Dynamics in Polymer Nanocomposites

Sangah Gam

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Abstract
Polymer diffusion and matrix morphology are investigated in polymer nanocomposites (PNCs). Using elastic recoil detection, tracer diffusion coefficients ($D$) of dPS and dPMMA are measured in PNCs containing polystyrene (PS) with phenyl-capped (Ph) silica, and poly(methyl methacrylate) (PMMA) with hydroxyl-terminated (OH) silica nanoparticles (NPs), respectively. As NP volume fraction increases or NP size decreases, polymer diffusion slows down. Moreover, $D$ plotted relative to diffusion in a pure PS matrix (i.e., $D/D_0$) falls on a master curve when plotted against the interparticle distance of NPs relative to the tracer radius of gyration, $ID/2R_g$. This slowing down with increasing confinement is consistent with an entropic barrier model which captures conformational entropy loss as macromolecules squeeze through a bottleneck (i.e., array of NPs). To investigate polymer-NP interactions, tracer diffusion of dPMMA is investigated in PMMA:OH-NP. Because of the attraction between dPMMA segments and OH groups on the NPs, tracer diffusion is slower than in the dPS system which involve weak interactions with the phenyl grafted NPs. Third, tracer diffusion is investigated in a bicontinuous structure. By adding NPs that segregate and jam at the interface during phase separation, a novel processing method was developed to prepare discrete or bicontinuous structures of PMMA-poly(styrene-ran-acrylonitrile) (SAN) films. A jamming map of the morphology summarizes the NP concentration and film thickness to produce either morphology. Diffusion of dPMMA in this bicontinuous structure is slower than in PMMA, a result attributed to the tortuosity of the continuous PMMA matrix phase. In summary, macromolecular diffusion has been investigated in PNCs as a function of tracer molecular weight and matrix properties including NP volume fraction, NP size, and NP interactions with tracer molecule. Understanding how to disperse NPs at high loadings is crucial for fabricating polymeric devices including membranes for fuel cells and organic solar cells. These diffusion studies are also practically important for selecting processing conditions to prepare hybrid materials. Finally, the bicontinuous morphology is attractive for applications requiring high interfacial area such as organic solar cells, membranes, catalysis, and fuel cells.

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DYNAMICS IN POLYMER NANOCOMPOSITES

Sangah Gam

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IN

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ABSTRACT

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Polymer diffusion and matrix morphology are investigated in polymer nanocomposites (PNCs). Using elastic recoil detection, tracer diffusion coefficients ($D$) of dPS and dPMMA are measured in PNCs containing polystyrene (PS) with phenyl-capped (Ph) silica, and poly(methyl methacrylate) (PMMA) with hydroxyl-terminated (OH) silica nanoparticles (NPs), respectively. As NP volume fraction increases or NP size decreases, polymer diffusion slows down. Moreover, $D$ plotted relative to diffusion in a pure PS matrix (i.e., $D/D_0$) falls on a master curve when plotted against the interparticle distance of NPs relative to the tracer radius of gyration, $ID/2R_g$. This slowing down with increasing confinement is consistent with an entropic barrier model which captures conformational entropy loss as macromolecules squeeze through a bottleneck (i.e., array of NPs). To investigate polymer-NP interactions, tracer diffusion of dPMMA is investigated in PMMA:OH-NP. Because of the attraction between dPMMA segments and OH groups on the NPs, tracer diffusion is slower than in the dPS system which involve weak interactions with the phenyl grafted NPs. Third, tracer diffusion is investigated in a bicontinuous structure. By adding NPs that segregate and jam at the interface during phase separation, a novel processing method was developed to prepare discrete or bicontinuous structures of PMMA:poly(styrene-ran-acrylonitrile)
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**Figure 7.8** A schematic showing the tracer molecule diffusing into a bicontinuous structure consisting of a penetrable PMMA phase (gray) and impenetrable SAN phase (black). Here, the bicontinuous structure represents a magnified image of the cross-section shown in Figure 7.6 (b). The dotted lines surrounding the nanoparticles at the interphase represents the “fast diffusion” region which is taken to have a thickness of $\sim 2R_g$.

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**Figure 7.10** Diffusion profiles of dPMMA in (a) PMMA and (b) PMMA : SAN films with a bicontinuous morphology after 2 h annealing at 195°C measured using ERD. Solid line is a fit of experimental data with Fick’s second law equation using $D$ values of (a) $7.8x10^{-15}$ cm$^2$ s$^{-1}$ and (b) $5.4x10^{-15}$ cm$^2$ s$^{-1}$. The dashed line represents the sum of...
the solid line and surface peak. The matrix polymers are denoted in the legends. The surface peaks in Figure 7.10 (b) is attributed to the impenetrable SAN phase.

**Figure 8.1** Small (a) and large NPs (b) can have same interparticle distance (double arrow) but different confined path length between NPs.

**Figure A.1** Cantilever schematic and analysis used in BE-NanoTA. (a) A heated tip locally heats the near surface of the film. The inset shows the contact mechanics model used for contact resonance frequency, contact area and Young’s modulus. (b) Amplitude of tip oscillations in vertical plane as a function of frequency caused by thermal expansion of the material under the tip. Simple harmonic oscillator (SHO) model fits contact resonance behavior well (black line is SHO fit). SHO model was used for determination of contact resonance frequency. (c) Contact resonance frequency as a function of temperature for pure PMMA and SAN films. The resonance frequency decreases as the polymer softens signifying that the near surface glass transition has been observed.

**Figure A.2** (a) Dependence of contact resonance frequency on temperature and Young’s modulus was modeled according to the Hertzian + creep model described in the text. Initial slow increase in the contact radius is due to creep of polymer (after ref. 29), sharp increase at temperature higher than 180 °C is due to decrease in Young’s modulus (Hertzian model). (b) Mechanical model used for description of polymer creep.

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similar for samples annealed at 0.5 h and 2 h, when the difference in domain structure of these samples is substantial (Figures A.3 (a), A.3 (b)). This illustrates the importance of high resolution $T_g$ mapping and added benefits of BE-NanoTA comparing with bulk methods of thermal analysis for studies of polymer phase separation.

**Figure A.4** Comparison of thermo-mechanical analysis methods and potential applications. The sensitivity in displacement measurements and spatial resolution for DMA, LTA: Wollaston Probe, LTA: Silicon Probe, and BE-NanoTA. The accuracy in displacement measurements and spatial resolution required for different applications, including the mechanical properties of the surfaces, analysis of pharmaceuticals, lithography masks, organic layers in OLEDs (blue/dark grey rectangle). Fundamental studies include the mechanics of single molecules (white/light ellipse); ferroelectric transitions and thermal expansion of the materials (red/light grey rectangle).
Chapter 1

Introduction

1.1 Polymer nanocomposites

Polymer nanocomposites, consisting of a polymer matrix with embedded nanoparticles (NPs), are attractive because they can exhibit better properties (e.g. creep) than the polymer alone, and by selecting the proper NP, exhibit new combinations of properties\(^1,2\). One advantage of nano-sized fillers is that a lower amount of them can generate properties comparable to those imparted by the addition of traditional micro-sized fillers. Moreover, certain properties can be enhanced by addition of NPs (e.g. toughness) while others (e.g. transparency) are not affected due to the small size of NPs. Performance enhancements mainly result from higher surface area created by the reduction of the filler size which increases total interfacial area and number density of NPs and decreases mean particle-particle separation when compared with traditional fillers at the same NP volume fraction. As particle size decreases, the relative volume of interface with respect to the particle volume increases, if the thickness of the interfacial region surrounding the particle is fixed, and the effect of the interface on the properties becomes increasingly important. Because they have a large surface area, nanoscale particles have more sites for bonding with matrix, which helps to improve the strength or resistance to heat and oxidation\(^3\). The strength of the interaction between polymer and NPs can control the interfacial properties and dispersion of NPs, affecting the physical
properties. Functionalization of NPs is one of methods used to tune the interaction. An attractive interaction between a polymer and NP will increase the glass transition temperature with increasing NP loading, while a repulsive interaction will decrease the glass transition temperature\(^4,5\). Covalent bonding between polymer and NP enhances the tensile modulus, strength, and toughness\(^6\). Also, the size of the polymer chain, expressed as \(R_g\) (radius of gyration), relative to the size of the NP is important in determining the properties of polymer nanocomposites. NP shape also affects the relative volume of interface with respect to the particle volume which increases as the shape changes from plate to rod to sphere\(^1\). Functionality, such as conductivity\(^7\)-\(^12\), photosensitivity\(^13\)-\(^17\), optical properties\(^18\)-\(^21\), and catalytic behavior\(^22\) can be added to the polymer nanocomposites depending on the characteristics of polymer and NP.

By incorporating NPs into polymers, the mechanical, optical, thermal, electrical, gas transport properties etc. can be greatly enhanced. The properties of polymer nanocomposites are highly related to the microstructures and control of NP dispersion is required to obtain the desired properties. For example, addition of carbon nanotubes increases electrical and thermal conductivities as well as reduces flammability by the formation of interconnected NP network\(^23,24\). Simulations predict that the modulus of fully aligned clay–polymer nanocomposites is much higher than that of randomly dispersed clay-polymer nanocomposites\(^25\) and that barrier properties of clay-polymer nanocomposite are also dependent of clay dispersion\(^26\). Polymer nanocomposites with conducting or semiconducting NPs are potentially useful for electronic and opto-electronic applications such as flexible electronics, photovoltaic devices, organic light-emitting devices. End-functional polythiophene enhances the performance of
polythiophene/CdSe nanocrystals solar cells by increasing the dispersion of CdSe nanocrystals\textsuperscript{27}. Higher molecular weight of the polymer in poly(3-hexylthiophene)/TiO\textsubscript{2} nanorod hybrid photovoltaic devices creates a more continuous absorption region and reduces the number of grain boundaries and thus, enhances the power conversion efficiency relative to that of lower molecular weight of the polymer\textsuperscript{28}. Also, a mixture of polythiophene and [6,6]-phenyl C61-butyric acid methyl ester (PCBM) has been used as the active layer in a polymer-based photovoltaic device\textsuperscript{29}. This blend undergoes phase separation into a bicontinuous morphology that enhances the device efficiency by controlling the sample preparation condition\textsuperscript{29}.

NPs can be added to polymers with different architectures such as block copolymers, dendrimers, polymer blends etc., which in turn can be used as a scaffold to control the spatial and orientational distribution of NPs\textsuperscript{30, 31}. Control of NP location in a block copolymer is determined by the interplay between particle-particle interaction, particle-polymer interaction, particle size and shape relative to the size and geometry of the host domains. Of particular interest for flexible data storage media, the spatial pattern of magnetic NPs such as iron, iron-platinum, iron–cobalt, and cobalt–nickel alloy NPs in a block copolymer can be achieved by the selective sequestration of NPs within one domain\textsuperscript{32, 33}. In addition to the spatial distribution of NPs, adding NPs to block copolymer or polymer blend films can change the microstructure of the polymer. For example, the incorporation of NPs to block copolymer can result in various morphologies ranging from spherical to lamellar\textsuperscript{34, 35} whereas, in polymer blends, the NPs can stabilize the morphology and change the structure from discrete to bicontinuous\textsuperscript{36, 37}. 

3
1.2 Polymer-nanoparticle interface in nanocomposites

The interface between NP and polymer is of great interest because the interfacial property can have a large impact on the macroscopic properties of polymer nanocomposites. The interface is defined as the region adjacent to the particle surface and the properties of a polymer chain less than a few $R_g$ from the particle surface can differ from those in the bulk because polymer dynamics are influenced by the particle surface. Compared to traditional micro-sized fillers, nano-sized fillers create higher interfacial area in the polymer matrix and thus, the volume fraction of polymer affected by the particles will be increased and the effect of the interface on the macroscopic properties will be more significant. Functionalization of the particle surface using short molecules or polymers is one approach to modify the polymer-NP interface. Short molecules, including silane coupling agents, can be covalently attached to the surface of particles, such as silicon, aluminum, titanium oxide, to tailor the interaction. Also, polymers can be grafted to particle surfaces using grafting-to and grafting-from methods. In the grafting-to method, polymers having functional end groups react with complementary surface sites on the particle. In this method, steric hindrance imposed by the previously grafted polymer chain limits grafting density. In the grafting-from method, chains grow by polymerization from preformed surface-grafted initiators and, relative to the grafting-to method, a high grafting density can be achieved at high molecular weight. Various polymerization methods such as atom transfer radical polymerization, nitroxide-mediated polymerization, chain transfer polymerization were used to modify the particle surface and thus polymer-particle interaction. For example, a favorable
interaction between polymer and NP achieved by functionalization enhances the miscibility and dispersion\textsuperscript{45}.

In addition to the enthalpic interaction between polymer and NPs, interfacial properties can be controlled by entropic energy contributions. Wettability between a polymer chain and a particle is mainly determined by entropy when the polymer brush is chemically identical to the matrix polymer. The NP grafted chain length ($N$), grafted chain density, particle size, and the degree of polymerization of the host polymer ($P$) are important variables to control the wetting behavior. The dispersion of NPs is enhanced as particle size decreases because of the weaker attraction between brushes, reduced chain stretching, and larger translational entropy of mixing\textsuperscript{19, 46}. Flory theory suggests that the grafted chains and matrix polymer chains are miscible when $P \leq N^{1.1}$\textsuperscript{47}. Experimentally, for gold NPs grafted with polystyrene (PS) in a PS matrix, Kim et al.\textsuperscript{48} found that the condition for miscibility is $P < 3N$. Namely, as the grafted chain length ($N$) increases, the wettability between polymer and NP is enhanced because of increased brush-melt penetration and high curvature of NPs.

To understand the effect of interface on local polymer relaxation, the glass transition temperature in thin films on a silicon substrate was measured as a function of film thickness\textsuperscript{4, 5}. As the thickness of a polystyrene film on a silicon substrate decreases (below ~ 200 nm), the glass transition temperature decreases due to the repulsive interaction between polystyrene and the substrate; however for film thicknesses greater than ~ 200 nm, the glass transition temperature is almost same as the bulk value, ~ 106 °C. This result demonstrates that a solid/polymer interface can influence a bulk property. For
PS with silica NPs, the glass transition temperature was observed to decrease as interparticle distance decreases (NP loading increases) indicating that the interparticle distance plays a role analogous to the thickness in thin polymer films$^5$. For a favorable interaction between polymer and NP, the glass transition temperature increases as interparticle distance decreases$^4$. Also, gas permeability increases as filler concentration increases because of an increase in the free volume resulting from the incorporation of NPs$^{49}$. In this dissertation, polymer tracer diffusion is measured in polymer nanocomposites that exhibit weak and strong attractive interactions between polymer and particle. In addition to enthalpic interaction, polymer dynamics is found to depend strongly on interparticle distance, radius of gyration of the tracer, and particle loading.

1.3 Outline of the dissertation

This dissertation focuses on polymer tracer diffusion in a series of polymer nanocomposites. These studies are designed to investigate the effects of (i) tracer molecular weight and NP loading, (ii) NP size and polydispersity, (iii) polymer-NP interaction, and (iv) matrix morphology (i.e., a bicontinuous structure). In chapter 2, the theoretical background is given for polymer diffusion in an entangled melt (i.e., reptation), random media, and confined media. The theory describing how NP dispersion depends on thermodynamic factors is also given. Chapter 3 describes experimental methods and characterization techniques. Chapter 4 to 7 gives the main experimental results and is summarized in Table 1.1. Chapter 8 suggests the possible future studies.
Appendix I describes morphology mapping of phase separated polymer blend films using nano-thermal analysis.

Table 1.1 Summary of Chapters 4 to 7, Appendix I

Chapter 4

<table>
<thead>
<tr>
<th>Title</th>
<th>Macromolecular diffusion in a crowded polymer nanocomposite</th>
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<tbody>
<tr>
<td>Objective</td>
<td>Understand the mechanism of polymer diffusion in a model polymer nanocomposite as a function of nanoparticle loading and tracer molecular weight</td>
</tr>
</tbody>
</table>
| Major findings | - As nanoparticle loading or tracer molecular weight increases, polymer diffusion slows down.  
  - The tracer diffusion coefficient of dPS in the nanocomposite relative to the pure PS matrix ($D/D_0$) plotted against the nanoparticle separation relative to the size of tracer molecule (i.e., $ID/2R_g$) falls on a master curve.  
  - Macromolecular diffusion through crowded polymer nanocomposites is controlled by entropic barriers.  
  - Published in *Macromolecules*, 44, 3494–3501 (2011) |

Chapter 5

<table>
<thead>
<tr>
<th>Title</th>
<th>Polymer diffusion in a polymer nanocomposite: Effect of nanoparticle diameter, nanoparticle polydispersity and interparticle polydispersity</th>
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<tbody>
<tr>
<td>Objective</td>
<td>Compare polymer diffusion as a function of nanoparticle size, nanoparticle polydispersity and interparticle polydispersity in identical polymer nanocomposites</td>
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</tbody>
</table>
| Major findings | - At the same nanoparticle volume fraction, smaller nanoparticles slow down polymer diffusion more than larger nanoparticles.  
  - The tracer diffusion coefficient of dPS in the nanocomposite relative to the pure PS matrix ($D/D_0$) plotted against the NP separation relative to the size of tracer molecule (i.e., $ID/2R_g$) is independent of nanoparticle size. |
- The interparticle distance is investigated as a function of the polydispersity and size (number and volume average) of the NPs.

- The collapse of $D/D_0$ plotted against $ID/2R_g$ is compared for monodisperse NPs (number and volume average) and polydisperse NPs; the best agreement is found when $ID$ is calculated using the number average size and polydispersity.

- In addition, $ID$ is calculated using monodisperse spheres having a distribution of $ID$: $D/D_0$ plotted against $ID/2R_g$ also collapses onto a master curve.

