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Structure Properties of Heterophase Hairy-Nanoparticles: Organic vs. Inorganic

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ABSTRACT

CHEMISTRY

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STRUCTURE PROPERTIES OF HETEROPHASE HAIRY-NANOPARTICLES:
ORGANIC VS. INORGANIC

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Dissertation dated July 2015

Substances that consist of nano-scale fillers dispersed in a polymer matrix are known as polymer-nanocomposites (PNCs). These materials are appealing since they have high potentials for applications, due to their mechanical, electrical, and thermo electrical properties. A common problem associated with PNCs is that the nano-fillers have a tendency to aggregate into clusters and form phase separated domains, which cause the desired properties of the system to either diminish or vanish all together. Hairy nanoparticles (HNPs) can avoid the issue of agglomeration that is commonly encountered by conventional PNCs. When polymer chains are grafted to a nanoparticle, and the coverage is high, the nanoparticles have decreased inter-particle interactions which allows for enhanced dispersion and mixing into a polymer matrix. By tailoring the architecture (functionalization of polymer chains, degree of polymerization, grafting density) of HNPs, it is possible to control the final properties of the system. An in depth
study was carried out to investigate the effects of hairy-nanoparticle architecture on the resulting properties of the material itself. Atom transfer radical polymerization and living anionic polymerization were used to synthesize the polymer chains, of the HNP systems, while various instrumental methods including differential scanning calorimetry (DSC) and scanning electron microscopy (SEM) were utilized to study the physical ageing affects and self-assembly of these systems.

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STRUCTURE PROPERTIES OF HETEROPHASE HAIRY-NANOPARTICLES:
ORGANIC VS. INORGANIC

A DISSERTATION
SUBMITTED TO THE FACULTY OF CLARK ATLANTA UNIVERSITY
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THE DEGREE OF DOCTOR OF PHILOSOPHY

BY
VERNECIA NICOLE PERSON

DEPARTMENT OF CHEMISTRY

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CHAPTER I

INTRODUCTION

The combination of new materials rather than their development is what will lift our technology to the next level. With the incorporation of nano-scale materials into composites, the enhanced materials are able to avoid the tradeoffs that restrict the performance of traditional engineering materials.¹

The term composite material comes from the Latin word “compositus” meaning to put together (com “together” + ponere “to place”). It is an intimate combination of two or more materials that differ in composition, structure, and form.¹ A composite is a heterogeneous engineering material with properties that arise from one phase being dispersed within another (reinforcing element/filler dispersed within a matrix/binder). In traditional composites, there are specific interphases that retain the chemical identity of each component without merging into one another. The phases are bonded either mechanically or chemically.¹

In the present time, there is a general reason that composites are used and that reason is financial. The financial aspect relates mainly to profit. If the production of a material results in the improvement of performance or a cheaper delivery of service, that material becomes more attractive and profitable. For example, the most environmentally friendly airliner, the Boeing Dreamliner, uses approximately 32 tons of composites in its construction. Its development was propelled in large part by environmental legislation
trends and increasing fuel prices.\textsuperscript{1} Anything that is mechanical and moves needs energy. The lighter the material, the less energy is needed to move it, and the less money is spent to use it.

Composite materials possess a combination of functions as a result of materials working in concert.\textsuperscript{1} For example, structural concrete consists of steel reinforcement embedded within the concrete matrix. The steel is responsible for mitigating the tension loads experienced by the material, while the concrete itself is responsible for mitigating the compression loads.\textsuperscript{1} The components of the composite act together to perform unique mechanical, chemical, thermal, optical, or electrical tasks, that alone would not be possible. In addition to the properties associated with combining the individual materials, the physical properties of the dispersed component and the matrix depends on the geometry, size, shape, roughness, and orientation of the dispersed component, as well as the nature of the interface between the minority inclusion and the host material.\textsuperscript{1} The same can be said for nanocomposites.

Nanocomposites are composed of a bulk material matrix with a reinforcing phase of one or more nanomaterials.\textsuperscript{2} Since nanoparticles are small, their high surface-to-volume ratio and surface energy, should promote bonding with the matrix material. This enhanced bonding should give the nanocomposite superior performance over composites filled with micrometer-sized materials.\textsuperscript{2}

It is well known that nanotechnology impacts both the inclusion and host materials, but what is it about these materials that makes them the best candidates for inclusion mediums in composites?\textsuperscript{1} What effect do nanomaterials have on the structure-property relationships between the filler and the matrix? Polymer chemistry has taught us
about the relationship between molecular weight, chain length, architecture, fillers, ordering, functional groups, etc. with solubility, rheology, mechanical properties, and chemical behavior; as well as the effects of solvent, size, chemistry, and fabrication conditions.¹ But what happens to polymers when nanomaterials are inserted? How do the various properties (physical, mechanical, and chemical) respond to nanometer inclusions of varying sizes, shapes, compositions, and orientations?¹ To answer these questions, an in depth study of polymer nanocomposites must be undertaken, and in particular, the study of hairy-nanoparticle (HNP) systems. Polymer nanocomposites (PNCs) fall under the category of composites. By definition, they are multicomponent systems in which the major component is a polymer and the minor component is a nanomaterial (with dimensions below 100 nm).³ The reinforcement of polymers with materials such as “short-fibers” is often done to improve mechanical or thermal properties. For example, polyamides are a thermoplastic polymers that can be reinforced with either carbon or glass fibers. Usually the fillers that are incorporated into the material are micron-sized.³ Again, the purpose of the filler is to improve the properties of the material as a whole. The polymer matrix and the filler are usually bonded together by weak intermolecular forces, while chemical bonding is rarely involved.³ If the reinforcing material in the composite can be dispersed in the polymer matrix at a nanometer level, improvements in the desired properties are possible. If the reinforced material interacts with the matrix by chemical bonding, i.e. hairy- nanoparticle, there should be a significant improvement in the properties compared to PNCs with no covalent bonding of polymer chains to their nanoparticle fillers.
1.1 Objective of Study

The purpose of this project is to investigate how the manipulation of the hairy-nanoparticle’s architecture will influence the properties of the resulting materials. This project is broken down into two parts. Part 1 of this dissertation, Hairy-Nanoparticles: General Brush Architecture, focuses on the physical aging studies of HNPs. The systems that are studied consist of silica particles (core) with polystyrene (PS) covalently tethered to the surface. These HNPs were synthesized via atom transfer radical polymerization (ATRP), and characterized using differential scanning calorimetry (DSC), nuclear magnetic resonance (NMR), gel permeation chromatography (GPC), thermal gravimetric analysis (TGA), small-angle X-ray scattering (SAXS), and dynamic light scattering (DLS). Molecular modeling was employed to study the morphology of these systems by simulating Coarse-grained models of polystyrene HNP systems using the MARTINI Force Field.

Part 2 of this dissertation focuses on the self-assembly of organic and inorganic HNP systems. The systems being investigated are microphase separated polymeric hairy nanoparticles (mHNPs) consisting of an organic core (polystyrene cross-linked with divinyl benzene) tethered to polydimethylsiloxane (PDMS); as well as two traditional hairy-nanoparticle systems composed of inorganic cores (silica particles) with either polystyrene or polydimethylsiloxane chains tethered to the surface of the core. These systems were synthesized via living anionic polymerization, and will be characterized using differential scanning calorimetry (DSC), proton nuclear magnetic resonance (\(^1\)H NMR), gel permeation chromatography (GPC), thermo-gravimetric analysis (TGA), and scanning electron microscope (SEM). Molecular modeling will be utilized to study the
self-assembly of the HNP systems. Coarse-grained (CG) models of polystyrene and polydimethylsiloxane HNP systems will be simulated with the use of the Transferable Potentials for Phase Equilibria (TraPPE) and the United-Atom Force Fields.

1.2 Dissertation Outline

This dissertation is focused on studying the physical aging and self-assembly effects of hairy-nanoparticle systems as it relates to their architecture. Chapter 2 introduces hairy-nanoparticles, briefly describing the theory behind their structure and the dynamics of their components. Chapter 3 focuses on computational methods that are used to simulate and study the morphology and self-assembly of the synthesized HNP systems. Chapter 4 describes the experimental methods and characterization techniques used to study each HNP system. Chapters 5 and 6 focus on the results and conclusion of the work done in Chapters 3 and 4.
CHAPTER II
HAIRY-NANOPARTICLES LITERATURE REVIEW

2.1 Hairy-Nanoparticle Systems

For the past three decades there has been an interest in the development of nanoparticle-filled polymer composites. The combination of inorganic nanoparticles and organic polymers can result in a variety of advanced materials with enhanced properties, i.e. thermal, barrier, mechanical, and electrical performance.\textsuperscript{6-10} These properties are strongly dependent on the dispersion characteristics of the nanoparticles in the polymer matrix which brings up the issue of structure control.\textsuperscript{9,12} Homogeneous dispersion requires the need for controlling the mesostructure of the polymer-nanocomposite. Structure control can be achieved through controlled processing techniques like blending conditions, or external stimuli (magnetic and electrical fields during synthesis).\textsuperscript{12,13} The scalability and reliability of these materials would be improved only if the desired structure and dispersion were stable properties that the material already possessed.

To enhance dispersion and mixing of the particles into the polymer matrix, polymer chains are tethered to the nanoparticle surface. The grafting of organic molecules onto inorganic particles was reported by van der Waarden in the early 1950s.\textsuperscript{14-16} Grafting stabilizes the particle in the matrix by creating a compatibilizing layer between the inorganic particle and the organic matrix.\textsuperscript{17,18}
Merging these different materials results in the formation of a “Hairy-Nanoparticle.” A hairy-nanoparticle (HNP), which is shown in Figure 2.1, is a material consisting of a central core tethered to an organic corona (hairs).

![Figure 2.1 Representation of hairy-nanoparticles.](image)

The material has the combined properties of the core (if inorganic: band gaps, dielectric properties, and superparamagnetism) and the mechanical properties that are associated with the organic component. The dispersion characteristics of HNPs have been shown to strongly depend on the architecture of the material (graft density (σ), type of corona (polymer), degree of polymerization of polymer chain (DP), etc.).

To distinguish HNPs from polymer-stabilized colloids (particles that can be dispersed in solvent), star polymers (which lack well-defined interface between the core and corona), and polymeric core-shell particles (cross-linked outer shells), the following criteria must be met:

1. The nanoparticle core dimensions must range between 1 and 100 nm;
2. The core must be either inorganic or macromolecular (rigid), with a well-defined interface between the core and corona;
3. The core must have organic molecules covalently or ionically bonded to the surface (non-cross-linked).

2.1.2 Theory of Structure Behavior: Scaling Models

A major factor that influences the properties of HNP systems is the material’s architecture. The architecture can be manipulated by:

1. Changing the chemistry of the core (metal, semiconductor, cross-linked-core macromolecules, etc.);
2. Adjusting the shape (spheres, rods, disks, etc.) and size of the core;
3. Choosing a specific organic molecule/polymer with:
   a. Specified composition
   b. Certain degree of polymerization (DP)
   c. Nature of grafting (covalent or ionic)
4. Varying the grafting density (σ).

But even with varying these parameters to get specific properties, there must be a conceptual approach to understand and evaluate the structure and interactions of polymer-grafted particle systems. The material that most closely resembles the behavior of a HNP is a star polymer, and the behavior of that material is described by a scaling model for planar brush geometries derived by Alexander and de Gennes, and extended by Daoud and Cotton. The Daoud-Cotton model is an approach used to describe the structure of star polymer systems. It assigns star polymers three conformational regimes that differ in the scaling of the segment density with the radial distance from the star center.
Polymer-grafted particles are categorized depending on the DP and grafting density ($\sigma$) of the surface grafted chains.\textsuperscript{26} At low molecular weights or grafting densities, the radius of gyration of the chains ($R_g$), doesn’t exceed the interchain spacing.\textsuperscript{27} As a result, individual chains do not interact with adjacent chains, and a mushroom-like conformation, shown in Figure 2.2 A\textsuperscript{27}, on the grafting surface is observed.

![Diagram](image)

Figure 2.2  Pictures A-C are schematic representation of the varied conformational behaviors of polymer brushes attached to spherical interfaces.\textsuperscript{27}

In the case of high grafting densities, segmental interactions give rise to extended chain conformations. In this limit the concentrated particle brush (CPB) regime (Figure 2.2 B) is observed.\textsuperscript{22} When there are reduced segmental interactions, more relaxed chain conformations are observed,\textsuperscript{26} and the chain density decreases as a result of the
emergence of the semi-dilute particle brush (SDPB) regime (Figure 2.2 C).\textsuperscript{26} Fukuda et al.\textsuperscript{23-24,28-33} expanded the Daoud-Cotton model to fit particle brush systems. The authors believed that a critical distance ($R_c$) should separate the CPB from the SDPB brush regime. The total particle size ($R_0 + h < R_c$) is assumed for particle brushes in the CPB regime, while ($R_0 + h > R_c$) represents the SDPB regime. The prediction of relaxed chain conformations in the SDPB regime suggests that the mechanical properties of particle brush assemblies can be enhanced if the segment length of the polymer chains, in the SDPB regime, can form chain entanglements.\textsuperscript{34-37} An important extension of the model is the critical radius:

$$R_c = R_0 \left(\sigma^*\right)^{\frac{1}{2}} \left(v^*\right)^{-1} \quad (2.1)$$

where $R_0$ is the radius of the core, $\sigma^*$ is the reduced grafting density, and $v^*$ is the effective excluded volume parameter.\textsuperscript{29} The critical radius determines whether a transition from the CPB regime to the SDPB regime will occur.\textsuperscript{5,23-24,27,29-33} The use of scaling models is based on an assumption that the models can capture structural transitions in particle-brush systems, resulting in an interpretation of the physical properties of the particle brush.\textsuperscript{22}

2.1.3 Assemblies of HNPs

Large and stable assemblies of HNPs can be held together in one of three ways; through van der Waals interactions on the outer surface of the corona, chemical interactions between functional groups of the polymer chain ends, or through a physical entanglement of the organic corona.\textsuperscript{5,38} When the corona possesses a length that will not allow a transition from the fully stretched CPB regime, the resulting material will be an
assembly of hard spheres that are brittle due to weak dispersion interactions of neighboring HNPs.\textsuperscript{5}

The reinforcement of mechanical properties via corona entanglement was reported by P. Akcora et al.\textsuperscript{39,40} and M. E. McEwan et al.\textsuperscript{41} In their work, poly(methylmethacrylate) grafted silica particles in a free-chain matrix proved that mechanical reinforcement can occur as a result of corona bridging from neighboring particles.\textsuperscript{39-41} This bridging usually occurs when the polymer chains of the corona are in the SPDB regime. The entangled brushes on neighboring particles can enhance the toughness and fracture resistance of HNP assemblies by dissipating the fracture energy through craze formation and plastic deformation.\textsuperscript{22} J. Choi et al.\textsuperscript{22} used the scaling laws described by Daoud and Cotton to develop an expression for determining the minimum degree of polymerization needed to create toughened arrays. For particle films having a brush length, \( N \), greater than \( N_{\min} \) (\( N_{\min} = 600 \), brush length for PS and PMMA brushes on 8 nm radius particles), the hardness and modulus of the materials resemble those of linear polymer chains. The value of those properties doubles with particles having shorter brushes.\textsuperscript{5,22} The authors of reference 22 showed that fracture toughness increases by \(~300\%\) as the systems become highly entangled. This is due to the particles forming network points in the polymer structures.\textsuperscript{22} Equation 2.2 is presented as a design guide to create toughened arrays of nanoparticles:

\[
N_{\min} = 2N_{c} + [a^{-1}(R_{c} - R_{0})]^{1/x}
\] (2.2)

where \( R_{c} \) is the radius at which the brush transitions from the CPB to the SDPB regime, \( x \) is the scaling parameter for the concentrated region, \( N_{c} \) is the entanglement length of the polymer, and \( a \) is the segment length of the polymer.\textsuperscript{22} Because \( R_{0} \) and \( R_{c} \) can be
manipulated, the rest of the variables depend on the choice of polymer used for the corona.

