective enhancement of mechanical properties.

Out of many simulation works, Hansoge *et al.*⁴⁰ recently predicted Young's modulus and toughness in brush particle assemblies with multiple parameters such as degree of polymerization, graft density, ligand-particle interaction and aspect ratio of the particle by using an updated

simulation method of metamodel-based design optimization. They observed a decrease in modulus and an enhancement of toughness when chains become longer in sparsely grafted particle films. The result also suggests that very dense functionalization is not suitable for applications requiring stiff and tough materials. Jiao and his coworkers³⁶ concluded that modulus of sparsely polymergrafted particle films does not change with degree of polymerization in the limit of the long chain regime.

5.1.2 Glass Transition in Brush Particle Assembly

Glass transition is a characteristic behavior of polymeric materials.⁴¹ When polymers are heated, they experience a macroscopic transition in dynamics from glassy to rubbery state. Glass transition temperature where the transition occurs is one of the most important thermophysical properties of amorphous polymers because of the distinct dynamics between before and after. Driven by high thermal energy, macromolecular chains slide by each other. The glass transition temperature of polymers depends on the degree of polymerization, chemical structure, cooling/heating ratio, etc. Glass transition behavior in brush particles has been explored in many researches.^{42–47} It was reported that glass transition temperature of polymerization due to the steric hindrance of brush chains and that glass transition temperature of particle brushes increases with the degree of polymerization as of homopolymers.^{43,44} However, the role of grafting density or bimodality on the glass transition temperature was not clearly revealed yet despite its significant impact.

5.1.3 Effect of Chain Length Dispersity on Physical Properties

Nevertheless, a study another molecular parameter of particle brush by any means has been mostly neglected both because of practical difficulty in synthesis of wide dispersed brush particles and

because of a need to clarify the influence of other easily-controllable parameters (particle size, chain length and degree of polymerization) on properties. Brush materials in this investigation cover a wide range of chain dispersity.

Early works putting an emphasis on the effect of dispersity of linear polymers on their collective properties dealt with bimodal (sometimes multimodal) molecular weights polymers, a system with two distinct molecular weight peaks.^{48–52} Progress in controlling molecular weight distribution (MWD) during synthesis widens the field into monomodal and wide-dispersed polymer materials.^{52–55} In linear polymers, a wide MWD at a given molecular weight average indicates an increase in the amount of a tail at short chain region. Short chains where molecular weights (MWs) are lower than $2M_e$ (entanglement molecular weight: 'average molecular weight between nearest entanglements on a chain') do not contribute to form entanglements, which greatly boost mechanical robustness or toughness.⁵⁵ We note that two times of entanglement molecular weight ($2M_e$) of poly(methyl) methacrylate (PMMA) is 27,500 g/mol for readers' information.⁵⁶ In other words, the increase in the portion of short chains results in the reduced entanglement density and consequently weakened mechanical properties. And, there is still an ongoing debate on "which molecular parameter between M_n and M_w relates to the physical properties?"

5.1.4 Motivations and Goals

Unfortunately, the effect of dispersity (or MWD) of ligands in particle brush materials has barely researched as mentioned above. A recent work by Bentz *et al.* scaled brush height of monomodal and wide-dispersed brush particles as a function of degree of polymerization.⁵⁷ However, the materials used had MWD depending on M_n , which means that a net effect of dispersity was not detected.

Recent advances in surface-initiated atom transfer radical polymerization (SI-ATRP) on nanoparticles set a milestone in that it realized the potential of polymer chain tethering from curved surfaces with precisely controlled chain architecture (such as the degree of polymerization *N* and the surface grafting density σ_s) as well as uniform grafting.^{19,58–62} Hui *et al.*⁵⁹ established essential SI-ATRP protocols that enable the surface modification with tetherable-initiators and the subsequent polymerization from varying curvatures. The authors succeeded in controlling the surface grafting density (a critical parameter that determines final structure; see details in next paragraphs) using inactive species (dummy initiators) of which the ends are chemically dormant so that polymerization is not initiated. Yan *et al.*⁶² and Wang *et al.*³⁷ developed synthetic strategies of SI-ATRP suitable for sparse grafting, bimodal grafting and wide-monomodal grafting.

Although the previous studies demonstrated the potential of particle brush materials with enhanced durability and stiffness in practical applications, these advancements were related mostly to narrow-monomodal brush particles. Bimodal brush architecture with distinct narrow molecular weights has been thought a perfect candidate for exploiting ligand interactions without sacrificing sufficient particle loading.^{63,64} However, the material synthesis is complicated, and cannot be done in one batch. Hence, wide-monomodal dispersed brush particle is a fair alternative in that we can still expect the advantages similar to bimodal materials with possibly facile fabrication. For these reasons, we aim to understand the role of molecular weight distribution of wide-monomodal ligands on physical properties.

5.2. Experimental Methods

5.2.1 Synthesis

To synthesize the particle brushes with diverse molecular weight (MW), dispersity (M_w/M_n), and grafting density (σ_s), a photoATRP approach was employed with only adjustments to copper concentrations (c_{Cu} , 0.01 – 100 ppm) and target degree of polymerization (DP_t, 375 – 1500).³⁷ 600 ppm of tris(2-(dimethylamino)ethyl)amine (Me₆TREN) were added in the reactions as ligand and reducing agent.⁶⁵ All reactions were allowed to proceed until the reaction became too viscous for a rare earth stir bar to further spin, at which point irreversible chemical crosslinking may start to take place.

Materials

Methyl methacrylate (MMA, Aldrich, 99%) were filtered through a basic alumina column to remove the inhibitor. 15.8 nm silica nanoparticles (MIBK-ST) were kindly donated by Nissan Chemical. Initiator-functionalized silica nanoparticles were synthesized according to previously reported procedures.^{60,66} Copper(II) bromide (CuBr₂, Aldrich, 99%), anisole (Aldrich, 99%), dimethylformamide (DMF, Fisher, 99%), hydrofluoric acid (HF, Aldrich, 48%), ammonium hydroxide (Fisher, 28%), tetrahydrofuran (THF, EMD, 99%) and tris(2-(dimethylamino)ethyl)amine (Me₆TREN, Alfa, 99%) were used as received.

Particle brush synthesis

In a typical reaction, 0.12 g functionalized silica nanoparticles $(2.1 \times 10^{19} \text{ nm}^2 \text{ of surface})$ were dispersed in a mixture of 2.8 mL (26 mmol, DP_t = 750 assuming 1 accessible Br/nm²) of MMA and 2.8 mL of anisole. 29 µL of 0.2 mg/mL (26 nmol, *i.e.* 1 ppm) CuBr₂ solution in DMF was added. The mixture was wrapped in foil and agitated in a ultrasonication bath for 2 h. 4.2 µL (16 µmol) of Me₆TREN and 25 mm × 12 mm oval extra power stir bar was added to the reaction. The

mixture was stirred at room temperature while exposed to UV irradiation at 365 nm (3.6 mW/cm², MelodySusie). The reaction was quenched by turning off the UV lamp and exposure to the air when the stir bar stopped moving. The particle brushes were purified by precipitation from methanol.

5.2.2 Size Exclusion Chromatography (SEC)

Number-average molecular weight (M_n) and dispersity were determined by size exclusion chromatography (SEC). Polymer-grafted nanoparticles were dispersed in THF and treated with HF before analysis in SEC. The SEC was conducted with a Waters 515 pump and Waters 410 differential refractometer using PSS columns (Styrogel 105, 103, 102 Å) in THF as an eluent at 35 °C and at a flow rate of 1 mL/min. Linear PMMA standards were used for calibration.

5.2.3 Thermogravimetric Analysis (TGA)

TGA with TA Instruments 2950 was used to measure the fraction of SiO₂ in the hybrids. The data were analyzed with TA Universal Analysis. The heating procedure involved four steps: (1) jump to 120 °C; (2) hold at 120 °C for 10 min; (3) ramp up at a rate of 20 °C/min to 800 °C; (4) hold for 2 min. The TGA plots were normalized to the total weight after holding at 120 °C.

5.2.4 Transmission Electron Microscopy (TEM)

Approximately monolayer films of all particle brush systems were prepared by drop-casting of dilute colloidal solutions (~1 mg/mL in toluene) on a carbon-supported copper grid. The particulate film morphology and craze formation were studied using TEM with a JEOL EX2000 electron microscope operated at 200 kV. Images with amplitude and phase contrast were obtained by a Gatan Orius SC600 high resolution camera.

5.2.5 Image Analysis

A quantitative analysis on TEM micrographs following a systematic processing was conducted using Matlab. A sequence for the analysis is shading correction – blurring – dilation – erosion – particle recognition – tessellation. Bandpass filter was applied to correct shading. As next steps, the combination of dilation and erosion was exploited to separate merged (neighboring) domains. Gaussian blurring is necessary to reduce detail for better recognition. Given that unstained TEM images provide two distinct contrast levels (dark (silica particles) and bright (polymer brush)), each domain was mapped by binarization. Then, effective domain of each particle was recognized, followed by Voronoi tessellation using centroid information.

5.2.6 Thick Film Preparation

Dispersed brush particles were processed in thick toluene solution (~ 30 mg/mL). Each solution was cast in a PTFE mold (15 mm × 5 mm × 300 μ m DWH) 4 times to thicken final specimens. To guarantee sufficient time to approach a nearly equilibrium state, solvent evaporation was delayed by semi-closed system and vapor-supplied atmosphere. Films were formed in the mold for three days and taken out to be annealed at a moderate temperature (~ 50 °C) in a mild low-pressure (~ 15 in.Hg) for a day to remove probable solvent residue.

5.2.7 Tensile Test

Thick films cast from the PTFE mold were mechanically characterized using TA instruments RSA-G2 solids analyzer. Tensile force was applied at strain rate of 0.001 mm/s from strain-free state. Data was analyzed using Matlab script (see attached in Appendix). Young's modulus (*E*) was obtained from the maximum gradient of stress-strain curve at the beginning stage (0–10 s). Toughness (U_T) was calculated by integrating area under stress-strain curve before fracture.

Systematic error in modulus and toughness was calculated by measuring 5 PMMA homopolymer films prepared in the same way and applied to all results.

5.2.8 Differential Scanning Calorimetry (DSC)

Thermal characterization was performed using a DSC-Q20 (TA Instruments) with 4 cycled repeats of heating and cooling across a temperature range of 60 °C < T < 160 °C. To get rid of instability of the first cycle, last three cycles of heating were analyzed to evaluate glass transition behavior. Glass transition temperature (T_g) was determined by inflection point, and breadth of glass transition was characterized by difference between onset and offset points (defined as intersections of tangents).

5.3. Results and Discussion

A series of PMMA brush particle materials with a variety of molecular weight distributions $(M_w/M_n = 1.18 \text{ to } 3.23; \text{ where } M_w \text{ is the weight average molecular weight and } M_n \text{ is the number}$ average molecular weight) was synthesized via surface-initiated photo atom transfer radical polymerization (SI-photoATRP) using established protocols as shown in Figure 5-1.^{19,37,58–60} The classification of dispersed brush particles into narrow-dispersed and wide-dispersed (sample ID: SiO₂-MMA-*n/w*) is based on the respective molecular weight distribution of grafted brush chains as illustrated in Figure 5-2.



Figure 5-1 SI-photoATRP of PMMA brush on silica nanoparticles functionalized with 3-(chlorodimethylsilyl)propyl 2-bromoisobutyrate, BiBSiCl) initiators.

Schulz-Zimm (SZ) distribution (Equation 5-2)^{67,68} was used to estimate MWDs of narrow- and wide-disperse brush particle materials as shown in Figure 5-1. The SZ distribution is widely acknowledged realistic representation of result of polymerization.⁶⁹ The number average molecular weight, Mn was fixed 50,000 g/mol to reflect intermediate chain length. Dispersity index, M_w/M_n for narrow-disperse system was set at 1.05 which is widely said experimental limit of uniform MWD while $M_w/M_n = 1.80$ was chosen to match representativeness of the minimum distribution as 1.05 does in narrow-disperse system:

$$p_{SZ}(M) = \frac{1}{\Gamma(\beta)} \alpha^{\beta} M^{\beta-1} e^{-\alpha M}$$
 Equation 5-2

where, *M* denoting molecular weight, Γ is the Gamma function, $\alpha = \beta/M_n$, $\beta = (M_w/M_n - 1)^{-1}$. We could confirm a great tail of short chains in the wide-disperse case from the MWDs that lead to reduced mechanical properties in the case of homopolymer. When it comes to particle brush, wide distribution is expected to lower N_c because short chains render more free volume to longer chains.⁷⁰ The lowered N_c amplifies formation of entanglements in the increased free volume. We expect the increased formation of entanglements in wide-dispersed brush system results in efficient toughening of films.



Figure 5-2 Comparison of chain architecture between uniform and dispersed brush particles. Plots under illustrations show molecular weight distribution of corresponding brush chain estimated by Schulz-Zimm distribution. As representative, 1.05 and 1.80 were chosen for M_w/M_n of uniform and dispersed regimes respectively.

Molecular characteristics of the materials used in this work were displayed in Table 5-1. Categorization into narrow- and wide-dispersed brush is based on dispersity index (narrow: $M_w/M_n \le 1.40$, wide: $M_w/M_n > 1.80$). 5 narrow-dispersed and 4 wide-dispersed brush particles were prepared to investigate the effect of molecular weight distribution on physical property. Moderate grafting was performed to maximize the efficiency of brush enhancing mechanical property as concluded in the Chapter 4.

Sample ID	N	<i>M</i> n (g/mol)	<i>M</i> _w (g/mol)	M _w /M _n	$f_{ m org}$	ф _{org}	σ₅ (nm ⁻²)
SiO ₂ -MMA-n1	219	21,890	30,650	1.40	0.74	0.84	0.23
SiO ₂ -MMA-n2	359	35,860	42,360	1.18	0.75	0.85	0.15
SiO ₂ -MMA-n3	362	36,150	49,700	1.37	0.73	0.83	0.13
SiO ₂ -MMA-n4	526	52,550	62,290	1.19	0.76	0.85	0.11
SiO ₂ -MMA-n5	490	49,000	67,700	1.38	0.87	0.93	0.25
SiO2-MMA-w1	375	37,500	70,500	1.88	0.77	0.86	0.16
SiO ₂ -MMA-w2	259	25,930	83,820	3.23	0.70	0.81	0.16
SiO ₂ -MMA-w3	605	60,480	120,500	1.99	0.76	0.86	0.10
SiO ₂ -MMA-w4	634	63,390	138,900	2.19	0.79	0.87	0.11

 Table 5-1 Molecular characteristics of poly(methyl methacrylate) grafted silica particles.

Variables represent the degree of polymerization of graft, N; the number average of molecular weight, M_n ; the weight average of molecular weight, M_w ; dispersity index, M_w/M_n ; weight fraction of polymer, f_{org} ; volume fraction of polymer, ϕ_{org} ; surface grafting density, σ_s .

5.3.1 Structure Formation of Dispersed Brush Particles

Transmission electron microscopy (TEM) was used to characterize the structure of particle brush films. Two pairs of materials were shown to evaluate the role of number- and weight-average molecular weights on structure. In Figure 5-3 (a–c), a narrow disperse brush SiO₂-MMA-*n*1 (M_n = 21,890 g/mol) and a wide disperse brush SiO₂-MMA-*w*2 (M_n = 25,930 g/mol) were analyzed. The similar number average molecular weight materials showed that increasing MWD of tethered chains results in decreasing degree of ordering (1–*FWHM*) as confirmed in Figure 5-3 (c). As information, the increase in average Voronoi cell area <*A*> and the increase in PMMA fraction ϕ_{PMMA} proves the larger M_w of SiO₂-MMA-*w*2. On the other hand, Figure 5-3 (d–f) compare a pair of similar weight average molecular weight samples: (d) SiO₂-MMA-*n*5 (M_w = 67,700 g/mol) and (e) SiO₂-MMA-*w*1 (M_w = 70,500 g/mol). These two materials do not present noteworthy distinctions in structure (ordering and areal fraction). For these reasons, M_w is more relevant parameter when structure of brush particle materials.



Figure 5-3 Bright field transmission electron micrographs of (a) SiO₂-MMA-*n*1, (b) SiO₂-MMA-*w*2, (d) SiO₂-MMA-*n*5 and (e) SiO₂-MMA-*w*1 with corresponding Voronoi area distributions (c and f). The combination of (a) SiO₂-MMA-*n*1 ($M_n = 21,890$ g/mol) and (b) SiO₂-MMA-*w*2 ($M_n = 25,930$ g/mol) is to compare similar number average molecular weight materials while the other (d) SiO₂-MMA-*n*5 ($M_w = 67,700$ g/mol) and (e) SiO₂-MMA-*w*1 ($M_w = 70,500$ g/mol) is to compare similar weight average molecular weight samples. <*A*> denotes the average Voronoi cell area in nm⁻², *FWHM*, the normalized full-width at half maximum and ϕ_{PMMA} , the fraction of PMMA domain in a micrograph. Line characteristic of distribution curves in (c and f) corresponds to the frame features of each micrograph. Scale bars are 100 nm.

5.3.2 Mechanical Properties of Dispersed Brush Particles

Young's modulus and toughness were characterized using tensile test of thick films (~ 100μ m). Representative stress-strain curves are displayed in Figure 5-4. The same materials chosen in Figure 5-3 are shown for consistent understanding. All films fractured between the grips (not on the grips). It is important because excessive strength of grabbing may lead to deformation at grip and influence upon test result. Modulus data is discussed in the next part. Toughness, the energy per volume dissipated prior to fracture, was calculated by integrating area under stress-strain curves. Apparent difference of toughness in narrow- and wide-dispersed systems was observed. High MWD brush particle films have larger fracture points, thus larger toughness. This observation supports our hypothesis that wide MWD contribute to the facile entanglement formation by lowering N_c .