**Chapter 6**

<table>
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<tr>
<th>Title</th>
<th>Polymer diffusion in a polymer nanocomposite: Effect of polymer-nanoparticle interaction</th>
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<tbody>
<tr>
<td>Objective</td>
<td>Study how attractive interactions between tracer polymer and nanoparticle affects polymer diffusion</td>
</tr>
<tr>
<td>Major findings</td>
<td>- The tracer diffusion coefficient of dPMMA in the nanocomposite relative to the pure PMMA matrix ($D/D_0$) plotted against the NP separation relative to the size of tracer molecule (i.e., $ID/2R_g$) collapse onto a master curve.</td>
</tr>
<tr>
<td></td>
<td>- Compared at same nanoparticle volume fraction and $ID/2R_g$, a favorable interaction between polymer and nanoparticle slows down polymer diffusion more than the weakly interacting matrix (Chapter 5).</td>
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<tr>
<td></td>
<td>- Diffusion of dPS in a PS matrix is faster if the surface group is phenyl ethyl compared to phenyl alone, possibly due to a weaker attraction.</td>
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<tr>
<td></td>
<td>- Based on the diffusion measurements, the difference in the enthalpic interaction energy in PS:ph-silica and PMMA:silica is found to be proportional to the interfacial area between PS (PMMA) and silica.</td>
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**Chapter 7**

<table>
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<tr>
<th>Title</th>
<th>Polymer diffusion into a bicontinuous polymer blend stabilized with nanoparticles</th>
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8
Objective | Understand how polymers diffuse through one continuous tortuous phase

Major findings | - Phase map against nanoparticle loading and film thickness dictates the condition for the formation of bicontinuous structure.

| - Polymer diffusion into a bicontinuous morphology is slower than homopolymer alone; factors that control diffusion include the accessible PMMA volume fraction, tortuosity of the PMMA phase as well as bulk vs interphase diffusion pathways.

| - By comparing the real tortuous path length to 1-D diffusion length, polymer diffusion near the interphase region (~2Rg) is shown to be faster than that in the center of PMMA phase.

| - Published (in part) in *Soft Matter*, Advance Article (2011)

Appendix I

| Title | Morphology mapping of phase separated polymer films using nano-thermal analysis

| Objective | Understand the phase evolution of polymer blend films by measuring the glass transition temperature in the near surface region

| Major findings | - AFM based band excitation nano thermal analysis (BE-NanoTA) can be used to measure the mechanical properties and glass transition temperature in the near surface region with a point-to-point lateral resolution of 50 nm.

| - BE-NanoTA analysis confirms the poly(styrene-ran-acrylonitrile) (SAN) : poly(methyl methacrylate) (PMMA) films undergo an early and intermediate stage of phase separation.

| - BE-NanoTA provided new observations including SAN and PMMA rich channels near the surface at early times, as well as SAN-rich domains trapped within PMMA domains that span the film during intermediate times.

| - Published in *Macromolecules*, 43, 6724–6730 (2010)
1.4 References

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Chapter 2

Theory of Polymer Diffusion in Melts, Confined Media, and Nanocomposites

2.1 Diffusion of high molecular weight polymers in an entangled polymer matrix

The diffusion of a linear, high molecular weight polymer chain in an entangled polymer matrix is controlled by two relaxation mechanisms: reptation\(^1, 2\) and/or constraint release\(^3-5\). Reptation was proposed by de Gennes\(^1, 2\) and Doi and Edwards\(^6\). The reptation model describes chain motion as being restricted to a confining tube-like region as shown in Figure 2.1. In the reptation model, polymer chain slides through the primitive path, while the motion is hindered normal to the primitive path by the topological constraints forming the tube which result from the entanglements with neighboring chains. The reptation model showed that tracer diffusion coefficient of a polymer chain depends only on its molecular weight when constraints defining the tube are relatively immobile. However, if constraints relax before the tracer has left the tube, an additional contribution to diffusion called constraint release can contribute. Below the entanglement molecular weight, the Rouse model\(^5\) explains the motion of chains.
2.1.1 Relaxation times and diffusion coefficients

In the reptation model, the chain diffuses by forming small loops along the contour of the primitive path. This curvilinear motion of the chain along its tube is characterized by the Rouse friction coefficient $\zeta$ and the curvilinear diffusion coefficient $D_C$ is obtained from the Einstein relation:

$$D_C = \frac{kT}{N\zeta}$$  \hspace{1cm} (1)

where $N$ is the degree of polymerization. The reptation time that it takes for the chain to diffuse out of the original tube of average length $<L>$ is

$$\tau_{rep} \approx \left(\frac{L}{D_C}\right)^2 \approx \frac{\zeta b^2 N^3}{kT N_e} = \frac{\zeta b^2}{kT} b N_e^2 \left(\frac{N}{N_e}\right)^3$$  \hspace{1cm} (2)

where the average contour length $<L>$ of the primitive path is the product of the entanglement strand length $a$ and the average number of entanglement strands per chain $N/N_e$, $<L> \approx a N/N_e \approx b^2 N / a \approx bN / \sqrt{N_e}$ and $b$ is the monomer size. The reptation time $\tau_{rep}$ is predicted to be proportional to the cube of the molecular mass whereas experimentally $\tau_{rep} \sim M^{3.4\pm 0.2}$. The chain moves a distance of order of its own size $R$, during its reptation time $\tau_{rep}$, since this is the time scale at which the tube is abandoned:

$$\frac{D_{rep}}{\tau_{rep}} \approx \frac{R^2}{kT} \frac{N_e}{\zeta N^2}$$  \hspace{1cm} (3)
where \( R \approx a \sqrt[\frac{N}{N_e}] \approx b \sqrt[\frac{N}{N_e}] \).

For times less than the reptation time, topological constraint imposed on a given chain can disappear when the neighboring chains defining the confining tube move away, leading to a modification of the confining tube. This chain motion is called constraint release. A single linear chain with \( N \) monomers in a melt of shorter \( P \)-mers has two relaxation mechanisms – reptation and constraint release. The \( N \)-chain is treated as a Rouse chain with \( \frac{N}{N_e} \) segments, where \( N_e \) is the average number of monomers in an entanglement strand. The relaxation time of a topological constraint imposed on the \( N \)-chain by surrounding \( P \)-chains is the reptation time of the \( P \)-chains \( \tau_{\text{rep}}(P) \). The relaxation time of the confining tube by constraint release is the Rouse time of \( \frac{N}{N_e} \) segments with segment relaxation time \( \tau_{\text{rep}}(P) \):

\[
\tau_{\text{tube}} \approx \tau_{\text{rep}}(P) \left( \frac{N}{N_e} \right)^2
\]

Since reptation and constraint release are independent mechanisms, the diffusion coefficient of a \( N \)-chain is the sum of two contributions:

\[
D \approx \frac{R^2}{\tau_{\text{rep}}(N)} + \frac{R^2}{\tau_{\text{tube}}}
\]

For long matrix chains (large \( P \)), reptation controls the motion of \( N \)-chains, while for short matrix chains (small \( P \)), constraint release controls the diffusion of \( N \)-chains. This was confirmed by experiments on tracer diffusion of deuterated polystyrene into a
polystyrene melt using elastic recoil detection (ERD) as shown in Figure 2.2\(^8\). An alternative method to describe the constraint release mechanism was proposed by Graessley\(^4\) who assumed that a \(N\)-chain moves in the lattice. When one of the segments on the \(N\)-chain moves laterally into a neighboring cell on the lattice by the removal of one of the \(z\) bars, the primitive path of the confining tube is changed. The diffusion coefficient from constraint release and reptation mechanisms is given by

\[
D \approx D_{rep} (1 + \alpha N_c^2 N \pi^{-3}), \text{ where } \alpha \approx (48 / 25) z (12 / \pi^2)^{-1}.
\]

2.1.2 Experimental techniques to measure tracer diffusion

Polymer diffusion in a polymer melt has been studied using a variety of techniques including elastic recoil detection (ERD)\(^8-10\), Rutherford backscattering spectrometry (RBS)\(^11,12\), dynamic secondary ion mass spectroscopy (DSIMS)\(^13\), nuclear reaction analysis\(^14,15\), neutron reflection (NR)\(^16\), and attenuated total reflection infra-red spectroscopy (ATR-IR)\(^17\). For example, Green et al.\(^8\) studied the effect of matrix (\(P\)) and tracer molecular weight (\(M\)) on the diffusion of long polymer chains using ERD and showed that for large \(P\), center of mass diffusion is in agreement with reptation and that the tracer diffusion coefficient is independent of \(P\) (\(D \sim M^2\)). For \(P\) less than a characteristic molecular weight (\(P^*\)) and greater than entanglement molecular weight (\(M_e\)), diffusion coefficient increases as \(P\) decreases due to the additional matrix contribution - constraint release as mentioned above. Also, temperature dependence of polymer tracer diffusion in a polystyrene melt was investigated using ERD and was described by the Vogel equation\(^10\). RBS was used to measure polymer diffusion by
detecting a motion of the marker (e.g. gold particle) at the interface of two polymer phase or by modifying one polymer with a heavy element (e.g. chlorine, bromine). Polymer diffusion was also measured using DSIMS by detecting deuterium and hydrogen profiles with a high resolution ~14 nm. Interdiffusion between two polymers has been studied using nuclear reaction analysis and NR by measuring the interfacial width as annealing time or annealing temperature increases. The measurement of interfacial width as a function of annealing time provides information about the short-time relaxation that reflects the characteristic time of segmental motion comparable to the tube diameter (Rouse time, $\tau_e$) up to center of mass relaxation time where the whole molecule has moved a radius of gyration and disengaged from its initial tube (reptation time, $\tau_{rep}$). Between these two limits, the Rouse relaxation time, $\tau_R$ indicates the time in which the motion of the single segments becomes coordinated over the entire length of the chain. ATR-IR was also used to observe interdiffusion between polymers.

2.2 Polymer dynamics in confined media

2.2.1 Models for polymer diffusion in random media

Molecular transport in heterogeneous media with impenetrable obstacles has been explained by the Maxwell model which was originally derived to describe thermal conductivity. In the case of diffusion, thermal conductivity is analogous to diffusivity. To describe diffusion through a composite medium with dispersed spherical particles, the Maxwell model expresses a diffusion coefficient as:
\[
\frac{D - D_2}{D + 2D_2} = \phi \frac{D_1 - D_2}{D_1 + 2D_2}
\]  

(6)

where \( D_1 \) is the diffusion coefficient in the dispersed particles, \( D_2 \) is the diffusion coefficient in the continuous medium, and \( \phi \) is the volume fraction of particles. If the particles are impenetrable \( (D_1 = 0) \), \( D = D_2 \left( \frac{1 - \phi}{1 + \phi / 2} \right) \) and as particle loading increases, the diffusion coefficient in the composite decreases. However, Maxwell model is derived under the assumption that particles are so sparsely distributed in the continuum that any interaction between them is negligible and thus, the volume fraction \( \phi \) of the particles should be small.

Ogston et al.\textsuperscript{21} described the transport of compact particles through fibrous obstacles using the stochastic or random-walk model of diffusional migration which regards diffusion as a succession of small unit displacements of individual particles. Diffusion rates of compact particles are reduced in the solution with fibrous obstacles according to the relationship:

\[
\frac{D}{D_0} = \exp\left(-kr^0.5\right)
\]  

(7)

where \( r \) is the radius of the particle, \( l \) is the length of the fibrous obstacles, and \( k \) is a dimensionless constant applying to all particles. The Ogston model has been found to be in agreement with the sedimentation rates of compact macromolecules in solution of hyaluronic acid\textsuperscript{22}. Moreover, the \( k (\pi^{0.5}) \) value is in reasonable agreement with the value estimated by Laurent et al\textsuperscript{23}. The Ogston model is valid only when the size of particle is smaller than a pore size\textsuperscript{21, 24}. Moreover, both Maxwell and Ogston models do not take
into account the change of chain conformation near the obstacles by entropic confinement or enthalpic interactions. Thus both models are insufficient to explain polymer diffusion in the presence of dispersed particles.

Polymer dynamics in randomly distributed impenetrable obstacles has been successfully described by the entropic barrier model (EBM)\textsuperscript{25-29} using Monte Carlo simulations and scaling arguments. In randomly distributed fixed obstacles, cages or cavities are separated by a bottleneck which acts as an entropic barrier. At the bottleneck, a polymer chain is squeezed leading to the reduction of the number of possible chain conformations and chain entropy as shown in Figure 2.3. Chain dynamics is investigated for $0 \leq$ volume fraction of obstacles ($\phi_{\text{obstacles}}$) $\leq 0.5$. By plotting the mean-square displacement of the center of mass of the chain, $R^2(t)$, against time $t$ three distinct regimes are observed as shown in Figure 2.4. In the early and later time regimes, $R^2(t) \sim t$ indicating classic diffusion. The duration of the intermediate crossover regime increases as the chain length ($N$) increases as shown in Figure 2.4 and as $\phi_{\text{obstacles}}$ increases (not shown). In the early regime, the diffusion coefficient scales as $N^{1.1 \pm 0.1}$ in accordance with the Rouse law while in the late regime, diffusion coefficient cannot be described by the reptation law, $D \sim N^2$, and $D$ scales as $N^3$ for sufficiently large values of $N$. This demonstrates that the chain dynamics in the presence of obstacles are slower than reptation, due to the slowing down of the chain at the bottleneck. For an activated process,

$$D = D_0 \exp(-\Delta F/k_B T)$$

(8)

where $D_0$ represents diffusion coefficient without any obstacles (i.e., $\phi_{\text{obstacles}} = 0$). $\Delta F (= F_2 - F_1)$ is a free energy difference in the cavities of size $C$ and bottlenecks of size $B$ (c.f.
Figure 2.3) and $F_1$ and $F_2$ are the scaling form for the confinement free energy per chain in a cavity and bottleneck, respectively. According to scaling arguments, $F_1$ and $F_2$ scale as $NC^{-1/\nu}$ and $NB^{-1/\nu}$, respectively, where $\nu$ is 0.5 for a Gaussian chain$^5$. Because the length of the bottleneck is not sufficiently large to confine the whole chain in it (Figure 2.3), partial confinement of a chain in the bottleneck is considered using the appropriate weighing factors and the free energy change is

$$\frac{\Delta F}{k_B T} = \left[ fF_2 + \frac{(1-f)}{z} F_1 \right] - F_1$$  \hspace{1cm} (9)

where $f$ is the fraction of monomers in the bottleneck and $z$ is the average number of cavities containing unconfined segments per bottleneck. Substituting eq. (9) and the scaling form for the confinement free energy into eq. (8),

$$\frac{D}{D_0} = \exp \left\{ -N \left[ fB^{-1/\nu} + \left( \frac{1-f}{z} - 1 \right) C^{-1/\nu} \right] \right\}$$  \hspace{1cm} (10)

To obtain the scaling form of $f$, we assume that the chain consists of $g$ blobs with size $B$ and each blob has $m$ segments ($B \sim m^\nu$). The total length of the chain $R$ is $R \sim gB \sim (N/m)B \sim (NB^{-1/\nu})B \sim NB^{1-1/\nu}$ and thus, $f \sim 1/R \sim N^{-1}B^{1/\nu-1}$. $f$ is 1 for $\zeta \leq 1$ and $N^{-1}B^{1/\nu-1}$ for $\zeta >> 1$ where $\zeta \sim R_a^2 R_b / B^2 h$ and $R_a$ and $R_b$ are the components of the radius of gyration of the chain in a plane perpendicular and parallel to the axis of the capillary with length $h$ in the bottleneck.

For $\zeta \leq 1$, $D/D_0$ decays exponentially with $N$ ($D / D_0 = \exp \left\{ -N \left[ B^{-1/\nu} - C^{-1/\nu} \right] \right\}$). However, when a polymer chain is highly confined ($\zeta >> 1$), the scaling form for $D/D_0$ is given by$^{25, 28, 29}$:

$$\ln(D / D_0) / N = A - s / N$$  \hspace{1cm} (11)
where \( s \) is proportional to \( B^\gamma (1 - z^{1/(B/C)})^{1/\nu} \). For \( 20 \leq N \leq 80 \), Monte Carlo simulations\(^{25,28,29} \) to determine \( D \) agree with the scaling predictions of eq. (11) and exhibit a slope that increases as the bottleneck size, \( B \), decreases.

This EBM captures the diffusion of linear polymers through porous glasses filled with solvent\(^{30,31} \). Moreover, the electrophoretic mobility of star and ring polymers is well-described by the EBM, which predicts topological independence at moderate confinement conditions\(^{32} \). However, the EBM has not been applied to the polymer melts with dispersed obstacles.

### 2.3 Polymer diffusion in nanocomposites

#### 2.3.1 Experimental studies of polymer diffusion in a polymer nanocomposite

Previously, polymer diffusion in a polymer nanocomposite has been studied using DSIMS\(^{33} \) and ERD methods\(^{34,35} \). While the tracer diffusion of deuterated polystyrene (dPS) measured by DSIMS was not influenced by adding 5 vol% clay to a polystyrene (PS) matrix, the same amount of clay added to poly(methyl methacrylate) (PMMA) was found to reduce the diffusion coefficient by a factor of 3\(^{33} \). For the tracer diffusion of dPS in a PS matrix containing carbon nanotubes (CNTs), diffusion initially decreased, reached a minimum, and then recovered as CNT concentration increased\(^{34,35} \). The minimum diffusion coefficient was observed at a concentration corresponding to the electrical percolation threshold. Theoretically, using molecular dynamics simulations, Kumar et al.\(^{36} \) showed that polymer diffusion slowed down by addition of NPs that attract the polymer, whereas diffusion was enhanced if this interaction was repulsive.
2.3.2 Hard sphere dispersion

Particle dispersion is a key factor in determining the polymer diffusion in a polymer nanocomposite because interparticle distance, which depends on particle size, loading, and dispersion, confines the diffusing chain. First, we assume that the distribution of particle size is monodisperse and thus, the number average and volume average diameters for monodisperse particles are the same. Under this assumption, the interparticle distance, $ID$, between the surfaces of neighboring particles is as follows:\(^{37}\):

$$ ID = d \left( \left( \frac{\phi_{\text{max}}}{\phi} \right)^{1/3} - 1 \right) $$  \hspace{1cm} (12)

where $d$ is the diameter of NPs, $\phi$ is NP volume fraction, and $\phi_{\text{max}}$ is the maximum packing density. As NP loading increases or NP size decreases, interparticle distance decreases resulting in the increase of confinement. $\phi_{\text{max}}$ depends on the packing type, such as simple cubic ($\phi_{\text{max}} = 0.5236$), face-centered cubic ($\phi_{\text{max}} = 0.7405$), body-centered cubic ($\phi_{\text{max}} = 0.6802$), and random dense packing ($\phi_{\text{max}} = 0.637 (=2/\pi)$).

When particle size is polydisperse, number average and volume average diameters of particle size will be different. In this case, the choice of one diameter to represent a distribution is problematic. As polydispersity of NP size increases at constant $\phi$, the number of particles per unit volume decreases and interparticle distance increases\(^{38},^{39}\). Also, if particles flocculate, the interparticle distance will increase\(^{38}\). Thus, all property measurements of nanocomposites must be accompanied by characterization of the size and dispersion of NPs.
2.3.3 Dispersion of nanoparticles with brushes in a polymer melt

The dispersion and the interparticle spacing between NPs are key factors that determine polymer chain dynamics and properties of polymer nanocomposites. NP diameter ($2R$), the degree of polymerization of the matrix polymer ($P$), the degree of polymerization of the grafted chain on NP ($N$), grafting density ($s$), surface functional groups on NP, and processing method can influence the NP dispersion in a polymer melt. NP dispersion in a polymer melt is mainly determined by translational and chain entropy if the grafted chains on NPs and a polymer melt are chemically identical. The wetting behavior between homopolymer and a chemically identical polymer brush on a particle surface has been studied using self-consistent field theory (SCFT)\textsuperscript{40,41}. Ferreira et al.\textsuperscript{40} showed that attractive interactions between two opposing polymer brushes occur when $s\sqrt{N} > (N/P)^2$ leading to particle aggregation and dewetting between polymer brush and polymer melt. Matsen et al.\textsuperscript{41} found that the attraction between two polymer brushes decreases when the molecular weight of a polymer melt is low, although the attraction between two brushes always exists. The effect of NP size on NP dispersion in a polymer melt was also investigated theoretically. As the core radius of NP becomes smaller than the size of grafted chains ($R < aN^{1/2}$), the polymer brushes on NP have a similar density profiles of a star polymer and less steric crowding, which weakens the attractive interaction between opposing brushes leading to the dispersion of NPs\textsuperscript{42}. When the size of a chain ($R_g$) in a polymer melt is larger than the total size of NP ($R_{NP}$) including the shell thickness ($R_g > R_{NP}$), chain stretching of a melt chain is reduced leading to NP dispersion\textsuperscript{43}. Moreover, because translational entropy depends on the volume fraction of
NPs ($\phi$) and NP diameter ($D$), NP dispersion is favored as NP size decreases $(F_{\text{trans}} \sim (\phi / ((D)^3)) \ln \phi)^{44,45}$.