An alternative to corona entanglement, for the toughening of HNP assemblies is the reversible or irreversible chemical interaction of the corona/polymer hairs. P. Agarwal et al.\textsuperscript{41} reported the synthesis of a shape memory material via the linking of HNP hairs on adjacent particles with covalent bonds. In this study, low molecular weight polyethyleneglycol (PEG), having a molecular weight of 5 kDa, was tethered onto silica particles. The hydroxyl functional groups of the PEG brushes were cross-linked using hexamethylene diisocyanate to form bridges between nanoparticle net-points. The resulting material exhibited the shape memory effect, even after it was deformed on heating.\textsuperscript{41}

2.1.4 Dynamics of HNPs

The spectrum of relaxation modes for polymer chains in HNP systems will depend on the molecular weight and grafting density of the tethered chains, as well as the distance of the chains from the core surface.\textsuperscript{5} If the ratio of core-to-corona volume is varied, a range of changes in the thermo-mechanical responses including the glass transition temperature ($T_g$), melt extensibility, tenacity, and physical aging should be realized.

D. A. Savin et al.\textsuperscript{25} studied the molecular weight dependence of glass transition temperature ($T_g$) on the corona of HNPs with high grafting density, compared with the molecular weight dependence of the $T_g$ of free polymer chains. They found that the $T_g$ of the corona is higher than that of the free polymer.\textsuperscript{25} The $T_g$ of a polymer is related to its freedom to relax. Shorter chains and higher grafting densities should result in stretched
and constrained chains (majority of chains in the CPB regime) that are unable to relax, thereby increasing the $T_g$. When the molecular weight is increased, the proportion of the chain in the semi-dilute (SDPB) regime increases, and the $T_g$ approaches that of the free polymer.$^{25}$

At lower grafting densities, the particle-particle interactions that are responsible for the packing frustration of freely jointed chains at a curved surface can lead to an increase or decrease in the glass transition of the HNP. The frustration of chain packing, as described by W. A. MacDonald,$^{42}$ refers to “any mechanism which while maintaining essential linearity and chain stiffness makes close and regular correlation into a 3D lattice difficult.$^{42}$” H. Y. Yu and D. L. Koch$^{43}$ studied the packing frustration found in HNP systems due to interstitial spaces. In this study, it was seen that the thermal cleavage of the tethering points can restore the $T_g$ to that of the bulk polymer. This suggests that suppression is a result of excess free volume that arises from frustrated packing. This frustrated packing was found to impact collective relaxation modes such as physical ageing.$^{43}$

### 2.2 Silica Nanoparticles and Their Surface Modifications

Among the many organic-inorganic hybrid materials, silica-polymer hybrid materials are the most studied and reported in literature.$^{49}$ This is due to the fact that silica can be easily synthesized, while its size and distribution can be precisely controlled.$^{49}$

Stöber et al.$^{50}$ reported the synthesis of monodisperse spherical particles, which proceeds with the hydrolysis and condensation of tetraethylorthosilicate (TEOS) in a mixture of alcohol, water, and ammonia (catalyst).$^{49,50}$ Scheme 2.1$^{49}$ shows a hydrolysis
reaction, which generally gives a singly hydrolyzed TEOS monomer. The hydrolyzed intermediate, shown in Scheme 2.2, then undergoes condensation to form silica.

\[
\text{Si(OR)}_4 + \text{H}_2\text{O} \rightarrow (\text{RO})_3\text{Si(OH)} + \text{ROH}
\]

\[
(\text{RO})_3\text{Si(OH)} + \text{H}_2\text{O} \rightarrow \text{SiO}_2 + 3\text{ROH}
\]

Scheme 2.1 Synthesis of Stöber spherical silica particles.

The resultant particles are stabilized by electrostatic repulsion due to the ions in the ammonia solution (Scheme 2.2).

\[
\text{Si(OHC}_2\text{CH}_3)_4 \text{TEOS} \xrightarrow{\text{NH}_3, \text{H}_2\text{O, CH}_3\text{CH}_2\text{OH}} \text{Silica}
\]

Scheme 2.2 Stabilization of the silica particles.

The chemical properties of the surface of the silica particles are determined by the types of silanol and siloxane groups that are present on the external structure of the particle. The hydroxyl groups that are located on the surface of the silica particles can be tailored with organic compounds or polymers. The most convenient technique for silica surface functionalization is shown in Scheme 2.3, via the reaction of silanol groups with suitable silane reagents.
Once the particles are functionalized, organic compounds/polymers can be attached to those functional groups by a method called grafting. This grafting can occur chemically (covalent bonding) or physically (physisorption).

Physisorption refers to the absorption of block copolymers with stick segments. The non-covalent adsorption makes the adsorption reversible especially during processing, and so, it is not a favorable technique. Chemical grafting techniques are preferred to enhance interfacial compatibility between two phases. Covalent grafting can occur by one of two methods, “grafting to” or “grafting from”.

The grafting to, shown in Figure 2.3, involves the reaction of preformed macromolecules with compatible surface groups. An advantage to using this method is that polymer chains can be characterized before being attached to the substrate.

![Scheme 2.3 Surface modification of silica nanoparticles.](image)

![Figure 2.3 Grafting to approach on the surface of the nanoparticle.](image)
The grafting from approach, Figure 2.4,\textsuperscript{49,52} is a process that involves the surface of the particle being modified with an initiator monolayer followed by the synthesis of the polymer chain.\textsuperscript{49,52}

The synthesis of the polymer chains used in both of these methods, grafting to and grafting from, can be accomplished by various polymerization methods such as free radical and ionic polymerization.\textsuperscript{49}

2.2.1 Surface Modifications of Silica Particles via Synthetic Methods

2.2.1.2 Conventional Radical Polymerization Methods

Free radical polymerization is the most common method for the synthesis of polymer chains used in polymer nanocomposites.\textsuperscript{49,53} Prucker and Rühle\textsuperscript{54} reported the use of free radical polymerization techniques to aid in the grafting from approach for the preparation of covalently attached polymers. This approach consists of grafting an azo (RN=NR’) initiator onto a particle or flat surface followed by polymerization.\textsuperscript{49} Figure 2.4 A shows a self-assembled monolayer (SAM), having an azo initiator, is grafted to the surface of the silica particle and is used for the radical chain.
polymerization of styrene (Scheme 2.4 B).\textsuperscript{49,54,55}

Scheme 2.4  Reaction scheme for the synthesis of covalently attached polystyrene on silica using surface-immobilized azo initiators.

These authors of references 49, 54, and 55 successfully produced high molecular weight polymer brushes with high grafting densities. Their kinetic investigations of their synthetic process revealed that the initiation and propagation of the polymer at low conversion was similar to that of solution polymerization.\textsuperscript{49,54,55}

Ueda et al.\textsuperscript{55} investigated the radical polymerization of vinyl monomers onto the surface of silica particles employing two different methods.\textsuperscript{49,55} In the first method, the azo group is introduced to the particle by the reaction of surface amino groups via the pretreatment of 3-aminopropyl-trioethoxysilane with 4,4’-azobis(4-cyanopentanoyl chloride).\textsuperscript{49,55} In the second method, surface immobilization was achieved by the reaction of surface amino groups; which were introduced by pretreatment of 3-aminopropyltrioethoxysilane with t-butyl-peroxy-2-methacryloxyethylcarbonate.\textsuperscript{49,55} The
silica nanoparticles coated with an azo initiator (Figure 2.5 A) and peroxy initiator (Figure 2.5 B) were prepared separately, and the radical chain polymerization was initiated by thermal decomposition. The authors of reference 16 reported a grafting density of 90% and the formation of un-grafted polymer was considerably reduced.\textsuperscript{49,55}

![Silica-Azo](image)

**(A) Silica-Azo**

![Silica-Peroxy](image)

**(B) Silica-Peroxy**

Figure 2.5  Silica nanoparticles functionalized with free radical initiators.\textsuperscript{55}

Propagation in traditional free radical polymerizations are pseudo first order reactions, while termination is second order in chain end radical concentration.\textsuperscript{57} The proportion of termination to propagation increases with increasing free radical concentrations.\textsuperscript{57} Because chain transfer and termination are impossible to control in this type of polymerization, this method is usually characterized by broad molecular weight distributions, poor control of molecular weight, and chain end functionality, and the inability to synthesize well defined block copolymers.\textsuperscript{57} Most of these issues can be overcome by using controlled free radical polymerization.\textsuperscript{49,57}
2.2.1.3 Controlled Radical Polymerization Techniques

Controlled radical polymerization has been used as an approach to incorporate different types of organic polymers with different architectures onto the surface of silica particles.\textsuperscript{49,58} Controlled Radical Polymerization techniques are preferred to traditional techniques for two reasons.\textsuperscript{59} First, the solid surface that the initiating groups are attached to place a mobility barrier for termination by coupling.\textsuperscript{59} Second, because there are a limited number of initiating groups that need to be attached to the surface to promote property changes, the concentration of free radicals present in the system should be reduced.\textsuperscript{59} When this technique is used, the initiator generates radicals that combine with monomer molecules to form polymer chains. In Figure 2.6\textsuperscript{59}, the radicals on the ends of the polymer chains are reversibly deactivated by the presence of capping groups.\textsuperscript{59}

![Diagram of reversible chain transfer in controlled free radical polymerization.](attachment:image.png)

Figure 2.6  Reversible chain transfer in controlled free radical polymerization.\textsuperscript{59}

The reaction of a radical polymer chain with a capping group eliminates the radical, temporarily stopping polymerization.\textsuperscript{59} The removal of the capping group allows the propagation to continue.\textsuperscript{59} The lifetime of the growing radical is controlled, resulting in the synthesis of polymers with predetermined molecular weights, low polydispersity indexes (PDI), and functionality.\textsuperscript{49,59} When this approach is used, the structure of the
polymer shell can be manipulated via changes in the grafting density and molar mass.\textsuperscript{49,59}

This type of polymerization can be achieved using techniques such as atom transfer radical polymerization (ATRP) and reversible addition fragmentation chain transfer (RAFT).\textsuperscript{49,59}

### 2.2.1.4 Atom Transfer Radical Polymerization (ATRP)

Atom transfer radical polymerization is an extension of the Kharasch addition reaction, which is also known as the atom transfer radical addition (ATRA).\textsuperscript{49,62} It’s a metal catalyzed polymerization (Scheme 2.5) that involves the reversible activation-deactivation reaction that occurs between the growing polymer chain, and the metal-ligand species.\textsuperscript{49}

\[
P-X + Cu(I)_{m} \xrightleftharpoons[k_{\text{dea}}]{k_{\text{act}}} P + X-Cu(II)_{m} + M \\
\xrightarrow[k_{p}]{k_{p}} P-P
\]

**Scheme 2.5** Metal catalyzed atom transfer radical polymerization.\textsuperscript{49}

The initiator in this synthetic method, either an ester or benzyl moiety, is activated in the presence of metals such as Cu, Ru, Fe, etc.,\textsuperscript{49,34,53,63} while the solubility and activity of the metal is enhanced by its complexation with aliphatic or aromatic amines.\textsuperscript{49,34,53,63} This method is very tolerant of impurities and functional groups, so a number of monomers can be polymerized with different architectures and morphologies in organic as well as aqueous phases.\textsuperscript{49,34,53,63}

The functionalization of silica nanoparticles with polymer brushes using ATRP was reported by Patten, et al.\textsuperscript{49,63} The approach taken to functionalize the particles
consisted of immobilizing the initiator molecule on the silica particle followed by the surface initiation via ATRP (Scheme 2.6).