Figure 5-4 Representative stress-strain curves of dispersed brush particle materials with photographs taken after test. (Red solid line, SiO₂-MMA-*n*1; blue solid line, SiO₂-MMA-*w*2; red dashed line, SiO₂-MMA-*n*5; blue dashed line, SiO₂-MMA-*w*1)

Young's moduli of the thick films were measured as gradient of stress-strain plot at the very beginning stage to capture elastic-only response. The results of modulus are shown as functions of $M_n, M_w, M_w/M_n$ and ϕ_{PMMA} in Figure 5-5. The narrow dispersed analog follows the result of Chapter 4: *E* increases and level-off with increasing M_n (or M_w). However, there is no clear trend of

modulus in the plots. This indicates that MWD does not play a critical role in elastic response which is measured in small strain region. Interestingly, *E* increases with the organic fraction (ϕ_{org}). In this intermediate grafting regime, all repeating units are expected to be in SDPB and so to contribute to dispersion interactions and the rise in modulus.



Figure 5-5 Young's modulus (*E*) of dispersed brush particles as functions of (a) M_n , (b) M_w , (c) M_w/M_n and (d) ϕ_{PMMA} . Data points are colored by dispersity categorization (red, narrow-dispersed; blue, wide-dispersed).

On the other hand, toughness (U_T) plotted as functions of the molecular parameters indicated featured trends as presented in Figure 5-6. The property did not show any explicit tendency in Figure 5-6 (a and d) which are plotted versus M_n and ϕ_{PMMA} . However, toughness increased with increasing weight average molecular weight and increasing dispersity index (Figure 5-6 (b and c))). It was found that wide-dispersed 4 samples capture high toughness compared to narrow analog. The toughening effect in the wide-dispersed brushes was attributed to the increased entanglement density due to the low N_c and super-long chains.^{63,71} Compared to the interpretation of modulus data, entanglements worked only against large strain (plastic) deformation.



Figure 5-6 Toughness (U_T) of dispersed brush particles as functions of (a) M_n , (b) M_w , (c) M_w/M_n and (d) ϕ_{PMMA} . Data points are colored by dispersity categorization (red, narrow-dispersed; blue, wide-dispersed).

The toughening effect was visualized by crazing when film is under fracture. Figure 5-7 shows failure mechanism when stress is applied on thin films. The narrow-dispersed short brush particles, SiO₂-MMA-*n*1 was found brittle because a simple crack formed. Other long and/or wide-disperse brush particles demonstrate their toughness by crazing which is a clue of the presence of entanglement. Compared to Fig. 5-7 (b) SiO₂-MMA-*w*2 and (d) SiO₂-MMA-*w*1, the morphology of crazes in (c) SiO₂-MMA-*n*5 is thinner probably due to insufficient density of interparticle entanglement. Thus, abundant entanglements in high MWD films result in the enhanced toughness.



Figure 5-7 Deformation behavior of dispersed brush particle films captured by TEM. (a) SiO₂-MMA-*n*1, (b) SiO₂-MMA-*w*2, (c) SiO₂-MMA-*n*5 and (d) SiO₂-MMA-*w*1. Scale bars are 200 nm.

5.3.3 Glass Transition of Dispersed Brush Particles

Thermal property of brush particle materials is also of our interest because a unique thermal behavior of amorphous polymers such as glass transition behavior can play another important role to widen its applicability. We could find out that wide distributed brush system has more broad window of glass transition and the breadth increases as grafted chains get dispersed. Glass transition temperature is determined by MW of chains constituting a bulk. A polymeric material with a wide variety of MWs as SiO₂-MMA-*w*2 gives broad glass transition.



Figure 5-8 Thermal history of dispersed brush particles when heating (a) SiO₂-MMA-*n*5 (red arrowed in c) and (b) SiO₂-MMA-*w*1 (blue arrowed in c), and (c) the breadth of glass transition

versus dispersity index (M_w/M_n) with a guideline (red, narrow-dispersed; blue, wide-dispersed). Arrows in (c) indicate the materials showing thermal history. Glass transition breadth was calculated the difference between onset and offset points of glass transition as described in (a) and (b).

5.4. Conclusion

Particle brush materials with a varying molecular weight distributions of functionalized polymers were studied. The material systems were differentiated by dispersity index M_w/M_n as narrowdisperse (≤ 1.40) and wide-disperse (> 1.80) brush particles. The structure formation in wide dispersed brush system is less ordered as confirmed by Voronoi tessellation. Tensile test results demonstrated that a high MWD substantially enhances mechanical resistance by the facile formation of entanglements in large strain deformation. It is because the considerable amount of short and very long chains respectively lower the critical degree of polymerization (for chain conformation change of concentrated-to-semidilute) and form sufficient entanglements which toughen the materials. Short strain (elastic) deformation is nearly independent of MWD. Glass transition width measured by differential scanning calorimetry clearly increases with increasing MWD. This can be interpreted statistically because glass transition temperature is known as a function of MW of chains. Hence, brush particles with more tails (composed of short and superlong chains) exhibited wide glass transition compared to uniform brush particles.

5.5. References

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6. Other works: Ligand-Induced Phase Transition in Particle Brushes

6.1. Polymer Ligand-Induced Reversible Phase Separation in Binary Particle Blends¹

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6.1.1 Background

The unique physical properties of nanocrystalline materials with controlled size and shape have rendered inorganic nanocrystals and their assembly structures an important platform to facilitate technological breakthroughs in areas ranging from sustainable energy technologies to magnetic storage or medical diagnostics.¹⁻³ A widely used approach to integrate particle-based materials into device structures relies upon the fabrication of films from particle dispersions.³ The process of structure formation in particle thin or thick films (hereafter referred to as 'particle solids') has thus been subject of intense research.^{4,5} Driven by the advancement of synthetic and particle size separation techniques as well as the understanding of the physics underlying the organization of colloidal systems, the controlled assembly of one- and two-component particle systems into uniform long-ranged ordered structures that mimic atomic crystal structures has been achieved.^{8,9} To augment the structure and properties of particle solids, the tethering of organic ligands to the surface of particles has emerged as an effective strategy. This approach takes advantage of the possibility to tailor the interactions between particle constituents by the deliberate design of the structure and composition of organic ligands. For example, Murray and coworkers demonstrated that the variation of aliphatic ligands in binary particle mixtures enables the controlled assembly of a range of binary particle superlattice structures.⁹ The tethering of DNA-based ligands that are

capable of directional interactions was shown to be an effective method to assemble particles into a range of open lattice structures.^{10,11}

Recent advances in surface-initiated controlled radical polymerization have further extended the range of possible ligand compositions to encompass polymer chains.¹² Properties of materials assembled from polymer-tethered particles were shown to sensitively depend on the grafting density and degree of polymerization of tethered chains as well as the size and geometry of the particle core.¹² For the special case of densely polymer-tethered particle systems (hereafter referred to as 'particle brushes') it was shown that increasing the chain length of ligands gives rise to a transition from hard sphere-type to soft interactions and a progressively more polymer-like response of particle solids.¹³ The tailoring of brush architectures has shown to offer intriguing opportunities to augment the properties of particle solids. For example, polymer ligands were shown to increase the elastic modulus and toughness of colloidal crystal-type particle solids, to enable their processing by solventless molding techniques and to facilitate hybrid materials with enhanced dielectric and novel phononic properties.¹⁴⁻¹⁹

Beyond the enhancement of mechanical properties, the macromolecular nature of polymers gives rise to unique physicochemical characteristics that could enable transformative advances in the development of high-throughput fabrication techniques of microstructured particle solid films. In this contribution we demonstrate that polymer-ligand interactions can induce upper or lower critical solution phase behavior in multicomponent particle solids depending on the polymer ligand composition. Hence, cooling (or heating) of particle brush blends with appropriate architecture below (or above) the upper (or lower) critical solution temperature (UCST/LCST) of the blend results in the formation of monotype particle microdomains with characteristic lengthscales that can be tuned by adjustment of the thermal annealing conditions. Thermal cycling of LCST particle

brush blends at temperatures above and below the critical temperature enables the *reversible* growth or shrinkage of mono-particle domain structures. This process could ultimately facilitate the reversible formation and dissolution of microstructures in multicomponent particle solids. Figure 6-1 illustrates the process for controlled organization in binary particle brush mixtures by harnessing polymer ligand-induced phase transitions.



Figure 6-1 Illustration of ligand-induced phase separation in particle brush blends. (A) Upper critical solution temperature (UCST) phase behavior. (B) Lower critical solution temperature (LCST) phase behavior. LCST blends allow for reversible cycling of blend through homogeneous one-phase (1P) and phase-separated two-phase (2P) states.

It is very well known that a pair of polymers have a tendency to be immiscible. Phase behavior of

binary polymer blends can be described using the Flory-Huggins model:

$$\frac{\Delta G_m}{RT} = \frac{\phi_1}{N_1} \ln \phi_1 + \frac{\phi_2}{N_2} \ln \phi_2 + \chi'_{12} \phi_1 \phi_2$$
 Equation 6-1
$$(\chi'_{12} \equiv \chi_{12} / V_{ref})$$

Where ΔG_m is the free energy of mixing per unit volume, *R* is the gas constant, *T* is the absolute temperature, ϕ_i is the volume fraction and N_i is the degree of polymerization of a component *i*, χ_{12} is the Flory-Huggins parameter, and V_{ref} is the molar volume of segment.²⁰ The first two

logarithmic terms indicate the combinational entropy of mixing. It can be easily deduced by that the condition, $0 < \phi < 1$, makes the two terms negative thus always promote mixing. For polymer blends, the molar volumes (V_1 and V_2) are both large. Hence, the third term, *i.e.*, the enthalpy of mixing determines the miscibility or immiscibility of the polymer blend. In most of polymer pairs, the enthalpy of mixing is positive. This is so why many polymer mixtures are immiscible.

$$\frac{d^2 \Delta G_m}{d\phi_2^2}\Big|_{\phi_2 = \phi'_{2,sp}} = \frac{d^2 \Delta G_m}{d\phi_2^2}\Big|_{\phi_2 = \phi''_{2,sp}} = 0$$
 Equation 6-2

$$\frac{d\Delta G_m}{d\phi_2}\Big|_{\phi_2=\phi_2'} = \frac{d\Delta G_m}{d\phi_2}\Big|_{\phi_2=\phi_2''} = \frac{\Delta G_m(\phi_2'') - \Delta G_m(\phi_2')}{\phi_2'' - \phi_2'} \qquad \text{Equation 6-3}$$

From the equation 6-1, spinodal and binodal curves can be calculated by the following equations 6-2 and 6-3 respectively. In Figure 6-2, an actual process to draw a phase diagram is described at three different temperatures including the critical point. For compositions within the binodal curve, phase separation arises. The binodal condition denotes the minimum of energy equilibrium state in the system. Within spinodal condition, the system is in 'stable' state. Hence, a specific area between the spinodal and binodal curve indicates the range of 'metastable' state.



Figure 6-2 An example of free energy of mixing versus volume fraction (left) and calculated phase diagram (right, solid: binodal, dashed: spinodal).²¹

Depending on the combinational entropy and the enthalpy of mixing, phase behavior varies. Archetypes of lower critical solution temperature (LCST) and upper critical solution temperature (UCST) behavior are described in Figure 6-3. Typically, UCST-type blend systems cannot be mixing even through thermal processing at higher than UCST that may induce the entropic terms dominant so as to cause mixing. Given most of polymers begin degraded ahead of reach to UCST, reversibility of phase separation is achievable when both of miscible and immiscible ranges of temperature coexist at a volume fraction. In that typical UCST is higher than the degradation temperature in UCST-type blends, single phase cannot be experimentally achievable at intermediate composition, indicating irreversible phase transition characteristics. Many of LCSTtype polymer blends, meanwhile, reveal reversible feature because LCST is lower than the degradation temperature. For this reason, LCST-type material systems have been of interest in terms of practical applications.



Figure 6-3 Representative phase diagrams of polymer blends (left: upper critical solution temperature behavior, right: lower critical solution temperature behavior, solid curve: binodal, dashed curve: spinodal).

In this work, Dr. Michael Schmitt spearheaded the first half (irreversible phase separation of PSand PMMA-grafted particles blend). The rest part, reversible phase separation of PSAN- and PMMA-grafted particles blend, was taken over by the author.

6.1.2 Experimental Methods

6.1.2.1 Particle brush synthesis

The synthesis of polymer-tethered particles was performed using surface-initiated atom transfer radical polymerization according to previously published procedures.²²⁻²⁴ In a typical synthetic procedure, silica nanoparticles were bound with initiator by using 5-hexen-1-ol, α -bromoisobutyryl bromide, and triethoxysilane to synthesize a tetherable ATRP initiator: 6-(triethoxysilyl)hexyl α -bromoisobutyrate. For the polymerization, a mixture of initiator-modified silica nanoparticles (SiO₂-Br) and anisole was stirred in a Schlenk flask for 24 h to form a homogenous suspension. Subsequently, styrene, *N*,*N*,*N'*,*N''*,*N'''*-pentamethyldiethylenetriamine (PMDETA) and CuBr₂ were added to the flask with a rare earth magnetic stir bar. The use of a sufficiently strong stir bar is required to prohibit vitrification that can occur, especially at high monomer conversion. The solution underwent three freeze-pump-thaw cycles before being

immersed in liquid nitrogen and then purged with nitrogen. Then, CuBr was added to the flask. The flask was sealed with a glass stopper and evacuated before being back-refilled with nitrogen three times. The reaction mixture was then warmed to room temperature and placed in an oil bath heated to 70 °C to initiate polymerization. The final molar ratios of reaction components in a typical reaction were approximately [Styrene]₀:[SiO₂-Br]₀:[CuBr]₀:[CuBr₂]₀:[PMDETA]₀ of 2000:1:2.5:0.25:2.75 with a volume fraction of non-reactive solvents of 5.4% dimethylformamide and 40% anisole in a 100 mL flask and stirred at approximately 1000 rpm. The polymerization was stopped by exposing the catalyst to oxygenated tetrahydrofuran after cooling under continuous stirring. The final product was dialyzed against tetrahydrofuran and methanol until the copper(II) catalyst was removed as evidenced by disappearance of its characteristic color.

Styrene (St, Aldrich, 99%) was purified by passing through a basic alumina column before use. Copper (I) bromide was prepared by reduction of an aqueous solution of $CuBr_2$ with an aqueous solution of ascorbic acid, and copper (I) chloride was prepared by reduction of CuCl₂ aqueous solution using an aqueous solution of sodium sulfite. Both copper halides were then sequentially filtered, washed with methanol, dried and stored under vacuum before use. Silica nanoparticles (SiO₂NP), 30% solution in isopropanol, were kindly donated by Nissan Chemical Corporation and used as received. 5-Hexen-1-ol (98%), α -bromoisobutyryl bromide (98%), triethoxysilane (95%), ethyl α -bromoisobutyrate (EBiB, 98%), 4,4'-dinonyl-2,2'-bipyridine (dNbpy, 99%), N,N,N',N'',N''-pentamethyldiethylenetriamine (PMDETA, 99%), and anisole (99%) were purchased from Aldrich and used as received. All other chemicals and solvents were supplied by Aldrich and Acros Organics.

Debromination procedure

The debromination was performed under an atmosphere of nitrogen. In a typical procedure, the asprepared SiO₂-PMMAN, SiO₂-PMMAN, or SiO₂-PSANN brush particles (0.03 mmol Br) and DMF (10 mL) were stirred in a Schlenk flask for 2 h to form a homogenous solution. Subsequently, thiophene (0.3 mmol) and triethylamine (TEA, 0.3 mmol) were added slowly to the flask under vigorous stirring. The flask was sealed with a glass stopper and evacuated before being backrefilled with nitrogen. The reaction mixture was immersed in an oil bath at 45 °C overnight. The product was precipitated by adding the reaction mixture to methanol and the solid was filtered and washed with methanol prior to drying in a vacuum oven at 60 °C.

6.1.2.2 Thermogravimetric Analysis (TGA)

Inorganic content of particle brushes and decomposition characteristics were made using weight fractions measured from thermogravimetric analysis (TGA) on a Q50 TGA analyzer from TA Instruments under nitrogen up to 850 °C at a scan rate of 20 °C /min. To study decomposition, temperature was held at a selected value (*i.e.* 250 °C) for a period of time, followed by a slowed scan period (5 °C /min) in order to accurate assess weight loss prior to continued scanning at the normal rate.

6.1.2.3 Gel Permeation Chromatography (GPC)

Molecular weight and dispersity were measured by gel permeation chromatography (GPC) using a Waters 515 pump and Waters 2414 differential refractometer ($\lambda = 930$ nm) and a Wyatt Technology DAWN EOS multiangle laser light scattering (MALLS) detector using PSS columns (Styrogel 10⁵, 10³, and 10² Å) for PS and Waters Microstyragel columns (guard, 10², 10³, and 10⁵ Å) in THF as an eluent (35 °C, flow rate of 1 mL/min) with toluene and diphenyl ether used as internal references. Linear PS or PMMA standard were used for calibration. Chains were cleaved from particles by etching of particles in HF in a polypropylene vial for 20 h, neutralized with ammonium hydroxide, and dried with magnesium sulfate before running GPC. Hydrofluoric acid (50 vol% HF) was purchased from Acros Organics and used as received. THF was purchased from Aldrich and used as received.