NP dispersion in a polymer melt was also studied experimentally using a mixture of polystyrene (PS) and PS-grafted gold NPs\textsuperscript{46,47}. Smaller NPs ($R \approx aN^{1/2}$, $R_{NP} < R_g$) enhanced miscibility of the NPs in a polymer melt due to a weaker attraction between brushes, less chain stretching, and larger translational entropy of mixing. Longer brush lengths on NPs also promote NP dispersion due to increased brush-melt penetration and high curvature of NPs ($R << aN^{1/2}$)\textsuperscript{46}. The phase diagram for NP dispersion in a polymer melt was plotted against $P$ and $N$ and shows that NPs are miscible with a polymer melt for $P/N < 3$\textsuperscript{47}. Mackey et al.\textsuperscript{48} studied NP dispersion in a mixture of linear PS and cross-linked PS NPs and showed that NP dispersion is enhanced when the radius of gyration of the linear polymer is larger than the radius of the NPs.

Functionalization of NPs is one way to control NP dispersion by changing the polymer-NP interaction. For example, CdSe/ZnS core–shell nanoparticles or gold nanoparticles with surface functionalization with thiol-terminated poly(ethylene oxide) (PEO) can be well dispersed in PMMA because PEO is miscible with PMMA\textsuperscript{49,50}. In addition to functionalization, Tuteja et al.\textsuperscript{51} found that the processing methods of PNCs affected the degree of NP dispersion, and viscosity of PS : fullerene nanocomposites decreased or increased with increasing fullerene concentration depending on the processing methods. Thermal annealing of a poly(3-hexylthiophene) (P3HT) and phenyl-C$_{61}$-butyric acid methyl ester (PCBM) film produces a nanoscale interpenetrating network that increases the power conversion efficiency compared to homogeneously distributed PCMB in the P3HT matrix\textsuperscript{52}. In this dissertation, silica NPs were well-
dispersed in a PS matrix by modifying the particle surface with phenyl groups that are
similar to the pendant phenyl group in PS and heating the substrate to prevent long range
diffusion of NPs during drying. For the dispersion of silica NPs in a PMMA matrix,
unmodified silica NPs (i.e. hydroxyl terminated) were miscible in this system due to the
favorable interaction between PMMA and silica NPs.

2.4 Summary

In this chapter, the basic concepts of polymer diffusion in an entangled matrix and
under the confinement are briefly reviewed. In section 2.1, polymer relaxation
mechanisms in an entangled matrix, such as reptation or constraint release, and examples
of measuring of polymer diffusion in a polymer melt using various methods are
introduced. In section 2.2, models for polymer diffusion in random media – Maxwell,
Ogston, and entropic barrier models are described. In section 2.3, experimental studies of
polymer diffusion and nanoparticle dispersion in polymer nanocomposites are reviewed.
2.5 References


Figure 2.1 Reptation model: $N$-chain trapped in a “tube” of surrounding of $P$-chains.

Taken from http://nobelprize.org.
Figure 2.2  Effect of matrix molecular weight ($P$) and tracer molecular weight ($M$) on tracer diffusion coefficient $D^*$ at a constant fractional free volume of 0.042. The tracer molecular weight are: (□) $M = 55,000$; (●) $M = 110,000$; (○) $M = 255,000$; (■) $M = 520,000$; (∇) $M = 915,000$. Depending on $P$ and $M$, diffusion of a polymer chain is classified with reptation, constraint release, and coil diffusion in unentangled matrices. $P$ ranges from less than to greater than $M_c = 18,000$ Da. Taken from Green et.al.
Figure 2.3 Randomly distributed obstacles create cavities separated by bottlenecks. A polymer chain reduces the number of chain conformations (i.e., entropy) as it squeezes through the bottleneck of diameter $B$ and length $h$. 
Figure 2.4 Double log plot of the mean-square displacement of the center of mass, $R^2(t)$, and that of one bead relative to the center of mass, $r^2(t)$, versus time $t$ for different chain lengths ($N$) and $p$ ($= 1 - \phi_{\text{obstacles}}$) = 0.6 showing three distinct regimes. Taken from Muthukumar\textsuperscript{35}.
Chapter 3

Experimental Methods and Characterization Techniques

3.1 Introduction

Whereas experimental methods are introduced in subsequent chapter, the purpose of this chapter is to provide details that describe the preparation of polymer nanocomposite films with well-dispersed nanoparticles (NPs) and thin deuterated polymer layers as well as strategies for minimizing ion beam damage to polymers during ion beam experiments. To probe diffusion in polymer nanocomposites, NPs in a polymer matrix must remain similarly dispersed across a wide range of concentrations. Polymer nanocomposite films with well-dispersed NPs are not easily achieved. Another challenge to overcome in regard to the diffusion studies is the adhesion of poly(methyl methacrylate) (PMMA) films to substrates. To prepare bilayers, the detachment of thin deuterated PMMA (dPMMA) films from silicon is required. Ion scattering is used to determine the depth profile, and subsequently diffusion coefficient, in dPMMA/PMMA:silica bilayers. Because PMMA readily degrades under the ion beam a method was developed to minimize beam damage so that depth profiles of dPMMA with sufficient statistics could be accumulated. Finally, techniques used to observe the structure of the polymer nanocomposite and determine polymer diffusion in polymer nanocomposites are described.
3.2 Preparation of polymer films with well-dispersed silica nanoparticles

3.2.1 Nanoparticle and polymer systems

Tracer diffusion is investigated in polystyrene (PS) and poly(methyl methacrylate) (PMMA) matrix polymers containing nanoparticles (NPs). PS ($M_w = 265,000$ g mol$^{-1}$, polydispersity, PDI = 2.45) is mixed with phenyl-capped silica nanoparticles (NPs) (28.8 nm diameter). A second PS system consists of PS ($M_w = 400,000$ g mol$^{-1}$, PDI = 1.06) with smaller phenyl-capped silica (12.8 nm diameter). The silica NPs were obtained from Aldrich (Ludox AS40) and Nissan Chemicals (DMAC-ST), respectively. The as received aqueous dispersion of silica NPs (28.8 nm) is transferred to dimethylformamide (DMF) and water boiled off. These NPs are reacted with either phenyltrimethoxysilane (PhTMS) or phenylethyltrimethoxysilane (PhETMS) as a coupling agent while mixing for several hours. The capping agent was added to achieve a grafting density of 2 molecules per nm$^2$ which was measured using size exclusion chromatography (SEC) coupled with an IR absorption detector. The particle diameter and polydispersity were measured by dynamic light scattering (DLS), small-angle X-ray scattering (SAXS), and transmission electron microscopy (TEM). The smaller silica NPs (12.8 nm) in dimethylacetamide (DMAC) were centrifuged twice at 11000 rpm for 3 h. After the second centrifuge, DMAC : toluene (50 : 50) were added to the NPs. PhTMS was added to the NP solution which was stirred under the nitrogen gas flow at 90 °C for 22 h. For the small NPs, the grafting density was determined by thermogravimetric analysis (TGA). The coverage of PhTMS was 1.5 and 0.54 chains nm$^{-2}$ for 28.8 nm and 12.8 nm silica NPs, respectively.
PMMA ($M_w = 337,000$ g mol$^{-1}$, PDI = 1.82) with the smaller silica NPs (12.8 nm) are also used as a matrix for diffusion studies. The silica NPs were obtained from Nissan Chemicals (DMAC-ST). The particle diameter and polydispersity were measured by small-angle X-ray scattering (SAXS). All polymers and NPs used for polymer nanocomposites containing well-dispersed NPs in this thesis are listed in Table 3.1.

Table 3.1 Matrix (polymer nanocomposites) and tracer (deuterated polymer)

<table>
<thead>
<tr>
<th>Matrix</th>
<th>Polymer</th>
<th>$M_w$ (g mol$^{-1}$)</th>
<th>PDI</th>
<th>Silica NPs (number average diameter, $d_n$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polystyrene</td>
<td>265,000</td>
<td>2.45</td>
<td></td>
<td>Phenyl-capped silica NPs ($d_n = 28.8$ nm)</td>
</tr>
<tr>
<td>Polystyrene</td>
<td>400,000</td>
<td>1.06</td>
<td></td>
<td>Phenyl-capped silica NPs ($d_n = 12.8$ nm)</td>
</tr>
<tr>
<td>Poly(methyl methacrylate)</td>
<td>337,000</td>
<td>1.82</td>
<td></td>
<td>Unmodified silica NPs ($d_n = 12.8$ nm)</td>
</tr>
<tr>
<td>Tracer</td>
<td>Deuterated polystyrene</td>
<td>49,000</td>
<td>1.03</td>
<td></td>
</tr>
<tr>
<td></td>
<td>168,000</td>
<td>1.03</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>532,000</td>
<td>1.05</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Deuterated poly(methyl methacrylate)</td>
<td>93,000</td>
<td>1.03</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>281,000</td>
<td>1.02</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

3.2.2 Polymer nanocomposite film formation with well-distributed NPs

The polymer and NPs were each dissolved in DMAC or DMF, and then mixed at the appropriate ratio. Films were prepared using a doctor blade to coat a solution on a heated glass substrate (~100 °C) to form a film of thickness ~10 μm. The NP
concentration in the films was measured using thermogravimetric analysis (TGA). Thick films were prepared by hot pressing at ~150 °C. For TGA measurements, films were heated at 20 °C min⁻¹ to 400 °C and then held at 400 °C for 3 h to burn off the polymer.

Silica NPs are thought to disperse in both PS and PMMA matrix because of the charge stabilization of silica in a non-aqueous solvent that acts as Lewis bases. Both unmodified and phenyl-capped silica NPs in DMF are charge stabilized, which was confirmed using ξ-potential, SAXS, and DLS. The values of ξ-potential for unmodified and phenyl-capped silica NPs were -38 ± 6 mV and -65 ± 12 mV and aggregation was not observed for both NPs in DMF. As solvent evaporates during film formation, the charged NP structure is maintained until some of the solvent has been evaporated. Subsequently, protons solvated by DMF adsorb back onto the surface of the silica NP. As a result, the charged double layer collapses, the surface charge decreases, and NPs attraction drives cluster formation. However, if the viscosity of a polymer matrix is high enough to suppress the NP diffusion, well-dispersed NPs can be retained in the polymer matrix. Also, to prevent NP clustering, the substrate temperature is increased to ~100 °C. At this temperature, DMF evaporates quickly resulting in a highly viscous matrix which limits NP diffusion.

3.3 Preparation of deuterated polymer film for tracer diffusion couple

In this dissertation, the tracer diffusion couples consist of the nanocomposite matrix film covered with a thin deuterated polystyrene (dPS) or poly(methyl
methacrylate) (dPMMA) film. The dPS film is spin coated on a silicon substrate. The dPS can be easily floated off in water and transferred onto the thick nanocomposite matrix if the dPS film immersed in water within one hour after spin coating. However, the dPMMA film does not easily detached from silicon due to the favorable interaction between dPMMA and the silicon oxide on the silicon substrate. To solve this problem, a water-soluble chitosan layer is used as a buffer layer. Chitosan cg10 (60kDa, deacetylation = 87%) is dissolved in water. Because chitosan is insoluble at pH 7, hydrochloric acid is added dropwise to the chitosan solution to low the pH to 2.64. The chitosan solution is filtered, spin coat on a silicon substrate, and dried in a chemical hood overnight. A dPMMA layer is spin coated from a toluene solution on the chitosan layer. Upon immersion in water, the dPMMA floats off because the chitosan layer dissolves in water. To confirm that chitosan is not attached to the dPMMA layer after floating, Fourier transform infrared spectroscopy (FTIR) is used to characterize dPMMA, dPMMA/chitosan, and dPMMA films after being floated off. Figure 3.1 shows the FTIR results for the three films. The peak at 1107 cm$^{-1}$ is observed for the dPMMA/chitosan film but not for the dPMMA film nor the dPMMA film after being floated off. This study indicates that the chitosan layer dissolves in water and does not remain attached to the dPMMA layer after detachment from the chitosan/silicon substrate.

### 3.4 dPMMA depth profiling using ERD

Light ions at MeV energies are slowed by collisions with electrons in a polymer target. Whereas PS mainly undergoes cross-linking, PMMA degrades by chain cession
which results in smaller molecules which volatilize\(^2\). To reduce beam damage in dPMMA, elastic recoil detection (ERD) experiments are performed with a very low beam current (< 2 nA). After annealing at 195 °C for 72.5 h, the depth profile of dPMMA in a PMMA matrix was collected at beam currents of 1, 2, 3, 4 nA. Figure 3.2 shows the depth profiles at 1 and 4 nA after collecting 2 \(\mu\)C of charge. As beam current increases, the peak height decreases from 31 to 27 and the background counts from channel 250 to 300 increases. Both changes could influence accuracy of the diffusion coefficient determined by fitting profiles to Fick’s second law. Also, to minimize beam damage, 2 \(\mu\)C of charge is collected on 5 fresh spots for a total of 10 \(\mu\)C. Even though the data are collected on 5 different spots at a low beam current, beam damage occurs and the measured film thickness is \(~12\) nm, about 8 nm less than the original film thickness (\(~20\) nm).

The film thickness measured from the dPMMA deuterium profile depends on the underlying substrate. Figure 3.3 shows the deuterium profiles from dPMMA films deposited on a silicon substrate, chitosan layer on silicon substrate, and a PMMA matrix on silicon. The area under the each profile is largest on silicon substrate and smallest on PMMA. The area under the each profile from 280 to 350 (channel) is \(~440\) on silicon substrate and \(~400\) on PMMA while that from 250 to 350 (channel) is \(~440\) on silicon substrate and \(~420\) on PMMA, indicating that more noises are observed in the dPMMA profile on PMMA. The film thickness values on chitosan and PMMA are \(~16\) nm and \(~12\) nm, respectively. This behavior may be attributed to damage in the underlying substrate that affects the deuterium profile.
3.5 Characterization techniques

The study of polymer tracer diffusion utilized transmission electron microscopy (TEM), Rutherford backscattering spectrometry (RBS), and elastic recoil detection (ERD). TEM was used to evaluate the distribution of silica nanoparticle (NP) in the polymer matrix from a cross-section removed from the thick sample using a microtome. RBS was used to determine the depth profiles of silicon and oxygen in PNCs to determine if the NPs were uniformly distributed with depth. Finally, ERD was used to determine the depth profiles of deuterated polystyrene (PS) or poly(methyl methacrylate) (PMMA) in the matrix.

To observe the morphologies of phase-separated PMMA : poly(styrene-ran-acrylonitrile) (SAN) blend films containing NPs, atomic force microscopy (AFM) and scanning electron microscopy (SEM) combined with focused ion beam (FIB) were used.

3.5.1 Ion beam scattering techniques: ERD and RBS

Elastic recoil detection (ERD), also known as forward recoil spectrometry (FRES), is used to determine the depth profiles of deuterium and hydrogen. In ERD, a $^4\text{He}^+$ or $^4\text{He}^{2+}$ ion beam is accelerated at 2 to 3 MeV, intersects the plane of the sample at an angle $\alpha_1$, and recoils $^1\text{H}$ and $^2\text{D}$ which are collected by a solid state detector as shown in Figure 3.4 (a). In front of the ERD detector, a stopper filter is placed to prevent the signal from the forward scattered He from masking the H and D signal. The incident $^4\text{He}$ ions and forward scattered atoms lose kinetic energy by colliding with electrons on their
inward and outward paths, respectively, as well as the stopper filter in front of the detector (e.g., $^1$H and $^2$D). The final energy of the recoiled H and D atom is described by

$$E = K(\text{incident energy} - \text{energy lost on inward path}) - \text{energy lost on outward path} - \text{energy lost passing through filter}$$

where the kinematic factor $K$ is

$$K = \frac{4M_{\text{in}}M_{\text{at}}}{(M_{\text{in}} + M_{\text{at}})^{\frac{3}{2}}} \cos^2 \theta.$$  

Energy loss resulting from the inelastic collisions in the sample and the stopper filter can be determined from the stopping power of the material using SRIM (the Stopping and Range of Ions in Matter) and by measuring the energy loss in the filter using several beam energies and a known film such as dPS:PS, respectively.

Rutherford backscattering spectrometry (RBS) determines the composition of materials by detecting the backscattered incident ions impinging on a sample as shown in Figure 3.4 (b). The energy of the backscattered ions is recorded with a solid state detector and no filter is needed in front of the detector. The detected energy of the backscattered ions is

$$E = K(\text{incident energy} - \text{energy lost on inward path}) - \text{energy lost on outward path}$$

where the kinematic factor $K$ is

$$K = \left(\frac{M_{\text{in}} - M_{\text{at}}}{M_{\text{in}} + M_{\text{at}}}\right)^2.$$  

To perform RBS, the angle between the sample and incident beam is changed from glancing to normal incidence to the sample and the position of a detector is also moved as shown in Figure 3.4. Whereas ERD can measure the depth profiles of H and D, RBS using He is insensitive to these
light elements. The fundamentals of ERD and RBS are described in books by Chu and Feldman\textsuperscript{5,6}. Ion beam techniques for polymer research and data conversion methods are reviewed by Composto et al.\textsuperscript{3}.