Scheme 2.6  Synthesis of polymer grafted silica by ATRP.$^{63}$

Shown in Figure 2.7$^{49,64,65}$, (2-(4-Chloromethylphenyl)dimethyloxysilane (CPTS), (3-(2-bromoisobutryl)propyl)dimethylethoxysilane (BPDS), and (3-(2-bromopropionyl)propyl)dimethylethoxysilane (BIDS) were used for the immobilization of the initiator on the silica surface.$^{49,64,65}$

![Chemical structures of initiators](image)

Figure 2.7  Structure of mono-siloxane initiators used for immobilization on the surface of silica particles.$^{64,65}$

After the silica was grafted with the initiator, the polymerization of styrene or methyl methacrylate (MMA) onto the particle was carried out.$^{64,65}$ The authors reported that the experimental number average molecular weight ($M_n$) was higher than that of the theoretical $M_n$. This discrepancy was attributed to an initiator efficiency of less than 100%.$^{64,65}$ The authors were able to show that the polymerization from small particles (~75 nm) exhibited a higher degree of control, while those of larger particles (~300 nm) had the opposite effect.$^{64,65}$ Their study also showed that larger particles with smaller
quantities of initiation sites resembled the kinetic and molecular weight evolution similar to those of flat substrates.\textsuperscript{64,65}

Another example of surface modification via ATRP was demonstrated by El Harrak et al.\textsuperscript{67} In this paper, surface initiated ATRP was used to control the interparticle aggregation of nanoparticles by grafting polystyrene chains onto particles.\textsuperscript{67} The silica particles were maintained in an organic suspension during surface modification. This is important because irreversible aggregation is often observed if the particles are redispersed after solvent removal. J. Pyun et al.\textsuperscript{66} reported similar work to Patten et al.\textsuperscript{64,65} where Cu(II)Br\textsubscript{2} was used as the deactivating transition metal.\textsuperscript{49} Styrene, n-butyl acrylate and methyl methacrylate (MMA) monomers were incorporated in this study, and various core-shell colloids containing tethered AB di-block copolymers were synthesized.

### 2.2.1.5 Reversible Addition-Fragmentation Chain Transfer (RAFT)

RAFT polymerization is a reversible deactivation radical polymerization that makes use of chain transfer agents in the form of thiocarbonylthio compounds to control the molecular weight and polydispersity during a free-radical polymerization. The mechanism for this synthetic method is shown in Schemes 2.7 (A – E).\textsuperscript{49,28} After initiation, the propagating radical (P\textsubscript{n}·) is added to a dithiocarbonyl compound, followed by the selective fragmentation of the intermediate radical.\textsuperscript{10,68}

\[
\text{Initiator} \quad \longrightarrow \quad \text{I} \quad \xrightarrow{M} \quad M \quad \xrightarrow{M} \quad P_{n}·
\]

Scheme 2.7(A)  Initiation and propagation steps of RAFT Polymerization.\textsuperscript{68}
This results in a polymeric thiocarbonylthio compound and a new radical ($R^\cdot$).\textsuperscript{49,68} The reaction of the radical ($R^\cdot$) with a monomer forms a new propagating radical ($P_{m^\cdot}$).

\[
P_n + S_{Z} \xrightarrow{k_{add}} P_n + S_{Z} \xrightarrow{k_{th}} P_m + R
\]

Scheme 2.7(B)  Reversible Chain Transfer step of RAFT polymerization.\textsuperscript{68}

The equilibrium between the active propagating radicals ($P_n^\cdot$ and $P_m^\cdot$) and the dormant polymeric thiocarbonylthio compounds provides an equal probability for all chains to grow; allowing for the production of polymers with narrow polydispersities.\textsuperscript{49,68}

\[
R^\cdot + R-M \xrightarrow{k_1} R-M^\cdot \xrightarrow{M} P_m^\cdot
\]

Scheme 2.7(C)  Reinitiating step for RAFT polymerization.\textsuperscript{28}

\[
P_m^\cdot + P_n \xrightarrow{k_p} P_n \xrightarrow{P_m^\cdot} P_m \xrightarrow{P_m^\cdot + P_m^\cdot} + P_m^\cdot
\]

Scheme 2.7(D)  Chain equilibration and propagation steps for RAFT polymerization.\textsuperscript{68}

\[
P_n^\cdot + P_m^\cdot \xrightarrow{k_t} \text{Dead Polymer}
\]

Scheme 2.7(E)  Termination step for RAFT polymerization.\textsuperscript{68}
The use of RAFT polymerization affords a number of advantages compared to ATRP which include, (a) the ability to carry out the synthesis under a wide range of conditions (bulk, solution, suspension, emulsion),\(^6^8\) (b) the formation of polymers with narrow molecular weight distributions,\(^6^8\) (c) the applicability to wide range of functionality in monomer types (-OH, -COOH, -CONR\(_2\), -NR\(_2\), -SO\(_3\)Na),\(^6^8\) and (d) with the majority of the chains in the product polymer possessing the S=C(Z)S- group, the polymerization can be continued in the presence of a second monomer resulting in a block copolymer.\(^6^8\)

The use of RAFT polymerization to grow polystyrene brushes on silica was first reported by Tsuji et al.\(^4^9,7^0\) In their work, an ATRP initiator was used as an anchor on the silica particle, and the polystyrene brushes were initially grown onto them.\(^4^9,7^0\) 1-phenylethyldithiobenzoate was reacted with the CuBr-4,4'-di-n-heptyl-2,2'-bipyridine (dHbipy) complex to convert the halogen end group from ATRP polymerization into a dithiobenzyl group for a RAFT technique reagent.\(^4^9,7^0\) The resulting silica particle (anchored PS-RAFT agent) was used to polymerize styrene in bulk in the presence of added free RAFT agent to effectively control polymerization.\(^4^9,7^0\)

C. Li and B. C. Benicewicz\(^4^9,7^1\) reported the use of the direct synthesis of brushes onto silica nanoparticles using a RAFT-silane coupling agent (Figure 2.8).

![RAFT-Silane coupling agent](image)

**Figure 2.8** RAFT-Silane coupling agent.\(^7^1\)
With the use of the RAFT agent, grafting densities with a range of 0.15-68 chains/nm² was reported upon the immobilization of the RAFT-silane coupling agent on the silica particle. The polymerization was then carried out at low conversions to avoid gelation or interparticle radical coupling.

2.2.2 Ionic Polymerization Methods

2.2.2.1 Anionic Polymerization

Anionic polymerization is a type of chain growth polymerization that involves the polymerization of vinyl monomers containing strongly electronegative groups. This synthetic method occurs in three steps: chain initiation, chain propagation, and chain termination, with propagation occurring by the repeated attack of a carbanion on a monomer. Living polymerizations can occur in anionic polymerizations if there are no formal termination pathways, allowing for this technique to be used as a powerful tool for preparing well-defined architectures with control over structure and composition.

The use of anionic polymerization in the grafting of polystyrene and poly styrene-b-polyisoprene (PI) to silica particles was reported by Oosterling et al. The synthesis was initiated by t-butyllithium, which was used to immobilize a double bond on the silica surface, by reacting vinyl benzyl trichlorosilane with silica nanoparticles. According to the authors, there was not much control in the synthesis of these materials. It is believed that the high molecular weights and molecular weight distribution were due to slow and inefficient initiation with t-BuLi.

Q. Zhou et al. reported use anionic polymerization in the controlled synthesis of polystyrene from silica nanoparticles. The initiator used was 1,1-diphenylethylene
(DPE).\textsuperscript{74} It was covalently functionalized onto a silica particle, with the polystyrene brushes synthesized from the initiator-silica particles using n-BuLi in benzene.\textsuperscript{74}

2.2.2.2 Cationic Polymerization

Cationic polymerization is a form a chain growth polymerization that occurs when a cationic initiator transfers charge to a monomer making it reactive.\textsuperscript{72} The reactive monomer species reacts in a similar manner with other monomers to form a polymer chain.\textsuperscript{72} The types of monomers used in cationic polymerizations are usually olefins with electron-donating substituents and heterocyclic compounds.\textsuperscript{72} This method can be used as a tool to bind polymeric chains onto nanoparticles with a controlled chain length and grafting density of the attached polymer brushes. There are limited reports on the use of cationic polymerization to synthesize polymer brushes, but the grafting of silica particles with polyisobutylene (PIB) has beneficial chemical and physical properties.\textsuperscript{72}

R. Zirbs et al.\textsuperscript{75} studied the grafting-from approach of isobutylene from silica nanoparticles (Scheme 2.8).

![Scheme 2.8](image)

Scheme 2.8 Modification of silica surface with polyisobutylene.\textsuperscript{75}

Living cationic polymerization was used to grow polymer chains onto the silica nanoparticles.\textsuperscript{75} The surface of the silica particle was silanized with the initiator chloro[2-[3-(2—chloropropane-2-yl)phenyl]}dimethylsilane; the polymerization of
isobutylene was catalyzed by titanium tetrachloride and di-t-butylpyridine (DTBP).\textsuperscript{75} Modified nanoparticles with well-defined PIB-polymeric shell were synthesized.\textsuperscript{75}

2.3 Modified Silica Nanoparticle and Their Applications

Control of particle aggregation is key to dispersing silica particles into various polymer matrices. As mentioned above, a method for preventing the aggregation of particles and producing sterically stabilized PNCs is to graft polymer chains to the nanomaterial’s surface. The grafted polymer chains control the aggregation of the neighboring nanomaterials via steric repulsions. The controlled aggregation leads to an improvement in mechanical properties in polymer-composites.\textsuperscript{77}

The brushes of molecularly imprinted polymers on silica particles can be used for chromatographic supports,\textsuperscript{78} as well as stationary phases for separation of triazinic herbicides. S. Blomber et al.\textsuperscript{76} reported the synthesis of hollow polymeric nanocapsules using silica nanoparticles. These materials can be used for the encapsulation of active substances such as drugs and dyes. Polymer-silica composites can be used for environmental pollution control processes, as was reported by T. Meyer et al.\textsuperscript{79} In this work, the use polymer-silica composites for the removal of heavy metal ions (cobalt and copper salts) from waste water. Because the silica particles have a well-defined pore size, pore shape, and large surface area, the specific binding sites of the polymer helped with the removal of these metals.
CHAPTER III
COMPUTATIONAL MODELS AND METHODS

3.1 Introduction: Molecular Dynamics

The optimization of polymer properties used in industrial applications can be achieved by controlling the details of their chemical composition. Generally this is achieved via expensive and time-consuming trial-and-error procedures. To speed up this process, computer methods, that predict changes in the material properties as a function of chemical composition, can be used.

Molecular dynamics is a computational method in which the dynamic and structural behavior of matter is simulated by using discrete representations of particles, interacting with each other. The basis of molecular dynamics is the force calculation, which is followed by the integration of the equations of motion. The forces that are involved in this method are the non-bonded interactions (electrostatic and van der Waals interactions), which act between dynamically formed pairs of particles; as well as bonded interactions (bond, bond angle bending, and dihedral angle interactions), which model the chemical bonds in a molecule. These interactions are extremely crucial in procuring a model that can predict molecular structure and macroscopic behavior.

3.1.2 Coarse-Grained Models

Despite the ever-growing computational resources, the simulations of polymer
Melts from atomistic models are subject to limitations that are associated with both the time and length scales of the phenomena that can be observed. For example, the simulation of the mechanical responses of polymeric materials requires simulations of tens or hundreds of microseconds, and a length scale of tens of nanometers, currently not accessible with fully atomistic descriptions. To overcome these limitations, coarse-graining strategies can be used.

When a polymeric structure is coarse-grained, the atoms are clustered together into super-atoms or beads, thereby reducing the total number of particles in the system. Since there is a reduction in the number of degrees of freedom and a use of smoother interaction potentials, coarse-grained (CG) models are computationally faster than atomistic ones, and they allow for longer time steps in molecular dynamics (MD) simulations. These chemically non-specific coarse-grained models of polymer chains are extremely useful in improving the understanding of the general features of the polymer structure and its dynamics. These freely jointed, bead-spring, and self-avoiding model chains don’t contain information on the specific chemistry of the polymer, so these generic models can’t be used to investigate the difference in material properties of different polymers.

In the last decade, there has been a need to develop coarse-grained models with chemical specificity; that will be used to capture some of the properties of polymer systems (specific chemical composition) without studying the molecules in detail at the atomic level. Most of the research that has been done on the development of specific coarse-grained models have focused on polymer chains such as polycarbonates, polystyrene, and polyamides.
A number of methodologies have been used to develop coarse-grained models for chemical specificity. For example, structure-based coarse-grained models have interaction parameters, derived from all-atom MD simulations. These parameters are tuned to accurately reproduce structural features of the systems, such as the radial distribution functions, but they suffer from some limitations. First, the transferability of the interaction parameters to different temperatures is generally poor. In the case of molecules such as ethylbenzene, the temperature dependence of the structure-based coarse-grained potential can be corrected, but this isn’t the case for most polymers. Second, structure-based models of polymer systems require additional parameterization if they are to be used in combination with solvents or other polymer species.

When comparing structured-based coarse-grained models to thermodynamics based models, the latter depends on an alternate coarse-graining strategy. If the thermodynamics based approach is used, the interaction parameters are chosen to reproduce the selected thermodynamic properties of the system, with only a few structural properties of the system. This approach is often used to simulate biological environments, and amphiphilic molecules. For example, S. Nielsen et al. developed a coarse-grained model for n-alkanes based on the reproduction of experimental bulk density and surface tension. This model was later adapted to combine a structure-based coarse-grained description of hydrophilic groups, which resulted in a model of amphiphilic molecules such as dimyristoyl-phosphatidylcholine and diblock copolymer, poly(ethyleneoxide)-poly(ethylethylene).
3.2 MARTINI Force Field

The MARTINI force field can be thought of as another form of thermodynamics based coarse-grained models. The name “MARTINI” force field was coined in 2007 with the release of version 2.0. It is nicknamed after a city called Groningen, which is located in the Netherlands. It is in this city where the force field was developed, and continues to be improved to this day. The name also reflects the universality of the cocktail with the same name, in which a few ingredients, or chemical building blocks, can be endlessly varied to create a complex palette of taste.