6.1.2.4 Atomic Force Microscopy (AFM)

Blended films of PMMA@SiO₂ and PS@SiO₂ were prepared by spin-coating concentrated solutions (~ 35 mg/mL) of particle brushes in toluene onto silicon substrates with their native oxide layer intact that were cleaned with acetone, isopropanol, and de-ionized water immediately prior to coating at 2000 rpm for 30 s. When annealing, temperature changes were introduced very rapidly (< 5 min) relative to the annealing times, such that the effect of the heating and cooling periods on structural evolution can be ignored. Vacuum annealed and not annealed samples were imaged for both height and phase using an NT-MDT SolverNEXT system in tapping mode under atmospheric conditions at scan sizes of 5 μ m x 5 μ m or smaller in order to reasonably discern phase separated domains using a silicon cantilever (40 Nm⁻¹ force constant, 300 kHz resonance frequency, tip radius < 10 nm). Film thickness was measured by scratching the film off and measuring the height change between the substrate and film surface.

6.1.2.5 Transmission Electron Microscopy (TEM)

Multilayer films were made by spin-coating concentrated solutions ($\approx 35 \text{ mg/mL}$) of particle brushes onto poly(acrylic acid) (PAA) films (PAA was obtained as a 25 wt% solution in water from Sigma Aldrich). Particle brush films were lifted off from the substrate by water immersion and subsequently transferred onto copper grids for analysis. The thickness of the films was approximately 110–140 nm as measured by a line scratch test with AFM.

6.1.3 Results and Discussion

6.1.3.1 Results

The binary blend systems in our study consist of silica particles (average radius $R_0 = 7.7 \pm 2$ nm and $R_0 = 60.3 \pm 4$ nm) tethered with poly(methyl methacrylate) (PMMA), polystyrene (PS) or poly(styrene-r-acrylonitrile) (PSAN) ligands. The tethered polymers are amorphous and exhibit high glass transition temperatures (*i.e.* $T_{g,PS} \approx 110 \text{ °C}$, $T_{g,PMMA} \approx 105 \text{ °C}$, and $T_{g,PSAN} \approx 118 \text{ °C}$) that enable the rapid vitrification of blend films for subsequent structural analysis. PS/PMMA ligands were chosen because the corresponding linear polymers present a widely studied prototype system for UCST polymer blends.²⁵ The Flory-Huggins interaction parameter for PS/PMMA is $\chi_{S/MMA} = 0.028 + 3.9/T$, where T is the absolute temperature.²⁶ Due to the strong repulsive interaction between repeat units and the low ceiling temperature of PMMA ($T_{ceil} \approx 220$ °C), miscibility in linear PS/PMMA blends (at T > UCST) can only be observed for low molecular weight systems.²⁵ As will be shown below, this precludes the possibility to accomplish reversible phase separation and dissolution in SiO₂-PS/SiO₂-PMMA particle brush blends. In contrast, PMMA/PSAN constitutes a miscible polymer blend with LCST behavior that shows reversible transition between miscible and phase separated states provided that the molar ratio v = n(AN):n(S)is within the miscibility window $0.09 \le v \le 0.38$.²⁷ The interaction parameter of the PSAN/PMMA system depends on both the constitution of PSAN as well as the composition of the blend. In the present study, the molar composition of the random co-polymer is S:AN = 3:1 – the corresponding interaction parameter is $\chi_{MMA/SAN} \approx -0.15$ (at $T \approx 25$ °C). The LCST of linear PMMA/PSAN blends is approximately 160°C for a polymer molecular weight $M_{\rm w} \approx 90,000$ g/mol.^{22,28}

Particle brush systems were synthesized by surface-initiated atom transfer radical polymerization (SI-ATRP) following to previously published procedures.^{23,24,29} To avoid crosslinking of polymer
tethers during prolonged thermal annealing, samples were debrominated after synthesis (see 'Materials and Methods' section). Silica particles were chosen as model systems, primarily because the strong covalent coupling of polymer tethers facilitates stable ligand bonds up to $T \approx 250 \text{ °C}$ (as evidenced by thermogravimetric analysis, not shown here). To enable the analysis of structure evolution on practical timescales the average particle size was chosen to be $R_0 = 7.7 \pm 2$ nm; however, for select systems a particle size of $R_0 = 60.3 \pm 4$ nm was tested to evaluate the role of particle size on ligand-induced phase separation. In total, ten types of particle brush systems were synthesized to elucidate the effect of composition and degree of polymerization of ligands on the phase separation of particle brush blends. The grafting density was approximately $\sigma_S \approx 0.5$ nm⁻² for all particle brush systems which is consistent with dense grafting. The molecular characteristics of all particle brush systems along with the respective sample IDs are summarized in Table 6-1.

Sample ID	Ν	$M_{\sf n, GPC}$	$M_{ m w}/M_{ m n}$	σ _s (nm ⁻²)	SiO₂ wt%
8SiO ₂ -S62	62	6500	1.22	0.76	56
8SiO ₂ -S205	205	21400	1.36	0.49	22
8SiO ₂ -S360	360	37900	1.14	0.64	14
60SiO2-S1300	1300	135200	1.29	0.59	25
8SiO2-MMA68	68	6800	1.30	0.41	58
8SiO2-MMA194	194	19400	1.17	0.65	25
8SiO ₂ -MMA257	257	25700	1.32	0.49	21
8SiO ₂ -MMA350	350	35000	1.12	0.56	13
60SiO2-MMA1470	1470	147000	1.18	0.93	16
8SiO ₂ -SAN262	262	22300	1.15	0.64	19

Table 6-1 Summary of molecular characteristics of particle brush systems.

Sample IDs reflect sample characteristics where the first number indicates the approximate particle radius in nanometer; 'S' refers to styrene, 'MMA' to methyl methacrylate, and 'SAN' to styrener-acrylonitrile with (S:AN) = 3:1 graft composition. N is the degree of polymerization of surface grafted chains, $M_{n, GPC}$ is the number average molecular weight as determined by GPC, M_w/M_n is the molecular weight dispersity, and σ_s is the surface grafting density.

Particle brush blend films with thickness of 110-140 nm (corresponding approximately to 5–8 particle layers) were prepared by spin casting from THF solution onto $\langle 100 \rangle$ silicon substrates with native oxide layer and subsequently vacuum annealed for up to seven days. Films were smooth

and contiguous; the absence of crosslinking was confirmed by film dissolution tests. The surface morphology was investigated using atomic force microscopy (AFM) driven in tapping mode. For each sample, several scans over distinct sample areas of 25 μ m² were conducted to ensure consistency. Because established processes to etch PMMA or PS domains (for example, by exposing samples to UV/ozone and subsequent immersion in acetic acid for PMMA or, by immersion in cyclohexane for PS) were not successful, transmission electron microscopy (TEM) was performed on select samples to identify the composition of phases. For electron imaging analysis, (100) silicon substrates were pre-coated with a thin (≈ 50 nm) film of poly(acrylic acid) prior to film deposition. Films were transferred to TEM grids after thermal annealing by immersion into water (we note that films of the low molecular 8SiO₂-MMA68/8SiO₂-S62 blend system could not be processed in this way due to the brittle nature of the films). The characteristic domain sizes of phase separated particle brush films were determined from AFM or TEM images using the line intersection method. FFT analysis (a frequently used method to determine correlation lengths) could not be applied in the present case because of the interference of the particle cores with the required image thresholding.

We first discuss the results on the $8SiO_2$ -PS/ $8SiO_2$ -PMMA particle brush systems with UCST phase behavior. Figure 6-4 depicts representative AFM phase images of symmetric molecular weight binary blends of $8SiO_2$ -MMA194/ $8SiO_2$ -S205 at varying compositions: MMA:S = 25:75 (Fig. 6-4 a & 6-4 b), 50:50 (Fig. 6-4 c & 6-4 d), and 75:25 (Fig. 6-4 e & 6-4 f) after *t* = 48h of thermal annealing at *T* = 200 °C (Fig. 6-4 a, 6-4 c, 6-4 e), 160 °C (Fig. 6-4 d), and 140 °C (Fig. 6-4 b) and 6-4 f). The micrographs reveal a transition from discrete island-type morphology, indicative of phase separation by nucleation and growth (NG) for asymmetric blend compositions to bicontinuous network-type structures indicative of phase separation initiated by spinodal

decomposition (SD) for symmetric blend compositions. The observed structural transitions show similarity to previous reports on phase separated structures of linear PS/PMMA polymer blend systems – this is illustrated in Figure 6-4 g that compiles the observed microstructures within a UCST phase diagram that was calculated for a PS/PMMA ($N_{PS} = 205$ and $N_{PS} = 194$) reference system using Flory-Huggins theory.²⁵ It should be noted that the depiction of a bulk-type UCST phase diagram (Fig. 6-4 g) serves to only illustrate the conceptual similarity between the observed morphologies in the 8SiO₂-MMA194/8SiO₂-S205 systems and the expected behavior for binary linear polymer blends. The influence of geometric confinement, polymer tethering as well as substrate interactions on structure evolution during phase separation are not considered in Figure 6-4 g.^{30,31} Nevertheless, the microstructures depicted in Figures 6-4 a – 6-4 f reveal remarkable agreement with the expected structure evolution in the unstable (SD) and metastable (NG) compositional range.



Figure 6-4 Phase separation in 8SiO₂-MMA194/8SiO₂-S205. AFM phase images of film morphologies at varying composition and annealing temperature after t = 48h of thermal annealing. Dark phase corresponds to PMMA. (A) PMMA:PS = 25:75; $T = 200 \,^{\circ}C$. (B) PMMA:PS = 25:75; $T = 140 \,^{\circ}C$. (C) PMMA:PS = 50:50; $T = 200 \,^{\circ}C$. (D) PMMA:PS = 50:50; $T = 160 \,^{\circ}C$. (E) PMMA:PS = 75:25; $T = 200 \,^{\circ}C$. (F) PMMA:PS = 75:25; $T = 140 \,^{\circ}C$. (G) UCST phase diagram for reference PS/PMMA homopolymer blend with $N_{PS} = 205$ and $N_{PMMA} = 194$ calculated using Flory-Huggins theory (see text for more details). Solid line indicates bimodal, the dotted line the spinodal. The region enclosed by the spinodal marks the 'unstable regime' where separation by spinodal decomposition is expected. Region highlighted in gray is not accessible to experiments due to thermal degradation of PMMA.

To identify phase compositions, electron imaging of select material systems was performed. Figure 6-5 depicts AFM and TEM images of $8SiO_2$ -MMA194/8SiO_2-S205 (50:50) at t = 0 and 24 h of thermal annealing at T = 140 °C. In TEM images PS appears as dark domain due to ruthenium tetroxide (RuO₄) stain. The figure reveals that as-spun films are approximately homogeneous (Fig. 6-5 a & 6-5 c) while a bicontinuous network structure is observed after thermal annealing for 24 h (Fig. 6-5 b & 6-5 d). It is noted that electron images of as-spun films (such as Fig. 6-5 a) reveal a shallow contrast variation that bears similarity to phase separated morphologies – an indication that phase separation commences already during the film fabrication process.

Analysis of the areal fraction of the respective phases in AFM and TEM images (for asymmetric blend compositions, not shown here) reveals that PMMA appears as darker domain in scanning probe images. Note that the uniform distribution of particle cores in electron images (Fig. 6-5 a & 6-5 b) confirms the contiguity as well as the approximately constant thickness of films since undulations of film thickness across the imaged area would result in fluctuations of the particle density in projection electron images.



Figure 6-5 Structure characterization of films before and after thermal annealing. Images show structure evolution in a symmetric blend of $8SiO_2$ -MMA194/8SiO_2-S205 (50:50). (A) Bright field TEM image after thermal annealing at T = 140 °C for t = 0. (B) Bright field TEM image after thermal annealing at T = 140 °C for t = 24 h. (C) AFM phase image after thermal annealing at T = 140 °C for t = 24 h. (C) AFM phase image after thermal annealing at T = 140 °C for t = 24 h. Insets in (B) & (D) show magnified view of phase separated structure. PS domain appears dark in (A) and (B) (RuO₄ stain); PS domain appears bright in (C) and (D). Electron micrographs further reveal uniform distribution of particle centers (small dark dots) thus confirming uniform film structure before and after thermal annealing. Scale bars are 500 nm in main figures and 250 nm in insets.

The uniform film thickness is confirmed by concurrent AFM height and phase image analysis shown in Figure 6-6 for the case of $8SiO_2$ -MMA194/8SiO_2-S205 (50:50) after 24 h of thermal annealing at T = 140 °C. The figure illustrates long wavelength height fluctuations with amplitude of about 15 nm (approximately equal to one particle brush diameter that is estimated to be ≈ 21 nm based on TEM analysis) across areas of the order of 1 μ m². This might be interpreted as terrace formation of particle films, possibly due to surface tension variations of the phases. No systematic growth of long wavelength fluctuations was observed during continued annealing. This may be due to pinning of phase separation that typically occurs in thin films from finite size effects. Within

terraces, height undulations of about 3 nm were observed on a length scale that corresponds to the size of individual domains; maxima correspond to PS, minima to PMMA domains (inferred by correlation of height and phase images). We hypothesize that – similar to PS/PMMA linear polymer blends – PS particle brushes 'stretch' toward the air/film interface due to the lower surface energy of the PS (*i.e.* $\gamma_{PS} = 40.7 \text{ mJ/m}^2$ as compared to $\gamma_{PMMA} = 41.1 \text{ mJ/m}^2$, where γ_i denotes the bulk surface tension of component *i*).^{25,32}



Figure 6-6 Structure and topology of phase separated films. (A) AFM height image of 8SiO₂-MMA194/8SiO₂-S205 (50:50) after 24 h of thermal annealing at T = 140 °C. (B) AFM phase image of same film. Z-scale in (A) is nm, Z-scale in (B) is degree. Black lines across scans in (A) and (B) indicate position used for line scans in (C–E). (C) shows line scan of height image depicting long wavelength corrugations with amplitude ≈ 15 nm that occur on the scale of 1–2 µm. Red box in (C) and (D) depicts short wavelength corrugations with amplitude ≈ 3 nm that coincide with domain positions. (E) and (F) show enlarged scans. Maxima in height images correspond to PS, minima to PMMA constituent; for phase images the PS domain corresponds to minima positions (indicated by green arrows).

To further interrogate the mechanism of phase separation, the kinetics of domain growth was analyzed. Figure 6-7 depicts the domain growth kinetics for the 8SiO₂-MMA194/8SiO₂-S205 (50:50) blend system annealed at T = 140 °C. Analysis of the data in terms of a scaling relation $d \sim t^{x}$ reveals that the bicontinuous morphology evolves with a scaling coefficient of $x \approx 0.22$ (see Fig. 6-7 a). The fraction of exposed surface coverage of 8SiO₂-MMA194 (determined from analysis of AFM phase images) is $f_a \approx 0.45$ and independent of the thermal annealing time. The observed depletion of PMMA-brushes from the air/film interface is consistent with previous reports on the morphology of PS/PMMA thin films on Si/SiO₂ substrates and is attributed to the preferential wetting of the silica by PMMA.²⁵ The reduction of f_a by approximately 5% suggests the formation of a 8SiO₂-MMA194 monolayer at the silica substrate/particle brush interface. The increase of domain size with annealing temperature (shown in inset of Fig. 6-7 a) is anticipated since the dynamical processes underlying the phase evolution process accelerate with increasing temperature.



Figure 6-7 Analysis of domain growth kinetics. (A) Characteristic distance *d* of 8SiO₂-MMA194/8SiO₂-S205 (50:50) blend system during thermal annealing at T = 140 °C as a function of annealing time, *t*, revealing the scaling relation $d \sim t^{0.22}$. The areal fraction of PMMA is $f_a = 0.45$ and independent of annealing time (error bars are within the symbol size). Inset of main figure shows the dependence of d on annealing temperature for a constant annealing time of t = 24 h. (B) AFM phase image of film at t = 12 h. (C) AFM phase image of film at t = 166 h. Scale bars are 1 μ m.

To illustrate the role of the size and degree of polymerization *N* of polymer ligands on the phase separation characteristics of binary particle brush blends, the microstructure formation in symmetric blends of $8SiO_2$ -MMA68/8SiO_2-S62, $8SiO_2$ -MMA194/8SiO_2-S205, and $8SiO_2$ -MMA350/8SiO_2-S360 after one week of thermal annealing at *T* = 140 °C are compared in Figure

6-8 (insets in Fig. 6-8 show the structures of the corresponding films prior to thermal annealing). The figure reveals that phase separation in particle brush blends requires a threshold degree of polymerization as can be inferred from the absence of any discernible phase separation in the 8SiO₂-MMA68/8SiO₂-S62 system. Interestingly, the characteristic domain size of the 8SiO₂-MMA194/8SiO₂-S205 system is larger than the domain size for the longer chain 8SiO₂-MMA350/8SiO₂-S360 system (218 nm *vs.* 167 nm). This is surprising since the thermodynamic force driving the phase separation process is expected to increase with degree of polymerization of tethered chains. Both observations point to a pronounced influence of the degree of polymerization of tethered chains on the balance between thermodynamic and dynamical characteristics of particle brush blends (see section 'Discussion').



Figure 6-8 Structure formation depends on degree of polymerization of tethered chains. (A) AFM phase images of symmetric blends $8SiO_2$ -MMA68/8SiO_2-S62, (B) $8SiO_2$ -MMA194/8SiO_2-S205, and (C) $8SiO_2$ -MMA350/8SiO_2-S360 after one week of thermal annealing at T = 140 °C. Insets show AFM phase images of respective samples before thermal annealing. All scale bars are 1 μ m. Short chain brush system (A) is found to remain uniform after thermal annealing while phase separation is observed in long chain brush particle systems (B & C). Non-uniformity of preannealed state is observed for long-chain ligands (inset of C) indicating that phase separation brush particles with increasing degree of polymerization of tethered chains: hard-sphere type in case of short polymer chains (concentrated particle brush regime) and polymer-like for long chain systems (semi-dilute particle brush regime), see section 'Discussion'.