In this dissertation, ERD and RBS were performed with an NEC minitandem Ion Accelerator (National Electrostatics Co.) at the Penn Regional Nanotechnology Facility at the University of Pennsylvania. In ERD, 3 MeV \(^4\)He\(^{++}\) ion and 10 \(\mu\)m Mylar foil were used to obtain dPS and dPMMA depth profiles at incident angle of 15\(^\circ\). The thin slab approach was applied to convert the energy to depth\textsuperscript{3}. The instrumental resolution is captured by the Gaussian function,

\[
y = \frac{1}{\sigma \sqrt{2\pi}} \exp\left(-\frac{x^2}{2\sigma^2}\right), \quad \text{where } \sigma = 30\text{--}39 \text{ nm.}
\]

The depth resolution and accessible depth are 60\text{--}78 nm and \(\sim 800 \text{ nm}\), respectively. The deuterium concentration profile in the matrix is measured by elastic recoil detection (ERD) and tracer diffusion coefficients obtained by fitting the profile to a one-dimensional (1-D) solution to Fick’s second law equation for a finite source in a semi-infinite medium\textsuperscript{7,8}. Diffusion coefficients were obtained from multiple measurements taken for each sample including those annealed at different times and only the profiles having a sufficient diffusion length were considered. A least squares fitting routine was used to determine tracer diffusion coefficient \((D)\) with \(\chi^2\) ranging from \(\sim 10^{-3}\) to \(\sim 10^{-4}\). RBS used 2 MeV \(^4\)He\(^+\) ion at a normal angle of 90\(^\circ\) to obtain silicon and oxygen depth profiles in polymer:silica films. The depth distribution of silica near the outer few microns is critical because that is the range over which the concentration profile is measured. XRUMP simulation program\textsuperscript{9} was used to convert the raw spectra (energy, yield) to a depth profile.
3.5.2 Transmission electron microscopy (TEM)

In transmission electron microscopy (TEM), electrons are accelerated at high voltage (100-1000 kV) and transmitted through an ultra thin (~100 nm) specimen. The contrast in a TEM image is attributed to the differences in electron density resulting from the thickness and composition of the specimen. TEM has a significantly higher resolution than optical microscopy due to the small wavelength of electrons. In this dissertation, the lateral distribution of silica NPs in PS and PMMA films was observed using TEM after cross-sectioning. Before imaging, the films were embedded in an epoxy, dried at ~ 60 °C overnight, and cross-sectioned using a microtome.

3.5.3 Atomic force microscopy (AFM)

Atomic force microscopy (AFM) is a scanning probe microscopy (SPM) technique that provides topography images of the specimen surface. The first SPM technique was scanning tunneling microscopy (STM) invented by Binnig and Rohrer\(^{10}\) in the early 1980s who received the Nobel Prize in Physics for this development. However, STM is used for imaging conducting or semiconducting surfaces, a limitation overcome by the development of AFM in 1986. AFM is capable of imaging almost any type of surface, including polymers, ceramics, and biological samples. AFM can be used to measure the height, depth, and lateral sizes of morphological features, in-plane molecular ordering, roughness, etc. The general components of the AFM instrument are a cantilever with a sharp pyramid tip (probe), laser beam, and detector. The movement of
the cantilever is driven by a tube piezoelement and the force between tip and sample results in the deflection of the cantilever when the tip is brought close to the sample surface. The deflection is measured by reflecting the laser beam from the top of the cantilever. In tapping mode, the cantilever oscillates vertically near its resonance frequency. The interaction between a tip and the sample surface decreases the amplitude of the oscillation as the tip approaches the surface. Both topography and phase information can be mapped during scanning.

In this dissertation, an Agilent MAC III AFM was used in tapping mode with silicon tips to scan the surface and internal morphologies of phase separated PMMA:SAN blend films. To observe the internal morphology, the PMMA phase was removed by first exposing the film to UV-ozone or an ion beam and then the film was immersed in an acetic acid bath to dissolve the PMMA. The tips have an average radius of less than 10 nm, a spring constant of \( \sim 40 \text{ N m}^{-1} \) and a resonance frequency of \( \sim 190 \text{ kHz} \). A line scan rate of \( 0.8 \sim 1 \text{ Hz} \) was used to image small areas (up to 20 mm x 20 mm). For larger scan areas, the rate was \( 0.4 \sim 0.6 \text{ Hz} \).

3.5.4 Focused ion beam (FIB) combined with scanning electron microscopy (SEM)

The focused ion beam (FIB) technique is commonly used for imaging, surface milling, or depositing hard materials. The FIB instrument operates similarly to a scanning electron microscopy (SEM) except that FIB uses a focused beam of ions, usually gallium ion (Ga\(^+\)) source, whereas SEM uses electrons. For imaging, the focused
beam of the ions rasters across the sample surface at low beam currents and secondary particles are collected. For surface milling, materials can be removed at high beam currents by sputtering which allows for cross-sectional images or modification of the structures. For material deposition, a precursor gas is introduced to the chamber, deposited on the samples surface, and reacts with the beam. Depending on the gases, platinum, tungsten, cobalt, gold etc. can be deposited. The deposited material can be also used to prevent the sample from being damaged by beam. The main applications of FIB are cross-sectional imaging, modification of the electrical structures on semiconductor devices, sample preparation for TEM, failure analysis, mask repair etc. FIB milling techniques for TEM sample preparation are reviewed by Giannuzzi et al.¹¹. To reduce the ion beam damage on the polymer films, Kim et al.¹² examined the sections exposed to an ion beam using SEM and TEM at varying beam currents and sample temperatures, and showed that ion beam heating damage was minimized at beam currents less than 100 pA and cooling down to -100 °C suppressed the beam damage.

Scanning electron microscopy (SEM) scans the sample with a high-energy beam of electrons and detects the secondary electrons from interactions of electron beam with atoms near the surface of the sample for imaging. The spatial resolution of the SEM depends on the size of the electron spot and cannot image individual atoms but can image comparatively large area of the sample surface.

In this dissertation (chapter 7), cross-sectional and top view images of thick PMMA:SAN films (thickness, $h > 1 \mu$m) were observed using SEM after FIB (FEI Strata DB235) etching. First, a Au/Pd coating was deposited on the films, which reduces
sample charging. Ga$^+$ ions (30 kV; 100~300 pA) were used to lightly etch a surface area of 10 µm x 10 µm or 20 µm x 20 µm for top view images as shown in Figure 3.5 (a). The Ga$^+$ ion beam current was increased to 300-1000 pA to etch trenches that penetrated through the film and into the substrate. These samples were tilted at 52° for cross-sectional images. Figure 3.5 (b) shows a schematic cartoon of FIB etching and SEM imaging of a phase separated polymer blend film with NPs at the interphase. Before repetitive cross-sectioning and imaging of three dimensional structures, thick Pt (thickness ~ 1 µm) layer was deposited on the film locally to reduce sample damaging from ion and electron beams.

3.6 Summary

This chapter describes the unique methods for preparing samples and characterizing nanocomposites. Methods for good dispersion of silica nanoparticles in a polymer matrix, preparation of thin deuterated polymer layers, minimization of ion beam damage on a polymer film were described. Because the polymer film is readily damaged by many types of radiation, a strategy to reduce the ion beam damage of dPMMA enabled the measurement of diffusion profiles. Finally, a description of the characterization techniques used to observe the structure of the polymer nanocomposites and study polymer diffusion in the polymer nanocomposite is provided.
3.7 References


Figure 3.1 FTIR spectra of dPMMA, dPMMA/chitosan, and a dPMMA film floated off a chitosan coated wafer. The peak at 1107 cm$^{-1}$ is observed only for the dPMMA/chitosan film indicating that a nearly pure dPMMA can be prepared using a sacrificial chitosan layer that is soluble in water.
Figure 3.2  dPMMA diffusion profiles in a PMMA matrix after annealing at 195 °C for 72.5 h using beam currents of 1 nA (circles) and 4 nA (squares). Higher beam currents decrease the area of the deuterium signal and increase background between channels 250 and 300. The integrated area from channels 250 to 350 is 470 at 1 nA and 430 at 4 nA.
Figure 3.3 Deuterium profiles collected from dPMMA/Si, dPMMA/chitosan/Si, and dPMMA/PMMA/Si. The area under the profiles from 280 to 350 (channel) is smallest on PMMA (440) and largest on silicon substrate (400).
Figure 3.4  Experimental setup for (a) ERD and (b) RBS.  ERD detects D or H ions recoiled from the sample, whereas RBS detects backscattered He ions.
Figure 3.5 A schematic cartoon of FIB etching and SEM imaging of a polymer blend film containing nanoparticles (small circles) at the interface between phases. (a) Top view of a polymer blend film can be observed at two different angles by slight etching with FIB near the surface. (b) Cross-sectional view is observed after making a small trench using FIB and tilting the sample.
Chapter 4

Macromolecular Diffusion in a Crowded Polymer Nanocomposite

4.1 Introduction

Polymer nanocomposites, consisting of a polymer matrix reinforced with nanosized fillers, are used in numerous existing and emerging engineering applications to improve mechanical, thermal, and electrical properties\(^1\). As with traditional micro-sized fillers, effects of nanoparticles (NPs) on the mechanical properties depend primarily on the particle size, shape, polymer-filler interaction, and degree of dispersion in a polymer matrix. However, the inherently high surface-to-volume ratios associated with NPs can provide dramatically improved properties in polymer nanocomposites\(^1-8\). The enormous total interfacial area between NPs and polymer dictates that the interphase between polymer and NP becomes one of the dominant factors that determine the properties\(^1,2,9,10\). Another consequence of the high surface-to-volume ratio in polymer nanocomposites is the potential of NPs to alter polymer dynamics. In this study, we probe the effect of NPs on macromolecular diffusion as a function of interparticle distance and observe a slowing down that is stronger than that predicted by simple tortuosity.

Typically, molecular transport in heterogeneous media has been explained by applying the Maxwell model\(^11\) for conductivity to describe diffusion. In this framework, the diffusion coefficient in composites with a sparse distribution of discrete particles decreases monotonically with filler concentration. However, the Maxwell model and subsequent refinement\(^12\), do not account for the impact of changes to chain conformation
in the vicinity of obstacles as a consequence of either entropic confinement or enthalpic interactions. Macromolecular diffusion in confined spaces such as gels and nanopores has been successfully described by the entropic barrier model (EBM)\textsuperscript{13-16}. Using Monte Carlo simulations and scaling arguments, it was shown that molecular diffusion through random media is slowed by bottlenecks which reduce the number of chain conformations and consequently the entropy available to the diffusing species. The EBM captures the diffusion of linear polymers through porous glasses filled with solvent\textsuperscript{17, 18}. Moreover, the electrophoretic mobility of star and ring polymers is well-described by the EBM, which predicts topological independence at moderate confinement conditions\textsuperscript{19}. The present study demonstrates that macromolecular diffusion through a polymer with well-defined, closely spaced obstacles is successfully described by the EBM.

Macromolecular diffusion in confined media is also relevant for understanding the structure and function of biological\textsuperscript{20-23} and bio-related\textsuperscript{24-27} systems. For example, although the cytoplasm of cells contains proteins and RNA molecules that comprise 20-30\% of the total volume\textsuperscript{21}, molecules are still able to fold, assemble and diffuse through such packed regions\textsuperscript{22}. Protein transport across a cellular membrane\textsuperscript{23}, m-RNA penetration into the nuclear membrane, and DNA injected from a virus into a cell all require translocation though constricted regions. In addition to \textit{in vivo} biological processes, bio-related systems also utilize molecular diffusion in confined media. For example, diffusion of nucleic acid polymers through nanopores enables single-molecule detection\textsuperscript{24}. DNA molecules can be separated using a microfabricated channel with many entropic traps that determines the translocation time\textsuperscript{25}. Similarly, silicon membranes with nanopores impose size-based molecular separation of proteins\textsuperscript{26} and gel electrophoresis
has long been used to separate DNA fragments\textsuperscript{27}. Thus, understanding macromolecular diffusion in confined regions is of great interest for both biological and bio-related systems.

Although polymer dynamics in confining environments containing a polymer matrix have received some attention, a unified picture has yet to emerge, even within a given system. Using neutron scattering, Richter et al.\textsuperscript{28, 29} observed a slowing down of poly(ethylene oxide) intermediate time-scale chain dynamics confined within cylindrical pores for chain dimensions larger and smaller than the pore size. Using molecular dynamics simulations, Kumar et al.\textsuperscript{30} found that polymer diffusion slowed down in the presence of NPs that attract the polymer, whereas diffusion was enhanced if this interaction was repulsive. Hu et al.\textsuperscript{31} showed that the tracer diffusion of deuterated polystyrene (dPS) measured by secondary ion mass spectrometry was not affected by adding 5 vol\% clay to a polystyrene (PS) matrix; however, the same amount of clay added to poly(methyl methacrylate) (PMMA) was found to reduce the diffusion coefficient by a factor of 3. For the tracer diffusion of dPS in a PS matrix containing carbon nanotubes (PS : CNT), Mu et al.\textsuperscript{32, 33} found that diffusion initially decreased, reached a minimum, and then recovered as CNT loading increased. The minimum diffusion coefficient was observed at a concentration corresponding to the percolation threshold. Segalman et al.\textsuperscript{34} showed that tracer diffusion of dPS through a semicrystalline PS matrix scaled inversely with probe size, a result attributed to the entropic barriers imposed by crystalline domains. Green et al.\textsuperscript{35} found that the diffusion of dPS or dPMMA into PS-b-PMMA is slower than that into homopolymer and attributed this behavior to the spatial orientation
of the domains, volume fraction of matrix accessible to the homopolymer, and tortuosity of the domains.

Here, we study macromolecular diffusion through a crowded system consisting of well-dispersed silica NPs in a PS matrix. The crowding imposed by the NPs is controlled by varying the volume fraction of NP, $\phi_{NP}$, from 0 to 0.5. A unique characteristic of this system is that a uniform dispersion is maintained even at 50 vol%. Thus, these nanocomposites are ideal for studying diffusion in a crowded system because the interparticle distance ($ID$) that defines confinement can be varied from much greater than to much less than the size of the macromolecular probe, $2R_g \sim 10$ to $\sim 40$ nm, where $R_g$ is the radius of gyration. A significant result, enabled by our ability to vary the relative length scales over a wide range, is that the tracer diffusion coefficients in the nanocomposite relative to pure PS ($D/D_0$) plotted against the NP separation relative to probe size (i.e., $ID/2R_g$) falls on a master curve indicating that crowding is a property of both the penetrant and the matrix. Moreover, the normalized diffusion coefficient decreases more rapidly when $ID/2R_g$ is less than $\sim 1$, suggesting strong confinement conditions. The scaling of the diffusion coefficient with chain length is in excellent agreement with the EBM$^{13-15}$, which has not previously been applied to polymer melts with well-defined and tunable barriers.

4.2 Experiment methods

4.2.1 Preparation and characterization of polymer nanocomposites

Polystyrene ($M_w = 265,000$ g mol$^{-1}$, polydispersity, PDI = 2.45) (PS) with phenyl-capped silica nanoparticles (NPs) is used as a matrix. These NPs were prepared using
phenyltrimethoxysilane (PhTMS) as a coupling agent. The particle diameter and polydispersity were measured by dynamic light scattering (28.7 nm, 0.1), small-angle X-ray scattering (28.7 nm, 0.1), and transmission electron microscopy (TEM) (26.3 nm, 0.2). We denote the diameter as 28 nm in this paper. After synthesis, the PhTMS capped silica particles were characterized using size exclusion chromatography (SEC) coupled with an IR absorption detector. The coverage of PhTMS was found to be 1.5 molecules nm\(^{-2}\). Using densities of 1.099 g cm\(^{-3}\) for PS and 2.113 g cm\(^{-3}\) for NPs, the volume fractions of NP (\(\phi_{NP}\)) in PS are 0, 0.01, 0.02, 0.05, 0.1, 0.2, 0.3, 0.5. The PS and phenyl-capped silica NPs were each dissolved in dimethylacetamide (DMAC) or dimethylformamide (DMF), and then mixed at the appropriate ratio. Films were prepared by doctor blading the solution on a heated glass substrate (~100 °C) to form a film of thickness ~10 \(\mu\text{m}\). The NP dispersion was observed using TEM after cross-sectioning the films using a microtome. Rutherford backscattering spectrometry (RBS) was used to obtain the depth profiles of the NPs in the composite film using 2 MeV He\(^+\) at 10 °. The depth resolution \(\delta r = \frac{\delta E}{[S_0]_{PNC}}\) is 40~45 nm depending on silica NP loading, where \(S_0\) is energy loss factor of the nanocomposite\(^{36}\). The NP concentration in the films was measured using thermogravimetric analysis (TGA). Thick films were prepared by hot pressing at ~150 °C. For TGA measurements, films were heated at 20 °C min\(^{-1}\) to 400 °C and then held at 400 °C for 3 h.

The glass transition temperatures \(T_g\) of PS (265k) and the nanocomposites were measured using differential scanning calorimetry (DSC). Approximately ~5 mg of material was placed in an aluminum pan. The scanning temperature range was 20 °C to
160 °C with a temperature ramp of 10 °C min\(^{-1}\) in N\(_2\) atmosphere. The \(T_g\) of pure PS (265k) was 105.2 ± 1 °C. For the nanocomposites, the \(T_g\) was 106.7±0.4 °C consistent with the findings of Bansal et al.\(^{37}\) for PS : PS grafted silica NP nanocomposites. These studies show that the \(T_g\) of PS did not change appreciably with the addition of particles and, therefore, changes in diffusion coefficient are not due to changes in \(T_g\).

4.2.2 Tracer diffusion couple and processing

The tracer diffusion couples consisted of the nanocomposite matrix film covered with the thin dPS tracer film. The matrix film was removed from the glass substrate by floating in water and then picked up by a silicon substrate. The matrix film on silicon was preannealed at ~150 °C for 3 days to age the film and remove any residual solvent. The dPS with molecular weights of 49,000 g mol\(^{-1}\) (PDI = 1.03), 168,000 g mol\(^{-1}\) (PDI = 1.03) and 532,000 g mol\(^{-1}\) (PDI = 1.05) was spin coated on silicon substrates to produce ~20 nm thick films as measured by ellipsometry. The dPS film was floated off in water and transferred onto the matrix film attached to the silicon substrate. Because of their wide range of diffusivities, the diffusion couples for dPS (49k), dPS (168k), and dPS (532k) were annealed in a vacuum oven at 145, 165, and 170 °C, respectively.

Molecular weight and polydispersity of PS and dPS were measured using SEC. The polymer was dissolved in tetrahydrofuran at various concentrations depending on its molecular weight.
4.2.3 Elastic recoil detection (ERD)

The dPS concentration profile in the matrix was measured by elastic recoil detection (ERD) and tracer diffusion coefficients obtained by fitting the profile to a one-dimensional (1-D) solution to Fick’s second law equation for a finite source in a semi-infinite medium \(12,38\). Diffusion coefficients were obtained from multiple measurements taken for each sample including those annealed at different times and only the profiles having a sufficient diffusion length were considered. In ERD, the He\(^{2+}\) ion beam was accelerated to 3 MeV and a 10 µm Mylar film was placed in front of the ERD detector to prevent the signal from the forward scattered He from masking the H and D signal. The incident beam intersects the plane of the sample at 15 ° and the recoiled H and D are collected by a solid state detector. The ERD spectra of counts versus channel are converted to a dPS volume fraction profile using in-house software. The instrumental resolution is captured by the Gaussian function, \(y = \frac{1}{\sigma\sqrt{2\pi}}\exp\left(-\frac{x^2}{2\sigma^2}\right)\), where \(\sigma = 39\) nm. The depth resolution and accessible depth are 78 nm and \(~800\) nm, respectively. In the least squares fitting to determine \(D\), \(\chi^2\) ranges from \(~10^{-3}\) to \(~10^{-4}\). Details of ERD have been reviewed elsewhere\(^{39}\).