In this approach, the interaction parameters are determined by regenerating densities and free energies of partitioning. There are several advantages to using the MARTINI approach: (1) it offers the possibility to build-up coarse-grained models for a large selection of molecules, since MARTINI has already been parameterized for a large number of chemical-building blocks; (2) parameterization of non-bonded (excluded volume and inter-molecular) interactions targets experimental data; and (3) the non-bonded interactions are modeled by simple Lennard-Jones and Coulomb functions, making the parameterizations of the new building blocks a simple task. The MARTINI force field approach does not generally take into account structural input during the parameterization stage. This very important fact can cause this approach to fail when trying to reproduce specific structural characteristics of polymer systems. To overcome this particular limitation of both structure-based and thermodynamics-based models, it is suggested to use a “hybrid approach,” in which the properties of both models are used as a target during parameterization.
3.3 Morphology Studies of Polystyrene Hairy-Nanoparticle Systems

The design of interface or surface-active polymer modifiers lacks crucial molecular scale information about the behavior and structure-property relationships of brushes that are grafted onto the surface of substrates. Polymeric systems are innately multi-scale problems that mandate the use of adapted molecular models. Studies in atomistic detail are known, but they focus on short oligomer like chains or low grafting densities; as well as polymer brushes simulated in the form of bead-spring type models, where the chemical specificity is lost. These types of models are valuable for understanding general dependencies on grafting density or chain length, but in order to directly compare them to experimental data, more specific models are needed. To gain a theoretical understanding of the hairy-nanoparticle at the molecular lever, the MARTINI force field was used to simulate CG models of the PNCs.

3.3.1 Development of Polystyrene MARTINI GC Models

The simulated polystyrene hairy-nanoparticles are described by means of the MARTINI-based coarse-grained model that was developed and validated by G. Rossi et al. Figure 3.1 is a representation of how the atomistic description of polystyrene is mapped into a description that is coarse-grained.
Each monomer unit is expressed in the form of four coarse-grained beads, representing two carbon atoms and their hydrogen atoms. This degree of coarse-graining allows for retaining the backbone-ring structure of the polystyrene chain. It’s also consistent with the 2-to-1 mapping scheme of the MARTINI force field.

### 3.3.2 Bonded Interactions

The bonds between the coarse-grained beads are described by harmonic functions. The equilibrium values and force constants are tuned to reproduce the peak position and width of their aromatic counterparts. These models don’t include any torsional angles at the coarse-grained level. The parameters that are used for the harmonic bonded interactions for the HNP systems are given in Table 3.1.

| Bond  | r<sub>eq</sub> (nm) | k<sub>b</sub> (kJ/mol nm)<sup>2</sup> | angle | θ<sub>eq</sub> (deg) | k<sub>a</sub> (kJ/mol deg)<sup>2</sup>
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<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>R-R</td>
<td>0.27</td>
<td>constr</td>
<td>R-B-R</td>
<td>120</td>
<td>25</td>
</tr>
<tr>
<td>B-R-R</td>
<td>136</td>
<td>100</td>
<td>B-R-R</td>
<td>8000</td>
<td>52</td>
</tr>
</tbody>
</table>

,B and R indicate backbone and ring beads. r<sub>eq</sub> (nm) and k<sub>b</sub> (kJ/mol nm)<sup>2</sup> are the equilibrium bond length and the elastic constant of the harmonic bond potential. Very narrow distributions lead to R-R bonds. θ<sub>eq</sub> (deg) and k<sub>a</sub> (kJ/mol deg)<sup>2</sup> are the equilibrium angle and the elastic constant of the harmonic angle potentials.
3.3.3 Non-Bonded Interactions

The non-bonded interactions between the non-charged beads are described by Lennard-Jones potentials. The MARTINI force field includes a large number of beads, with each bead describing a chemical building block, characterized by a specific degree of polarity. The Lennard-Jones interactions of MARTINI beads are allocated to reproduce experimental thermodynamic data, such as densities and free energies of transfer between water and oil. While G. Rossi et al. use parameterizations that are aimed at the reproduction of the density and radius of gyration of polystyrene in the melt, the parameterizations in this study incorporate the inter-particle distance (IPD) of the HNP systems as they are being equilibrated. The optimized values for the σ and ε parameters of the Lennard-Jones interactions (backbone-backbone (B-B), backbone-ring (B-R) and ring-ring (R-R) interactions) are given in Table 3.2.

Table 3.2 Optimized Values of ε and σ Lennard-Jones parameters for the CG MARTINI PS Model.

<table>
<thead>
<tr>
<th>parameter</th>
<th>σ_{B-B}</th>
<th>ε_{B-B}</th>
<th>σ_{B-R}</th>
<th>ε_{B-R}</th>
<th>σ_{R-R}</th>
<th>ε_{R-R}</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS model</td>
<td>0.43</td>
<td>2.625</td>
<td>0.43</td>
<td>2.325</td>
<td>0.41</td>
<td>2.4</td>
</tr>
</tbody>
</table>

3.3.4 Construction of Polystyrene HNPs and Simulation Cells

A total of nine hairy-nanoparticles systems with three molecular weights, ranging from 20k to 100k, were constructed using Material Studio 7.0 software. As shown in Table 3.3, each HNP system has one of three grafting densities, a certain number of chains per particle, a specific number of monomers per chain, as well as a certain number of beads in each system.
Table 3.3  Simulated PS HNP Systems.

<table>
<thead>
<tr>
<th>MW</th>
<th>Graft Density (chains/nm)^2</th>
<th>Chains/particle</th>
<th>Mers/Chain</th>
<th>Beads/system</th>
</tr>
</thead>
<tbody>
<tr>
<td>20 k</td>
<td>0.01</td>
<td>20</td>
<td>200</td>
<td>64,000</td>
</tr>
<tr>
<td></td>
<td>0.05</td>
<td>100</td>
<td></td>
<td>320,000</td>
</tr>
<tr>
<td></td>
<td>0.10</td>
<td>200</td>
<td></td>
<td>640,000</td>
</tr>
<tr>
<td>60 k</td>
<td>0.01</td>
<td>20</td>
<td>600</td>
<td>192,000</td>
</tr>
<tr>
<td></td>
<td>0.05</td>
<td>100</td>
<td></td>
<td>960,000</td>
</tr>
<tr>
<td></td>
<td>0.10</td>
<td>200</td>
<td></td>
<td>1,920,000</td>
</tr>
<tr>
<td>100 k</td>
<td>0.01</td>
<td>20</td>
<td>1000</td>
<td>320,000</td>
</tr>
<tr>
<td></td>
<td>0.05</td>
<td>100</td>
<td></td>
<td>1,600,000</td>
</tr>
<tr>
<td></td>
<td>0.10</td>
<td>200</td>
<td></td>
<td>3,200,000</td>
</tr>
</tbody>
</table>

After the polymer chains are constructed, they are inserted into a simulation cell along with four beads, representing the silica nanoparticles (Figure 3.2).

Figure 3.2  Simulation Cell containing HNP systems before densification.
Figure 3.3  Simulation Cell containing HNP systems after densification.

Using NPT dynamics (isothermal–isobaric ensemble), the simulation cell is densified (Figure 3.3) at a temperature of 500K and a pressure of 1 atm.
The systems are then equilibrated until the correct inter-particle distance for that particular system is obtained (Figures 3.4, 3.5, 3.6, and 3.7).

Figure 3.4 20 k PS HNP system equilibration at T=500K (200 mers/chain, $\sigma = 0.01$ chains/nm$^2$). (A) Equilibration chart, inter-particle distance vs. time step. (B) Isolated polystyrene HNP. (C) 4 PS HNP systems in simulation box.

Figure 3.5 20 k PS HNP system equilibration at T=500K (200 mers/chain, $\sigma = 0.05$ chains/nm$^2$). (A) Equilibration chart, inter-particle distance vs. time step. (B) Isolated polystyrene HNP. (C) 4 PS HNP systems in simulation box.
Figure 3.6 20 k PS HNP system equilibration at T=500K (200 mers/chain, $\sigma = 0.1$ chains/nm$^2$). (A) Equilibration chart, inter-particle distance vs. time step. (B) Isolated polystyrene HNP. (C) 4 PS HNP systems in simulation box.

Figure 3.7 20 k HNP system equilibration at T = 500K, 200 mers/chain, $\sigma = 0.01, 0.05, 0.1$ chains/nm$^2$. 
3.4 TraPPE Force Field

TraPPE is an acronym for transferable potentials for phase equilibria. This force field is parameterized against fluid-phase equilibria data with a strong emphasis on transferability. The word transferable suggests that the force field parameters are used to describe a given interaction site in different molecules; and the force field is applicable to predict different properties, such thermodynamic, structural, or transport, across a wide range of state points like pressure, temperature, or composition.

3.4.1 TraPPE-United Atom Force Field

In the united atom approach, computational efficiency is an important consideration. To reduce the computational cost and time in a simulation, the number of interaction sites in the force field are kept as small as possible without sacrificing too much accuracy from the polymer being modeled. This is done by using pseudo-atoms to represent a carbon atom together with all of its bonded hydrogen atoms. Typical pseudo-atoms in TraPPE–UA include CH₄, CH₃, CH₂, CH and C, while polar atoms, such as oxygen, nitrogen and sulfur (and any hydrogen atoms bonded to them) are treated as explicit interaction sites. The TraPPE-UA force field utilizes pseudo-atoms that are located at the sites of heavy atoms. The non-bonded interactions of these heavy atoms are described by pairwise-additive Lennard-Jones (LJ) 12-6 potentials of the form:

\[ u_{LJ}(r_{ij}) = 4\epsilon_{ij} \left[ \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{6} \right] \]  (3.1)
where \( r_{ij} \), \( \epsilon_{ij} \), and \( \sigma_{ij} \) represent the bead-bead separation, the Lennard-Jones well depth, and the Lennard-Jones diameter for beads i and j respectively.\(^{100}\) These potentials are used for interactions between pseudo-atoms belonging to different or the same molecules, whose interactions are not accounted for by any intra-molecular bonded potentials.\(^{100}\) The term \( u_{LJ}(r_{ij}) \) describes all intermolecular site-site interactions, as well as intra-molecular non-bonded interactions for atoms separated by more than three bonds. Lennard-Jones parameters for the interactions of unlike pseudo atoms are calculated using the standard Lorentz-Berthelot combining rules (Equation 3.2).\(^{100}\)

\[
\sigma_{ij} = \frac{1}{2}(\sigma_{ii} + \sigma_{jj}) = \epsilon_{ij} \sqrt{\epsilon_{ij} \epsilon_{jj}}
\]  
(3.2)

There is a potential cutoff distance of 1 nm. Attractive tail corrections are applied to the energy and pressure using standard analytical expressions that assume a uniform density distribution beyond the cutoff.\(^{102}\) All of the bond lengths are kept rigid using a relative tolerance of \( 10^{-4} \) (SHAKE method).\(^{103}\) A harmonic potential is used to control bond angle bending:

\[
u_{\text{bend}} = \frac{k_0}{2} (\theta - \theta_0)^2
\]

(3.3)

where \( \theta \), \( \theta_0 \), and \( k_0 \) are the measured bending angle, the equilibrium angle, and the force constant respectively.\(^{103}\) The torsional potentials describe the rotations along the bonds in the aliphatic backbone.\(^{101}\) They are used to restrict the dihedral rotations around bonds connecting two methylene pseudo-atoms and around bonds connecting a methylene pseudo-atoms that are sp\(^2\) hybridized.\(^{100}\) The torsional potentials have the functional form

\[
U_{\text{tors}} = C_0 + C_1 [1 + \cos(\phi)] + C_2 [1 - \cos(2\phi)] + C_3 [1 + \cos(3\phi)]
\]

(3.4)
The coefficients $c_0$, $c_1$, $c_2$, and $c_3$ are taken from information reported by C. Wick et al.\textsuperscript{100}

To keep sets of four atoms in a specific configuration, a set of improper dihedral-angle interactions having the following form are used:

$$u_{impr}(\xi) = \frac{1}{2} k_\xi (\xi - \xi_0)^2$$

(3.5)

where $\xi$ is the improper dihedral angle. The values for the constants $k_\xi$ and $\xi_0$ are taken from the GROMOS force field.\textsuperscript{104} When the polystyrene models are constructed, the improper dihedral-potentials are used to keep the phenyl rings planar and maintain the tetrahedral configuration around the sp\textsuperscript{3} hybridized carbons within the benzene rings.\textsuperscript{101} Table 3.4 contains the parameters that were entered into material studio before the traditional PS HNP models were densified and equilibrated in their simulation boxes.
Table 3.4  Atomistic TraPPE Forcefield for Polystyrene.