Note that N also affects the structure of films in the pre-annealed state. In particular, AFM phase

images of the long chain system 8SiO2-MMA350/8SiO2-S360 prior to annealing reveal a partially

phase separated structure that resembles the morphology of the annealed system (see inset in Fig. 6-8 c). An analogous behavior (albeit less pronounced) is observed in case of $8SiO_2$ -MMA194/8SiO_2-S205 (see inset in Fig. 6-8 b). Phase separation therefore commences already during the vitrification of the film – similar observations have been reported for linear polymer blends with UCST behavior for which it is generally difficult to generate fully homogenized initial states.²³ To test whether ligand-interactions can drive phase separation also in case of larger colloidal systems, the microstructure formation of a symmetric blend of 60SiO₂-MMA1470/60SiO₂-S1300 was evaluated after 24 h of thermal annealing at *T* = 140 °C. No phase separation was observed in the pristine blend system (not shown here); however, the addition of 15% of dimethylphthalate (DMP) resulted in the formation of bicontinuous type structures similar to small particle brush analogs as revealed in Figure 6-9. This demonstrates both the role of particle brush size and architecture on the kinetics of the separation as a method to control the microstructure of multicomponent colloidal assemblies.



Figure 6-9 Ligand-induced phase separation in large particle blend system. Bright field TEM images of monolayer films of $60SiO_2$ -MMA1470/ $60SiO_2$ -S1300 (50:50) blends in presence of 15% DMP revealing spinodal-decomposition type phase separation. (A) As-cast film. (B) After t = 24 h of thermal annealing at T = 140 °C. Dark phase corresponds to PS (RuO₄ stain). Insets show magnified image. Scale bars are 500 nm in main figure and 200 nm in insets.

In contrast to UCST systems, LCST blends are miscible at low temperatures and phase separate only when temperature is raised above the LCST. LCST polymer blends have attracted much interest as model systems in the study of polymer phase separation due to the better control of the separation process and the possibility to reversibly cycle systems between mixed and phase separated states by subsequent heating and cooling through the LCST. For mixed particle brush materials, the prospect of reversible phase separation is particularly interesting as it promises intriguing new opportunities to dynamically control the structure (and hence properties) of particle solids. To demonstrate LCST behavior and to test the feasibility of reversible mixing and phase separation of particle brush blends, the structure evolution in the binary system 8SiO₂-MMA257/8SiO₂-SAN262 was analyzed. To accelerate phase separation, a small amount (10 wt%) of DMP was added to the system. This system was chosen because of its similar molecular characteristics to the 8SiO₂-MMA194/8SiO₂-S205 UCST system, and the suitable line-up of thermal transitions (i.e. LCST ≈ 160 °C > $T_g \approx 75$ °C > 25 °C) that enables the vitrification of blend microstructures for structural characterization (note that the T_g is lowered from approximately 115 °C to 75 °C by DMP addition). Here, it is assumed that the LCST of the 8SiO₂-PMMA/8SiO₂-PSAN particle brush blends is \approx 160 °C, equal to the LCST of corresponding linear PMMA/PSAN blends. To evaluate structure evolution during heating/cooling through LCST, particle brush blend films with thickness of ≈ 150 nm were sequentially annealed at 130 °C (24 h), 170 °C (24 h), and 130 °C/110 °C (48 h). The phase-separated microstructures were probed using TEM after 24 h annealing steps. Figure 6-10 illustrates the thermal processing history as well as the structure evolution of the 8SiO2-MMA257/8SiO2-SAN262 blend system during sequential annealing cycles.



Figure 6-10 Reversible structure evolution in $8SiO_2$ -MMA257/8SiO_2-SAN262 (50:50) LCST system. 10% of DMP were added to accelerate kinetics. (A) Illustration of thermal processing steps: annealing at 130 °C for 24 h; 170 °C for 24 h; and 110 °C/130 °C for 48 h along with corresponding domain size *d* (see text for more detail). The star symbol corresponds to pre-annealed state, filled black circles represent annealing states of which microstructures are presented. The dotted blue line at $T \approx 351$ K (75 °C) indicates the T_g of the blend in the presence of DMP. TEM images depict film microstructures after subsequent annealing steps (RuO₄ stain of PSAN component). (B) 24 h at 130 °C. (C) 24 h annealing at 170 °C. (D) 24 h annealing at 110 °C. (E) 48 h at 110 °C. Scale bars are 200 nm. The micrographs reveal a transition from uniformly mixed structure (B) to bicontinuous phase separated structure (C) after annealing at T > LCST. Subsequent annealing at T < LCST results in progressive reduction of domain size (D & E).

Films in the pre-annealed state exhibited a weakly phase-separated structure similar to UCST blends (not shown here). This can be rationalized by considering Hildebrand solubility parameters $(\delta_{THF} = 18.6 \text{ MPa}^{1/2}, \delta_{PMMA} = 19.0 \text{ MPa}^{1/2}, \text{ and } \delta_{PSAN} = 19.6 \text{ MPa}^{1/2}, \delta_{DMP} = 21.9 \text{ MPa}^{1/2}).^{33}$ The weak affinity of the solvent (THF) toward PMMA alters the thermodynamics of mixing and possibly results in partial phase separation during casting of films.³³ Annealing of films for 24 h at T = 130 °C resulted in completely homogeneous microstructures (see Fig. 6-10 b). The dissolution of the partially phase-separated structure is expected since LCST > 130 °C. It confirms the miscibility of the blend and also that the addition of DMP does not significantly alter the expected LCST characteristics.³⁴ Subsequent annealing at T = 170 °C for 24 h resulted in the formation of a bicontinuous morphology (Fig. 6-10 c) with a characteristic correlation length of d= 325 nm (determined by line intersection method from electron micrographs). The latter is consistent with a spinodal-type phase separation for a blend with near critical composition at T >LCST.²⁴ Interestingly, subsequent annealing of phase-separated films at T = 110 °C and 130 °C resulted in the progressive decrease of d along with the reduction of the contrast between adjacent domains (see Fig. 6-10 d & 6-10 e), indicating the gradual 'dissolution' of domains. The reduction of domain size was more pronounced when annealed at 110 °C (see Fig. 6-10 a) – this is interpreted as a consequence of the more negative interaction or ' χ ' parameter at lower T that raised the thermodynamic driving force for mixing. In summary, the results displayed in Figure 6-10 confirm LCST behavior of the 8SiO₂-MMA257/8SiO₂-SAN262 system and correlate well with the expected behavior of linear PMMA/PSAN blends with LCST ≈ 160 °C.³¹

6.1.3.2 Discussion

Our results demonstrate that the interaction between polymeric ligands with distinct composition can drive UCST- or LCST-type phase separation processes in mixed particle brush systems in a similar way to the corresponding linear polymer blends. However, while the general trends are similar, the data also brings out several pertinent features that point to a more complex parameter space governing phase separation in particle brush blends that will be discussed in the following. These features include: first, the existence of a threshold degree of polymerization to enable phase separation that exceeds the corresponding value for linear polymer blends. The latter is demonstrated by the 8SiO₂-MMA68/8SiO₂-S62 system that remains miscible (see Fig. 6-8 a) despite of its degree of segregation $\chi \langle N \rangle \approx 2.43$ that exceeds the critical value '2' for phase separation in the corresponding linear polymer blend ($\chi \langle N \rangle$ is calculated assuming $\chi = 0.037$ at *T* = 140 °C and an average degree of polymerization $\langle N \rangle = 65$ for polymeric tethers). Second, a reduced scaling coefficient of domain growth as well as a significantly smaller domain size, as compared to those of linear polymer blends for analogous annealing conditions.

To gain insight into the role of the degree of polymerization *N* of tethered chains on the phase separation process in particle brush blends, we first consider the effect of chain conformation on the interaction between polymer-tethered particles. It has been shown that the geometric constraints on chains that are tethered to a curved interface give rise to two chain conformational regimes: In the vicinity of the particle core (*i.e.* in the limit of small *N*), the concentrated brush regime (CPB) is observed in which chains assume stretched chain conformations (experimental studies on particle brush melts suggest $h_{CPB} \sim N_{CPB}^{0.8}$ where h_{CPB} denotes the brush height). In contrast, for sufficiently large *N* the semi-dilute brush regime (SDPB) is observed that is characterized by relaxed chain conformations ($h_{SDPB} \sim N_{SDPB}^{0.5}$).^{18,33,35} An approximate model to predict the transition between CPB and SDPB regimes was introduced by Fukuda and coworkers who extended the Daoud-Cotton model for star polymer systems to derive a 'critical distance' that marks the CPB/SDPB transition.^{35,36} Applied to the 'small' SiO₂ particles ($R_0 = 7.7$ nm) used in

the present study, the model suggests the CPB/SDPB transition to occur at a critical degree of polymerization $N_{\text{crit.}} \approx 250^{18}$ The analysis thus reveals that both $8SiO_2$ -MMA68 and $8SiO_2$ -S62 particle systems are in the 'stretched' chain regime while other particle systems are in the semidilute brush regime - this conclusion is also consistent with the analysis of the particle brush height using electron micrographs of particle monolayers (not shown here). The apparent miscibility of the 8SiO₂-MMA68/8SiO₂-S62 blend system (see Fig. 6-8 a) can then be rationalized as the consequence of two major contributing factors that reduce the thermodynamic driving force of phase separation. First, the dense packing of chains in CPB brush particles hinders brush interdigitation and hence reduces the number of segmental contacts between chemically distinct chains. This is supported by light scattering experiments on solutions of brush particles that revealed CPB particle brushes to interact via hard sphere-type potentials.¹⁵ It is also consistent with the results of prior studies on the structure and interactions of brush particles in polymer melts. These studies have shown that 'dense ligand layers' are rather impenetrable to melt polymer chains of similar molecular size.^{37,38} The reduced number of contacts between chemically distinct chains decreases the specific energy gain upon phase separation and hence the (chemical) potential gradient that drives the separation process. However, whereas in in the case of particle brush/polymer blends the presence of a mobile phase (i.e. the melt) provides a kinetic path for phase separation even in weakly phase separating systems, we hypothesize that the absence of a mobile phase in conjunction with the reduced driving force 'freezes' CPB blends in the mixed state.³⁹ In this context it is interesting to note that contact angle measurements revealed a significant decrease of the surface energy of particle brush films as compared to linear homopolymer analogs (*i.e.*, $\gamma_{8SiO2-MMA194} \approx 26 \text{ mJ/m}^2$, $\gamma_{8SiO2-S205} \approx 33 \text{ mJ/m}^2$, $\gamma_{PMMA} \approx 41 \text{ mJ/m}^2$, $\gamma_{PS} \approx 40 \text{ mJ/m}^2$). While the origin of this decrease of surface tension in the case of particle brush

films remains unresolved (we hypothesize it to be related to a more pronounced contribution of end groups in conjunction with fewer segmental contacts due to the repulsion between brushes), the similarity of surface tension between brush particles with distinct composition is an indicator for the reduced driving force of phase separation in CPB blend systems.

A further contribution to the reduction of the driving force of phase separation stems from the smaller number density of segment contacts due to the presence of particle cores. For example, assuming complete brush interdigitation, the cumulative pairwise interactions between ligands in brush particles will be reduced approximately by a factor of $(1-\phi)$ as compared to the analogous linear polymer blend (with ϕ denoting the inorganic volume fraction). Since ϕ is large for CPB particles ($\phi > 0.3$), this 'dilution effect' is more pronounced for CPB particle systems whereas for SDPB systems the inorganic content is comparatively small (see Table 1).

A second interesting observation pertains to the kinetics of domain growth in the 8SiO₂-MMA194/8SiO₂-S205 (50:50) blend system (shown in Fig. 6-7) that scales with time as $d \sim t^{0.22}$ which is significantly less than the expected value of 1/3 for diffusion controlled domain coarsening.⁴⁰ Scaling coefficients less than 1/3 were reported for thin film polymer blends in the literature and have been rationalized as a consequence of geometric constraints that limit domain coarsening when the domain size becomes comparable to the thickness of films.³¹ Here we want to point to an additional distinguishing feature between particle brush and linear polymer blends that could contribute to a reduction of the scaling coefficient. In principle, phase separation by SD is initiated by the spontaneous growth of composition fluctuations as the system is being quenched into the unstable region of the phase diagram. Three stages of domain growth are distinguished. During the first stage of phase separation, the amplitude of fluctuations increases yet their wavelength remains constant. This is followed by a diffusion controlled intermediate stage during

which both composition and domain size change $(d \sim t^{1/3})$ and a final hydrodynamic-driven stage where only domain size increases $(d \sim t)$.⁴¹ The characteristic spinodal wavelength is typically of the order of the size of the constituent polymer chains and can be influenced by the quench depth and composition of the system.⁴² Given the limited (time) resolution of our experiments, the first stage of phase separation could not be observed in our study. However, literature reports on the phase separation in star polymer systems have shown that the spinodal wavelength of star and linear polymers is approximately equal.⁴³ We therefore hypothesize that the spinodal wavelength in brush particle blends is similar to star and linear polymer blend analogs. Note that this implies the spinodal wavelength in particle brush materials to be less than the size of individual brush particles - a constraint that could alter domain growth. For example, de Gennes analyzed the kinetics of SD under the constraint that the spinodal wavelength is less than the distance between entanglement points and concluded for such systems normal diffusional growth to be preceded by an 'anomalous growth regime' with a scaling coefficient of 1/5 (i.e. close to the experimental value of 0.22).⁴⁴ To further elucidate the role of brush architecture on the structure evolution process, it would be an interesting subject for future research.

Finally, we want to comment on the domain size in phase-separated particle brush blends that is substantially smaller (by about one order of magnitude) than values reported for linear polymer blends.²⁵ To illustrate this point we note that a reference system comprised of a symmetric blend of PS/PMMA homopolymers with degree of polymerization $N_{PMMA} = 204$ and $N_{PS} = 216$ (comparable to PS/PMMA tethers in the 8SiO₂-MMA194/8SiO₂-S205 system shown in Figs. 6-5 and 6-4) did show final stage separation after annealing for 24 h at T = 140 °C (see Fig. S6-1). We rationalize the small domain size in particle brush blends as a consequence of the combination of the reduced thermodynamic driving force (see discussion above) as well as the reduced diffusion

kinetics. The latter can be appreciated by comparison with the topologically related system of star polymers, for which dynamical properties have been extensively studied. For example, Klein and coworkers proposed the self-diffusion coefficient in star polymer melts to depend on the degree of polymerization of branch chains (N_b) and the number of chains (f) as $D(N_b, f) \sim \exp[-CN_b(f-2)]$; where C is a constant.⁴⁵ Given that the number of graft chains for 15 nm particles is ≈ 350 (assuming a grafting density of $\sigma = 0.5$ nm⁻²) the particle brush mobility is expected to be significantly reduced as compared to linear polymer systems. For practical purposes this reduction in diffusional kinetics might be balanced by the addition of small molecular additives that raise molecular mobility as demonstrated for the case of 60SiO₂-MMA1470/60SiO₂-S1300 (see Fig. 6-9). Hence, the reduced separation kinetics does not preclude the concept of 'ligand-induced phase separation' to be applied to larger particle systems. Finally, we note that the exponential decrease of D with $N_{\rm b}$ also suggests the existence of an 'optimum' N for maximizing domain growth that is determined by the balance of thermodynamic driving force and diffusivity. Indeed, the increased domain size in case of the intermediate 8SiO2-MMA194/8SiO2-S205 system confirms this proposition, although the currently available data does not allow for a more quantitative analysis.

6.1.4 Conclusion

Ligand interactions in blends of polymer-tethered nanoparticles can impart UCST- and LCST-type phase behavior on particle mixtures similar to the phase behavior of the respective linear polymer blends. Cooling (or heating) of particle brush blends with appropriate architecture below (or above) the UCST (or LCST) thus results in the formation of mono-particle domain structures with characteristic size and shape that can be tuned by variation of the composition and thermal annealing conditions. The ability to autonomously organize multicomponent particle mixtures into mono-type microdomain structures of controlled size and shape by harnessing phase separation

processes could enable transformative advances in the high-throughput fabrication of microstructured particle solid films. The latter play an important role in a wide range of particleenabled material technologies including, for example, photovoltaics or nano-enabled solid state lighting technologies. Furthermore, the reversible formation and dissolution of microstructures in multicomponent particle solids by thermal cycling of LCST particle brush blends through the critical temperature could enable important advances in the development of smart and adaptive coating technologies. To facilitate these advances, better understanding of the governing parameters that control the structure evolution in particle brush blends should be accomplished. In particular, while the structure evolution is consistent with phase separation by nucleation and growth or spinodal decomposition, the kinetics of structure evolution shows distinctive differences (such as a reduced scaling coefficient) as compared to linear blends. Given the complex parameter space in polymer-tethered particles, this might also provide opportunities to gain novel physical insights into the role of geometric constraints on phase separation in polymer systems.