4.3 Results and discussion

4.3.1 Distribution of nanoparticles in polymer nanocomposites

The fabrication of polymer nanocomposites with well-dispersed nanoparticles (NPs) is particularly challenging at high loadings. In our polymer nanocomposites, good dispersion is achieved by modifying the surface of silica NPs with phenyl groups that are
similar to the pendant phenyl group found on the PS molecules in the matrix. Figure 4.1 (a) shows the chemical structure of PS and a schematic of the phenyl-capped silica NPs, which have a diameter of 28 nm. The cross-sectional TEM image in Figure 4.1 (b) shows that NPs are well dispersed at low concentration, \( \phi_{NP} = 0.02 \). Figure 4.1 (c) shows that these NPs remain well dispersed even up to extremely high loading, \( \phi_{NP} = 0.5 \). We have also performed selected TEM studies on PNC’s that were annealed for conditions corresponding to the diffusion experiments and observe no change in NP dispersion. As described later, the interparticle spacing for this crowded system is about 2 nm, which is a factor of \(~0.2\) and \(0.05\) smaller than the smallest and largest tracer molecules, respectively. The insets show that the sample surfaces have a similar distribution as the bulk.

To complement the lateral structure observed by TEM, depth profiles of the NPs were determined by RBS. Figure 4.1 (d) shows the RBS spectra from a nanocomposite with \( \phi_{NP} = 0.5 \). The energy (channel) and normalized yield correspond to depth and elemental concentration, respectively. The silicon and oxygen atoms located at the surface of the film are denoted with arrows. For both elements, the normalized yield is consistent with a uniform distribution of NPs. Using XRUMP\textsuperscript{®}, the spectrum was simulated (solid line) using a nanocomposite film (> 2 \(\mu\)m) containing 50 vol% of NPs uniformly dispersed in 50 vol% PS\textsuperscript{40}. The depth resolution is 38 nm\textsuperscript{36}. The simulation is in excellent agreement with the RBS data and shows that NPs are uniformly distributed in the near surface region (i.e., no depletion or enrichment), consistent with TEM observations. We have also performed RBS on selected PNC’s that were annealed for
conditions corresponding to the diffusion experiments and observe no change in NP dispersion within the resolution of RBS. These TEM and RBS results are representative of nanocomposite films at all NP loadings, demonstrating that phenyl-capped silica NPs are uniformly distributed at length scales probed by the diffusion studies, as required to quantitatively interpret the diffusion results. Furthermore, using the Stokes-Einstein equation and the appropriate PS viscosity\textsuperscript{41,42}, the NP diffusion coefficient at 170 °C is 4.0x10\textsuperscript{-17} cm\textsuperscript{2} s\textsuperscript{-1}. This is much smaller than the dPS diffusion coefficient at 170 °C which ranges from 10\textsuperscript{-12} to 10\textsuperscript{-15} cm\textsuperscript{2} s\textsuperscript{-1}. Thus, the NPs are relatively immobile relative to the tracer molecules which diffuse ~300 nm. Using TEM and RBS we have established that these PS-based nanocomposites are model materials with well-dispersed NPs that persist throughout the diffusion experiments.

### 4.3.2 Tracer diffusion in nanocomposites

Macromolecular diffusion through the nanocomposites was investigated using tracer diffusion experiments. A thin dPS layer (~20 nm) was deposited on a thick (~10 μm) nanocomposite film. The dPS volume fraction profiles, \( \phi(x) \), were determined using ERD after annealing, as we have described recently\textsuperscript{32,33}. The tracer diffusion coefficient \( D \) was determined by fitting the experimental \( \phi(x) \) with the appropriate solution to Fick’s second law. For an initial tracer thickness \( h \), \( \phi(x) \) is given by\textsuperscript{12,38}:

\[
\phi(x) = \frac{1}{2} \left[ \text{erf} \left( \frac{h-x}{\sqrt{4Dt}} \right) + \text{erf} \left( \frac{h+x}{\sqrt{4Dt}} \right) \right] \tag{1}
\]

where \( \text{erf} \) denotes the error function and \( t \) is annealing time. This expression was convoluted with a Gaussian function whose standard deviation corresponds to the depth
resolution of 78 nm. Using least-square fitting, $D$ is varied until the simulation matches the experimental profile by minimizing $\chi^2$.

The effect of confinement on diffusion can be evaluated by determining how the tracer diffusion coefficient depends on both the volume fraction of NP ($\phi_{NP}$) in the nanocomposite matrix and the molecular weight of the tracer ($M$). To test the former, dPS ($M = 168k$) was diffused into nanocomposite films containing $\phi_{NP} = 0.02$ and 0.3 by annealing at 165 °C for 4 and 12.5 h, respectively. Whereas the dPS profile shown in Figure 4.2 (a) follows the expected Fickian diffusion shape at $\phi_{NP} = 0.02$, the dPS profile for diffusion into the matrix at the higher loading exhibits a surface peak as shown in Figure 4.2 (b). The surface peak results from a reduced flux at the interface possibly caused by some additional crowding of the NPs. The reduced flux scales with the volume fraction of NPs and therefore the surface peak becomes more pronounced as loading increases. Our observation that, as annealing time increases (i.e., dPS penetration into the matrix increases), the surface peak decreases (as shown in Supplementary Figure 4.S1) is also consistent with this mechanism. A more detailed theoretical and experimental investigation of the origins of the surface peak will be the subject of a future publication.

Segalman et al.\textsuperscript{34} also observed a surface peak for diffusion into semicrystalline polymers wherein the crystalline domains are effectively impenetrable. The solid lines in Figures 4.2 (a) and 4.2 (b) represent best fits of the experimental data with eq. (1) with $D = 2.3 \times 10^{-14}$ cm$^2$ s$^{-1}$ and $9.8 \times 10^{-15}$ cm$^2$ s$^{-1}$, respectively. The dashed line in Figure 4.2 (b) represents the sum of the solid line and a surface peak from a reduced flux due to the impenetrable NPs. Thus, at fixed tracer molecular weight, the diffusion coefficient is
reduced by a factor of ~2 as $\phi_{\text{NP}}$ increases from 0.02 to 0.3, consistent with slowing down due to greater confinement. To investigate the effect of tracer size, dPS with $M = 49k$ and $532k$ was diffused into nanocomposites having a fixed NP concentration of $\phi_{\text{NP}} = 0.1$. Figures 4.2 (c) and 4.2 (d) show the volume fraction profiles after annealing at 145 °C for 7 h and 170 °C for 25 h, respectively. The temperatures and times are selected to provide an optimum diffusion distance of ~300 nm for ERD measurements. In Figure 4.2 (c), the depth profile of the shorter tracer chains shows a Fickian type profile (solid line), whereas the profile for the longer chains (dashed line) in Figure 4.2 (d) indicates a surface peak overlapping with the Fickian type profile (solid line). Thus, a surface peak is observed either when the matrix is crowded (i.e., high $\phi_{\text{NP}}$) or at large probe sizes (i.e., high $M$), as noted in Figures 4.2 (b) and 4.2 (d), respectively.

The dPS tracer diffusion coefficients are shown in Figure 4.3 for $M = 49k$, 168k, and 532k at 170°C. Diffusion coefficients for dPS (49k) and dPS (168k) measured at 145 °C and 165 °C, respectively, were converted to values at 170 °C using the Vogel-Fulcher equation\textsuperscript{43}. To test the role of matrix molecular weight polydispersity, tracer diffusion measurements in nanocomposites containing PS ($M_w = 400,000$ g mol\textsuperscript{-1}, PDI=1.06) were performed. These studies are in agreement with the data shown in Figure 4.3 indicating that polydispersity does not significantly affect diffusion in PNCs containing entangled polymers. As $M$ increases from 49k to 532k, Figure 4.3 shows that the diffusion coefficient decreases strongly at a fixed $\phi_{\text{NP}}$. As $\phi_{\text{NP}}$ increases, the diffusion coefficient decreases for all dPS molecular weights. At low loadings, $\phi_{\text{NP}} < 0.1$, this reduction in $D$ becomes stronger as $M$ increases, consistent with greater slowing down of larger
molecules as they squeeze past constraints. For example, $D$ decreases by 30% and 60% as $M$ increases from 49k to 532k at $\phi_{NP} = 0.1$. The open symbols in Figure 4.3 denote diffusion couples with volume fraction profiles captured by Fickian diffusion (i.e., eq. (1)), whereas the closed symbols represent couples that exhibit a surface peak. As $M$ increases, the maximum volume fraction of NP at which eq. (1) fits the dPS profile decreases from 0.1 to 0.01 as $M$ increases from 49k to 532k, respectively. In summary, larger molecules are more strongly influenced by diffusion in confined media than smaller ones.

The two length scales that are relevant for the diffusion of probe molecules through bottlenecks are\textsuperscript{44,45}: (1) the molecular size, which for polymers corresponds to the radius of gyration and (2) the bottleneck size, or in the case of a polymer nanocomposite, where confinement is imposed by the discrete, impenetrable particles (c.f., Figure 4.2 top), the average interparticle distance, $ID$, between particles. Assuming that NPs are randomly distributed in the polymer matrix, $ID$ is given by\textsuperscript{46}:

$$ID = d \left[ \left( \frac{2}{\pi \phi_{NP}} \right)^{1/3} - 1 \right]$$

where $d$ is the NP diameter (28 nm). As shown in Figure 4.4 (a), $ID$ initially decreases strongly, by nearly an order of magnitude, as $\phi_{NP}$ increases from 0.01 to 0.20, and then decreases more slowly between 0.20 and 0.50. The symbols represent the NP volume fractions that satisfy the confinement condition $ID \sim 2R_g$. For $M = 49k, 168k$ and 532k, this condition is satisfied at $\phi_{NP} = 0.23, 0.12$, and 0.05, respectively. The probe is considered to be diffusing in a crowded matrix if $ID < 2R_g$, e.g. the probe size is larger
than the spacing between NPs. For example, diffusion of dPS (49k) is highly constrained for $\phi_{\text{NP}} > 0.23$ because molecules must undergo large conformational energy changes to squeeze between NPs spaced closer than $2R_g$. As $M$ increases, the concentration of NP that induces strong confinement decreases. Thus, comparing diffusion in nanocomposites as a function of the reduced variable $ID/2R_g$ should be insightful.

Motivated by the confinement conditions described above, Figure 4.4 (b) shows that all data collapse onto a master curve when the reduced diffusion coefficient ($D/D_0$), where $D$ is normalized by the tracer diffusion coefficient in pure PS ($D_0$), is plotted against the dimensionless quantity $ID/2R_g$. As $ID/2R_g$ decreases from 3 to $\sim 1.5$, $D/D_0$ decreases weakly. This regime mainly represents diffusion couples that exhibit diffusion profiles without a surface peak (open symbols). For $ID/2R_g < 1$ (i.e., crowded conditions), $D/D_0$ decreases strongly as $ID/2R_g$ decreases. This regime corresponds to diffusion couples that exhibit a surface peak (closed symbols). This strong slowing down may be attributed to the loss of chain conformations as tracer molecules squeeze between closely spaced NPs.

4.3.3 Applying the entropic barrier model

While the collapse of the data onto a master curve provides a valuable empirical representation of the dynamics of polymers in confined systems, we turn our attention to the entropic barrier model (EBM) to gain insight into the underlying physical mechanisms. Prior to this work, the EBM has not been applied to polymer melts with well-defined and tunable barriers because of the difficulty in fabricating uniformly distributed barriers at high loadings. In our nanocomposites, the spaces between NPs define cages or cavities
that enclose dPS chains either in whole or in part, depending on the NP concentration and the corresponding cage size. In the framework of the EBM, the cavities are separated by bottlenecks (i.e., entropic barriers) as illustrated in Figure 4.5 (a), and macromolecular diffusion through random media such as porous glasses, concentrated polymer solutions, gels and semicrystalline polymers deviates from reptation behavior because the media contains entropic traps that perturb chain dynamics. As noted earlier, the NPs are capped with phenyl groups and therefore enthalpic interactions with tracer chains should be small. Thus, the free energy barrier $\Delta F$ in Figure 4.5 (a) should be dominated by the loss of chain conformations as chains pass through bottlenecks formed by neighboring NPs. For an activated process $D = D_0 \exp(-\Delta F/k_B T)$, where $D_0$ represents diffusion without barriers (i.e., $\phi_{NP} = 0$). Because chain motion occurs between cavities of size $C$, separated by bottlenecks of size $B$, the diffusion coefficient decreases exponentially with $\Delta F (= F_2 - F_1)$, where $F_1$ and $F_2$ are the confinement free energy for a chain in a cavity and bottleneck, respectively. According to scaling arguments, $F_1$ and $F_2$ are proportional to $NC^{-1/v}$ and $NB^{-1/v}$, where $N$ is the degree of polymerization and $v$ is 0.5 for a Gaussian chain$^{42}$. The scaling form for $D/D_0$ is given by$^{13-15}$:

$$\ln(D/D_0)/N = A - s/N$$

(3)

where $s$ is proportional to $B^{-1}(1-z^{1/(B/C)^{1/v}})$ and $z$ is the average number of cavities containing unconfined segments per bottleneck. For $20 \leq N \leq 80$, Monte Carlo simulations$^{13-15}$ to determine $D$ agree with the scaling predictions of eq. (3) and exhibit a slope that increases as the bottleneck size, $B$, decreases.
To test if the EBM captures dPS diffusion in nanocomposite matrices, \( \ln(D/D_0)/N \) is plotted against \( 1/N \) for \( \phi_{\text{NP}} = 0.1, 0.2, 0.3 \) and \( 0.5 \). Figure 4.5 (b) shows that the EBM scaling relationship is in good agreement with the experimental data. For tracer diffusion into a semicrystalline polymer, Segalman\(^{34}\) also observed that \( D \) decreases as \( 1/N \), consistent with the EBM. However, because the barrier dimensions were ill defined for that system, a rigorous test of the EBM model was not possible. Figure 4.5 (b) also shows that the slope, \( s \), increases as \( \phi_{\text{NP}} \) increases in qualitative agreement with eq. (3). Since \( s \sim B^{-1} \) and \( B \) is determined by \( ID \), we can relate \( s \) to \( \phi_{\text{NP}} \) via eq. (2), namely \( s \sim B^{-1} \sim ID^{-1} \sim \phi_{\text{NP}}^{1/3} \). The inset of Figure 4.5 (b) shows that \( s \) increases linearly with \( \phi_{\text{NP}}^{1/3} \) indicating that an increase in NP loading does indeed slow down tracer diffusion in accordance with the EBM. Thus, our studies are a systematic experimental verification of the relationship between the slope, \( s \), and the confining media.

In applying the EBM model several assumptions are made. First, we use eq. (2) to estimate an average \( ID \) that is used in the EBM model. A log normal distribution of \( ID \) values is likely and correspondingly a distribution of bottleneck and cavity sizes. Ultra small angle X-ray scattering studies are in progress to quantify the spatial distribution of NPs as a function of loading. Second, enthalpic contributions could influence diffusion behavior. For example, polymer diffusion along an attractive surface is slower than through the bulk\(^{47}\). Also, molecular dynamics simulations show that chain diffusion can be enhanced or reduced when interactions are repulsive or attractive, respectively\(^{30}\). Because NPs in this study are capped with phenyl groups to minimize interactions with dPS, the interaction between NP and tracer molecule should be weak. Third, Muthukumar\(^{48}\) modified the original EBM to include enthalpic interactions and found
that for a polymer escaping from a nanopore, the entropic barrier mechanism dominates for short pores while pore-polymer interactions dominant for pores longer than a critical length. The narrowest section of the bottleneck as noted in Figure 4.5 (a) is relatively short, further justifying the use of the EBM for describing dPS diffusion in crowded nanocomposites. While both the master curve and EBM capture experimental results, a quantitative relationship between these two descriptions of polymer diffusion in crowded systems is of great interest and the subject of future study.

4.4 Conclusions

Polymer diffusion was investigated in nanocomposites containing silica nanoparticles (NPs). The lateral and depth distributions of the NPs were found to be uniform, even at 50 vol% NP, indicating that nanocomposites are a model system for testing how macromolecules diffuse through crowded systems. Tracer diffusion slows down as NP loading increases and this reduction is strongest for the largest tracer chains. Significantly, we find that the reduced diffusion coefficient, $D/D_0$, collapses onto a master curve when plotted versus $ID/2R_g$, indicating that confinement is determined by the spacing between particles relative to the size of the tracer molecule. Our results are in excellent agreement with the entropic barrier model indicating that the slowing down of the molecular diffusion in the presence of NPs is mainly attributed to the loss of chain conformations as molecules squeeze through bottlenecks formed by neighboring particles. These studies of diffusion in a crowded system inspire a series of future studies including the effect of particle shape on tracer diffusion\textsuperscript{32, 33, 49}, as well as designing polymer nanocomposites having interactions between the tracer molecules and particles. Such
studies are technologically important for ultrafiltration, DNA separation and melt processing of polymer nanocomposites, and also can provide new insight into the dynamics of biological systems where macromolecular crowding is ubiquitous.