<table>
<thead>
<tr>
<th>nonbonded LJ parameters</th>
<th>$\epsilon$ (kJ/mol)</th>
<th>$\sigma$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_3$ (sp$^3$)</td>
<td>0.8159</td>
<td>3.75</td>
</tr>
<tr>
<td>CH$_2$ (sp$^3$)</td>
<td>0.3828</td>
<td>3.95</td>
</tr>
<tr>
<td>CH (sp$^3$)</td>
<td>0.0831</td>
<td>4.65</td>
</tr>
<tr>
<td>CH$_{aro}$ (aromatic)</td>
<td>0.4197</td>
<td>3.695</td>
</tr>
<tr>
<td>C$_{aro}$ (aromatic link)</td>
<td>0.2494</td>
<td>3.70</td>
</tr>
<tr>
<td>bonds (rigid) l$_0$ (Å)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH$_3$-CH$_2$</td>
<td>1.54</td>
<td></td>
</tr>
<tr>
<td>CH$_2$-CH</td>
<td>1.54</td>
<td></td>
</tr>
<tr>
<td>CH-C$_{aro}$</td>
<td>1.51</td>
<td></td>
</tr>
<tr>
<td>CH$<em>{aro}$-CH$</em>{aro}$</td>
<td>1.40</td>
<td></td>
</tr>
<tr>
<td>bond bending type k$_\theta$ (kJ/mol/rad$^2$)</td>
<td>$\theta_0$ (deg)</td>
<td></td>
</tr>
<tr>
<td>CH$_3$-CH-CH$_2$</td>
<td>520</td>
<td>112</td>
</tr>
<tr>
<td>CH$_1$-CH$_2$-CH$_1$</td>
<td>520</td>
<td>114</td>
</tr>
<tr>
<td>C$<em>{aro}$-CH$</em>{aro}$-CH$_{aro}$</td>
<td>1000</td>
<td>120</td>
</tr>
<tr>
<td>CH$<em>{aro}$-CH$</em>{aro}$-C$_{aro}$</td>
<td>1000</td>
<td>120</td>
</tr>
<tr>
<td>CH$<em>{aro}$-C$</em>{aro}$-CH</td>
<td>1000</td>
<td>120</td>
</tr>
<tr>
<td>torsion type c$_0$ (kJ/mol)</td>
<td>c$_1$ (kJ/mol)</td>
<td>c$_2$ (kJ/mol)</td>
</tr>
<tr>
<td>CH$_x$-CH$_1$-CH$_2$-CH</td>
<td>0.0</td>
<td>2.952</td>
</tr>
<tr>
<td>improper dihedral k$_\xi$ (kJ/mol/rad$^2$)</td>
<td>$\xi_0$ (deg)</td>
<td></td>
</tr>
<tr>
<td>CH$<em>{aro}$-CH$</em>{aro}$-CH$<em>{aro}$-CH$</em>{aro}$</td>
<td>167.4</td>
<td>0</td>
</tr>
<tr>
<td>C$<em>{aro}$-CH$</em>{aro}$-CH$_{aro}$-CH</td>
<td>167.4</td>
<td>0</td>
</tr>
<tr>
<td>CH-CH$_x$-CH$<em>y$-C$</em>{aro}$</td>
<td>35.26</td>
<td>0</td>
</tr>
</tbody>
</table>

3.4.2 Development of Polystyrene HNP TraPPE-UA CG Models

Polystyrene is the most commonly studied commercial polymers in the experimental and the computational world. The structural and short time local dynamical characteristics of polystyrene have been modeled at the atomistic level using either molecular dynamics or Monte Carlo simulations. If all-atom or united-
atom models are used to simulate PS, experimental data on the density and the structure are able to be reproduced; but due to time limitations, only single chain systems\textsuperscript{106,107} or very short chains of the order of about 10 monomers can be used.\textsuperscript{105,108} To study both the structural and dynamical properties of the polystyrene chain grafted to a silica particle, a combination of atomistic and mesoscopic simulations will be used (TraPPE-UA) model.

The simulated traditional polystyrene hairy-nanoparticles are described by means of the TraPPE-UA model that was developed and validated by V. Harmandaris et al. and the \textit{Siepmann Group} from the University of Minnesota.\textsuperscript{99-101} A total of 9 traditional PS HNP systems (TraPPE-UA model) with three molecular weights ranging from 2k to 10k will were constructed (Table 3.5) using Material Studio 7.0. The polystyrene monomer units are represented by 8 pseudo-atoms containing either C atoms, or C and H atoms together (Figure 3.8)

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure_3.8.png}
\caption{(A) Coarse-grained United Atom Model of polystyrene. (B) Material Studio representation of CG-UA model of polystyrene.}
\end{figure}
Each traditional HNP system will have one of three grafting densities, a certain number of chains per particle, a specific number of monomers per chain, as well as a certain number of beads in each system (Table 3.5).

<table>
<thead>
<tr>
<th>Molecular Weight</th>
<th>Graft Density</th>
<th>Chains/Particle</th>
<th>Mers/Chain</th>
<th>Beads/system</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 k PS Chains</td>
<td>0.01</td>
<td>6</td>
<td>20</td>
<td>960</td>
</tr>
<tr>
<td></td>
<td>0.05</td>
<td>27</td>
<td>20</td>
<td>4,320</td>
</tr>
<tr>
<td></td>
<td>0.1</td>
<td>53</td>
<td>20</td>
<td>8,480</td>
</tr>
<tr>
<td>5 k PS Chains</td>
<td>0.01</td>
<td>6</td>
<td>50</td>
<td>2,400</td>
</tr>
<tr>
<td></td>
<td>0.05</td>
<td>27</td>
<td>50</td>
<td>10,800</td>
</tr>
<tr>
<td></td>
<td>0.1</td>
<td>53</td>
<td>50</td>
<td>21,200</td>
</tr>
<tr>
<td>10 k PS Chains</td>
<td>0.01</td>
<td>6</td>
<td>100</td>
<td>4,800</td>
</tr>
<tr>
<td></td>
<td>0.05</td>
<td>27</td>
<td>100</td>
<td>21,600</td>
</tr>
<tr>
<td></td>
<td>0.1</td>
<td>53</td>
<td>100</td>
<td>42,400</td>
</tr>
</tbody>
</table>

3.4.3 Development of Polydimethylosiloxane (PDMS) HNP TraPPE-UA CG Models

S. W. Sides et al.\textsuperscript{110} compared the results from wide-angle X-ray scattering, molecular dynamics simulations, and polymer reference interaction site theory (PRISM) for a study of the structure of PDMS melts.\textsuperscript{111} The authors found that MD simulations using the explicit atom (EA) model approach was in excellent agreement with the experimental structure factor, whereas a united atom (UA) model approach, presented by
Sok et al.\textsuperscript{112} was found to be in poor agreement with experiments due to the model’s inability to predict the correct pressure-volume-temperature (PVT) properties. It is desirable to use a united atom force field for PDMS, since simulations with a united atom potential are faster than simulations with explicit ones.\textsuperscript{111} To develop an improved United-Atom force field for PDMS that captures all of the possible features of the explicit atom model, potentials from both approaches will be used for the parameters of the traditional PDMS HNP systems.

The simulated traditional polydimethylsiloxane hairy-nanoparticles are described by means of the TraPPE-UA model that was developed by A. Frischknecht and J. G. Curro.\textsuperscript{135} The united atom models for polydimethylsiloxane, shown in Figure 3.9, treats each methyl group as a single atom, reducing the number of atoms per monomer from ten to four.\textsuperscript{111}

![Figure 3.9 Coarse-grained United Atom Model of polydimethylsiloxane.](image)

Table 3.6 shows a total of 9 traditional PDMS HNP systems (TraPPE-UA model) with molecular weights, ranging from 2k to 10k, that will be constructed using Material Studio 7.0.
Table 3.6  Traditional PDMS HNP TraPPE-UA Systems.

<table>
<thead>
<tr>
<th>Molecular Weight</th>
<th>Graft Density</th>
<th>Chains/Particle</th>
<th>Mers/Chain</th>
<th># of Beads</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 k PDMS Chains</td>
<td>0.01</td>
<td>6</td>
<td>27</td>
<td>648</td>
</tr>
<tr>
<td></td>
<td>0.05</td>
<td>27</td>
<td>27</td>
<td>2916</td>
</tr>
<tr>
<td></td>
<td>0.1</td>
<td>53</td>
<td>27</td>
<td>5724</td>
</tr>
<tr>
<td>5 k PDMS Chains</td>
<td>0.01</td>
<td>6</td>
<td>68</td>
<td>1632</td>
</tr>
<tr>
<td></td>
<td>0.05</td>
<td>27</td>
<td>68</td>
<td>7344</td>
</tr>
<tr>
<td></td>
<td>0.1</td>
<td>53</td>
<td>68</td>
<td>14416</td>
</tr>
<tr>
<td>10 k PDMS Chains</td>
<td>0.01</td>
<td>6</td>
<td>135</td>
<td>3240</td>
</tr>
<tr>
<td></td>
<td>0.05</td>
<td>27</td>
<td>135</td>
<td>14580</td>
</tr>
<tr>
<td></td>
<td>0.1</td>
<td>53</td>
<td>135</td>
<td>28620</td>
</tr>
</tbody>
</table>

This improved united atom model will include potentials (for parameterization) from the explicit model and the united atom model, which are shown in Table 3.7.
Table 3.7  Force Field Parameters for Traditional PDMS HNP TraPPE-UA Systems.

<table>
<thead>
<tr>
<th>Nonbonded (LJ + Coulomb) Parameters</th>
<th>( \varepsilon ) (kcal/mol)</th>
<th>( \sigma ) (Å)</th>
<th>q (e)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si-Si</td>
<td>0.131</td>
<td>4.29</td>
<td>0.3</td>
</tr>
<tr>
<td>Si-O</td>
<td>0.0772</td>
<td>3.94</td>
<td>n/a</td>
</tr>
<tr>
<td>Si-CH(_3)</td>
<td>0.1596</td>
<td>3.83</td>
<td>n/a</td>
</tr>
<tr>
<td>O-O</td>
<td>0.08</td>
<td>3.3</td>
<td>-0.3</td>
</tr>
<tr>
<td>O-CH(_3)</td>
<td>0.1247</td>
<td>3.38</td>
<td>n/a</td>
</tr>
<tr>
<td>CH(_3)-CH(_3)</td>
<td>0.1944</td>
<td>3.73</td>
<td>0</td>
</tr>
<tr>
<td>Bonds (Harmonic)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>r(_0) [Å]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Si-O</td>
<td>1.64</td>
<td>350.12</td>
<td></td>
</tr>
<tr>
<td>Si-CH(_3)</td>
<td>1.9</td>
<td>189.65</td>
<td></td>
</tr>
<tr>
<td>Angles (Harmonic)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \theta_0 ) (deg)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Si-O-Si</td>
<td>146.46</td>
<td>14.14</td>
<td></td>
</tr>
<tr>
<td>O-Si-O</td>
<td>107.82</td>
<td>94.5</td>
<td></td>
</tr>
<tr>
<td>CH(_3)-Si-CH(_3)</td>
<td>109.24</td>
<td>49.97</td>
<td></td>
</tr>
<tr>
<td>O-Si-CH(_3)</td>
<td>110.69</td>
<td>49.97</td>
<td></td>
</tr>
<tr>
<td>Dihedrals (CHARMM)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>n</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Si-O-Si-O</td>
<td>1</td>
<td>0.225</td>
<td></td>
</tr>
<tr>
<td>Si-O-Si-CH(_3)</td>
<td>3</td>
<td>0.01</td>
<td></td>
</tr>
</tbody>
</table>
CHAPTER IV
EXPERIMENTAL PROCEDURES

4.1 Hairy-Nanoparticles: General Brush Architecture

4.1.2 Introduction

Grafting polymer chains onto a nanoparticle surface has emerged as a standard motif in the polymer nanocomposite community to disperse and stabilize nanoparticles in a broad range of matrices, including linear polymers, solvents, and reactive resins. Recent work has also demonstrated that these polymer-grafted nanoparticles (or hairy nanoparticles, HNPs) provide an exciting alternative to the traditionally blended PNCs. These so-called “single component” hybrid nanocomposites (or assemblies of hairy nanoparticles, aHNPs) avoid the complexities associated with blending functionalized nanoparticles with a separate polymer matrix phase. Rather, the architecture of the grafted polymer, such as its molecular weight and grafting density, is designed so that the polymeric canopies of near-neighbor nanoparticles interpenetrate, affording uniform dispersion, nanoscopic order and viscoelastic response without the presence of a linear chain matrix. Similar to reports for blended PNCs, aHNPs also show increased modulus. Additionally, aHNPs have been reported with optical transparency up to 30 vol%, improved dielectric breakdown, and as room temperature liquids with
inorganic loadings of up to 30 vol%. These properties are challenging to achieve with blended PNCs, especially at relatively high inorganic volume fractions (>20%)

The single component nature may also afford longer term stability relative to a multicomponent blend. However, as with any glassy or thermoplastic material, physical ageing and the associated evolution of density, specific volume, enthalpy, and relaxation rates is well known to result in significant changes to thermal, optical and gas transport properties; as well as premature mechanical failure and limited device shelf life due to fracture, dewetting, and/or crazing. How the architecture of the HNP and the nanoscopic ordered confinement of the canopy impacts these processes is unknown.

At a coarse-grained level, HNPs are soft colloids, where the particles interact through a distance-dependent repulsive-steric potential that decreases with distance from the nanoparticle surface. Other examples of soft colloids are star polymers, block-copolymer micelles, and super-paramagnetic particles in a varying external field. Prior studies have pointed out the analogy between HNPs, star polymers, and polymer brushes on curved surfaces; and adopted the models and approaches of Daoud-Cotton, K. Ohno et al., S. T. Milner et al., and Wijmans-Zhulina as a framework to understand the relationship between the architecture of the grafted polymeric canopy and the structure and properties of the HNP and its assembly. A significant feature of this extension is the critical radius

\[ r_c = r_0 \sigma^*^{1/2} \nu^*^{-1} \]  

(4.1)

where \( r_0, \sigma^* \), and \( \nu^* \) are the particle radius, reduced polymer grafting density and reduced excluded volume parameter, respectively. This critical radius determines the transition of the canopy from a concentrated polymer brush (CPB), where the grafted polymer is
stretched, to a semi-dilute polymer brush (SDPB) where the chains are solution-like. Experimentally, a large number of HNPs have been reported utilizing oxides (SiO$_2$, Fe$_3$O$_4$, TiO$_2$), metals (Au, Ag, Pd, PtFe), biologic and carbon cores with PS, PEO, PMMA, polyolefin, protein, and ionic liquid canopies. In general, the physical characteristics of these permutations are primarily correlated to the canopy architecture, the chain dynamics at the observation temperature, and the size, shape and associated distributions of the nanoparticle core. Recent modelling builds upon a simplified pairwise additive, soft-colloid framework, and confirms these primary correlations. In the solvent-free, assembled HNP limit, the interaction potentials are no longer pairwise additive if the length of the tethered chain is of the order of the radius of the particle, due to the constraint that these tethered chains fill the interstitial voids between the closed packed HNPs. aHNPs were predicted to form glasses, isotropic aggregates, anisotropic aggregates, and star fluids as a function of grafting density, core size, and temperature. At higher temperatures, the dynamics of the end groups of the polymer chains act as an unconnected solvent, swelling the tethered chains. Thus, assembled HNPs may adopt numerous local packing geometries and behave as incompressible single-component fluids or as a suspension of spheres depending on temperature and canopy architecture. Experimentally, different local HNP packing in blends with liner chains as well as solvent free assemblies have been reported for different canopy architectures and $r_c$. Rheology and NMR of nano-scale ionic liquids are consistent with self-suspending fluid behavior.