6.1.5 References

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6.2. Ligand-Induced Structure Formation of Block Copolymer Particle Brushes

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6.2.1 Background

The dispersion of nanoparticles in polymers, metals, or ceramic matrixes can dramatically improve the properties of the composite material.¹⁻³ Inorganic nanoparticles can be added to polymer matrices as nanofillers to tune a material's the mechanical properties.⁴⁻⁵ While uniform nanoparticle spatial distribution is usually the focus of hybrid particle synthesis and dispersion procedures, many situations take advantage of spatially non-uniform, anisotropic nanoparticle organization. Controlling the dispersion of unmodified nanoparticles into polymer matrices is a significant challenge facing achievement of the proclaimed property improvements promised by polymer nanocomposites,⁶ as inorganic particles are typically immiscible with an organic phase.⁷⁻ ⁸ Polymer nanocomposites formed by one-component polymer grafted nanoparticles, which are also referred to as matrix-free nanocomposites, overcome this "demixing" issue in traditional nanoparticles filled matrix systems.⁹⁻¹¹

An interesting property of polymer grafted nanoparticles is their tendency to self-assemble into various well-defined structures in solution, or in a polymer matrix, including assembly into sheets and strings.¹²⁻¹³ The dispersion of nanoparticles in polymer nanocomposites mainly depends on polymer graft density and the ratio of the molecular weights of the grafted polymer to the matrix polymer. Generally, co-assembly of performed nanoparticles and block copolymer (BCP) has been considered to be an efficient way of forming hybrid aggregates with controlled morphology and nanoparticles distribution.¹⁴ This property arises from mesoscopic phase separation between

inorganic and polymer parts of the nanoparticles and resembles the self-assembly characteristics of a BCP.¹⁵ As an example, nanoparticles can alter the orientation of BCP microdomains and tailor the morphology of the nanocomposite.¹⁶⁻¹⁷ Examples of a close packed BCP brush particle (driven by excluded volume interactions in brush layer) and a bicontinuous structure (driven by polymer phase behavior) are shown in Figure 6-11. Theory predicts the formation of various structures by the self-assembly of particles with few attached polymer chains,¹⁸ depending on the particle size, molecular weight of attached polymers and chain grafting density. These structures, which include lamellae, cylinders, and lattices, exhibit unique properties.¹⁹⁻²¹ Analogous to the mesostructure formation in phase separated diblock/triblock copolymers, the morphology of these hybrid nanoparticles could be highly sensitive to even a small fraction of unattached free polymer chains, therefore, a precise knowledge of the structure and composition of materials based on hybrid particles is of paramount importance for the successful design of bottom-up composites.²²



Figure 6-11 Examples of assembly structure in BCP brush particles with corresponding illustrations. (left: close packed, right: lamellae)

One key advantage of atom transfer radical polymerization (ATRP) over conventional radical polymerization is feasibility of BCP synthesis.²³⁻²⁴ The ability to control both the length scale and the spatial organization of BCP brush morphologies on nanoparticles makes these materials particularly attractive as scaffolds for engineering of nanostructures.²⁵⁻²⁷ The grafting density of the polymer brushes and fraction of free self-initiated polymer can be changed by altering the targeted degree of polymerization (DP) of SiO₂-*g*-PS particle brush, hence changing the [SiO₂-Br]₀.²² The interdependence of grafting density, initiation efficiency and initiator concentration can be used to prepare particle brushes with PMMA-*b*-PS BCPs through simple chain extension reactions from pre-synthesized SiO₂-*g*-PMMA particle brushes. When nanoparticles are sparsely grafted with hydrophobic polymer chains, some parts of the particle surface are covered by the grafted chains while the other unmodified hydrophilic parts are exposed, resulting in formation of anisotropic self-assembled morphologies, *e.g.* strings, sheets.²⁸⁻³⁰

6.2.2 Experimental Methods

6.2.2.1 Materials Synthesis

Materials

Monomers: styrene (S, 99%, Aldrich), methyl methacrylate (MMA, 99%, Aldrich) were purified by passing through a column filled with basic alumina to remove the inhibitor. Tris(2dimethylaminoethyl)amine (Me₆TREN, 99%, Alfa), 4,4'-dinonyl-2,2'-bipyridyne (dNbpy, 97%, Aldrich), anisole (99%, Aldrich), tetrahydrofuran (THF, 99%, VWR), methanol (99%, VWR), hexane (99%, VWR), acetone (99%, VWR), *N*,*N*-dimethylformamide (DMF, 99%, VWR), copper(II) bromide (CuBr₂, 99%, Aldrich), copper(II) chloride (CuCl₂, 99%, Aldrich), copper(I) chloride (CuCl, 97%, Sigma-Aldrich), tin(II) 2-ethylhexanoate (Sn(EH)₂, 95%, Aldrich), hexane (Fluka), 48% hydrofluoric acid aqueous solution (HF, >99.99%, Aldrich), ammonium hydroxide aqueous solution (NH₄OH, 28.0-30.0%, Fisher), anhydrous magnesium sulfate (MgSO₄, Fisher) were used as received without further purification. Copper (I) bromide (CuBr, 98%, Acros), was washed with glacial acetic acid to remove any soluble oxidized species, filtered, washed twice with anhydrous ethyl ether, dried and kept under vacuum. Silica nanoparticles, 30 wt % solution in methyl isobutyl ketone (MIBK-ST), effective diameter $d \approx 15.8$ nm, were kindly donated by Nissan Chemical Corp. and used as received. The tethered ATRP initiator 1-(chlorodimethylsilyl)propyl-2-bromoisobutyrate and surface modified silica (SiO₂-Br) were prepared using previous reported procedures.¹⁻² The surface initiator densities are moderated with a "dummy" initiator chlorotrimethylsilane (99%, Aldrich).

Procedures

Procedures for synthesis of bimodal SiO₂-g-PMMA-b-PS particle brushes via ARGET ATRP. SiO₂-g-PMMA particle brushes synthesis.

Initiator (SiO₂-Br), monomer (MMA), solvents (anisole, DMF), CuCl₂, and dNbpy (molar ratio shown as subscript of Table 6-1) were mixed thoroughly in a sealed Schlenk flask. The mixture was degassed by bubbling with nitrogen. Then, the mixture was flash-frozen by immersion in liquid nitrogen under continuous nitrogen purge and CuCl was immediately added. Another 10 min of nitrogen purge removed residual air from the flask. The reaction mixture was thawed by immersing the flask in water then subsequently placed in an oil bath set at the desired temperature. The conversion and molecular weight (MW) of polymer were monitored by gravimetric analysis and SEC, respectively.

Chain extension with styrene by ARGET ATRP.

Initiator (SiO₂-*g*-PMMA-Br particle brushes), monomer (S), solvents (anisole, DMF), CuBr₂, and Me₆TREN were mixed thoroughly in a sealed Schlenk flask. A stock solution of Sn(EH)₂ in anisole was prepared. Both mixtures were degassed by nitrogen purging, then the Sn(EH)₂ solution was injected into the Schlenk flask to activate the catalyst complex and the flask was immediately put into an oil bath. The MW of the polymer was measured by SEC.

6.2.2.2 Transmission electron microscopy (TEM)

Transmission electron microscopy (TEM) was carried out using a JEOL 2000 EX electron microscope operated at 200 kV. The spatial distribution, radius and inter-particle distances of the SiO₂ nanoparticles were determined from statistical analysis of the TEM micrographs using ImageJ software.

6.2.2.3 Thermogravimetric Analysis (TGA)

Thermogravimetric analysis (TGA) with TA Instruments 2950 was used to measure the fraction of SiO₂ in the hybrids. The data were analyzed with TA Universal Analysis. The heating procedure involved four steps: (1) jump to 120 °C; (2) hold at 120 °C for 10 min; (3) ramp up at a rate of 20 °C/min to 800 °C; (4) hold for 2 min. The TGA plots were normalized to the total weight after holding at 120 °C.

6.2.2.4 Image Analysis

A description of image analysis done in this study was provided in detail in Appendix at the end of this document.

6.2.3 Results and Discussion

A system based on bimodal polymer grafted nanoparticles was examined. The synthesis of SiO_2 g-PMMA-*b*-PS particle brushes was accomplished using surface initiated atom transfer radical polymerization (SI-ATRP).³¹⁻³⁴ First, PMMA blocks were "grafted from" the surface of the SiO₂ particles by normal SI-ATRP. The grafting density was tuned by altering the ratio between tetherable ATRP initiator ((chlorodimethylsilyl)propyl-2-bromoisobutyrate) and "dummy" initiator (chlorotrimethylsilane).²¹ Three SiO₂-Br nanoparticles were prepared for initial grafting of PMMA chains with controlled grafting densities (Table 6-2, Figure 6-12). The second PS blocks were formed using a low-ppm Cu catalyst ATRP procedure comprising of catalyst complexes with highly activating ligands.



Figure 6-12 Synthesis of SiO₂-*g*-PMMA particle brushes with different grafting densities. Block copolymers can self-assemble into various morphologies after annealing.^{15,35-37} In contrast to linear block copolymers, self-assembly of block copolymer particle brushes are not only affected by polymer chain composition, but are also strongly associated to the grafting density of polymer ligands on the surface of the nanoparticles. Three SiO₂-*g*-PMMA-*b*-PS particle brush systems were investigated to study the effect of chain composition and grafting density on the self-assembly of block copolymer particle brushes. First, three SiO₂-*g*-PMMA particle brushes (PMMA-H1/M1/L1) with different grafting densities (high: 0.75 nm⁻², medium: 0.15 nm⁻², low: 0.05 nm⁻²) but with a similar degree of polymerizations (DP ~ 450–550) were prepared, Table 6-2. Before chain extension, the morphologies of SiO₂-*g*-PMMA particle brushes were characterized

by TEM, Figure S6-13, which showed that the decreased distance between particle cores with decreasing grafting density. The outer PS blocks were prepared by ARGET ATRP chain extension with the same initial macro-initiator concentration ([SiO₂-g-PMMA-Br]₀), (50 ppm). Polymer ligands were characterized by SEC after etching the SiO₂ cores, the bimodal features and high dispersity values from the SEC traces (Figures S6-6–S6-8) indicated only a partial chain extension from the tethered PMMA blocks. After deconvolution of the SEC traces, the composition of polymer ligands (PMMA and PMMA-*b*-PS) are listed in Table S6-3, which shows that the fraction of PMMA-*b*-PS ligands prepared under these conditions was 30% to 45%.

Table 6-2 Result of syntheses of SiO₂-g-PMMA nanoparticles with different grafting density.

Entry ^a	<i>M</i> _n ^b	$M_{\rm w}/M_{\rm n}{}^{\rm b}$	<i>f</i> _{ino} (%) ^c	σ (nm ⁻²) ^d
PMMA-H1	44,500	1.16	8.9	0.763
M-b-S-1	97,100	2.46	5.3	0.609
PMMA-M1	56,300	1.12	26.2	0.165
M-b-S-2	113,000	1.93	15.8	0.156
PMMA-L1	47,700	1.13	57.7	0.051
M-b-S-3	152,400	4.41	36.7	0.038

^a Reaction condition: M-*b*-S-1~3: [S]₀/[SiO₂-*g*-PMMA-Br]₀/[CuBr₂]₀/[Me₆TREN]₀/[Sn(EH)₂]₀ = 20000:1:2:20:2; PMMA-H1/M1/L1: [MMA]₀/[SiO₂-Br]₀/[CuCl₂]₀/[dNbpy]₀/CuCl]₀ = 4000:1:0.4:8:3.6 with 45 vol% anisole, 5 vol% DMF at 60 °C. ^b Determined by SEC. ^c *f*_{ino} (inorganic content), determined by TGA. ^d σ (grafting density), calculated according to TGA data. Although the three block copolymer particle brushes (M-*b*-S-1~3) have comparable ligand compositions, *i.e.* similar PMMA blocks and block copolymer ligand fractions, their morphologies are dramatically different. Figure 6-13 shows the TEM images of M-*b*-S-1–3 particle brushes with the same magnification. The high grafting density particle brush (M-*b*-S-1) showed a relatively uniform structure in the monolayer film on Cu grids, Figures 6-13 a–b. On the other hand, the medium grafting density and low grafting density samples exhibited strongly anisotropic morphological features, as connecting strings (M-*b*-S-2, Figures 6-13 c–d) and continuous cluster networks (M-*b*-S-3, Figures 6-13 e–f), respectively. These unique assembly behaviors are attributed to the different grafting densities and resulting chain conformations of polymer ligands

on the silica nanoparticles surfaces. The apparent grafting densities (σ_2) of PMMA-*b*-PS block, which are calculated using the grafting density of SiO₂-*g*-PMMA particle brush (σ , Table 6-2) and the fraction of block copolymer ligands after chain extension are listed in Table S6-3. In the case of high grafting density particle brush, the grafting density of PMMA-*b*-PS ligands is 0.192 nm⁻², which is still in the medium and high grafting density region. With sufficient PS outer layers, this leads to a relatively uniform structure.

Meanwhile, the grafting density of block copolymer ligands in the intermediately grafted particle brush (M-b-S-2) is 0.07 nm^{-2} , which falls into the typical sparsely grafted particle brush region. The medium grafting density system displays a connected single SiO₂-g-PMMA particle brush domain covered with PS outer shell structure, which agrees with the ligands composition. The grafting density of PMMA-b-PS chains in the sparsely grafted particle brush sample is only 0.01 nm⁻², and the surface area of a 15 nm silica nanoparticle is around 700 nm², giving an average of 7 BCP chains per particle. According to an estimation based on a kinetic analysis in literature,³⁸ a fair proportion of particle brush in the system will be nearly bare SiO₂-g-PMMA (5 extended chains or less: 29.6%; 7 or less: 59.5%, see Figure S6-15), possibly explaining the "cluster" structure in the SiO₂-g-PMMA domain due to the strong particle-particle attraction. Although quantitative analysis of the TEM images (Figure 6-13 e-f) was difficult because of visual overlapping of particles within the images, the aforementioned fractions of 29.6% and 59.5% roughly correspond to the percentages of particles lying within the cluster and on the surface. The schematic illustrations of block copolymer particle brush structures and monolayer film morphologies are shown in the top scheme of Figure 6-13.

Compared to the high and medium grafting density systems, the sparsely grafted SiO_2 particle brushes showed more unique self-assembly behaviors. To further investigate the synthesis of bimodal copolymer particle brush with low grafting density, we utilized our findings that the bimodality of the particle brushes and the population of conjugated PS blocks can be easily tuned by altering the concentration of the pre-synthesized SiO₂-*g*-PMMA particle brush macro-initiators in the reaction. The chain composition strongly influences the morphology and aggregation states of the block hybrid particles in bulk and in solution. Single particles and cluster string-like structures were observed, the top scheme in Figure 6-14. These hierarchical architectures present a promising approach to prepare novel functional materials.



Figure 6-13 Schematic graph of the synthesis and assembly of bimodal SiO₂-*g*-PMMA/PMMA*b*-PS particle brushes and TEM images of SiO₂-*g*-PMMA-*b*-PS particle brushes. (a–b) M-*b*-S-1, (c–d) M-*b*-S-2: (e–f) M-*b*-S-3. Scale bar, (a), (c), (e): 500 nm, (b), (d), (f), 100 nm.

Table 6-3 Result of syntheses of sparsely grafted SiO₂-g-PMMA/PMMA-b-PS particle brushes.

Entry ^a	$M_{ m n}{}^{ m b}$	$M_{\rm w}/M_{\rm n}^{\rm b}$	f _{ino} (%) ^c	σ (nm ⁻²) ^d
PMMA-L2	133,500	1.18	35.10	0.046
M- <i>b</i> -S-4	209,400	2.66	24.52	0.049
M- <i>b</i> -S-5	241,800	2.11	24.15	0.044
PMMA-L3	23,200	1.23	77.20	0.042
M- <i>b</i> -S-6	206,800	3.17	27.52	0.042
M-b-S-7	80,600	1.68	21.98	0.043

^a Reaction condition: M-*b*-S-4–5: $[S]_0/[SiO_2-g-PMMA-Br]_0/[CuBr_2]_0/[Me_6TREN]_0/[Sn(EH)_2]_0 = 50000:1/2:5:50:5; M-$ *b* $-S-6–7: <math>[S]_0/[SiO_2-g-PMMA-Br]_0/[CuBr_2]_0/[Me_6TREN]_0/[Sn(EH)_2]_0 = 10000:1/2:1:10:1; PMMA-L2–3: [MMA]_0/[SiO_2-Br]_0/[CuCl_2]_0/[dNbpy]_0/CuCl]_0 = 3000:1/4:0.4:8:3.6 with 45 vol% anisole, 5 vol% DMF at 60 °C. ^b Determined by SEC. ^c f_{ino} (inorganic content), determined by TGA. ^d <math>\sigma$ (grafting density), calculated according to TGA data.

Table 6-3 shows the compositions of two sparsely grafted SiO₂-*g*-PMMA NPs synthesized by normal ATRP, PMMA-L2 with DP = 1335, grafting density 0.046 chains/nm² and PMMA-L3 with DP = 232, grafting density 0.042 chains/nm², respectively. In order to achieve bimodal structures, low initiator concentrations of 20 and 40 ppm were used, for chain extension experiments with styrene monomers, samples M-*b*-S-4/5. After polymerization and purification, the samples were characterized by TEM and SEC. SEC traces of polymers cleaved from nanoparticles indicated clear bimodal features (Figures S6-9 and S6-10). The number-averaged molecular weight (M_n), dispersities and PMMA/PMMA-*b*-PS chain fractions were calculated by deconvolution of SEC traces. As shown in Table S6-3, under high target DP conditions, 50,000 and 25,000, only 7% and 11% of PMMA-Br chains were chain extended. Constant grafting density values before and after chain extensions suggested that the amount of new chains, which are free homo-polymers generated from thermal-self initiation of styrene monomers, is negligible.





Figure 6-14 Schematic graph of the synthesis and assembly of bimodal SiO₂-*g*-PMMA/PMMA*b*-PS particle brushes and TEM images of SiO₂-g-PMMA-*b*-PS particle brushes. (a) M-*b*-S-4, (b) M-*b*-S-5: (c) M-*b*-S-6: (d) M-*b*-S-7. Scale bar: 500 nm, inset scale bar: 100 nm.