4.5 Appendix

: Temperature dependence of polymer diffusion in a polymer nanocomposite

To investigate the effect of annealing temperature on polymer diffusion, dPS (168k) / PS : \( \phi_{NP} = 0 \), 0.2 nanocomposite films were annealed at 137 °C, 146 °C, 156 °C, 162 °C, 172 °C. Previously, the temperature dependence of tracer polymer diffusion in a polymer matrix was studied by Green et al\(^{43}\) in a dPS / PS system and described by the Vogel-Fulcher equation:

\[
\log \left( \frac{D}{T} \right) = A' - \frac{B}{(T - T_\infty)}
\]

where \( B \) and \( T_\infty \) are 710 and 49 °C, and obtained empirically from viscosity measurements for PS\(^{50}\). Figures 4.6 (a) and (b) show the log \((D/T)\) plotted against 1/(\(T - T_\infty\)) for dPS (168k) / PS : \( \phi_{NP} = 0 \) and dPS (168k) / PS : \( \phi_{NP} = 0.2 \), respectively. The solid line is a fit with eq. (4) using \( T_\infty = 49 \) °C, and \( B \) values of 669 and 659 for \( \phi_{NP} = 0 \) and \( \phi_{NP} = 0.2 \), respectively, similar to the previous study\(^{50}\). It is demonstrated that temperature dependence of polymer diffusion in a polymer nanocomposite as well as a pure polymer matrix can be described by the Vogel-Fulcher equation as shown in Figure 4.6.
4.6 References


Figure 4.1 Characterization of PS : silica NP nanocomposites. (a) The chemical structure of PS (left) and a cartoon of the phenyl-capped silica NP (right). (b), (c) Cross-sectional TEM images showing NP distribution for PS : $\phi_{NP} = 0.02$ and PS : $\phi_{NP} = 0.5$ nanocomposite films, respectively. Insets: cross-sectional TEM images of the near surface. Particles are uniformly dispersed in all nanocomposite films. (d) Silicon and oxygen concentration profile measured via RBS for PS : $\phi_{NP} = 0.5$ nanocomposite film. Closed square symbols represent the silicon and oxygen yield from the surface (arrows) and near surface ($< 2 \mu m$) regions. The solid line is a simulation assuming a uniform distribution of NPs corresponding to a PS : $\phi_{NP} = 0.5$ nanocomposite film.
Figure 4.2  Diffusion profiles of dPS in PS : NP nanocomposites measured using ERD to investigate the effect of NP volume fraction and tracer molecular weight. Solid line is a fit of experimental data with eq. (1) using appropriate $D$ values, whereas the dashed line represents the sum of the solid line and a surface peak. Tracer molecular weight ($M$) and NP volume fraction ($\phi_{NP}$) are denoted in the legends. (a) $D = 2.3 \times 10^{-14} \text{ cm}^2 \text{ s}^{-1}$ at 165 °C. (b) $D = 9.8 \times 10^{-15} \text{ cm}^2 \text{ s}^{-1}$ at 165 °C. (c) $D = 1.4 \times 10^{-14} \text{ cm}^2 \text{ s}^{-1}$ at 145 °C. (d) $D = 3.8 \times 10^{-15} \text{ cm}^2 \text{ s}^{-1}$ at 170 °C. Note that surface peaks are observed for profiles in Figure 4.2 (b) and 4.2 (d). The cartoons (top) represent the tracer and matrix conditions that correspond to diffusion profiles without and with a surface peak.
Figure 4.3  Diffusion coefficient versus NP loading. Diffusion coefficients of dPS ($M = 49k, 168k, 532k$) at $170^\circ$C are plotted as a function of NP volume fraction. Closed and open symbols represent diffusion with and without surface peaks, respectively. The error bars represent the standard deviation determined from measurements taken on samples annealed for different times.
Figure 4.4 Effect of relative size of probe and interparticle distance on diffusion. (a) Interparticle distance ($ID$) is plotted as a function of the volume fraction of NP ($\phi_{NP}$) under the assumption that NPs are randomly distributed in a polymer matrix according to eq. (2). (b) Reduced diffusion coefficients ($D/D_0$) of dPS ($M = 49k, 168k, 532k$) plotted against $ID/2R_g$ create a master curve. Closed and open symbols represent diffusion with and without surface peaks, respectively. The error bars represent the standard deviation determined from measurements taken on samples annealed for different times.
Figure 4.5 Entropic barrier model. (a) Free energies and chain conformations as a probe chain diffuses from one cavity to another cavity through a bottleneck of size $B$. In the bottlenecks, the number of chain conformations is reduced resulting in the formation of an energy barrier with a height $\Delta F$ that depends on the size of the bottleneck. (b) $\ln(D/D_0)/N$ is plotted against $1/N$ at $\phi_{NP} = 0.1, 0.2, 0.3, 0.5$, where $N$ is the degree of polymerization of the tracer. Inset: slope $s$ versus $\phi_{NP}^{1/3}$ ($\sim JD^{-1}$). This scaling behavior is in agreement with the entropic barrier model.
Figures 4.6  log \((D/T)\) is plotted against \(1/(T - T_\infty)\) for (a) dPS (168k) / PS : \(\phi_{NP} = 0\) and (b) dPS (168k) / PS : \(\phi_{NP} = 0.2\), respectively. The solid line is a fit with eq. (4) using \(T_\infty = 49\) °C, and \(B\) values of 669 and 659 for \(\phi_{NP} = 0\) and \(\phi_{NP} = 0.2\), respectively. The Vogel-Fulcher equation is observed to capture the temperature dependence of diffusion in both the pure polymer and polymer nanocomposite matrices.
SUPPLEMENTAL INFORMATION

S1: Diffusion is Independent of Annealing Time

Figure 4.S1 Diffusion profiles of dPS after two different annealing times. (a), (b) dPS (168k) was diffused into PS : $\phi_{NP} = 0.2$ nanocomposite after annealing at 165 °C for 4 and 12.5 h, respectively. Solid line is a fit of experimental data with eq. (1) using the same value of $D$, $1.9 \times 10^{-14}$ cm² s⁻¹, while dashed line represents the sum of the solid line and a surface peak. As annealing time increases, the area of the surface peak decreases.
Chapter 5

Polymer Diffusion in a Polymer Nanocomposite: Effect of Nanoparticle Diameter, Nanoparticle Polydispersity and Interparticle Distance Polydispersity

5.1 Introduction

Polymer nanocomposites, nanoparticles (NPs) dispersed in a polymer matrix are of great interest because adding NPs to a polymer matrix can enhance its performance\(^1\). The performance enhancements mainly result from the reduction of the particle size which induces the higher interfacial area and number density of particles, and smaller mean particle-particle separation compared with micro-sized particles at the same particle volume fraction. Even for NPs, the decreases of NP size improved mechanical, thermal, electrical properties of polymer nanocomposites\(^2\)\(^-\)\(^4\). For examples, Ash et al.\(^2\) found that addition of alumina NPs (< 1 wt% of 38 nm NPs or < 0.5 wt% of 17 nm NPs) to poly(methyl methacrylate) (PMMA) decreases glass transition temperature by 25 °C and this dependence of glass transition temperature on particle size is a function of the interfacial area between PMMA and NPs. Also, theoretical calculation by Ji et al.\(^3\) showed that decrease in radius of spherical particles from 90 nm to 3 nm increases tensile modulus more than twice only at 4 vol% NP loading. As thickness and radius of particles vary from 90 nm to 3 nm for plate and cylindrical particles, respectively, the modulus increases but not as much as that by the addition of spherical NPs. NP size also affects
the properties of NP itself. El-Sayed et al.\textsuperscript{5} observed the red-shifts of plasmon absorption on gold NPs with increasing NP diameter from 8.9 nm to 99.3 nm. Dielectric and magnetic properties of NPs were also dependent of the size of NPs\textsuperscript{6,7}. In our study, the effect of NP size on polymer diffusion in a polymer nanocomposite is investigated using elastic recoil detection (ERD).

At a given NP volume fraction, as NP size decreases, the interfacial area between polymer matrix and NP increases. For example, as NP size is reduced by half, the number density and total interfacial area increases by 8 times and 2 times, respectively, for well dispersed NPs. As the contact area between polymer and NP increases, the total enthalpic interaction energy increases resulting in a reduced diffusion coefficient in a polymer nanocomposite because the total enthalpic interaction energy is proportional to the contact area. This slowing down of polymer diffusion would be enhanced if the interaction is attractive, relative to a repulsive or neutral interaction.

NP size also affects particle-particle spacing in a polymer nanocomposite which imparts the confinement for polymer diffusion. The reduction of NP size decreases interparticle distance at same volume fraction of NPs. Interparticle distance for monodisperse NPs is given by\textsuperscript{8}

\[ ID(d_n) = d_n \left( \frac{\phi_{\text{max}}}{\phi_{NP}} \right)^{1/3} - 1 \]  

(1)

where \( d_n \) is the number average diameter of NPs, \( \phi_{NP} \) is NP volume fraction, and \( \phi_{\text{max}} \) is maximum packing density. \( \phi_{\text{max}} \) depends on the packing type such as simple cubic (\( \phi_{\text{max}} = 0.5236 \)), face-centered cubic (\( \phi_{\text{max}} = 0.7405 \)), body-centered cubic (\( \phi_{\text{max}} = 0.6802 \)),...
random dense packing ($\phi_{\text{max}} = 0.637 (=2/\pi)$). However, the occurrence of monodisperse NP system is rare and polydisperse NP systems are common for real nanocomposites. To obtain the interparticle distance for polydisperse NPs, it is important to define the average particle size statistically, first. The distribution of particle size can be measured using small x-ray scattering (SAXS), dynamic light scattering (DLS), transmission electron microscopy (TEM), etc. and described by binomial, Gaussian, log-normal, and gamma distribution functions etc. For example, if NP diameter ($d_i$) obeys a log-normal distribution, a frequency $W(d_i)$ is given by

$$W(d_i) = \frac{1}{\sqrt{2\pi \ln\sigma}} \exp \left[ -\frac{(\ln d_i - \ln d_m)^2}{2\ln^2 \sigma} \right]$$

(2)

where $d_m$, the geometric mean (median) diameter, and $\sigma$, the geometric mean standard deviation (polydispersity), are given by

$$\ln d_m = \frac{\sum_{i=1}^{N} n_i \ln d_i}{\sum_{i=1}^{N} n_i} \quad \text{and} \quad \ln \sigma = \sqrt{\frac{\sum_{i=1}^{N} n_i (\ln d_i - \ln d_m)^2}{\sum_{i=1}^{N} n_i}}$$

(3)

The value of $\sigma$ represents the breadth of the distribution. For monodisperse and polydisperse NPs, $\sigma = 1$ and, $\sigma > 1$, respectively. Number average and volume average diameters are defined as $d_n = \frac{\sum_{i=1}^{N} n_i d_i}{\sum_{i=1}^{N} n_i}$ and $d_v = \left( \frac{1}{N} \frac{\sum_{i=1}^{N} n_i d_i^3}{\sum_{i=1}^{N} n_i} \right)^{1/3}$, respectively. As the distribution of particle size becomes polydisperse, the number of particles per unit volume decreases and interparticle distance increases at the same volume fraction of
NPs\textsuperscript{10-16}. Theoretical calculation by Lu et al.\textsuperscript{10} showed that the mean nearest surface-surface distance (here, interparticle distance) increases with increasing the polydispersity of NP size. Wu\textsuperscript{11} and Liu et al.\textsuperscript{12-16} derived the equation for interparticle distance in a mixture of polymer and particle as a function of particle size, polydispersity of particle size, volume fraction of particle, and particle distribution to study the brittle-tough transition of the mixture. The brittle-tough transition of rubber toughened polymers is determined by the interparticle distance\textsuperscript{12-16}. Also, the interparticle distance in a dispersion of clusters is larger than that in well-dispersed particles\textsuperscript{11, 12, 16}. The particle-particle separation in the continuous phase of pseudonetwork morphology is smaller than that in well-dispersed particles\textsuperscript{12, 15}. Because the interparticle distance depends on size, size distribution, and dispersion of particles, our experimental studies of tracer diffusion and their relationship to the interparticle distance provides new insight into the appropriate length scale (e.g., number or volume average size) that dictate molecular relaxations in confined systems.

In our previous study (chapter 4)\textsuperscript{17}, polystyrene (PS) with well-dispersed 28.8 nm diameter silica NPs was used as a matrix and three different molecular weight of deuterated PS (dPS) was diffused into the matrix. The volume fraction of NPs ($\phi_{NP}$) is from 0 to 0.5. As tracer molecular weight or NP loading increases, polymer diffusion slows down. The tracer diffusion coefficient of dPS in the nanocomposite relative to the pure PS matrix ($D/D_0$) can be normalized with respect to the interparticle distance relative to the size of tracer molecule (i.e., $ID/2R_g$). This slowing down is described by
entropic barrier model\textsuperscript{18-22} in which a polymer chain is squeezed through a bottleneck reducing the number of chain conformation.

Here, we investigate tracer diffusion of deuterated polystyrene (dPS) in a matrix of PS containing large and small phenyl-grafted silica NPs with number average diameters $d_n$ of 28.8 nm and 12.8 nm, respectively. In addition to their size difference, the NPs have a narrow and broad distribution of diameters corresponding to 1.12 and 1.39, respectively, using a log-normal distribution. The interparticle distance, $ID (d_n)$ is first calculated using the number average diameters ($d_n$) and a random distribution in the PS. The tracer diffusion coefficients in the nanocomposite relative to pure PS ($D/D_0$) against the $ID (d_n)$ relative to tracer size (i.e., $ID/2R_g$) collapses onto a master curve for the large and small NPs. This result indicates that the mechanism(s) of diffusion is independent of NP size at least for the range of NPs investigated here. To account for the distribution of NP size, the interparticle distance $ID (d_n, \sigma)$ of polydisperse NPs is calculated assuming a log-normal distribution of diameters. For completeness, the interparticle distance $ID (d_n)$ is also determined from the volume average diameters of NPs to see if this weighted average similarly captures the scaling behavior of $D/D_0$. By including polydispersity $ID (d_n, \sigma)$ or using $ID (d_v)$, $D/D_0$ versus $ID/2R_g$ obeys a master curve. Statistically, the collapse of $D/D_0$ onto a master curve is slightly better when $ID$ is calculated using $d_n$ and including polydispersity. A third way to describe $ID$ is to assume a monodisperse distribution but explicitly account for the range of spacing between randomly spaced NPs. A one-dimensional spacing ($x$) is calculated and the reduced diffusion coefficients ($D/D_0$) collapses onto a master curve when plotted against
\[
\left(\frac{x}{2R_g}\right)^{2/3}, \text{ although not as well as in the prior normalization. Although the interparticle distance is captured by one diameter for the silica NP systems having a relatively low polydispersity in size, many real composites such as rubber toughened polymers have a much wider distribution and therefore such polydispersity would greatly impact properties, including whether the composite is brittle or ductile.}
\]

5.2 Materials and experimental methods

5.2.1 Preparation and characterization of polymer nanocomposites

Polystyrene \((M_w = 265,000 \text{ g mol}^{-1}, \text{ polydispersity, PDI} = 2.45)\) (PS) with phenyl-grafted 28.8 nm diameter silica nanoparticles (NPs) and PS \((M_w = 400,000 \text{ g mol}^{-1}, \text{ PDI} = 1.06)\) with phenyl-grafted 12.8 nm diameter silica NPs are used as a matrix. 28.8 nm and 12.8 nm silica NPs were from Aldrich (Ludox AS40) and from Nissan Chemicals (DMAC-ST), respectively. The particle diameter and polydispersity were measured using small-angle X-ray scattering (SAXS). These NPs were mixed with phenyltrimethoxysilane (PhTMS), a coupling agent for NP dispersion in a PS matrix. Grafting densities of PhTMS on 28.8 nm and 12.8 nm silica NPs were characterized using size exclusion chromatography (SEC) coupled with an IR absorption detector and thermogravimetric analysis (TGA), respectively and were found to be 1.5 and 0.54 chains nm\(^{-2}\), respectively. The volume fractions of NP \((\phi_{NP})\) in PS are 0, 0.01, 0.02, 0.05, 0.1, 0.2, 0.3, 0.5 for 28.8 nm diameter NPs and 0, 0.03, 0.1 for 12.8 nm diameter NPs. The PS and phenyl-grafted silica NPs were each dissolved in dimethylacetamide (DMAC) or
dimethylformamide (DMF), and then mixed at the appropriate ratio. Transparent films were prepared by doctor blading the solution on a heated glass substrate (≈100 °C) to produce a film of thickness 5 ~ 10 µm. The NP dispersion in a PS matrix was observed using TEM after cross-sectioning the nanocomposite film using a microtome (thickness ~100 nm). Rutherford backscattering spectrometry (RBS) was used to obtain the depth profiles of the NPs in the nanocomposite film using 2 MeV He⁺ at incident angle of 10°. The depth resolution $\delta r = \frac{\delta E}{[S_0]_{PNC}}$ depends on silica NP loading, where $S_0$ is energy loss factor of the nanocomposite and is improved from 40~45 nm to 20 nm after rebuilding the electronics. The NP volume fraction in the nanocomposite film was measured using TGA. For TGA measurements, the film was heated at 20 °C min⁻¹ to 400 °C and then held at 400 °C for 3 h.

5.2.2 Tracer diffusion couple and processing

The tracer diffusion couples consisted of the nanocomposite matrix film covered with ~20 nm thick dPS tracer film. The nanocomposite matrix film was soaked in water and floated off from the glass substrate and then picked up by a silicon substrate. The matrix film on silicon substrate was dried in air overnight and preannealed at ~150 °C for 3 days to age the film and remove any residual solvent. Three different molecular weights of dPS - 49,000 g mol⁻¹ (PDI = 1.03), 168,000 g mol⁻¹ (PDI = 1.03) and 532,000 g mol⁻¹ (PDI = 1.05) were used as a tracer. The dPS was spin coated on silicon substrates to produce ~20 nm thick films as measured by ellipsometry. The dPS film was floated
off in water and transferred onto the matrix film attached to the silicon substrate. The
diffusion couples containing 12.8 nm NPs for dPS (49k), dPS (168k), and dPS (532k)
were annealed in a vacuum oven at 137, 156, and 162 °C, respectively because of their
wide range of diffusivities. The annealing condition for the diffusion couples containing
28.8 nm NPs is mentioned in our previous paper17.

Molecular weight and polydispersity of PS and dPS were measured using SEC.
The polymer was dissolved in tetrahydrofuran at various concentrations depending on its
molecular weight.

5.2.3 Elastic recoil detection (ERD)

The dPS concentration profile in the matrix was obtained by elastic recoil
detection (ERD). In ERD, the He\(^{2+}\) ion beam was accelerated to 3 MeV and intersects the
surface of the sample at 15 °. The recoiled H and D are collected by a ERD detector and
a 10 µm Mylar film was placed in front of the ERD detector to prevent the signal from
the forward scattered He from masking the H and D signal. The ERD spectra of counts
versus channel are converted to a dPS volume fraction profile using the thin slab
approach\(^{24}\). The instrumental resolution is captured by the Gaussian function,

$$
y = \frac{1}{p\sqrt{2\pi}} \exp\left(-\frac{x^2}{2p^2}\right),
$$

and enhanced from 78 nm \((p = 39 \text{ nm})\) to 60 nm \((p = 30 \text{ nm})\)
after rebuilding the electronics. The accessible depth is ~ 800 nm. The tracer diffusion
coefficients were obtained by fitting the profile to a one-dimensional (1-D) solution to
Fick’s second law equation for a finite source in a semi-infinite medium\(^{25,26}\). In the least
squares fitting to determine tracer diffusion coefficients, $\chi^2$ ranges from $\sim 10^{-3}$ to $\sim 10^{-4}$. Diffusion coefficients were obtained from multiple measurements taken for each sample including those annealed at different times and only the profiles having a sufficient diffusion length (300 ~ 500 nm) were considered. Details of ERD have been described elsewhere\textsuperscript{27}.

5.3 Results and discussion

5.3.1 The size and size distribution of NPs

To understand how the size of NPs influences polymer diffusion in a polymer nanocomposite, large and small silica NPs with the same surface functionality were added to a polystyrene (PS) matrix. The NPs were dispersed in DMAC and DMF for small and large NPs, respectively, and their size and polydispersity measured using SAXS. Log-normal distribution was applied to obtain the diameter and polydispersity of NPs. Figure 5.1 shows the log-normal distribution of particle diameters for the small and large NPs, and their corresponding median $d_m$, number average $d_n$, and volume average $d_v$ diameters. Figure 5.1 indicates that the smaller NPs are more polydisperse than the larger NPs. For the smaller NPs, the median, number average, and volume average diameters are 12.1 nm, 12.8 nm, and 14.2 nm, and the polydispersity ($\sigma$) is 1.39. Correspondingly, the diameters for the larger NPs are 28.6 nm, 28.8, and 29.2 nm, respectively, with polydispersity of 1.12. In a previous study\textsuperscript{17}, we reported the size of the larger NPs in terms of the number average diameters determined by averaging results from SAXS,
dynamic light scattering (DLS), and TEM. The diameter of 28 nm was then used to
calculate the interparticle distance as a function of NP volume fraction.