The architecture of the HNP canopy and the confined interstitial volume within the aHNP is also anticipated to impact the glass transition temperature ($T_g$) and longer-
time relaxation processes (\(\tau > 1\) sec), key features that govern glassy behavior and physical aging. In general, interfaces, confined volume, and macromolecular structure are known to impact relaxation processes that drive the non-equilibrium, glassy structure toward its thermodynamic equilibrium state. For example, both accelerated and reduced physical aging have been observed with decreasing thickness of thermoplastic film.\(^{128,129}\) In most cases, thin (\(h < 30\) nm),\(^{130}\) supported PS films show a decrease in relaxation rates and glass transition temperatures. However, residual internal stresses due to processing also play a major role, leading to an increase in the physical aging rate at certain pre-strains.\(^{129,130}\) Glassy relaxation modes also depend on macromolecular architecture; star-shaped macromolecules exhibit a significant slowing of the physical aging rate relative to their linear analogues (\(T_a - T_g = -35\) to \(-50^\circ C\)).\(^{132}\) Nano-fillers have also been shown to alter physical aging in blended PNCs.\(^{133}\) Depending on interactions between the polymer matrix and nanoparticles, no effect, increase or decrease in \(T_g\), relative to the linear matrix have been observed.\(^{133,134}\) For example, Boucher et al.\(^{135}\) showed that local dynamics observed via dielectric spectroscopy increased in PMMA/SiO\(_2\) relative to PS/SiO\(_2\) systems.\(^{135,136}\) On the other hand, A. L. Flory et al.\(^{137}\) showed a large increase in \(T_g\) (+17\(^\circ C\)) with the modification of the PMMA/carbon nanotube surface; but no significant change in the activation energy of the enthalpy relaxation process or fragility index.\(^{137}\) Older studies of hyper-confinement (< 5 nm) of PS chains in layered silicate PNCs reported a marked suppression or absence of some cooperative relaxation modes.\(^{138}\) Modeling results of PNC dynamics by A.Y. H. Liu et al.\(^{139}\) are consistent with this view that nanoparticle-matrix interactions may increase (repulsive) or decrease (attractive) local mobility of polymer segments relative to regions far from the
nanoparticle (d > 2.5\sigma), and thus manifest in either an increase or decrease in local physical aging rates.\textsuperscript{139} Recently, broadened and reduced glass transition temperatures (\(\Delta T \sim -30^\circ C\)) have been reported for PS-TiO\textsubscript{2} and PS-SiO\textsubscript{2} aHNPs relative to their linear PS analogs, and attributed to frustrated packing and increased local free volume of the tethered polymer due to the nanoparticle separation being less than the polymer coil size (\(R_g\)). Unfortunately, insufficient data is available to build upon prior reports of thin films and blended PNCs to develop an understanding of the relative impact of nanoparticle-chain interaction and canopy confinement on the cooperative and glassy relaxation processes in aHNPs.

Toward this goal, the physical aging via calorimetry of silica-based aHNPs with various canopy architectures (molecular weight, grafting density (\(\sigma\))) composed of polystyrene and silica (core) will be reported.

4.1.3 Materials

All chemicals were purchased from Sigma-Aldrich Co., USA. Aminopropyltriethoxysilane (APTES) silane derivative, ethyl \(\alpha\)-bromoisobutyrate (EBIB) (initiator), N,N,N',N'',N''-Pentamethyldiethylenetriamine (PMDETA) (ligand), sodium azide, dimethylacetamide (DMAC), and dimethylformamide (DMF) were used as received from Sigma-Aldrich. The inhibitor in the styrene monomer was removed by passage through a column of basic alumina. Copper(I) bromide was purified by washing several times with glacial acetic acid and stored (dry) under a blanket of nitrogen.
4.2 Experimental Procedures

4.2.1 Synthesis of Polystyrene via ATRP

The synthesis of the polymer chains was carried out using Atom Transfer Radical Polymerization as described in references 140 and 141. A 250 mL schlenk flask was obtained, and to it 40 mL of purified styrene, 60 mL of ethyl α-bromisobutyrate (EBIB initiator), and N,N,N',N",N"-Pentamethyldiethylenetriamine (PMDETA) (ligand) were added. The flask was then placed in a liquid nitrogen bath under vacuum, where it was allowed to solidify. Once frozen, the flask was exposed to a flow of argon gas, and allowed to thaw out completely. This process was repeated three times. When the mixture was frozen once more, it was transferred to a hood, where under a blanket of nitrogen gas, .036g of Cu(I)Br was quickly added to the flask. The flask was closed, transferred to a flow of argon gas, and allowed to warm to room temperature. The room temperature mixture was then transferred to an oil bath, at a fixed temperature of 90˚C, and left to stir for 7-8 hours (Scheme 4.1).

Scheme 4.1 Synthesis of Polystyrene chains (with azide end cap) via ATRP.

To monitor the molecular weight of each batch of polystyrene that was synthesized, aliquots were taken from the flask 7-8 hours after synthesis began and checked for the desired molecular weight via gel permeation chromatography (GPC). The reaction was stopped by opening the flask and exposing the catalyst to air.
Once the desired molecular weight for the polymer was obtained, the samples were washed and dried. Some of the free polymer from each synthesized batch was set aside for later experiments to compare results against HNP systems of the corresponding MW. The remaining free polymer was transferred to a solution of dimethylformamide (DMF) and reacted with sodium azide (NaN₃) to create an active site on the end of the PS chain that aids in the formation of the hairy-nanoparticle.

### 4.2.2 Silanization of Colloidal Silica Nanoparticles in DMAc

The silanization of the colloidal silica nanoparticles was carried out by a method described by C. Chevigny et al. A dilute Ludox (40wt%) solution (silica particles) was obtained from Sigma-Aldrich. The silanization of the silica particles could not take place in a 40wt% solution (water), so it had to be diluted to a 5wt% solution. To dilute the 40wt% solution to 5wt%, a 250 mL round bottom flask containing the ludox solution was placed in an oil bath and maintained at a temperature of 110°C. As the water in the 40wt% solution was evaporated off in increments of 50 mL to 100 mL, dimethylacetamide (DMAC) was added to the flask until the the ludox solution reached 5wt%. The silane derivative, aminopropyltriethoxysilane (APTES) (395 mg), and 6.6 mL of methanol were added to that flask, and left to stir for 24 hours at room temperature (Scheme 4.2).

![Scheme 4.2  Silanization of silica particles (ATRP).](image-url)
The reaction mixture was washed 4 times using a Millipore Ultra-filtration apparatus, with a 30,000 dalton pores diameter filter (regenerated cellulose), to remove unreacted silanes. Each time 100mL of the solution was filtered through the apparatus, 200 mL of DMAc was added to return the solution to its initial volume.

4.2.3 Click Reaction

Lutz et al. used click chemistry for the preparation of end-functionalized ATRP polymers. The brominated chain ends of the polymer were transformed into an azide group and reacted with terminal alkynes to create different functional groups. The information provided from their work motivated the decision to use azide functionalized polymer chains, and silanized silica particles with alkyne end groups, to form the polystyrene hairy-nanoparticles (Scheme 4.3).

\[
\text{PS-}N_3 + \text{CuSO}_4 \cdot 5\text{H}_2\text{O} + \text{Na ASC/H}_2\text{O} \xrightarrow{\text{DMAC}} \text{SiO}_2\text{-PS}
\]

Scheme 4.3 Click Reaction between polystyrene chains and silica particles.

4.3 Characterization Methods

4.3.1 Thermo-gravimetric analysis (TGA)

The grafting densities (silane, initiator, and polymer) of the HNPs were determined by Thermo-gravimetric analysis (TA instrument Q50). A scan rate of 10°C/min to 800°C, under nitrogen flow was used for the sample runs. The grafting densities were determined by using the equation below:

\[
\text{Grafting Densit} = \frac{S_{spe}}{M_{gr-N_A}} \times \frac{W_{tot}-W_{ref}}{100-(W_{tot}-W_{ref})}
\]
$S_{spe}$ is the specific surface (nm$^2$/g) of the silica, $M_{gr}$ is the molar mass of the grafted molecule, $N_a$ is Avogadro’s number, $W_{tot}$ and $W_{ref}$ are the weight loss of the grafted sample and weight loss of the reference sample (silica for determining the initiator grafting and initiator-grafted silica from the polymer).\textsuperscript{141}

### 4.3.2 Differential Scanning Calorimetry (DSC)

Glassy polymers are inherently unstable when their physical and mechanical properties change with time until they reach equilibrium.\textsuperscript{143} This phenomena is known as structural relaxation or physical ageing, and it is responsible for the time-dependent changes of the polymer’s physical properties, such as the specific volume, thermal conductivity, gas permeability, and optical properties.\textsuperscript{132} Physical properties are used to differentiate this phenomena from chemical ageing. When chemical ageing occurs, an irreversible change takes place in the materials chemical structure.\textsuperscript{143} During physical ageing, there is a reversible change in the polymer’s properties without permanent change in the chemical structure, resulting in a modification of the macromolecular configuration via enthalpy or volume relaxation, or from the transport phenomena which can involve solvent penetration, or migration of additives.\textsuperscript{143}

Differential scanning calorimetry was used to study the physical ageing effect, induced by annealing the polystyrene (tethered to silica nanoparticle) at annealing temperatures ($T_a$) below the polymers $T_g$ at different annealing times ($\Delta t_a$). The samples were cooled from a higher temperature than the $T_g$ to room temperature using specific cooling rates.
4.4 Self-Assembly of Hairy Nanoparticles: Organic vs. Inorganic

4.4.1 Organic Hairy-Nanoparticles: Introduction

Self-assembly, the spontaneous organization of matter into ordered arrangements, is a fundamental and ubiquitous process in nature and found at all length scales.\textsuperscript{144,145} The assembly of atomic, molecular, nano and micro-scale building blocks into macroscopic structures is a theme that runs through chemistry, biology and material science.\textsuperscript{146-148} The past decades have witnessed the unprecedented development in the synthesis of diverse building blocks\textsuperscript{149-153} for self-assembly ranging from copolymers,\textsuperscript{154-160} dendrimers,\textsuperscript{161} core-shell nanoparticles,\textsuperscript{162} to DNA coated colloidal particles.\textsuperscript{161} These advances have led to the emergence of numerous self-assembled supra-structures for a wide variety of applications, including optoelectronic, catalysis, sensing, and drug delivery.

Most notably, Wang et al.\textsuperscript{161} devised a novel assembly strategy by mimicking atomic bonding via DNA hybridization. The approach that was taken by Wang and his colleagues was to decorate the surface of the colloidal particles with sticky patches made of synthetic organic or biological molecules in specific locations.\textsuperscript{161} Bonding between particles occurs through patch-patch interactions, so that in principal the location and functionality of the patches can endow particles with bonding directionality and valence.\textsuperscript{161} The concept of particles with surface functional groups as valency has been inspiring scientists to develop atomic-bonding mediated self-assembly systems. For this reason, we decided to synthesize a class of micro-phase separated polymeric hairy nanoparticles (mHNPs) to explore atomic-bonding-driven self-assembly systems. To do so, we have used living anionic polymerization via the “one-pot synthesis” approach.
Living anionic polymerization allows the precise control of the size and composition of both core and shell components. The hairy core-shell nanoparticles with surface functional groups serve as building blocks that self-assemble into well-ordered hierarchical structures. The self-assembled mHNPs will be a tremendous boost for the development of supra-structures with potential applications in emerging industries such as high-density microelectronic materials, lithography, porous catalysis and cryo-electrodes.

4.4.2 Materials

Sec-Butyllithium (sec-BuLi, 1.4 M in cyclohexane, Aldrich) was used as received. Tetrahydrofuran (THF) (certified ACS), styrene (99%), divinylbenzene (technical grade, 80%), hexamethylocyclosilotoxane (D₃, 98%), chlorodimethylsiloxane (99%) were purchased from Aldrich.

THF was purified by refluxing over sodium metal, with benzophenone being used as a color indicator and distilled on the vacuum line before use. Styrene and divinylbenzene were mixed in a predetermined molar ratio, and stirred over calcium hydride (CaH₂) at room temperature for 2 days, and then degassed on the vacuum line before distillation into ampules and flame-sealed. Hexamethyl(cyclotrisiloxane) (D₃) was dissolved in pre-dried THF, and stirred over CaH₂ at room temperature for 2 days, then degassed on the vacuum before distillation into ampules and flame-sealed. Chlorodimethylsiloxane was purified as described for the mixture of styrene and divinylbenzene. All other chemicals were purchased from commercial sources and used without further purification.
4.5 Experimental Procedures

4.5.1 Synthesis of Organic (PS-PDMS) Hairy-Nanoparticles

All synthetic manipulations were conducted with standard all-glass high-vacuum techniques. The two-step sequential copolymerization was performed in a glass reactor equipped with a magnetic stir bar, connected with a vacuum distillation apparatus for THF and a septum inlet. The break-sealed ampules containing the mixture of monomer and cross-linker, hexamethyl(cyclotrisiloxane) (D₃) and chlorodimethylsiloxane were connected in advance to the reactor. Pre-dried THF (25 mL) was degassed on the vacuum line and distilled into a completely flame-dried reactor. Afterwards, the reactor was sealed by flame to separate it from the THF distillation apparatus.

Synthesis of the organic hairy-nanoparticle core began with the breaking of the seal containing the mixture of styrene monomer (1.50 g) and divinylbenzene (0.22 g). Sec-BuLi (0.5 mL of 1.4 M in cyclohexane) was rapidly added to the reactor at -78°C under vigorous stirring. The color of the reaction mixture immediately turn red indicating the occurrence of polymerization. This first step of the synthetic procedure was allowed to run for 1.5 h. From the resulting polymerization mixture, 3 mL of sample was withdrawn from the reactor and terminated by means of the addition of methanol.

The addition of the polymer hairs to the organic core began with the breaking of the seal containing 1.80 g of D₃ in THF. The resulting reaction mixture gradually warmed to room temperature for approximately an hour. The red color eventually became orange, then completely disappeared. The synthesis of the organic HNP was allowed to run for 13 hours at room temperature. The break seal of chlorodimethylsiloxane was crushed to terminate the entire copolymerization, followed the addition of 3 mL of triethylamine to
neutralize the polymerization mixture solution. Both the core particles and target hairy nanoparticles were obtained by precipitation of the reaction mixture into methanol, and further dried at 50°C under vacuum to give 0.10 g of core particles and 1.35 g of hairy nanoparticles with PDMS brushes (Scheme 4.4).