TEM was used to investigate the morphology of the particle brush assemblies. Representative images are shown in Figure 6-14. Figures 6-14 a–b shows that PMMA-g-SiO₂ particles were well-dispersed on the grid. Sparsely grafted particle brushes have low grafting density and tend to self-assemble to anisotropic string-like structures, which can be observed in the higher magnification TEM image, Figure 6-14 b (inset). This tendency of the particles to link directionally is due to the non-uniform chain distribution on the surface of nanoparticles. Even after partial chain extension with a PS block, the low grafting density SiO₂-g-PMMA particles remained connected with each other and formed predominately one dimensional short string composed of several particles, Figure 6-14 b. A decrease of BCP chain fraction to 6.9% resulted in the formation of a more elaborately branched and thicker network structure, accompanied by interpenetrating higher DP chains at the junction points (Figure 6-14 a). The basis for the self-assembly process is illustrated in the top scheme of Figure 6-14. The images show that the nanoparticles are not in direct contact with each

other, since there is an average 15–30 nm gap between each nanoparticle pair along the string orientation. This gap represents the presence of a shell formed by the collapsed PMMA domains. It is important to note that the self-assembly mechanism of these bimodal polymer grafted particle brushes is different from most of the polymer-directed colloidal assemblies previously reported. In this case, sparsely grafted homopolymer/BCP brushes result in direct anisotropic assembly, which originates from the phase separation of immiscible polymer brushes without the need of any post-polymerization procedures. It is noted that due to the self-assembly of particle brush to a string-like structure, some void spaces are observed in TEM images of the monolayer sample films (Figures 6-14 a–b), which confirm the ligand-induced self-assembly behavior and also the absence of free PS polymers from thermal-self initiation. The volume of the void space can be diminished when the DP of PS blocks are increased.

PMMA-L3, SiO₂-*g*-PMMA hybrid particles with shorter PMMA chains were prepared to confirm the mechanism of self-assembly of bimodal BCP particle brushes. As shown in Figures 6-14 c–d, the inter-particle distance decreased significantly for the bimodal BCP particle brushes with similar grafting density, but lower DP (DP = 232), due to the shrinkage of the collapsed PMMA polymer shell. The self-assembly of sparsely grafted NPs can no longer be observed in TEM images (Figure S6-14 b). This also leads to a thinner PMMA phase in the BCP particle brushes (M-*b*-S-6–7) after chain extension. Lower target DPs, 10,000 and 5,000, were also examined in the chain extension reactions with the expectation of forming a higher fraction of PMMA-*b*-PS in the products. SEC traces, Figures 6-14 c and 6-14 d, showed that when compared to samples M*b*-S-4–5, the PMMA peaks in M-*b*-S-6–7 were much smaller, implying higher PMMA-*b*-PS fractions. After deconvolution of the traces, the chain compositions of the PMMA-*b*-PS fractions were 55% and 80%, respectively. Although no clear string-like structures were observed in the
images of the SiO₂-*g*-PMMA samples before chain extension, and no obvious PMMA phase was found in TEM images after chain extension, the images from the PMMA-*b*-PS sample with a higher block fraction of 80%, displayed a string-like structure (Figure 6-14 d). On the other hand, some clusters structures were observed in Figure 6-14 c with only 55% of PMMA-*b*-PS.



Figure 6-15 Schematic graph of the synthesis and assembly of bimodal SiO₂-*g*-PMMA/PMMA*b*-PS particle brushes and TEM images of a mixture of SiO₂-*g*-PMMA-*b*-PS and SiO₂-*g*-PMMA particle brushes. (a) M-*b*-S-2 with PMMA-L1, mass ratio=1:4; (b) M-*b*-S-7 with PMMA-L1, mass ratio=1:4. Scale bar: 500 nm, inset scale bar: 100 nm.

To further investigate if the self-assembly mechanism of non-chain-extended SiO_2 -g-PMMA particle brushes would form a "cluster-like" structure, which is surrounded by SiO_2 -g-PMMA-b-PS particle brushes, sparsely grafted SiO_2 -g-PMMA particle brushes (PMMA-L1) were mixed with two SiO_2 -g-PMMA-b-PS particle brushes (M-b-S-2 and M-b-S-7) separately in THF solution, with a mass ratio of 4:1. The morphology of the mixtures was studied by TEM. As shown in Figure

6-15 a, after adding a large amount of SiO₂-*g*-PMMA particle brushes, the "string-like" structure of M-*b*-S-2 (Figure 6-13 d) evolved to a "cluster-string" structure. Due to the lower grafting density of the adding particle brushes, PMMA-L1, it is easy to distinguish the two distinct PMMA regions, one where the SiO₂-*g*-PMMA-*b*-PS particle brushes are located outside of the cluster and another where the SiO₂-*g*-PMMA particle brushes are inside the cluster. A similar evolution can be observed in sparsely grafted bimodal copolymer particle brush system (M-*b*-S-7) with a smaller PMMA phase. These observations not only confirm the self-assembly mechanism we proposed but also show that adding SiO₂-*g*-PMMA particle brushes can enrich the PMMA phase in the system, overall enhancing the design and fabrication of unique and elaborate network structures.

6.2.4 Conclusion

Our results demonstrate that in the presence of a copper catalyst formed with highly activating ligands under a low ppm catalyst loading condition, SiO₂-*g*-PMMA/PMMA-*b*-PS particle brushes were successfully synthesized by SI-ATRP. By altering the grafting density and concentration of the hybrid initiator, SiO₂-*g*-PMMA-Br, predesigned bimodality chain compositions were achieved. Bimodal homo-/block copolymer particle brushes were obtained through simple chain extensions from PMMA grafted silica particle brushes that formed anisotropic string-like and continuous cluster network morphologies. The self-assembly of BCPs grafted from strategically designed nanocomposites provides a new route toward hierarchically ordered quasi-one component materials as a result of the morphology of the grafted homo-/block copolymer brushes. This provides new perspectives for engineering high-performance composite materials that require localized or specifically oriented particles, ultimately allowing for efficient capitalization of these materials distinct properties.

6.2.5 References

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7 Conclusions and Perspectives

7.1. Conclusions

This work explores the molecular parameters (*i.e.*, surface grafting density and molecular weight distribution of tethered polymer chains) governing the interactions and physical properties of particle brush materials. Chapter 4 discusses the role of grafting density on the structure formation and consequent interactions and mechanical properties. Precedent works mainly focused on densely functionalized brush particle films to demonstrate reinforcement effect of particle solids as functions of chain length, particle size and monomer chemistry. This study extended the field to the intermediately and sparsely polymer-grafted particle assembly. To be specific, we successfully demonstrated the effective stiffening effect in the moderate grafting particle brush as well as the unique anisotropy (string-like structure) formation and mechanical properties as observed in effective medium models in the sparse brush particles. A quantitative estimation of dispersion interactions in the system support the efficient increase of cohesive interactions in intermediate grafting brush materials compared to the dense analog. Our result of structure formation in the sparse system agrees with previous studies. From the structure, we observed an opposite trend in modulus and hardness: decrease and level-off. We suggested that this distinct observation was attributed to the anisotropic structure of the sparse brush materials, which made the mechanical property of the materials to transition gradually from silica- to polymer-like characteristics. As a conclusion, the hypothesis that reducing grafting density thins the concentrated brush layer (resulting in thickening the semi-dilute brush layer) and increase brush interactions was successfully demonstrated.

Chapter 5 explores the impact of another molecular parameter, the dispersity index. Integrated studies including Chapter 4 demonstrated the applicability of particle brush materials as a building

block for organic-inorganic hybrid materials that take advantages of functionality from inorganic nanoparticles and mechanical ductility from organic brushes. However, those were casting light on very uniform brush particles, or did not consider dispersity in molecular weight of chains. Indeed, mechanical and thermal properties in wide-dispersed brush particles were very different from those of narrow-dispersed (or uniform) analog. At a given grafting density, wider distribution in molecular weight of grafted chains leads to more facile formation of entanglements that increase toughness in bulk films, which demonstrated the underlying hypothesis. Another interesting observation was the broadened glass transition in wide-dispersed brush system. The assumption that increasing chain dispersity lowers the critical degree of polymerization for CPB-to-SDPB transition and increase chain entanglements that result in toughened films.

Chapter 6 discusses other projects conducted including the reversible phase transition in a binary mixture of particle brushes and the structure formation of block copolymer (BCP) brush particle assembly. The hypothesis that grafted polymer chains induce phase behavior in a blend of particle brushes was demonstrated. Also, the phase separation was reversible via a series of thermal process in case that a LCST-type mixture was chosen. This achievement opens a field that has not been discovered and demonstrated the hypothesis that polymer ligands induce self-assembly behavior as observed in homopolymer system. The other work explores the phase formation of block copolymer tethered nanoparticles, and found out that particles form string-like structure in different level depending on grafting density. Dense BCP brush particles form into 1-D structure (connected particles) in first brush and particle core regimes respectively. These hierarchical architectures are expected promising in designing novel functional materials.

7.2. Future Perspectives

While this work uncovered governing parameters of interactions and properties in particle brush materials and explored the possibility of polymer modification with varying architectures into mechanically robust hybrid materials, there remain a lot of both fundamental and practical questions that need to be addressed.

The foremost thing would be the quantitative explanation about the interactions in sparse brush particle films. There is a limitation to interpret the trend in Young's modulus and hardness using an effective medium theory that needs multiple approximations. This complex system is required to clarify the structure formation more systematically. The simple Daoud-Cotton model is probably not accurate enough to describe chain conformation in this regime due to the presence of huge free volume resulting from increased ungrafted area on surface.

An experimental study using X-ray scattering might improve the structure-property relationship research which still is an active area of investigation and could extend to 3D assembly in a fine fashion. This study can also clarify the more sparse grafting materials. Computational simulation suggested that particles are expected to undergo a transition in the structure throughout distributed–string–sheet–3D aggregates. Field studies are needed to demonstrate the structure-property relationship of particle brush materials with various architectures in 3D.

For last two decades, researchers have discovered and predicted a number of features of this hybrid material. There is no doubt that particle brush will continue to play a building block role taking both advantages. Studies from many different fields will entertain scientists and researchers with novel discoveries in the coming years, as it has been.

Appendix

Matlab Scripts

Voronoi tessellation

```
clf.
clear all
shade = strel('disk',30);
hsize = 10;
sigma = 10;
h = fspecial('gaussian',hsize,sigma);
sensitivityforparticle = 0.38;
sedilation = strel('disk',7);
seerosion = strel('disk',9);
openW = 400;
openB = 200;
hist.limit = 3.0*10^3;
s1 = 'JY-10-101 \ 20k';
s2 = '.jpg';
a0 = imread(strcat(s1,s2));
sizea0 = size(a0);
Atotal = sizea0(1,1) * sizea0(1,2);
figure(1)
subplot(2,4,1); imshow(a0); title('original');
a1 = 255 - a0;
a1 = imfilter(a1,h);
a1 = 255 - a1;
subplot(2,4,2); imshow(a1); title('blurred by Gaussian');
a2 = imdilate(a1, sedilation);
subplot(2,4,3); imshow(a2); title('dilated');
a3 = imerode(a2, seerosion);
subplot(2,4,4); imshow(a3); title('eroded');
   = imbinarize(a3,
                         'adaptive', 'ForegroundPolarity', 'dark', 'Sensitivity',
a4
sensitivityforparticle);
a4 = bwareaopen(a4, openW);
a4 = 1 - a4;
a4 = bwareaopen(a4, openB, 4);
a4 = 1 - a4;
subplot(2,4,5); imshow(a4); title('noise removed');
a5 = 1 - a4;
cc = bwconncomp(a5);
props = regionprops(cc);
centroids = cat(1, props.Centroid);
ANPs = sum(cat(1, props.Area));
a5 = 1 - a5;
subplot(2,4,6); imshow(a5); title('centroids'); hold on
plot(centroids(:,1), centroids(:,2), 'w+'); hold off
subplot(2,4,7);
voronoi(centroids(:,1), centroids(:,2)); ax = gca; set(ax, 'Visible', 'off');
```

```
pbaspect([1 1 1]); axis([0 sizea0(1,1) 0 sizea0(1,2)]);
title('Voronoi diagram');
set(findall(gca, 'type', 'text'), 'visible', 'on'); ax.YDir = 'reverse';
subplot(2,4,8);
imshow(a0);
hold on
voronoi(centroids(:,1), centroids(:,2),'-y');
title('Result');
ax = gca; set(ax, 'Visible', 'off'); ax.YDir = 'reverse';
hold off
figure(2)
imshow(a0);
hold on
voronoi(centroids(:,1), centroids(:,2),'-y');
ax = gca; set(ax,'Visible','off'); ax.YDir = 'reverse';
hold off
[V,C] = voronoin(centroids);
for i = 1 : size(C,1)
    ind = C{i};
    tess area(i,1) = polyarea(V(ind,1), V(ind,2)) / 3.08<sup>2</sup>; % pixel / nm!!!!
    if tess area(i,1) > hist.limit
        tess area(i,1) = NaN;
    end
end
mean = nanmean(tess area);
stdev = nanstd(tess area);
FWHM = 2.355 * \text{stdev};
nstdev = nanstd(tess area/mean);
nFWHM = 2.355 * nstdev;
figure(3)
h = histfit(tess area, 15, 'normal');
h(1).FaceColor = [.8 1 .8];
h(2).Color = [.6 .2 .2];
title(['mean: ' num2str(mean), ' FWHM: ',num2str(FWHM)],'fontsize',20)
xlabel('Voronoi cell area','fontsize',20)
ylabel('count','fontsize',20)
legend('number distribution', 'normal distribution','fontsize',20)
set(gca, 'fontsize', 20, 'XTickLabelRotation', 45)
fNPs = ANPs / Atotal;
APMMA = Atotal - ANPs;
fPMMA = APMMA / Atotal;
figure(4)
x = -mean:4*mean/1000:3*mean;
pd = makedist('Normal', 'mu', mean, 'sigma', stdev);
y = pdf(pd, x);
y2 = pdf('Normal', x, mean, stdev);
plot(x/mean,y,'LineWidth',4,'Color','r')
                                          ',num2str(nFWHM),'
title(['normalized
                          FWHM:
                                                                              \phi {PMMA}:
',num2str(fPMMA)],'fontsize',20)
xlabel('\bf\it A/<A>','fontsize',40)
ylabel('\bf \nu','fontsize',40)
set(gca,'xtick',[0.5
                                      1.5], 'xticklabel', [], 'ticklength',
                                                                                    [0.05,
                       1
0.05], 'ytick', [], 'linewidth', 4)
axis([0 2 0 inf])
axis square
s3 = '.svg';
saveas(figure(1),strcat(s1,'(1)',s3));
```

```
saveas(figure(2),strcat(s1,'(2)',s3));
saveas(figure(3),strcat(s1,'(3)',s3));
saveas(figure(4),strcat(s1,'(4)',s3));
```

Phase Mapping of Block Copolymer-Grafted Nanoparticles

```
clf
clear all
sensitivityforparticle = 0.38;
sensitivityforPS = 0.68;
hsize = 3;
sigma = 0.5;
h = fspecial('gaussian',hsize,sigma);
sedilation = strel('disk',1);
seerosion = strel('disk',1);
openW = 100; % maximum size of white dots to be removed
openB = 20; % maximum size of black dots to be removed
Atotal = 1200 * 1200; % total area
a0 = imread('MbS1 ZW-7-13 10k.jpg');
a0 = imcrop(a0, [145 1 1199 1199]); %% only for M-b-S-1
imshow(a0); title('original','FontSize',30);
a1 = 255 - a0;
a1 = imfilter(a1,h);
a1 = 255 - a1;
figure, imshow(al); title('blurred by Gaussian', 'FontSize', 30);
a2 = imdilate(a1, sedilation);
figure, imshow(a2); title('dilated', 'FontSize', 30);
a3 = imerode(a2, seerosion);
figure, imshow(a3); title('eroded', 'FontSize', 30);
a4 = imbinarize(a3,
                           'adaptive',
                                        'ForegroundPolarity',
                                                                 'dark', 'Sensitivity',
sensitivityforparticle);
                           'adaptive',
                                                                           'Sensitivity',
a5 = imbinarize(a3,
                                        'ForegroundPolarity',
                                                                 'dark',
sensitivityforPS);
a4 = bwareaopen(a4, openW);
a4 = 1 - a4;
a4 = bwareaopen(a4, openB, 4);
a4 = 1 - a4;
a5 = bwareaopen(a5, openW);
a5 = 1 - a5;
a5 = bwareaopen(a5, openB, 4);
a5 = 1 - a5;
figure, imshow(a4); title('NPs', 'FontSize',30);
figure, imshow(a5); title('domain mapping', 'FontSize',30);
cc1 = bwconncomp(1 - a4);
props1 = regionprops(cc1);
ANPs = sum(cat(1, props1.Area));
cc2 = bwconncomp(1 - a5);
props2 = regionprops(cc2);
APS = sum(cat(1, props2.Area)) - ANPs;
APMMA = Atotal - ANPs - APS;
fPS = APS / Atotal;
fPMMA = APMMA / Atotal;
fSiO2 = 1 - fPS - fPMMA;
```