5.3.2 The dispersion of NPs in polymer nanocomposites

Surface grafting and processing are used to ensure that NPs are well dispersed in
the matrix. First, to minimize repulsion between NP and matrix chains, the surface of the
silica NPs is modified with phenyl groups that mimic the pendant phenyl groups on the
PS matrix chains. Second, while using a doctor blade to uniformly spread the matrix
solution, the glass substrate is heated to ~100 °C so that solvent evaporates quickly,
before long range diffusion of NPs can occur. Using the number average diameters, 12.8
nm and 28.8 nm, the number density of particles, interfacial area and interparticle
distance for well dispersed small and large NPs are compared at same volume fraction of
NPs in Figure 5.2 (a). For the smaller NPs, the number of particles per unit volume and
total interfacial area are ~12 times and 2.3 times greater than the larger NPs, whereas the
interparticle distance decreases by 66%. One objective of this study is to determine if
these changes in number density and, interfacial area, and interparticle distance have an
effect on the mechanism of polymer diffusion in a polymer nanocomposite.

For the volume fractions of NPs in this study, the large and small NPs are well-
dispersed in PS matrices. The cross-sectional TEM images in Figures 5.2 (b) and (c)
show that large and small NPs are well-dispersed at $\phi_{NP} = 0.1$. This result indicates that
the lower phenyl grafting density on the smaller NPs is sufficient to achieve a good
dispersion. The insets of Figures 5.2 (b) and (c) show the NP dispersion near the surface indicating that no segregation or depletion of NPs is observed near the surface. Whereas TEM provides information about the lateral distribution of NPs, RBS is used to determine the depth profile of the silica NPs in the PS matrix. Figure 5.2 (d) shows the depth profile of the smaller silica (SiO₂) NPs in a PS matrix for \( \phi_{NP} = 0.1 \). The energy (channel) and normalized yield correspond to depth and elemental concentrations, respectively. Arrows indicate backscattering from the silicon and oxygen atoms located at the surface of the film. For both elements, the normalized yield is consistent with a uniform distribution of NPs which is simulated using XRUMP®️. The simulation (solid line) represents a nanocomposite film (> 2 µm) containing 10 vol% of silica NPs uniformly dispersed in 90 vol% PS which is in good agreement with the RBS data (close square symbols). The depth resolution is ~ 20 nm. For the larger NPs \( (d_p = 28.8 \text{ nm}) \), the depth profile of silica NPs in a PS matrix for \( \phi_{NP} = 0.5 \) was published in a previous paper. For all volume fractions, the depth profiles of silica are consistent with a uniform dispersion near the outer ~1.5 µm and within the resolution of RBS, no measurable depletion or enrichment of NPs. Taken together, TEM and RBS studies show that nanocomposites of PS with up to 50 vol% of silica NPs are well dispersed over length scales probed by diffusion.

To compare tracer diffusion through matrices with the smaller and larger NPs, the diffusion of the NPs themselves must be evaluated. As NP size decreases, the diffusion coefficient is expected to increase according to the Stokes-Einstein (SE) prediction,

\[
D = \frac{k_B T}{6\pi \eta r}
\]

where \( \eta \) is the matrix viscosity and \( r \) is a radius of particle. Although the
diameter of the smaller NP is 44% less than the larger one, the higher molecular weight of the matrix (400k vs 265k) compensates by increasing the PS matrix viscosity. Assuming that the SE prediction is valid for NPs, the NP diffusion coefficient of the smaller \( (d_n = 12.8 \text{ nm}) \) NPs is \( \sim 10^{-17} \text{ cm}^2 \text{ s}^{-1} \) at 170 °C, similar to the \( D \) of the larger \( (d_n = 28.8 \text{ nm}) \) NP at 170 °C\textsuperscript{17,30}. In both cases, the NP diffusion coefficients are smaller than the diffusion coefficients of dPS tracer molecules \( (M = 49k, 168k, 532k) \) at 170 °C which range from \( 10^{-12} \) to \( 10^{-15} \text{ cm}^2 \text{ s}^{-1} \). Thus, the smaller and larger NPs are immobile on the time scale of the tracer diffusion in this study. Because they are well-dispersed (TEM, RBS) and relatively immobile, PS containing phenyl grafted NPs with diameters of 28.8 nm and 12.8 nm appears to be a model matrix for investigating tracer diffusion.

5.3.3 Effect of NP size

Tracer diffusion of deuterated PS (dPS) is measured in a PS matrix containing small and large silica NPs. The tracer diffusion couple is a bilayer of a thin \( (\sim 20 \text{ nm}) \) dPS layer deposited on a thick \( (5\sim 10 \mu\text{m}) \) PS:silica nanocomposite film. After thermal annealing, the dPS volume fraction profile in the matrix is measured by ERD. The tracer diffusion coefficient \( (D) \) is determined by fitting the dPS volume fraction profiles, \( \phi(x) \), with the appropriate solution to Fick’s second law\textsuperscript{25}:

\[
\phi(x) = \frac{1}{2} \left[ \text{erf}\left(\frac{h-x}{\sqrt{4Dt}}\right) + \text{erf}\left(\frac{h+x}{\sqrt{4Dt}}\right) \right]
\]
where $h$ is the dPS film thickness, $t$ is annealing time and $erf$ denotes the error function. This equation was convoluted with a Gaussian function which represents the depth resolution. For diffusion in the larger and smaller NP systems, the depth resolutions are 78 nm and 60 nm, respectively. Using least-square fitting, $D$ is varied to achieve a best fit between eq. (4) and the experimental data.

Previous studies of tracer diffusion into PS containing the larger NPs (28.8 nm) \(^1\) investigated how the tracer diffusion coefficient depends on both the NP volume fraction ($\phi_{NP}$) and tracer molecular weight ($M$). The tracer diffusion coefficient was found to decrease as the NP volume fraction or tracer molecular weight increased. To test whether these trends apply to the smaller NPs (12.8 nm), dPS tracer diffusion with $M = 49k$, 168k, 532k was measured into matrices containing $\phi_{NP} = 0, 0.03, 0.1$. Figures 5.3 (a) and (b) show the diffusion profiles of dPS ($M = 168k$) into matrices containing $\phi_{NP} = 0$ and 0.03 after annealing at 156 °C for 5.5 and 15.5 h, respectively. Similar to our prior studies\(^1\), the dPS diffusion profile into the matrix at high loading exhibits a surface peak as shown in Figure 5.3 (b) as opposed to the expected Fickian diffusion profile in Figure 5.3 (a). The surface peak results from a reduced flux at the interface attributed to the impenetrable NPs. A detailed discussion about the origin of the surface peak was presented in our previous paper\(^1\). The solid lines in Figures 5.3 (a) and (b) represent best fits of eq. (4) to the experimental data using $D = 1.2 \times 10^{-14} \text{ cm}^2 \text{ s}^{-1}$ and $6.9 \times 10^{-15} \text{ cm}^2 \text{ s}^{-1}$, respectively. The dashed line in Figure 5.3 (b) represents the sum of a surface peak and the Fickian profile (solid line). Thus, the addition of 3 vol% NPs decreases the tracer diffusion coefficient by almost 50%, consistent with slowing down due to confinement.
Figures 5.3 (c) and (d) show the volume fraction profiles of dPS ($M = 49k$ and 532k) into nanocomposite films containing $\phi_{NP} = 0.1$ after annealing at 137 °C for 27 h and at 162 °C for 143 h, respectively. The annealing temperatures are adjusted so that reasonable annealing times produce a diffusion distance of ~ 300 nm. The profile for the shorter tracer chains, Figure 5.3 (c), shows a typical Fickian shape (solid line) whereas a surface peak is observed for the longer tracer chains (dashed line) as shown in Figure 5.3 (d). Consistent with the results for larger NPs, a surface peak is observed by increasing the volume fraction of the smaller NPs (e.g., Figs. 5.3 (a) and 5.3 (b)) or the size of the tracer molecules (e.g., Figs. 5.3 (c) and 5.3 (d)). Figure 5.4 shows the reduced diffusion coefficient, which is the tracer diffusion coefficient in the nanocomposite relative to that in pure PS ($D/D_0$), as a function of NP volume fraction ($\phi_{NP}$). As NP volume fraction increases, the reduction in $D/D_0$ decreases more strongly as the three tracer molecular weight increases. The close and open symbols represent nanocomposites with large (28.8 nm) and small (12.8 nm) NPs, respectively. To accentuate any differences due to the size of NPs, Figures 5.4 (b), (c), and (d) show $D/D_0$ plotted up to $\phi_{NP} = 0.1$ for $M = 49k$, 168k and 532k, respectively. For dPS (49k), $D/D_0$ decreases slightly as $\phi_{NP}$ increases and no effect of NP size is observed, which is attributed to the condition that $ID > 2R_g$ for both smaller and larger NPs. Prior study with the larger NPs showed that for $ID > 2R_g$, $D/D_0$ decreases quite slowly as $\phi_{NP}$ increases whereas for $ID < 2R_g$, $D/D_0$ decreases more rapidly. Figure 5.4 (c) shows that for dPS (168k), $D/D_0$ for smaller NPs is much smaller than that for larger NPs at $\phi_{NP} = 0.1$. This difference may be attributed to the larger number density of smaller NPs which results in $ID < 2R_g$ for smaller NPs whereas $ID >$
$2R_g$ for the larger NPs. For dPS(532k), the $D/D_0$ values at $\phi_{NP} = 0.1$ are similar for smaller and larger NPs because $ID/2R_g$ is similar for both NPs.

Previously, we found that the reduced diffusion coefficient ($D/D_0$) plotted against the interparticle distance relative to probe size (i.e., $ID/2R_g$) collapses onto a master curve indicating that interparticle separation and probe size determine how confinement due to NPs slows diffusion in nanocomposites and the number average diameter based on TEM, SAXS and DLS was used\textsuperscript{17}. To be consistent, here we only use the SAXS measurements to investigate how the master curve depends (if at all) on the type of average as well as polydispersity of NP size. First, interparticle distance is calculated assuming monodisperse NPs, randomly distributed in a polymer matrix\textsuperscript{8}:

$$ID(d_n) = d_n \left( \frac{2}{\pi \phi_{NP}} \right)^{1/3} - 1$$

(5)

where $d_n$, the number average diameters for the large and small NPs are 28.8 nm and 12.8 nm, respectively. In Figure 5.5 (a), the interparticle distance is plotted against NP volume fraction for both NPs using eq. (5). At a given $\phi_{NP}$, NPs are 44% closer for the smaller NPs. For example, Figure 5.5 (a) shows that at $\phi_{NP} = 3\%$ (vertical dotted line), the interparticle distances are 50.9 nm and 22.6 nm for 28.8 nm and 12.8 nm NPs, respectively.

If $ID < 2R_g$, the tracer molecule is expected to be highly constrained by the nanoparticles in the matrix and, corresponding, $D/D_0$ decreases rapidly as $ID/2R_g$ decreases as shown in our previous study\textsuperscript{17}. Figure 5.5 (b) shows that $D/D_0$ plotted against $ID(d_n)/2R_g$ are in reasonable agreement with a master curve (dashed line is guide
to eye) for both the large (close square) and small (open square) NPs. For \( ID(d_n)/2R_g < 1 \) polymer diffusion slows down more rapidly because of confinement due to the NP. Whereas these results indicate that tracer diffusion is subject to both tracer size and interparticle distance, \( D/D_0 \) for the smaller NPs (open symbols) is slightly greater than for the larger NPs (closed symbol). So far \( ID \) has been determined for each nanocomposite using the number average diameter as noted in Figure 5.5 (a). In the next section, we show that polydispersity of NP size via \( ID \) has a measurable effect on the collapse of \( D/D_0 \) onto a master curve.

5.3.4 The polydispersity of NP diameter increases the interparticle distance

Because NPs have a range of sizes, polydispersity can change (increase) the value of \( ID \) and therefore the collapse of \( D/D_0 \) on a master curve. NP diameter \( (d_i) \) obeys a log-normal distribution having a frequency \( W(d_i) \) for 28.8 nm and 12.8 nm NPs as shown in Figure 5.1. Under the assumption that the NPs occupy a simple cubic lattice (see Appendix),

\[
ID(\sigma) = d_m \left( \frac{\pi}{6\phi_{NP}} \right)^{1/3} \left[ \exp\left(1.5(\ln \sigma)^2\right) \right] - \exp\left(0.5(\ln \sigma)^2\right) \tag{6}
\]

Using the number average diameter \( (d_n) \) rather than the median diameter \( (d_m) \), eq. (6) becomes

\[
ID(\sigma) = d_n \left( \frac{\pi}{6\phi} \right)^{1/3} \left[ \exp(\ln \sigma)^2 \right] - 1 \tag{7}
\]
For NPs in a simple cubic lattice, the ratio $ID(\sigma)/ID(1)$ is given by

$$ID(\sigma)/ID(1) = \left(\frac{\pi}{6\phi_{NP}}\right)^{1/3} \left[\exp(\ln \sigma^2) - 1\right] / \left(\frac{\pi}{6\phi_{NP}}\right)^{1/3} \left[\exp(\ln \sigma^2) - 1\right]$$  \hspace{1cm} (8)

and plotted as a function of polydispersity, $\sigma$, in Figure 5.6 (a). For NPs randomly distributed as in a polymer matrix, the ratio $ID(\sigma)/ID(1)$ is given by

$$ID(\sigma)/ID(1) = \left(\frac{2}{\pi\phi_{NP}^2}\right)^{1/3} \left[\exp(\ln \sigma^2) - 1\right] / \left(\frac{2}{\pi\phi_{NP}^2}\right)^{1/3} \left[\exp(\ln \sigma^2) - 1\right]$$  \hspace{1cm} (9)

and plotted against polydispersity, $\sigma$, in Figure 5.6 (b). Regardless of distribution, $ID(\sigma)/ID(1)$ increases as the polydispersity of NP size increases at constant volume fraction. Moreover, for a given polydispersity, nanocomposites with a higher volume fraction of NPs are more strongly affected by polydispersity. Comparing Figures 5.6 (a) and (b) shows that $ID(\sigma)/ID(1)$ is greater for the simple cubic distribution relative to the random distribution when compared at the same polydispersity and volume fraction of NPs. For the present study, the $ID$ for the small NPs are 19% (18%) and 27% (25%) greater than the monodisperse at $\phi_{NP} = 0.03$ and 0.1, respectively for the simple cubic (random) distribution. For the larger NPs $ID$ is increased by 2% (2%) and 3% (3%) at $\phi_{NP} = 0.03$ and 0.1, respectively, for the simple cubic (random) distribution. Thus, the effect of size polydispersity on the interparticle spacing for the large NPs is small but significant particularly for the smaller NPs. In general, size polydispersity plays a very significant role at higher loading and/or $\sigma > 2$. 

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The large and small silica NPs used in this study can be described as having a narrow ($\sigma=1.12$) and moderate ($\sigma=1.39$) distribution of diameters for 28.8 nm and 12.8 nm NPs, respectively. To determine the importance of size polydispersity in the present studies, Figure 5.6 (c) shows the interparticle distance for the small NPs if they are monodisperse or polydisperse. The monodisperse cases are calculated using the number and volume average diameters whereas the polydisperse case uses the number average values. As expected, interparticle distance decreases as the NP volume fraction increases. The interparticle distance of the polydisperse NPs (dotted line) is larger than that of monodisperse NPs (solid line) and the increment of the interparticle distance due to the polydispersity depends on the volume fraction of NPs, as expected from Figure 5.6 (b). To test other weighted averages, the interparticle distance is calculated using eq. (3) assuming the volume averaged diameter, $d_v$ instead of $d_n$. Figure 5.1 (a) shows that $d_v$ is greater than $d_n$ and therefore $ID (d_v)$ is always larger than $ID (d_n)$ for a distribution that is log-normal. Because $d_v = 14.2$ and $d_n = 12.8$ nm, $ID$ only increase by 11%, which is smaller than the effect of polydispersity previously noted.

To determine whether including the NP size distribution improves the master curve shown in Figure 5.5 (b), $D/D_0$ is plotted against $ID/2R_g$ where $ID (d_n, \sigma)$ and $ID (d_v)$ are calculated using eqs. (7) and (5) and shown in Figure 5.7 (a) and (b), respectively. Because $ID (d_n, \sigma)$ and $ID (d_v)$ are slightly larger than $ID (d_n)$ (c.f., Figure 5.6 (c)), $ID/2R_g$ is shifted towards higher values and this shift is greater for the smaller NPs because of their higher polydispersity. The experimental data points in Figures 5.5 (b), 5.7 (a) and 5.7 (b) are compared with the fitted lines ($D/D_0 = a\ln(ID/2R_g) + b$) where $a$ and $b$ are
constants. The difference between experimental data and fitted lines is least for $ID (d_n, \sigma)$ and largest for $ID (d_v)$. A comparison of Figure 5.5 (b) with Figures 5.7 (a) and 5.7 (b) suggests that inclusion of polydispersity either via $\sigma$ or $d_v$ slightly improves the collapse of the data. However, because the polydispersities of the small and large NPs are small ($\sigma = 1.12, 1.39$), $D/D_0$ against $ID/2R_g$ is not very sensitive to the distribution of NP size. However, for $\sigma > 2$, we expect that a monodisperse distribution using either $d_n$ or $d_v$ would fail to give $ID$ values that collapse $D/D_0$ onto a master curve. Thus, for the small and large NPs studied here, inclusion of size distribution is similarly captured by the breadth of the distribution and the volume average diameter. Future studies using a broad distribution of NPs would lead to differentiating between these two parameters.

5.3.5 Accounting for dispersion of interparticle distance in one dimension

In tracer diffusion in real polymer nanocomposites, the separation between randomly placed monodisperse nanoparticles (i.e., confining region) follows a statistical distribution that depends on the dimensionality. Assuming that confinement is 1-D, the matrix can be discretized into a lattice of unit size, $\bar{a} = \pi d / 4$, where each lattice site is either occupied with a probability of $\phi$, or unoccupied with a probability of $1 - \phi$ and $d$ is a particle diameter. The probability that the first site to be occupied relative to any given occupied site $i (= 1, 2, 3 \ldots)$ is given by $\psi(i) = \phi(1 - \phi)^{i-1}$, which is the product of the probability that all intervening $i-1$ sites are unoccupied and the probability that site $i$ is occupied. This discrete probability distribution function can be rewritten as,

$$\psi_{\text{discrete}} = \phi \exp \left\{ \ln(1 - \phi) \frac{x}{\bar{a}} \right\}$$

(10)
where \( a_i \equiv i - 1 \) such that \( a_i \equiv 0 \) corresponds to zero separation between two occupied nearest neighbor sites. If the continuous distribution is assumed to take the same form as eq. (10), the probability of finding a particle between \( x \) and \( x + dx \), is given by,

\[
B \exp \left\{ \ln(1 - \phi) \frac{x}{a} \right\} dx
\]

(11)

where \( B \) is a normalization constant found from the condition that \( \int_{0}^{\infty} \psi_{\text{continuous}}(x) dx = 1 \).