4.6 Characterization Methods

4.6.1 Proton Nuclear Magnetic Resonance (1H NMR)

The spectra from the 1H NMR (500 MHz) was used for the structure determination of the organic hairy-nanoparticle systems. The spectra was recorded on a Bruker AVANCE III-500 spectrometer (Figure 4.1).
Figure 4.1  $^1$H NMR (CDCl$_3$) spectra of the representative hairy-nanoparticle sample PDMS@P(S/DVB)-1 (b) and its corresponding core particle sample P(S/DVB)-1 (a).

4.6.2 Differential Scanning Calorimetry (DSC)

DSC measurements were performed using a Seiko DSC 220C or TA DSC Q2000, which was calibrated for both temperature and enthalpy using an indium standard, under a nitrogen gas atmosphere with powder samples, at a cooling rate of 5 °C/min, or heating
rate of 10 °C/min. The glass transition temperature, $T_g$, was defined as the midpoint of the change in heat capacity.

### 4.6.3 Scanning Electron Microscope (SEM)

Scanning electron microscope (SEM) images were obtained on an Agilent Technologies 8500FE-SEM instrument with a 1.0 kV accelerating voltage and an upper secondary electron detector. Prior to SEM analysis, the samples (core particles and hairy nanoparticles) were prepared by drop-casting a dilute particle solution in THF on a silicon wafer followed by air-drying and coating with gold via direct sputtering using a Technics Hummer Sputter Coater.

### 4.7 Traditional Hairy-Nanoparticles

Chemists have been inspired by the spontaneous organization of molecular building blocks into complex structures.\(^{160}\) The formation of these structures are usually driven by non-covalent attractive and repulsive intermolecular interactions.\(^{160}\) Colloidal inorganic nanoparticles are wonderful candidates for the building blocks of self-assembly, since they possess the desired optical, electronic, or magnetic properties that are associated with the surface and quantum effects that arise from their small size.\(^{160}\) These inorganic nanoparticles include gold (Au) and silver (Ag), which have strong surface plasmon resonances in the visible range,\(^{164,165}\) metals such Fe and Co, metal oxide (Fe$_2$O$_3$) magnetic nanoparticles,\(^{166}\) and semiconductor quantum dots (CdSe, CdS, PbSe, core/shell CdSe/ZnS) with stable, size-tunable fluorescence at high quantum yield.\(^{160,167}\)

However, the controlled assembly of these materials into one, two, and three dimensional superstructures remains an ongoing challenge.\(^{168,169}\) To meet this challenge, the surface of these inorganic nanoparticles can be functionalized with organic ligands that can
modify the interactions between neighboring nanoparticles or between nanoparticles and the surrounding medium.\textsuperscript{160} In this approach, the balance between attractive and repulsive interactions can be used to facilitate the organization of particles into 2D and 3D periodic super lattice structures.\textsuperscript{22} The resulting hairy-nanoparticle can be regarded as a building block that combines the optical, electronic, or magnetic properties of the inorganic core with the mechanical strength, flexibility, processability, and dielectric properties of the grafted polymer chains.\textsuperscript{169-172} To study the formation of highly ordered structures via self-assembly, the architecture (molecular weight, grafting density, etc.) of these materials will be varied from system to system.

4.7.1 Materials

All chemicals were purchased from Sigma-Aldrich Co., USA. For the synthesis of the traditional PS HNP systems, n-Butyllithium (2 M in cyclohexane, Aldrich), and dichlorodimethylsiloxane (> 99.5%), were purged under nitrogen or argon gas before they were used. Benzene and styrene monomer were dried over calcium hydride (CaH\textsubscript{2}), for 24 hours. Benzene was left drying until it was distilled over to a reaction flask for the synthesis of the polymer chains or silanization of the silica nanoparticles. The styrene monomer was distilled to a round bottom flask where it was purged and sealed, until it was needed for synthesis. The ludox (40wt\%) solution was freeze dried for 2 days to obtain the silica nanoparticles.

4.8 Experimental Procedures

4.8.1 Silanization of Colloidal Silica Nanoparticles in Benzene

A vacuum distillation apparatus was set up with one flask containing the benzene-CaH\textsubscript{2} solution, and a 100mL two neck round bottom flask (reaction flask) containing bare
silica particles and a magnetic stir bar. Heat was applied to the flask containing the dried benzene, and 50 mL of the solution was distilled into the reaction flask, while under a constant nitrogen flow. Once the purified benzene was obtained, the flask was stoppered and sealed. This process was repeated with another 100 mL round bottom flask. The flasks were labeled silanated (#2) and bare (#3). Flask #3 was sealed and allowed to stir, while flask #2 was transferred to a glove box, along with purged syringes, and a sealed flask containing a designated amount of purged dichlorodimethylsiloxane. The glove box was filled with either nitrogen or argon gas, for approximately 10 minutes. After the 10 minutes, the designated amount of cholorosilane derivatie was added to flask #2. The flask was then resealed, and allowed to stir for 3 days. The color of the flask was slightly turbid, indicating the particles were being silanated (Scheme 4.5).

Scheme 4.5  The silanization of the silica particles (Living Anionic polymerization).^{173}

4.8.2 Synthesis of Traditional Polystyrene (PS) Hairy-Nanoparticles

To begin the synthesis of polystyrene, a vacuum distillation apparatus was set up, with one flask containing the benzene-CaH₂ solution, and a 50mL reaction flask with a magnetic stir bar. Heat was applied to the flask containing the dried benzene, and 20-25 mL of the solution was distilled into the reaction flask, while under a constant nitrogen.
flow. Once the purified benzene was obtained, the flask was stoppered, sealed, and transferred to a glove box, along with two purged syringes, the purified styrene monomer, and the purged initiator, n-butylithium. The glove box was then filled with either nitrogen or argon gas for approximately 10 minutes. The volume ratio of monomer to solvent is 1:10, so 2 mL of styrene monomer had to be added to the reaction flask. The next step was to add the designated amount of initiator, for the desired molecular weight, to the reaction flask drop wise. While the drops were being added to the flask, a pale yellow color appeared. The color became darker, and eventually turned ruby red with the final addition of the initiator. These colors are indicative of the polymerization occurring. The reaction flask was resealed, as well as the initiator and monomer containers, and removed from the glove box. The reaction flask was then left to stir for 24 hours (Scheme 4.6 A).

Scheme 4.6(A) Initiation and propagation steps in the synthesis of polystyrene chains (Living Anionic Polymerization).

After 24 hours, the reaction flask was returned to the glove box along with a flask containing a designated amount of dichlorodimethylsiloxane (flask #1), a flask containing
the silanated silica particles (flask #2), a flask containing bare silica particles (flask #3), a sealed flask containing methanol (flask #4), and 4 purged syringes.

From the reaction flask, two aliquots of polystyrene were taken. The aliquots appeared to be ruby red. Since living anionic polymerization was used to synthesize the polymer, the reaction continued until it was purposely terminated. One of the aliquots was added to a flask containing methanol (flask #4), terminating the reaction. The polymer sample was used for structure determination and the determination of the molecular weight of the polymer chains.

The second aliquot was added to flask #1 for the silanization of the polymer chain. The color of the reaction mixture became clear, indicating termination of the synthesis. A sample of this mixture was used for structure determination to show that the polymer chains had been silanated. The mixture that was left in flask #1 was transferred to flask #3, and left to stir for 3 days (termination method 2) (Scheme 4.6 B).

![Scheme 4.6(B) Termination Method 2: End capping of living polymer chain with dichlorodimethylsilane (Me₂SiCl₂), followed by the reaction of the chain with bare silica particles.](image)

The mixture left in the reaction flask was transferred to flask #2, and left to stir for three days (termination method #1) (Scheme 4.6 C).
Scheme 4.6(C) Termination Method 1: Reaction of living polymer chains with silanated silica particles.\textsuperscript{173}

In order to recover the HNP and polymer samples, all of the mixtures were precipitated in chilled methanol (drop wise), rinsed with methanol and water, and oven dried to remove solvent from the samples, leaving behind powdery substances.

4.9 Characterization

The characterization of the traditional PS HNP systems will be carried out using the same methods and instruments that were mentioned in section 4.2.3.
CHAPTER V
RESULTS AND DISCUSSION

5.1 Hairy-Nanoparticles: General Brush Architecture: Results

5.1.2 Morphology Studies of the MARTINI Coarse-Grained Polystyrene HNP Systems

With the use of the parameters from the MARTINI force field, nine models were simulated to study the effects that resulted from the manipulation of the hairy-nanoparticle’s architecture (grafting density ($\sigma$), and molecular weight). Figure 5.1 displays results for the 20k polystyrene HNP systems at their various grafting densities.

![Figure 5.1](image)

Figure 5.1  MARTINI-COARSE GRAINED Polystyrene Hairy-Nanoparticles: Single bead representation of HNP and model of HNP represented by 4 beads, in a simulation box. Molecular weight 20k, graft density: .01, .05, and 0.1 chains/nm$^2$. 

67
These models are solvent free, so when the polymer chains adhere to the surface of the bead, they form what seems to be stripes or worm-like micelle structures. A trend is seen for all nine of the systems, regardless of the molecular weight of the simulated polymer chains. As the grafting density is increased from 0.01 chains/nm\(^2\) to 0.1 chains/nm\(^2\), there is a uniform coverage of polymer chains about the bead. It is known that when these inorganic nanoparticles have polymer chains covalently tethered to them, and there is a high coverage of chains about the particle, the particle becomes sterically stabilized, which allows for an enhanced dispersion and mixing of the nanoparticle into a polymer matrix.\(^{150}\) This uniform coverage is representative of enhanced dispersion and mixing of the hairy nanoparticle into a polymer matrix.

Molecular dynamics (MD) is generally used to gain insight into what may be happening to organic systems at the molecular level. The main reason that MD is incorporated in this study is to make educated predictions about the simulated systems before the materials are physically produced. So along with the conclusion that has been made from these simulations, two predictions are made about the experimental work that will follow in the coming sections.

First, because the polymer chains are covalently tethered to the inorganic particle, a restriction has been introduced to the polymer chains. It is predicted that when the chains equilibrate or relax to their natural state, the time frame that it usually takes for them to return will be longer than the corresponding free polymer chains with no restrictions. This may be due to the broad size distribution of the nanoparticles. Because the graft densities are different, the local environment of the polymer is different from particle to particle, and therefore, the breadth of the relaxation time should be broader.\(^{150}\)
Second, when the molecular weight and grafting density of each system is increased, the glass transition should increase until a critical molecular weight is reached. It is known in polymer chemistry that the glass transition temperature of a polymer chain increases with molecular weight, branching, pendant groups etc.\textsuperscript{72} When the molecular weight is increased along with the grafting density, the polymer chains from neighboring particles can become entangled with each other. This imposed restriction should cause the glass transition temperature of the HNP to increase.

5.1.3 Experimental Results

The mHNPs are new members in the family of PDMS-based microphase separated materials. The self-assembly of these materials has become an important approach for the fabrication of nanostructures with different morphologies\textsuperscript{174,175} such as spheres, cylinders, hexagonally perforated lamellae, and lamellae.\textsuperscript{174,175} Three Polystyrene HNP systems, and polymer chains with the corresponding molecular weights were prepared via atom transfer radical polymerization. The molecular weights ranged from 11k – 230k (Table 5.1 and 5.2). Hard sphere center-to-center distance (L\textsubscript{hs}) and hard sphere volume fraction (\(\phi\textsubscript{hs}\)) were determined by small-angle X-ray scattering (SAXS). The grafting density (\(\sigma\)) was determined by TGA measurements.

<table>
<thead>
<tr>
<th>HNP</th>
<th>DP graft</th>
<th>MW</th>
<th>(\sigma) chains/nm\textsuperscript{2}</th>
<th>T\textsubscript{g} *\textdegree C</th>
<th>L\textsubscript{hs}/2 nm</th>
<th>(\phi\textsubscript{hs})</th>
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<td>aHNP-</td>
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</tr>
<tr>
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<td>11k</td>
<td>0.61</td>
<td>105.1</td>
<td>12.2</td>
<td>0.28</td>
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Table 5.2 Molecular Weights and T₆s of Free Polystyrene Chains.

<table>
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<th>Polymer Standards</th>
<th>DP</th>
<th>MW</th>
<th>T₆ (°C)</th>
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<td>104.4</td>
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<td>PS-230k</td>
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</tbody>
</table>

It is seen that the hairy-nanoparticle systems exhibit higher glass transition temperatures (T₆) than the linear chains of comparable molecular weight. This can be a consequence of a higher “effective” molecular weight. For example, the chains of the HNPs are tethered to a common core, at grafting densities of 0.6 chains/nm², the number of chains per particle is ~480, and thus the total molecular weight for the HNP (aHNP-PS-18) can reach 10³ kDa for a short tether size of 10 kDa.

5.1.3.1 Characterization

5.1.3.2 Physical Ageing Studies (DSC)

Physical ageing studies were performed on both the polystyrene HNP, and free polymer chains with the corresponding molecular weights. Figure 5.2 provides representative examples of calorimetric aging studies of one of the PS HNP systems at intermediate and high silica loading.
In Figure 5.2 A, the sample is physically aged at a specific annealing temperature, \((T_a = T_g - 20°C)\), at different increased annealing times \((\Delta t_a)\), 5 to 1000 minutes with increasing peak height. The excess enthalpy per mass of polymer, \(\Delta H\), is measured as an exothermic peak on top of the heat capacity change that accompanies the transition of the polymer from a glass to a melt upon heating.\(^{176}\) The enthalpy of relaxation is seen in the \(T_g\) overshoot (peak superimposing the step). The inset (Figure 5.2 A) shows glass transition temperature after the sample has been thermally erased.