Estimation of Dispersion Interactions in Particle Brush Materials

```
clear all
clf
% constants
kB = 1.38E-23; % Boltzmann constant /J/K
T = 298; % temperature /K
EPS0 = 1.0; % dielectric constant of vacumm/air
n0 = 1.0; % refractive index of vacumm/air
h = 6.63E-34; % Planck constant /Js
% parameters
R = 7.5E-9; % particle radius /m
d = 0:0.1E-10:50E-9; % interparticle distance /m
L = 0:0.1E-10:50E-9; % chain length /m
Ad = 0.335E-9; % correction parameter in CPB (PS 0.335, PMMA 0.273)
Bd = 1.71E-9; % correction parameter in SDPB (PS 1.71, PMMA 1.65)
Bi = 0.907E-9; % correction parameter in SDPB (PS 0.907, PMMA 0.835)
Ncd = 230; % critical degree of polymerization of dense system PS230 PMMA400
Nci = 1; % critical degree of polymerization of intermediate system
Ncs = 0; % critical degree of polymerization of sparse system
EPSp = 3.8; % dielectric constant of SiO2 particle
EPS1 = 2.55; % dielectric constant of PS ligands
np = 1.448; % refractive index of SiO2 particle
nl = 1.557; % refractive index of PS ligands
NUp = 3.2E15; % Apsorption frequency of SiO2 particles //s
NUl = 2.3E15; % Apsorption frequency of SiO2 particles //s
lambda = 0.252E-9; % repeat unit length of PS ligands /m
x = 0.4E-9; % interligand distance /m
NA = 6.02E+23; % Avogadro's number
RHO = NA*1050000/104.15; % number density of monomers //m^3
dc = Ad*Ncd^0.8; % critical interparticle distance /m
% secondary parameters
% interparticle Hamaker constant /J
Ap
           =
                       3/4*kB*T*((EPSp-EPS1)/(EPSp+EPS1)).^2+3*h*NUp/16/sqrt(2)*(np.^2-
nl.^2).^2/(np.^2+nl.^2).^(3/2);
% interligand Hamaker constant /J
           =
                       3/4*kB*T*((EPS1-EPS0)/(EPS1+EPS0)).^2+3*h*NUl/16/sqrt(2)*(nl.^2-
Al
n0.^2).^2/(nl.^2+n0.^2).^(3/2);
% interligand interaction constant /(Jm<sup>6</sup>)
Cl = Al/(pi*RHO).^{2};
% vdW interaction between 2 particles
Uc = -Ap/6 * (2*R.^2./(4*R+d)./d + 2*R.^2./(2*R+d).^2 + log((4*R+d).*d./(2*R+d).^2));
Uc(1) = -1e-14;
% interaction between 2 chains
Ul = -Cl*3*pi*L/8/lambda.^2/x.^5;
% DP
N = 0:0.2:1000;
dd = zeros(size(N));
% scaled interparticle distance
for i=1:length(N)
    if N(i)<Ncd
        dd(i) = Ad*N(i)^{0.8};
    else
        dd(i) = Bd*N(i)^{0.5};
    end
end
di = Bi*N.^{0.5};
```

```
% volume of particle core /ok/
Vcore = 4/3*pi*R^3;
% total volume of the unit cell (d/i) /ok/
Vtotald = 1/sqrt(2)*(2*R+dd).^3 - 2.386485386504597e-24 + Vcore;
Vtotali = 1/sqrt(2)*(2*R+di).^3 - 2.386485386504597e-24 + Vcore;
% Vtotals = 1/sqrt(2)*(2*R+2*lambda*Ncs.^0.3*N.^0.5).^3;
% core-core interaction per unit particle brush cell /ok/
Ucc = 12*Uc;
% ligand-ligand interaction per unit particle brush cell /ok/
Ull = 6*Ul*lambda/L*(RHO/16)*(1/sqrt(2)*(2*R+d).^3-4/3*pi*R.^3) + 1.156095079546237e-
16;
% effective core-core interaction per unit particle brush cell /ok/
Ucceff = -12 * Ap/6 * (2*R.^2./(4*R+dd)./dd + 2*R.^2./(2*R+dd).^2 +
log((4*R+dd).*dd./(2*R+dd).^2));
Ucceff(1) = -1;
% effective ligand-ligand interaction per unit particle brush cell /ok/
Ulleff = 6*(-Cl*3*pi/8/lambda.^2/x.^5)*lambda*RHO/16*(1/sqrt(2)*(2*R+dd).^3-
4/3*pi*(R+dc/2).^3);
% effective volume for ligand-ligand interaction in the unit cell /ok/
Veffd = Vtotald-4/3*pi*(R+Ad*Ncd.^0.8/2).^3 - 1.187746222216336e-23;
Veffi = Vtotali-4/3*pi*(R+Bi*Nci.^0.5/2).^3 - 1.192784323475795e-25;
% Veffs = Vtotals-4/3*pi*(R+lambda*Ncs.^0.8).^3);
% effective ligand-ligand interaction per unit cell (d/i) /ok/
Ulleffd = 6*Ul./L*lambda*RHO/16.*Veffd./Vtotald;
Ulleffi = 6*Ul./L*lambda*RHO/16.*Veffi./Vtotali;
% Ulleffs = 6*Ul./L*lambda*RHO/16.*Veffs./Vtotals;
Ulleffd leveloff = min(Ulleffd);
Ulleffi leveloff = min(Ulleffi);
Ulleff leveloff = min(Ulleffd leveloff,Ulleffi leveloff);
Ulleffd normalized = Ulleffd/Ulleff leveloff;
Ulleffi normalized = Ulleffi/Ulleff leveloff;
% volume fraction of organic content
PHIorgd = 1 - Vcore./Vtotald;
PHIorgi = 1 - Vcore./Vtotali;
% Young's modulus /GPa
Ed = -Ulleffd * 8.1;
Ei =- Ulleffi * 8.1;
N Ed = [120 0.55]
136
      0.61
204
      0.50
      1.25
212
226
      1.06
      0.93
231
231
      1.22
355
      1.20
365
      1.26
365
      1.08
400
      0.98
      0.96
432
549
      1.13
638
      1.22
762
      0.99
      1.06
829
841
      1.10
890
      0.82
     1.25
1087
```

```
1777
     0.93
      1.04]; %% experimental N vs E of dense
1800
N Ei = [221 \quad 0.432413209]
255
      0.4907969164
313
       1.151282051
328
       0.6746900418
440
       1.000682778
758
      1.096445462
1103 1.273269927]; %% experimental N vs E of intermediate
% figure(1)
% plot(d,Ucc,'k','LineWidth',2)
% grid
% axis([0 5E-8 -1E-20 2E-21])
% % title('\fontsize{20}vdW interaction between particles')
% xlabel('\fontsize{30}\it\bfd \rm/m')
% ylabel('\fontsize{30}\it\bfU_{\rm\bfcc} \rm/J')
% set(gca, 'FontSize', 30)
% figure(2)
% plot(L,Ull,'m','LineWidth',2)
% grid
% axis([0 5E-8 -inf inf])
% % title('\fontsize{20} interaction between ligands')
% xlabel('\fontsize{30}\it\bfL \rm/m')
% ylabel('\fontsize{30}\it\bfU {\rm\bfll} \rm/J')
% set(gca, 'FontSize', 30)
figure(1)
plot(d,Ucc,'k',d,Ull,'m','LineWidth',2)
arid
axis([0 50E-9 -2E-14 4E-15])
% axis([0 1E-9 -2E-18 0.4E-18])
xlabel('\fontsize{30}\it\bfd \rm/m')
ylabel('\fontsize{30}\it\bfU \rm/J')
% legend('\fontsize{30}\it\bfU {\rm\bfcc}','\fontsize{30}\bf\itU {\rm\bfl}')
set(gca, 'FontSize',30)
figure(2)
plot(d,Ucc,'k',d,Ull,'m','LineWidth',2)
grid
axis([0 0.5E-9 -5E-18 1E-18])
% axis([0 1E-9 -2E-18 0.4E-18])
xlabel('\fontsize{30}\it\bfd \rm/m')
ylabel('\fontsize{30}\it\bfU \rm/J')
% legend('\fontsize{30}\it\bfU_{\rm\bfcc}','\fontsize{30}\bf\itU_{\rm\bfl}')
set(gca, 'FontSize', 30)
% figure(4)
% plot(dd,Ucceff,'k',dd,Ulleff,'m','LineWidth',2)
% grid
% axis([0 5E-8 -4E-15 0])
% % axis([0 1E-9 -2E-18 0.4E-18])
% xlabel('\fontsize{30}\it\bfd \rm/m')
% ylabel('\fontsize{30}\it\bfU \rm/J')
% % legend('\fontsize{30}\it\bfU {\rm\bfcc}','\fontsize{30}\bf\itU {\rm\bfl}')
% set(gca, 'FontSize', 30)
figure(5)
yyaxis left
fig5 = plot(N,Ulleffd/1E6,N,Ulleffi/1E6,'-','LineWidth',2);
set(fig5(1), 'color', [1 0 0])
set(fig5(2), 'color', [0 0.5 0])
set(gca, 'YColor', 'k');
```

```
grid off
axis([0 1000 -200 0])
% title('\fontsize{20}comparison of effective interactions')
xlabel('\fontsize{30}\it\bf N ')
ylabel('\fontsize{30}\bf\itIPCED \rm/MPa','Color','k')
yyaxis right
ylim([-1.61 0])
ylabel('\fontsize{30}\bf\itE \rm/GPa','Color','k')
set(gca, 'YColor', 'k');
% legend('\fontsize{30}Dense','\fontsize{30}Intermediate')
set(gca, 'FontSize', 30)
figure(6)
fig6 = plot(N,Ulleffd normalized,N,Ulleffi normalized, 'LineWidth',2);
set(fig6(1), 'color', [1 0 0])
set(fig6(2), 'color', [0 0.5 0])
hold on
sz = 50;
fiq62
                    scatter(N Ed(:,1),N Ed(:,2),sz,'filled','MarkerEdgeColor',[1
                                                                                          0
            =
0], 'MarkerFaceColor', [1 0 0]);
fiq63
          =
                  scatter(N_Ei(:,1),N_Ei(:,2),sz,'filled','MarkerEdgeColor',[0
                                                                                        0.5
0], 'MarkerFaceColor', [0 0.5 0]);
hold off
grid
axis([0 1000 0 1.3])
% title('\fontsize{20}comparison of effective interactions')
xlabel('\fontsize{30}\it\bf N ')
ylabel('\fontsize{30}\bf\itE/E_{\rm\bflevel-off}')
% legend('\fontsize{30}Dense','\fontsize{30}Intermediate')
set(gca, 'FontSize', 30)
% figure(6)
% plot(N,Vtotald,'r',N,Vtotali,'g','LineWidth',2)
% arid
% % axis([0 1000 -inf 0])
% % title('\fontsize{20}Volume of PB unit cell')
% xlabel('\fontsize{20}\it\bf N ')
% ylabel('\fontsize{20}\it\bfV \rm/m^3')
% legend('\fontsize{20}Dense','\fontsize{20}Intermediate')
% set(gca, 'FontSize', 30)
figure(7)
fig7 = plot(PHIorgd,Ulleffd/1E6,PHIorgi,Ulleffi/1E6,'LineWidth',2);
set(fig7(1), 'color', [1 0 0])
set(fig7(2), 'color', [0 0.5 0])
grid off
axis([0.8 1.0 -200 0])
% title('\fontsize{20}Volume of PB unit cell')
xlabel('\fontsize{30}\bf\phi {org} ')
ylabel('\fontsize{30}\bf\itIPCED \rm/MPa')
% legend('\fontsize{30}Dense','\fontsize{30}Intermediate')
set(gca, 'FontSize', 30)
% figure(8)
% loglog(N,dd,'r',N,di,'g','LineWidth',2)
% grid
% axis([1 1000 1E-9 1E-7])
% % title('\fontsize{20}Volume of PB unit cell')
% xlabel('\fontsize{20}\it\bf N ')
% ylabel('\fontsize{20}\it\bfd \rm/m')
% legend('\fontsize{20}Dense','\fontsize{20}Intermediate')
% set(gca, 'FontSize',30)
```

Tensile Test Data Analysis

```
clear all
clf.
filename = 'PMMA1200.xlsx';
[status, sheet name] = xlsfinfo(filename);
data = double.empty;
Ut = double.empty;
E = double.empty;
strain = double.empty;
stress = double.empty;
i = double.empty;
for k=1:numel(sheet name)
  data{k} = xlsread(filename, sheet name{k});
  strain{k} = data{k}(:,3)/100;
  stress{k} = data{k}(:,4);
  figure(k)
  plot(100*strain{k},-stress{k},'LineWidth',2)
  axis([0 inf 0 inf])
  xlabel('\it\bf\epsilon (%)')
  ylabel('\it\bf\sigma \rm/Pa')
  title(sheet name{k})
  set(gca, 'FontSize', 30)
  Ut{k} = -trapz(strain{k},stress{k});
  i{k} = find(data{k}(:,3) > 0,1);
 E\{k\} = - \min(data\{k\}(i\{k\}+1:i\{k\}+10,5));
end
figure(numel(sheet name)+1)
hold on
for k=1:numel(sheet name)
    fprintf('s: E = %.2f GPa, K = %.2f MPa\n', sheet_name{k}, E{k}/1E9, Ut{k}/1E6)
    plot(100*strain{k},-stress{k},'LineWidth',2,'DisplayName',sheet_name{k})
end
hold off
axis([0 inf 0 inf])
xlabel('\it\bf\epsilon \rm(%)')
ylabel('\it\bf\sigma \rm/Pa')
set(gca, 'FontSize', 30)
```

legend show

Supporting Information for Chapter 4

Calculation of surface grafting density Graft densities were calculated using the following equation:

The value for f_{SiO_2} , in the equation, is the weight fraction of silica measured by TGA after exclusion of any residual solvent; N_A is the Avogadro number; ρ_{SiO_2} is the density of silica NPs; d is the average diameter of silica NPs; M_n is the number average MW of polymer brushes.

Calculation of Poisson's ratio of composite materials

Poisson's ratio of brush particle materials were calculated using the Voigt model for composite materials¹:

$$v = v_{org} \phi_{org} + v_{SiO_2} \phi_{SiO_2}$$
 Eq

where, v_i is the Poisson's ratio of component *i* and ϕ_i is the volume fraction of component *i*.

Table S4-1 Additional material information of (intermediate dense) poly(methyl methacrylate)

 brush particles.

N	$M_{ m w}/M_{ m n}$	$f_{ m org}$	ф _{org}	σ₅ (nm ⁻²)
321	1.20	0.81	0.89	0.44
359	1.15	0.82	0.90	0.42
391	1.23	0.85	0.91	0.46
527	1.21	0.87	0.93	0.43
	N 321 359 391 527	N Mw/Mn 321 1.20 359 1.15 391 1.23 527 1.21	N M _w /M _n f _{org} 321 1.20 0.81 359 1.15 0.82 391 1.23 0.85 527 1.21 0.87	Ν M _w /M _n f _{org} φ _{org} 321 1.20 0.81 0.89 359 1.15 0.82 0.90 391 1.23 0.85 0.91 527 1.21 0.87 0.93

Variables represent the degree of polymerization of graft, N; dispersity index, M_w/M_n ; weight fraction of polymer, f_{org} ; volume fraction of polymer, ϕ_{org} ; surface grafting density, σ_s . Sample ID: SiO₂-(σ_s regime: d (dense) /i (intermediate) /s (sparse))-(monomer)N.



Figure S4-1 Representative bright field transmission electron micrographs and corresponding schemes of structure for the (a) dense (SiO₂-*d*-MMA445), (b) intermediate (SiO₂-*i*-MMA563) and (c) sparse (SiO₂-*s*-MMA365) PMMA-brush systems with similar degrees of polymerization. All scale bars are 50 nm (20 nm in inset).

Quantitative analysis of domain structure using TEM micrographs

A quantitative analysis on TEM micrographs following a systematic processing was conducted using Matlab. A sequence for the analysis is shading correction – blurring – dilation – erosion – particle recognition – tessellation. Bandpass filter was applied to correct shading. As next steps, the combination of dilation and erosion was exploited to separate merged (neighboring) domains. Gaussian blurring is necessary to reduce detail for better recognition. Given that unstained TEM images provide three distinct contrast levels (dark (silica particles) and bright (polymer brush)), each domain was mapped by binarization. Then, particle domain was recognized, followed by Voronoi tessellation using centroid information. The results at each step are shown in Figure S4-2.



Figure S4-2 A representative image processing of a TEM micrograph (SiO₂-*d*-MMA445) for Voronoi tessellation.



Figure S4-3 Histograms of spacing between adjacent particle cores in dense (a: SiO_2 -*d*-S365), intermediate (b: SiO_2 -*i*-S328) and sparse (c: SiO_2 -*s*-S432) systems. Monomodal distributions in the dense and intermediate materials indicate 'isotropic' microstructure while bimodal distribution in the sparse brush particles demonstrates 'anisotropic' structure.



Figure S4-4 Representative load-displacement curves of (a) dense (SiO₂-*d*-S890), (b) intermediate (SiO₂-*i*-S328) and (c) sparse (SiO₂-*s*-S432) brush particulate films during nanoindentation measurements. Insets are corresponding topographs taken by AFM. All scale bars are 1 μ m.

Comparison of cohesive energy contributed from core-core interaction and ligand-ligand interaction

A quantitative analysis of the effect of interpenetration between ligands is carried out. Herein we assume that there are only van der Waals interactions between nanoparticle cores, and London dispersion interactions between ligands. The model system we adopt for the estimation is silica nanoparticles ($r_0 = 7.9$ nm) grafted by PS chains. We also assumed the additivity of interactions to simplify the estimation.

First, the van der Waals interactions between two identical hard spheres² is:

$$U_c(d) = -\frac{A_{\text{SiO}_2}}{6} \left\{ \frac{2r_0^2}{(4r_0 + d)d} + \frac{2r_0^2}{(2r_0 + d)^2} + \ln\frac{(4r_0 + d)d}{(2r_0 + d)^2} \right\}$$
Eq S4-3

where, A_{SiO_2} is the Hamaker constant of silica in PS medium (~ 3.3×10^{-21} J), r_0 is the radius of spherical particles, and d is the distance between particles. This cohesive energy is considerable when particles are very closely located. Otherwise, it is negligible.