Picture B shows a plot for the enthalpic relaxation \((\Delta H)\) versus ageing time \((\Delta t_a)\) (open circles). This data is fitted with the Kohlrausch-Williams-Watts Stretched Exponential Function (KWW).\(^{177}\)

Again, all of the PS HNP systems and the corresponding free polymers were aged at different temperatures (75°C, 85°C, and 95°C) during different times (Figure 5.3).
The observed endothermic peaks should show jumps in heat capacity associated with the recoverable amount of structural relaxation for different annealing times and temperatures. When the change in heat capacity (ΔCP) increases, it’s indicative of the chains being restricted in mobility. The physical aging process leads to a densification of the chain packing and reduction in chain mobility. What you see in the overshoot is the stress relief the chains are experiencing when they are able to expand. A larger peak or higher ΔCP value means the chains had less freedom in the state they were physically aged into.

The enthalpies excesses (area of the enthalpic overshoot) are calculated by taking the difference between the raw DSC data and the annealed DSC data. Once these values
are obtained, they are plotted and fitted with the KWW equation to yield enthalpic relaxation plots (Figure 5.4). These enthalpy excesses should increase with ageing times $\Delta t_a$ and temperatures.\(^{143}\)

![Graphs showing enthalpic relaxation plots for different temperatures](image)

**Figure 5.4** Enthalpic Relaxation Plots for aHNP-PS-52k at different annealing temperatures (75°C, 85°C, and 95°C).

After this data is plotted, the $\beta$ parameter is obtained. It defines the width/broadness of the spectrum of relaxation time. The lower the $\beta$ value, the broader the distribution of the relaxation times, and vice versa (The higher the $\beta$ value, the narrower the distribution of the relaxation times). These enthalpy relaxation studies reveal a trend for all synthesized HNP systems where deviations in the dynamics of aHNPs lead to slower (suppressed)
relaxation times compared to neat PS close to the $T_g$ ($\beta$ values of HNPs lower than free polymer) (refer to Table 5.3).

Table 5.3 $\beta$ values for 52k PS Free Polymer and PS-HNP at different Annealing Temperatures.

<table>
<thead>
<tr>
<th>Molecular Weight 52 k</th>
<th>Free Polystyrene Chains</th>
<th>Polystyrene HNPs</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_a = 75$</td>
<td>.93</td>
<td>.54</td>
</tr>
<tr>
<td>$T_a = 85$</td>
<td>.75</td>
<td>.53</td>
</tr>
<tr>
<td>$T_a = 95$</td>
<td>.44</td>
<td>.30</td>
</tr>
</tbody>
</table>

The suppression of enthalpy relaxation can be explained via confinement effects.\textsuperscript{178} When the polymer chains are covalently attached to the silica surface, a restriction is introduced onto the polymer chain, which causes a reduction of chain mobility.\textsuperscript{143,178} This tethering of chain ends also leads to frustration of dynamics (hindered reptation) and reduction in free volume due to a reduced number of chain ends.\textsuperscript{179} These results are akin to work on PS in thin films or within nano-pores in which suppression and slowing of the enthalpy relaxation process has been observed,\textsuperscript{178} as well as polymer chains confined within 1 nm thin galleries in layered silicate PNCs.\textsuperscript{179}

5.2 Self-Assembly of HNPs: Organic vs. Inorganic, Results

5.2.1 Organic Hairy-Nanoparticles: Experimental Results

Two organic hairy-nanoparticles systems were synthesized, composed of polystyrene as the core, and polydimethylsiloxane as the polymer hairs (Table 5.4). The diameters of the polystyrene cores were determined by using the SEM, while the material’s glass transition temperatures were determined by using the DSC.
Table 5.4 Organic HNP systems and their morphological characteristics.

<table>
<thead>
<tr>
<th>Organic HNP Samples</th>
<th>Molar ratio of S/DVB</th>
<th>Molar ratio of sec-BuLi to S+DVB</th>
<th>Shell surface functional group</th>
<th>Molar content of PDMS in particle %</th>
<th>$D_h$ SEM nm</th>
<th>$T_g$ PDMS °C</th>
<th>$T_g$ PS °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>P(S/DVB)-1</td>
<td>90/10</td>
<td>1/46</td>
<td>—CH$_2$-Ph</td>
<td>0</td>
<td>172</td>
<td>N/A</td>
<td>85</td>
</tr>
<tr>
<td>P(S/DVB)-2</td>
<td>90/10</td>
<td>1/13</td>
<td>—CH$_2$-Ph</td>
<td>0</td>
<td>95</td>
<td>N/A</td>
<td>82</td>
</tr>
<tr>
<td>PDMS@P(S/DVB)-1</td>
<td>90/10</td>
<td>1/46</td>
<td>—Si(CH$_3$)$_2$OH</td>
<td>45.85</td>
<td>445</td>
<td>-115.7</td>
<td>75</td>
</tr>
<tr>
<td>PDMS@P(S/DVB)-2</td>
<td>90/10</td>
<td>1/13</td>
<td>—Si(CH$_3$)$_2$H</td>
<td>71.75</td>
<td>490$^d$</td>
<td>-118.9</td>
<td>41</td>
</tr>
</tbody>
</table>

5.2.1.2 Characterization

5.2.1.2.1 Differential Scanning Calorimetry (DSC)

Differential scanning calorimetry (DSC) data showed two distinct glass transition temperatures in the mHNPs. A glass transition was observed for the polydimethylsiloxane chains, $T_g = -115.7$ and -118.9°C for PDMS@P(S/DVB)-1 and PDMS@P(S/DVB)-2 (Figure 5.5);
Figure 5.5  DSC thermograms of the hairy nanoparticle samples. PDMS@P(S/DVB)-1 and P(S/DVB)-2. The cooling rate is 5°C/min. The glass transition temperature, \( T_g \), was defined as the midpoint of the change in heat capacity.

and the polystyrene core, \( T_g = 75.0 \) and 40.7 °C for samples PDMS@P(S/DVB)-1 and PDMS@P(S/DVB)-2 (Figure 5.5). The lowering of the \( T_g \) of polystyrene and the slightly higher \( T_g \) polydimethylsiloxane in the mHNPs are attributed to the interplay between both of the polymer’s segments. The plasticizing effects of the flexible PDMS segments leads to a \( T_g \) of 45°C for the polystyrene core. This glass transition temperature corresponds to PS being cross-linked in the PDMS-b-PS copolymer.\(^{180}\)

5.2.1.2.2 Scanning Electron Microscope (SEM)

Scanning electron microscopy (SEM) was employed to observe the self-assembly of the organic HNP systems. The PS core particles possessed a non-covalently connected nanoporous network with diameters varying from 95 to 172 nm (Figures 5.6 A).
The mHNPs with 46 mol. % of PDMS (sample PDMS@P(S/DVB)-1) showed multiple-sized spherical morphology (Figure 5.6 B) with the diameters ranging from 445 to 3690 nm. Remarkably, two small spherical hairy nanoparticles (ca. 445 nm in diameter) are able to connect and fuse together to form a larger particle (ca. 760 nm in diameter) (Figure 5.7).
Figure 5.7 SEM images of mHNPs at various sizes after fusing into each other.

Similarly, the larger particles can combine with other particles to form larger particles (ca. 1340 nm in diameter), and so on. The largest particle (ca. 3690 nm in diameter) is equivalent to fusing together of 10 of the smallest particles. The mHNPs showed spherical morphologies. Similar phenomenon was observed on sample PDMS@P(S/DVB)-2. An emerging question arises as to how theses smaller particles grow into larger particles with different sizes. The answer lies with the end-capping of the PDMS chain ends with silane derivatives.

This “dynamic particle growth” is quite unique and may be explained by the following scenario. The surface of the particles (the end of siloxane hairs) were functionalized by either silanol (-Si(CH\(_3\))\(_2\)-OH) or silane (-Si(CH\(_3\))\(_2\)-H) groups (Figure 5.8).
Furthermore, the terminal functional group (-Si(CH₃)₂-H) can be easily oxidized into a silanol functional group (-Si(CH₃)₂-OH). The condensation of silanol groups to form siloxane bonds (-Si-O-Si-) easily takes place at room temperature. Therefore, two surface silanol functionalized HNPs are linked together via the silanol condensation reaction to produce a larger particle (Figures 5.9). The surface tension of PDMS (γ = 19.9 mN/m) is dramatically lower than that of PS (γ = 40.7 mN/m), which drives PDMS to preferentially segregate at the air/polymer interface. Initially, the two-fused particle have dumbbell shapes (Figure 5.9).
Figure 5.9  Formation of dumbbell shaped mHNP.

The two-fused dumbbell shaped particles over time transform into a spherical particle (Figure 5.9). It is believed that thermodynamics is the driving force for formation of the spherical particles. The two cores come together and push out the surface-active PDMS to the outer layer. As a result, a thermodynamically stable particle with a doubled diameter was formed due to the involvement of covalent bonding (Figures 5.7). As such, the particles with multiple-fold sizes in diameter are formed in such a way. After the spheres reach a size of 3690 nm, further growth is not observed. Two of the larger particles can come together without fusing into one another. Particles can grow along orthogonal directions to generate a T-type or tetrahedral cluster (Figure 5.9). Therefore, particles can grow in a three-dimensional way to form symmetrically fused larger spherical particles.

Figure 5.10 depicts three different higher ordered structures obtained by imaging an air-dried sample formed by drop-casting a THF solution of PDMS@P(S/DVB)-2 with 72 mol% of PDMS on a silicon wafer.
The dried sample had a gradient concentration of mHNPs ranging from nearly single to many layer thicknesses. When the local particle concentration is very low (1 layer of drop-casted THF sample solution on the silicon wafer), individual particles were clearly observed to organize in a square lattice (Figure 5.10 a and d). When the local particle concentration is medium (a second layer of THF sample solution drop-casted on the first-layered thin film), the particles associate to form small-sized clusters, and then subesequently self-assemble into well-ordered super patterns (Figure 5.10 b and e). When the local particle concentration is very high (a third layer was drop-casted on the two previous layers), the mHNPs self-assembled into highly ordered porous suprastructures (Figure 5.10 c and f). For this sample, three-layered porous structure was observed with the layers completely aligned (Figure 5.11).
To elucidate the self-assembly process of the mHNPs, three prototype patterns (Material Studio representations) were constructed (Figures 5.11 d, e, and f). The patterns were based on a simple cubic (SC) pattern consistent with experimental SEM images.

Figure 5.11 Three layered structure of mHNPs drop cast in tetrahydrofuran.
CHAPTER VI

CONCLUSION

6.1 Hairy-Nanoparticles General Brush Architecture

6.1.2 Morphology Studies of Polystyrene Hairy-Nanoparticles Systems

Molecular dynamics was employed to give insight into the dispersion behavior of HNP systems at the molecular level. This work relied on coarse-grained models of PS, which were based on the MARTINI coarse-grained force field. Nine systems were simulated with various molecular weights and grafting densities. The increase in the brush chain length leads to thicker grafted brushes, which aids in the miscibility of the nanoparticles within a polymer matrix. The density distributions of polymer chains about the silica particle depends on the grafting density of the polymer chains. As the grafting density ($\sigma$) is increased, the particle bead transitions from sparse looking beads to beads that are uniformly covered. This uniform coverage is representative of the miscibility of the nanoparticles within the polymer matrix.

6.1.2.1 Physical Ageing Studies

This study shows that physically ageing the HNP systems induces a reduction in the molecular mobility of the polymer chains, preventing a rapid return to the equilibrium state. It also shows that the system’s architecture impacts free volume and should therefore lead to changes in cooperative relaxation, mechanical, and optical properties.
Further factors that contribute to differences in these properties are nanoparticle core size distribution, distribution in graft density and molecular weight. At grafting densities of 0.6 chains/nm$^2$ the polymer architecture changes significantly radially from particle surface into bulk and local rigidity close to the core is increased, affecting both the $T_g$ and enthalpy relaxation rates (decrease). A dense concentrated polymer brush layer surrounding the particles makes up a large portion of less mobile polymer which also excludes interaction of polymer chains with the particle core from other particles in the system.

6.2 Self-Assembly of Hairy-Nanoparticles: Organic vs. Inorganic

6.2.1 Self-assembly of Organic HNPs

As observed in SEM images, organic HNPs with PDMS brushes and PS cores form 1D, 2D and 3D self-assemblies owing to their unique structures. The hierarchal ordering on a macroscopic scale is attributed to the large $\chi$ parameter of PS-PDMS and exceptionally low surface energy of the PDMS brushes. Most importantly, the self-assembly processes are intrinsically driven in much the same way that atoms combine to form molecules as formed SiO$_2$ in nature. Our findings confirmed the prophecy in the seminal research work by A. H. Groeschel et al.$^{182}$ as the soft patchy nanoparticles is remarkably analogous to the principal atomic-bonding-mediated self-assembly. The self-assembly of such core-shell mHNPs is an efficient strategy for producing appealing superstructures with complex, hierarchical architectures for potential applications in materials science and engineering.
6.3 Future Work

The work reported in this dissertation is only a starting point for the study of the structure-property relationships of hairy-nanoparticle systems. All the addressed topics should be further explored, in order to obtain a clear understanding of how to control the parameters of these materials and develop them for specific applications. There are four aspects that should be investigated and performed:

1. Toughening Studies
   - Determine the optimal grafting density and degree of polymerization for polystyrene HNPs that can facilitate the assembly of nanoparticles into mechanically robust, ordered solid structures with polymer-like elastic and fracture characteristics;

2. Simulation of MARTINI CG PS HNP models
   - Construction of cooling curves to validate experimental glass transition temperatures;
   - Probe non-isotropic polymer distribution (predict how and where polymer chains covalently attach to silica particle);
   - Simulate Physical ageing of neat polymer and HNPs systems;

3. Simulation of polystyrene and polydimethylsiloxane HNP TraPPE-UA CG models
   - Simulate the self-assembly of the traditional HNP systems (polystyrene and polydimethylsiloxane);

4. Synthesis and characterization of Traditional HNP systems (polystyrene and polydimethylsiloxane)
   - Study the parameters that have an effect on the self-assembly of the HNP.
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