The other interaction we consider is between overlapped (side-on) ligands. Dispersion interactions between end-on chains is insignificant as mentioned above. The interaction between two parallel ligands³ is:

where $C_{\text{PS}} \sim 7.1 \times 10^{-79} \text{ J} \cdot \text{m}^6$ is the interaction constant, *L* is the length of overlap between two parallel chains, λ is the contour length of the repeat unit (~ 0.252 nm), *x* is the intermolecular spacing between chains (~ 0.4 nm).⁴ We then extended the two interactions to our system. Assemblies of particle brush with relatively high grafting density have been known to form close packed structure in 2D⁵⁻¹⁰ and face-centered cubic (FCC) or hexagonal close packed (HCP) structure in 3D.⁸⁻¹⁰ Hence, each particle core is considered to neighbor with 12 cores at the closest distance with polymer buffer layer and forms a rhombic-dodecahedral unit cell. Similarly, each polymeric chain has 6 neighboring chains when closely packed. Under an assumption that densely grafted particles form a closed packed structure and are separated by a distance, *d*, the core-core interaction, U_{cc} , and the total ligand-ligand interaction, U_{ll} , per unit cell can be estimated as follows:

$$U_{cc}(d) = 12U_{c}(d) = -2A_{\text{SiO}_{2}} \left\{ \frac{2r_{0}^{2}}{(4r_{0}+d)d} + \frac{2r_{0}^{2}}{(2r_{0}+d)^{2}} + \ln\frac{(4r_{0}+d)d}{(2r_{0}+d)^{2}} \right\} \qquad \text{Eq}$$

$$U_{ll}(d) = 6U_l(L)\frac{\lambda}{L}\rho_{St}V(d) = -6C_{PS}\frac{3\pi}{8\lambda x^5}\rho_{St}\left\{\frac{\sqrt{2}}{2}(2r_0+d)^3 - \frac{4}{3}\pi r_0^3\right\} \qquad \text{Eq}$$

As shown in Figure S4-5, U_{II} is much stronger except for at extremely short separations (< 1 Å). For this reason, the core-core interaction is not considered when calculating an effective cohesive energy, U_{eff} , in particle brush assembly.



Figure S4-5 Comparison of interactions between inter-core, U_{cc} , and inter-ligand, U_{ll} . The interligand dispersion interactions are dominant except for contact.

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Supporting Information for Chapter 5

Figure S5-1 Glass transition temperature as functions of (a) M_n , (b) M_w , (c) M_w/M_n and (d) ϕ_{PMMA} . Data points are color-mapped scaled in grayscale by dispersity index as displayed.

Supporting Information for Chapter 6.1



Figure S6-1 Phase separation in PS/PMMA polymer blend. AFM phase images of thin film of 50:50 PS/PMMA blend with $N_{PMMA} = 204$ and $N_{PS} = 216$. (A) Before thermal annealing. (B) After t = 24 h of thermal annealing at T = 140 °C. Dark phase corresponds to PMMA. Some non-uniformity is observed in as-cast film (A) due to partial phase separation of blend during film fabrication. Phase separated structure (B) reveals large spherical domains indicative late stage of film separation process.

Supporting Information for Chapter 6.2

Grafting density was calculated using formula (Eq S6-1).

$$\sigma_{\text{TGA}} = \frac{(1 - f_{\text{SiO2}})N_{\text{Av}} \rho_{\text{SiO2}} d}{6 f_{\text{SiO2}} M_n} \qquad \text{Eq S6-1}$$

where f_{SiO2} is the SiO₂ fraction measured by TGA, N_{Av} is the Avogadro number, ρ_{SiO2} is the density of SiO₂ nanoparticles (2.2 g/cm3), d is the average diameter of SiO₂ nanoparticles (15.8 nm), M_n is the overall number-average MW of the cleaved polymer brushes.

Number-average molecular weights (M_n) and MWDs were determined by size exclusion chromatography (SEC). The SEC was conducted with a Waters 515 pump and Waters 410 differential refractometer using PSS columns (Styrogel 105, 103, 102 Å) in THF as an eluent at 35 °C and at a flow rate of 1 mL min⁻¹. Linear PS and PMMA standards were used for calibration. Conversion was calculated by gravimetric analysis. The fraction of short PMMA and long PS-*b*-PMMA long brushes were calculated by deconvolution of differential refractive index (*d*RI) vs elution volume (V_e), in Origin 9.0 assuming both of the polymer signals follow Gaussian distribution.¹

Example of the deconvolution of PMMA-b-PS SEC traces

1. Intensity vs. Elution time plot

The example PMMA-*b*-PS sample was first characterized by SEC with PMMA standard calibration.

The M_n of PMMA macro-initiator is 133,500, with $M_w/M_n=1.18$ The M_n of PMMA-*b*-PS is 241,800, with $M_w/M_n=2.11$.



Figure S6-2 SEC traces of PMMA-b-PS polymer ligand (intensity vs. elution time)

Raw data was obtained from SEC, intensity vs. elution time graph was plotted as shown in Figure S6-2. A clear bimodal feature was observed.

2. Fitting to obtain different peaks in Origin 9.0



Figure S6-3 Fitting plots of SEC traces by Origin 9.0, black curve: raw data, blue: added fitting curves, red: three different unimodal curves.

It was assumed that all of the polymer signals follow Gaussian distribution. As shown in Figure S6-3, after fitting in Origin 9.0, three curves (red) were obtained. The added curve (blue) has great overlap with the original curve, which suggested the fitting's good accuracy.

3. Fit data into two PMMA and PMMA-b-PS curves



Figure S6-4 Added fitting curve, red: PMMA, green: PMMA-*b*-PS, black: original curve. According to the mechanism reported, the curve 1 in Figure S6-3 corresponds to un-extended PMMA polymer ligands. The green curve in Figure S6-3 is the sum of curve 2 and curve 3 in Figure S6-3, which corresponds to PMMA-*b*-PS.

4. Calculation of the Mn and Mw/Mn of two fitting curves and their chain compositions

Each time in elution time plot corresponds to a molar mass and after calculation in the raw data; the data obtained is summarized in Table S6-1 and shows the Mn and M_w/M_n of two fitting curves and their chain compositions.

Table 50-1 Summary of TwiwiA/1 wiwiA-0-1 S molecular weight and machons							
Entry	PMMA		PMMA-b-PS		fрмма ^с	<i>f</i> _{PMMA-b-PS} ^c	
	$M_{ m n}$	$M_{ m w}/M_{ m n}$	$M_{ m n}$	$M_{ m w}/M_{ m n}$	(%)	(%)	
PMMA-b-PS ^a	145,000	1.22	773,000	1.35	79.6	20.4	
PMMA^b	133,500	1.18			100	0	

Table S6-1 Summary of PMMA/PMMA-b-PS molecular weight and fractions

^a Fitting curve and deconvolution data, ^b Original PMMA-Br marco-initiator data as comparison, ^c mol% fraction of PMMA and PMMA-*b*-PS.

5. Normalization with $d_n/d_c(eff)$

The refractive indexes of PMMA (1.4813) and PS (1.5717) under wave length 1.052 μ m are very different. The dn/dc values used in SEC for PMMA and PS are 0.09 and 0.18, respectively, which leads to different signal intensities in the same curve. Therefore, to achieve more accurate chain composition, normalization to provide d_n/d_c (eff) for PMMA-*b*-PS blocks is necessary.

$$d_n/d_c(eff) = \frac{M_n(PMMA)}{M_n(PMMA-b-PS)} \times d_n/d_c(PMMA) + \frac{M_n(PMMA-b-PS) - M_n(PMMA)}{M_n(PMMA-b-PS)} \times d_n/d_c(PS)$$
Eq S6-2

Equation (S4-2) was used to calculate the d_n/d_c (eff) for PMMA-*b*-PS blocks, in where M_n (PMMA) and M_n (PMMA-*b*-PS) were obtained from Table S4-1. After calculation, we have the d_n/d_c (eff) = 0.163 for PMMA-*b*-PS blocks. In Figure S6-4, the d_n/d_c value for PMMA-*b*-PS was assumed to be the same as PMMA. After normalization with new d_n/d_c (eff), Figure S6-5 was plotted, with new PMMA-*b*-PS in green dash curve, which is much less intense than the previous one. The peak values didn't move, which means the M_n of PMMA-*b*-PS would not change after normalization. The intensity decrease leads to a lower fraction of PMMA-*b*-PS. (Table S6-2)



Figure S6-5 SEC trace after normalization with $d_n/d_c(eff)$ for PMMA-*b*-PS blocks, black: Original curve, red: PMMA curve, green solid: PMMA-*b*-PS curve with $d_n/d_c(PMMA)$, green dash: PMMA-*b*-PS curve with $d_n/d_c(eff)$.

Entry	PMMA		PMMA-b-F	rs –	fPMMA ^c	<i>f</i> PMMA- <i>b</i> -PS ^c
Entry	Mn	<i>M</i> _w / <i>M</i> n	Mn	$M_{\rm w}/M_{\rm n}$	(%)	(%)
PMMA-b-PS ^a	145,000	1.22	773,000	1.35	79.6	20.4
PMMA- <i>b</i> -PS [♭]	145,000	1.22	773,000	1.35	88.6	11.4
PMMA ^c	133,500	1.18			100	0

Table S6-2 Summary of PMMA/PMMA-b-PS molecular weight and fractions after normalization

^a Fitting curve and deconvolution data, ^b Original PMMA-Br macro-initiator data as comparison, ^b PMMA-*b*-PS Mn and fractions after normalization, ^b Original PMMA-Br macro-initiator data as comparison, ^c mol% fraction of PMMA and PMMA-*b*-PS.

As shown in Table S6-2, after normalization, the M_n and M_w/M_n for PMMA-*b*-PS did not change. However, the molar compositions changed significantly. Supplementary data



1000

Figure S6-7 SEC trace of PMMA-M1 and M-b-S-2.

10000

100000 1000000

Molecular weight

1Ė7



Figure S6-9 SEC trace of PMMA-L2 and M-b-S-4





Figure S6-12 SEC trace of PMMA-L3 and M-b-S-7



Figure S6-13 TEM image of SiO₂-*g*-PMMA particle brushes: (a) PMMA-H1, (b) PMMA-M1, (c) PMMA-L1, scale bar: 100 nm.



Figure S6-14 TEM image of SiO₂-*g*-PMMA particle brushes: (a) PMMA-L2, (b) PMMA-L3, scale bar: 100 nm.

Image analysis

A quantitative analysis on TEM micrographs following a systematic processing was conducted. A sequence for the analysis is shading correction – blurring – dilation – erosion – domain mapping. Bandpass filter was applied to correct shading. Gaussian blurring is necessary to reduce detail for better recognition. As next steps, the combination of dilation and erosion was exploited to separate merged (neighboring) domains. Given that unstained TEM images provide 3 distinct contrast levels (dark: silica, intermediate: PS, and bright: PMMA), each domain was mapped by binarization. The results at each step are shown in Figure S6-15–21.



Figure S6-15 Image analysis of M-*b*-S-1 (a) shading-corrected, (b) blurred, (c) dilated, (d) eroded, (e) particle domain recognized, and (f) PS+particle domain recognized images.



Figure S6-16 Image analysis of M-*b*-S-2 (a) shading-corrected, (b) blurred, (c) dilated, (d) eroded, (e) particle domain recognized, and (f) PS+particle domain recognized images.



Figure S6-17 Image analysis of M-*b*-S-3 (a) shading-corrected, (b) blurred, (c) dilated, (d) eroded, (e) particle domain recognized, and (f) PS+particle domain recognized images.



Figure S6-18 Image analysis of M-*b*-S-4 (a) shading-corrected, (b) blurred, (c) dilated, (d) eroded, (e) particle domain recognized, and (f) PS+particle domain recognized images.



Figure S6-19 Image analysis of M-*b*-S-5 (a) shading-corrected, (b) blurred, (c) dilated, (d) eroded, (e) particle domain recognized, and (f) PS+particle domain recognized images.



Figure S6-20 Image analysis of M-*b*-S-6 (a) shading-corrected, (b) blurred, (c) dilated, (d) eroded, (e) particle domain recognized, and (f) PS+particle domain recognized images.


Figure S6-21 Image analysis of M-*b*-S-7 (a) shading-corrected, (b) blurred, (c) dilated, (d) eroded, (e) particle domain recognized, and (f) PS+particle domain recognized images.

Entry	PMMA		PMMA-b-PS		f _{PMMA} ^b	σ1	<i>f</i> _{PMMA-b-PS} ^b	σ ₂ (nm ⁻
	$M_{ m n}$	$M_{ m w}/M_{ m n}$	$M_{ m n}$	$M_{ m w}/M_{ m n}$	(%)	(nm ⁻²) ^a	(%)	²) ^a
M-b-S-1	46,000	1.32	141,000	1.75	68.5	0.417	31.5	0.192
M- <i>b</i> -S-2	50,200	1.35	168,000	1.85	54.9	0.086	45.1	0.070
M-b-S-3	47,900	1.28	395,000	2.02	70.6	0.027	29.4	0.011
M- <i>b</i> -S-4	142,000	1.41	1,150,000	1.85	93.1	0.043	6.9	0.006
M-b-S-5	145,000	1.22	773,000	1.75	88.6	0.035	11.4	0.009
M- <i>b</i> -S-6	36,200	1.34	503,000	1.81	45.2	0.019	54.8	0.023
M-b-S-7	24,100	1.35	121,000	2.04	19.7	0.009	80.3	0.035

Table S6-3 Deconvolution results of SiO₂-g-PMMA/PMMA-b-PS SEC traces

a Calculated according to TGA data, $\sigma = \sigma_1 + \sigma_2$, b mol% fraction.

 Table S6-4 Composition analysis of SiO₂-g-PMMA/PMMA-b-PS particle brushes

Entry	F _{PMMA} (vol%) ^a	F _{PS} (vol%) ^a	F _{SiO2} (vol%) ^a	S _{PMMA} (vol%)b	S _{PS} (vol%) ^b	S _{SiO2} (vol%) ^b
M- <i>b</i> -S-1	46.8	50.8	2.4	29.6	63.6	6.8
M- <i>b</i> -S-2	32.9	59.7	7.2	25.6	65.6	8.8
M-b-S-3	16.8	66.5	16.7	13.4	77.8	8.8
M- <i>b</i> -S-4	50.9	38.1	11	29.1	53.8	17.1
M-b-S-5	48.2	40.9	10.9	38.9	46.0	15.1
M- <i>b</i> -S-6	7.3	80.2	12.5	14.3	74.5	11.2
M- <i>b</i> -S-7	12.9	77.1	10	18.7	70.9	10.4

^a Determined by SEC traces, and calculated by Eq S6-3–S6-8, F_{PMMA} is the volume fraction of PMMA, F_{PS} is the volume fraction of PS, ^b Determined by image analysis from TEM images using a Matlab script, S_{PMMA} is the area fraction of PMMA domain, S_{PS} is the area fraction of PS domain, S_{SiO2} is the area fraction of SiO₂ domain.

 $F_{PMMA}^{**} = \frac{f_{PMMA} \times M_{w,PMMA}}{f_{PMMA} \times M_{w,PMMA} + f_{PMMA-b-PS} \times M_{w,PMMA-b-PS}} + \frac{M_{w,PMMA}}{M_{w,PMMA-b-PS}} \times \frac{f_{PMMA-b-PS} \times M_{w,PMMA-b-PS}}{F_{PMMA} \times M_{w,PMMA} + f_{PMMA-b-PS} \times M_{w,PMMA-b-PS}} = Eq S6-3$ $F_{PMMA}^{*}(vol\%) = \frac{F_{PMMA}^{**}/1.18}{F_{PMMA}^{**}/1.18 + (1-F_{PMMA}^{*})/1.05} \times 100 \quad Eq S6-4$ $F_{PS}^{*}(vol\%) = 100 - F_{PMMA}^{*} \quad Eq S6-5$ $F_{Si02}(vol\%) = f_{Si02}/\rho_{Si02} \quad Eq S6-6$ $F_{PMMA}(vol\%) = F_{PMMA}^{*} \times (100 - F_{Si02})/100 \quad Eq S6-7$ $F_{PS}(vol\%) = 100 - F_{Si02} - F_{PMMA} \quad Eq S6-8$

Eq. S6-3 calculated the weight fraction of PMMA (F_{PMMA}^{**}) in the polymer ligands, which includes the PMMA ligands and the PMMA blocks in the PMMA-*b*-PS ligands. Eq. S6-4 normalized the volume fraction of PMMA with density of bulk PMMA (1.18 g/cm3) and bulk PS (1.05 g/cm³). Eq. S6-7 normalized the volume fraction of PMMA after considering the volume fraction of SiO₂ nanoparticles.

Estimation of the graft number distribution

Understanding statistical characteristics of the grafts is especially critical in sparsely tethered cases because the proportion of (completely or nearly) bare particles is not negligible. Hakem *et al.* successfully derived a model to describe incomplete chemical modification using kinetic analysis.² The statistical expression is applied to estimate the distribution of the number of grafts per particle as follows.

$$v(g) = {g_{max} \choose g} e^{-g_{max}f} (e^f - 1)^g \qquad \text{Eq S6-9}$$

where, g is the number of grafted chains, v is the fraction of particles grafted with g chains, g_{max} is the initial number of reactive sites on a particle (*i.e.*, the maximum number of grafts), and f is the ratio of reacted sites at the time to g_{max} . The maximum grafting density is assumed 1.00 nm⁻², thus g_{max} is approximately 700 since the surface area of a 15 nm (diameter) spherical particle is ~ 700 nm². The ratio of reacted sites to the total sites is 0.01 in the sparse system. Figure S6-22 shows the anticipated distribution of graft number. It is found that 30% of the particle surface is nearly bare (5 chains or less), which leads to structures displaying cluster or string-like structure formation.



Figure S6-22 Plot of particle fraction (number-average) *vs.* number of ligands in SiO₂-*g*-PMMA*b*-PS particle brushes (M-*b*-S-3).

(1)Tung, L. H.; Runyon, J. R., Calibration of instrumental spreading for GPC. Journal of Applied *Polym. Sci.* **1969**, 13 (11), 2397-2409

(2)Hakem, I. F.; Leech, A. M.; Johnson, J. D.; Donahue, S. J.; Walker, J. P.; Bockstaller, M. R., Understanding Ligand Distributions in Modified Particle and Particlelike Systems. *J. Am. Chem. Soc.* **2010**, 132 (46), 16593-16598.