Thus, \( \psi_{\text{continuous}}(x) dx = \frac{-\ln(1 - \phi)}{a} \exp \left\{ \ln(1 - \phi) \frac{x}{a} \right\} dx \)

(12)

By rescaling the \( x \)-coordinate in terms of the probe size, the probability of finding a particle between \( y \) and \( dy \) is given by,

\[
\psi_{\text{continuous}}(y) = \frac{-2R_g}{a} \ln(1 - \phi) \exp \left\{ \ln(1 - \phi) \frac{2R_g}{a} y \right\} dy
\]

(13)

where \( y = x/2R_g \). The average \( \langle y^2 \rangle_{1-D} \) is then,

\[
\langle y^2 \rangle_{1-D} = \left\langle \left( \frac{x}{2R_g} \right)^2 \right\rangle = \frac{\int y^2 \psi(y) dy}{\int \psi(y) dy} = \frac{1}{2} \left( \frac{a}{R_g \ln(1 - \phi)} \right)^2
\]

(14)

and, \( \psi(y) = \sqrt[\langle y^2 \rangle_{1-D}]{\frac{2}{\sqrt[\langle y^2 \rangle_{1-D}]{y}}} \exp \left\{ -\sqrt[\langle y^2 \rangle_{1-D}]{y} \right\} \)

(15)

The expression \( \left\langle \left( \frac{x}{2R_g} \right)^2 \right\rangle \) is a more generalized form of \( ID/2R_g \) because it accounts for the statistical spatial distribution between NPs. In Figure 5.8, \( D/D_0 \) is plotted against \( \sqrt[\langle y^2 \rangle_{1-D}]{\left\langle \left( \frac{x}{2R_g} \right)^2 \right\rangle} \) and is found to collapse the results for the smaller and larger NPs onto one master curve. Although this model provides a similar quality master curve as the single spacing (i.e., \( ID \)) approach, this approach is more physically insightful because it
accounts for the tracer diffusion to be dominated by the tail end of the distribution where nanoparticle separation is largest. Thus, as opposed to a uniform distribution of spacing, this model is consistent with a smaller entropic penalty for diffusing species navigating through the composite when it encounters NPs spaced further apart than its random coil size.

5.4 Conclusions

Polymer diffusion in polymer nanocomposites was investigated for two different sizes of NPs ($d_n = 28.8, 12.8$ nm). Phenyl-grafted silica NPs are well dispersed in a PS matrix at length scales probed by the diffusion studies, which was confirmed by TEM and RBS. Smaller NPs have higher number density of particles, larger total interfacial area, and smaller interparticle distance. As NP loading or tracer size increases, tracer diffusion slows down. Compared at the same NP volume fraction, the tracer diffusion coefficient decreases as NP size decreases. When interparticle distance, $ID$, is calculated for monodisperse NPs that are randomly dispersed, the reduced diffusion coefficient, $D/D_0$, against $ID/2R_g$ for all NPs collapses onto a master curve, indicating that polymer diffusion is determined by the spacing between particles relative to the size of the tracer molecule. When the interparticle distance is calculated by including polydispersity of NP size or using the volume average diameter of NPs, a plot of $D/D_0$ against $ID/2R_g$ also falls on a master curve. Because these NPs have a narrow size distribution, the effect of the polydispersity of NP size on $ID$ is small. However, the collapse of $D/D_0$ against $ID/2R_g$ is slightly improved relative to the monodisperse case. In addition to polydispersity of NP size, the dispersity of $ID$ in 1-D is also considered. In this case, $D/D_0$ plotted against
the root mean square interparticle distance relative to tracer size is also found to collapse onto a master curve. These studies show that properties of PNCs can be tune by varying the polydispersity of particle size. Studies of polymer diffusion in a polymer nanocomposite are important for applications involving ultrafiltration, melt processing of polymer nanocomposites, and welding of multi-layer coatings.

5.5 Appendix

: Derivation of interparticle distance of polydisperse nanoparticles

Under the assumption that particles occupy the simple cubic lattice and one particle is in one simple cubic as shown in Figure 5.9, average volume of particle, $\langle V_{\text{particle}} \rangle$, and volume fraction of particles, $(\phi_{NP})$, are given by $\langle V_{\text{particle}} \rangle = \frac{\pi}{6} \langle d^3 \rangle$ and $\phi_{NP} = \frac{\pi}{6} \langle d^3 \rangle / b^3$, where $\langle d \rangle$ is average diameter of particle and $b$ is a length of a cubic lattice.

Thus, $b = \left( \frac{\pi}{6 \phi_{NP} \langle d^3 \rangle} \right)^{1/3}$

$ID(\sigma) = 2b - 2 < d > = \left( \frac{\pi}{6 \phi_{NP} \langle d^3 \rangle} \right)^{1/3} - < d >$

Because $\langle d \rangle = \exp \left( \ln d_m + \frac{(\ln \sigma)^2}{2} \right)$ and $\langle d^3 \rangle = \exp \left( 3 \ln d_m + 4.5(\ln \sigma)^2 \right)$ in the log-normal distribution$^9$, 

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\[ ID(\sigma) = d_m \left\{ \left( \frac{\pi}{6\phi_{NP}} \right)^{1/3} \left[ \exp(1.5(\ln \sigma)^2) \right] - \exp\left[ 0.5(\ln \sigma)^2 \right] \right\} \]

If number averaged diameter \( d_n = \langle d \rangle \) is used instead of median diameter \( d_m \),

\[ ID(\sigma) = d_n \left\{ \left( \frac{\pi}{6\phi} \right)^{1/3} \left[ \exp(\ln \sigma)^2 \right] - 1 \right\} \]

The ratio \( ID(\sigma) / ID(1) \) is given by

\[ ID(\sigma) / ID(1) = \left\{ \left( \frac{\pi}{6\phi_{NP}} \right)^{1/3} \left[ \exp(\ln \sigma)^2 \right] - 1 \right\} / \left\{ \left( \frac{\pi}{6\phi_{NP}} \right)^{1/3} - 1 \right\} \]
5.6 References


Figure 5.1. The distribution of particle diameter is measured using SAXS and the frequency, $W(d_i)$, is plotted against particle diameter for two different NPs. The size distribution of the smaller NPs (a) is broader than that of the larger NP (b). $d_m$, $d_n$, $d_v$, and $\sigma$ represent median, number average, volume average diameters and polydispersity, respectively and are listed for two different NPs in (c).
Figure 5.2 (a) As NP diameter decreases from 28.8 nm to 12.8 nm, number density and total interfacial area increase and interparticle distance decreases at same NP volume fraction. (b), (c) Cross-sectional TEM images of PS : $\phi_{NP} = 0.1$ nanocomposite film containing silica NPs with number average diameters of 28.8 nm and 12.8 nm, respectively. Insets: cross-sectional TEM images of the near surface (dotted line). NPs are well dispersed in all nanocomposite films. (d) Silicon and oxygen concentration profile measured via RBS for PS : $\phi_{NP} = 0.1$ nanocomposite film containing 12.8 nm diameter silica NPs. Symbols represent the silicon and oxygen yield from the surface (arrows) and near surface ($< 2 \mu$m) regions. The solid line (red) is a simulation assuming a uniform distribution of NPs corresponding to a PS : $\phi_{NP} = 0.1$ nanocomposite film.
Figure 5.3 Concentration profiles of dPS in PS : NP nanocomposites measured using ERD to investigate the effect of NP volume fraction and tracer molecular weight. Solid line is a fit of experimental data with eq. (4) using appropriate $D$ values, whereas the dashed line represents the sum of the solid line and a surface peak. Tracer molecular weight ($M$) and NP volume fraction ($\phi_{NP}$) are denoted in the legends. (a) $D = 1.2 \times 10^{-14}$ cm$^2$ s$^{-1}$ at 156 °C. (b) $D = 6.9 \times 10^{-15}$ cm$^2$ s$^{-1}$ at 156 °C. (c) $D = 1.4 \times 10^{-14}$ cm$^2$ s$^{-1}$ at 137 °C. (d) $D = 3.8 \times 10^{-15}$ cm$^2$ s$^{-1}$ at 162 °C. Surface peaks are observed for profiles in Figures 3 (b) and 3 (d) which have higher NP concentration and tracer molecular weight, respectively.
Figure 5.4  Closed and open symbols correspond to NPs with 28.8 nm and 12.8 nm diameters, respectively.  (a) Reduced diffusion coefficient as a function of NP volume fraction for all NPs.  Reduced diffusion coefficients of (b) 49kdPS, (c) 168kdPS, and (d) 532kdPS tracer molecules are plotted against NP volume fraction up to $\phi_{NP} = 0.1$ to observe the effect of NP size on polymer diffusion.  As NP size decreases, polymer diffusion slows down and the slowing down depends on the ratio of interparticle distance and tracer size.
Figure 5.5 (a) Interparticle distance (ID) is plotted against NP volume fraction ($\phi_{NP}$) using eq. (5) and number average diameter of NP ($d_n$) under the assumption that NPs are monodisperse and randomly distributed in a polymer matrix. As NP size decreases or NP volume fraction increases, interparticle distance decreases. (b) Reduced diffusion coefficient ($D/D_0$) is plotting against interparticle distance $ID$ ($d_n$) against tracer size and interparticle distance. Reduced diffusion coefficient ($D/D_0$) against $ID (d_n)/2R_g$ collapses onto a master curve for all NPs. As $ID (d_n)/2R_g$ decreases, polymer diffusion is highly constrained and slows down rapidly. Open and closed symbols represent the data for 12.8 nm and 28.8 nm NPs, respectively.
Figure 5.6  \( ID(\sigma)/ID(1) \) for (a) simple cubic and (b) random distribution of NPs is plotted against the polydispersity of NP size (\( \sigma \)) using eq. (8) and eq. (9), respectively. As polydispersity of NP size or NP volume fraction increases, \( ID(\sigma)/ID(1) \) increases for both NP distributions and \( ID(\sigma)/ID(1) \) in simple cubic distribution is larger than that in
random distribution at same polydispersity and volume fraction of NPs.  (c) Interparticle distance is plotted against NP volume fraction for 12.8 nm NPs ($\sigma = 1.39$). Interparticle distance is calculated using eq. (7) and $d_n$, $\sigma$ (dotted line), and using eq. (5) and $d_v$ (dashed line) to investigate the effect of polydispersity of NP size on interparticle distance. Solid line is interparticle distance for monodisperse NPs calculated using eq. (5) and $d_n$ as a reference. The polydispersity of NPs increases interparticle distance as expected from Figures 5.6 (b) and 5.6 (c).
Figure 5.7 Reduced diffusion coefficient ($D/D_0$) is plotted against interparticle distance against tracer size and interparticle distance. $ID(d_n, \sigma)$ and $ID(d_v)$ are calculated using eq. (7) and $d_n$, $\sigma$, and eq. (5) and $d_v$, respectively. Reduced diffusion coefficient ($D/D_0$) plotted against $ID(d_n, \sigma)/2R_g$ and $ID(d_v)/2R_g$ collapses onto a master curve for all NPs. Open and closed symbols represent the data for small and large NPs, respectively.
Figure 5.8 Reduced diffusion coefficient \((D/D_0)\) is plotted against root mean square 1-D average spacing between particles relative tracer size \(\sqrt{\langle (x/2R_g)^2 \rangle}\) for all NPs. All data points collapse onto a master curve and open and closed symbols represent the data for 12.8 nm and 28.8 nm NPs, respectively.
Figure 5.9  When each particle is occupied at the center of a simple cubic, interparticle distance (*ID*) is calculated considering a polydispersity of NP diameter.
Chapter 6

Polymer Diffusion in a Polymer Nanocomposite: Effect of Polymer-Nanoparticle Interaction

6.1 Introduction

Polymer nanocomposites have attracted great attention because addition of nanoparticles (NPs) to a polymer matrix enhances properties and provides possibility for numerous applications. With decreasing particle size, surface area-to-volume ratio of particle increases and interfacial region between particle and polymer becomes crucial to determine the properties of polymer nanocomposites. A major challenge is to control the spatial distribution of NPs in a polymer melt. Many researchers have functionalized the particle surface using short molecules or polymers to modify the polymer-NP interaction and control the dispersion. For example, NPs are grafted with a chemically identical or attractive brush to a polymer matrix for good dispersion of NPs in a homopolymer or self-assembly of NPs in a block copolymer or a polymer blend. This modification of the particle surface can also improve mechanical, thermal, and electrical properties etc. Winey et al. enhanced tensile strength and toughness of the composites by covalently bonding of single wall carbon nanotubes (SWCNTs) to the nylon matrix via alkyl segments. Ramanathan et al. also improved not only mechanical properties but also thermal and electrical properties of neat poly(methyl methacrylate) (PMMA) or PMMA containing non-functionalized SWCNTs or graphene sheets by adding functionalized...
SWCNTs or graphene sheets which may form covalent or hydrogen bonds with PMMA, respectively. Rong et al.\textsuperscript{10, 11} modified the surface of silica NPs by grafting various polymers such as polystyrene (PS), PMMA, polyvinyl acetate (PVA) etc. to improve interfacial adhesion between polypropylene (PP) and NPs and thus, mechanical property of PP.

In the present study, we investigate NPs that are strongly attractive towards the matrix as well as weakly attractive. Silica NPs are well dispersed in a PMMA matrix without any surface modification due to the favorable interaction between PMMA and colloidal silica NP (i.e. hydroxyl terminated). Good dispersion of silica NPs is also achieved by modifying the surface of particles with phenylethyltrimethoxysilane (PhETMS) as well as phenyltrimethoxysilane (PhTMS) due to the phenyl groups on the silica NPs that are similar to the pendant phenyl group in the PS molecules. The glass transition temperature and physical aging rate in PS or PMMA nanocomposites containing silica NPs have been studied using differential scanning calorimetry (DSC), fluorescence spectroscopy, and dielectric spectroscopy\textsuperscript{12-14}. As silica NP concentration in a PMMA matrix increases up to 0.6 vol\%, the glass transition temperature increases by \( \sim 5 \) °C and physical aging rate is reduced relative to neat PMMA\textsuperscript{13, 14}. In contrast, upon addition of up to 40 wt\% silica NPs to a PS matrix, the glass transition temperature decreases by \( \sim 11 \) °C and no change in the physical aging is observed\textsuperscript{12-14}. The hindered mobility of PMMA containing silica NPs is attributed to the hydrogen bonding between PMMA ester side groups and hydroxyl units on the surface of the silica NPs. In addition to the nanocomposite, the glass transition temperature and physical aging rate of homopolymer films on silica substrates are investigated as film thickness decreases\textsuperscript{15, 16}. 

At the polymer-silica substrate interface, cooperative segmental mobility of PMMA is suppressed due to hydrogen bonding, leading to an increase in the glass transition temperature and also, the formation of hydrogen bonds suppresses segmental relaxation and reduces the physical aging rate.

Here, polymer diffusion in polymer nanocomposites is investigated to study how the interaction between polymer and NP influences dynamics. The nanocomposite systems include NPs (12.8 nm) that are strongly and weakly attractive towards the diffusing species. Using elastic recoil detection (ERD) to measure the tracer diffusion coefficient, dPMMA diffusion into a PMMA:hydroxyl-terminated silica matrix (PMMA:OH-NP) is found to be slower than that of dPS into a PS:phenyl-terminated silica matrix (PS:Ph-NP). This result is attributed to the stronger attractive interaction between dPMMA segments and hydroxyl groups relative to the dPS segmental attraction to phenyl groups. For the PMMA:OH-NP and PS:Ph-NP systems, the reduced diffusion coefficients \( \frac{D}{D_0} \) plotted against interparticle distance relative to tracer size \( \frac{ID}{2R_g} \) collapse onto master curves. These results indicate that the collapse of \( \frac{D}{D_0} \) is a general property of polymer nanocomposites. To further test the effect of NP-polymer interaction, dPS diffusion is measured in PS matrices containing phenyl ethyl and phenyl-terminated silica (28.8nm). Faster diffusion of dPS is observed in the phenyl ethyl-terminated silica NPs possibly because the ethyl spacer weakens the attraction between dPS segments and the phenyl ethyl groups. Based on the tracer diffusion measurements, the enthalpic interaction energy difference between PMMA:OH-NP and PS:Ph-NP \( (\Delta H_{dPMMA} - \Delta H_{dPS}) \) is estimated as \( 0.2 \sim 1.0k_BT \), indicating that PMMA segments and
hydroxyl groups are more attractive than PS and phenyl groups. As NP volume fraction increases from 0.035 to 0.14, $\Delta H_{d_{PMMA}} - \Delta H_{d_{PS}}$ increases from $\sim 0.2k_BT$ to $\sim 0.96k_BT$ demonstrating that the enthalpic interaction energy increases as the interfacial area between polymer and NP increases. This provides guidelines for controlling the processibility of polymer nanocomposites which exhibit a range of polymer-NP interactions depending on the desired application (e.g., metal NPs for optical properties).

6.2 Materials and experimental methods

6.2.1 Preparation and characterization of polymer nanocomposites

Polystyrene ($M_w = 400,000 g mol^{-1}$, polydispersity, PDI = 1.06) (PS) with phenyl-capped silica NPs and poly(methyl methacrylate) ($M_w = 337,000 g mol^{-1}$, PDI = 1.82) (PMMA) with unmodified silica nanoparticles (NPs) are used as matrices. Silica NPs from Nissan Chemicals (DMAC-ST) were characterized by small-angle X-ray scattering (SAXS) and number average diameter ($d_n$) and polydispersity ($\sigma$) were 12.8 nm and 1.39, respectively. These silica NPs were mixed with PMMA. To disperse silica NPs in PS, these silica NPs were grafted with phenyltrimethoxysilane (PhTMS). Silica NPs in dimethylacetamide (DMAC) were centrifuged twice at 11000 rpm for 3 h. After the second centrifuge, DMAC : toluene (50 : 50) were added to the NPs which were reacted with PhTMS by stirring under the nitrogen gas flow at 90 °C for 22 h. The grafting density of PhTMS on silica NPs was measured using thermogravimetric analysis (TGA) and was found to be 0.54 chains nm$^{-2}$. 

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Polymer and NPs were each dissolved in dimethylacetamide (DMAC), and then mixed at the appropriate ratio. The volume fractions of NP ($\phi_{NP}$) in PS are 0, 0.03, 0.1 and those in PMMA are 0, 0.005, 0.035, 0.07, 0.14, 0.25. The polymer nanocomposite films were prepared by doctorblading the solution on a heated glass substrate (~100 °C) to produce a film with thicknesses from 5 to 10 µm. The NP concentration in the films was measured using TGA. For TGA measurements, films were heated at 20 °C min\(^{-1}\) to 400 °C and then held at 400 °C for 3 h. The NP dispersion in the films was observed using transmission electron microscopy (TEM) after cross-sectioning using a microtome. Depth profiles of the NPs in the films were obtained using Rutherford backscattering spectrometry (RBS) at 2 MeV He\(^{+}\) and incident angle of 10°. The depth resolution was ~20 nm.

To understand the role of brush type, diffusion was studied in polystyrene ($M_w = 265,000$ g mol\(^{-1}\), PDI = 2.45) (PS) matrices containing phenyl-grafted or phenyl ethyl-grafted silica NPs ($d_n = 28.8$ nm). The silica NPs (Aldrich, Ludox AS40) were functionalized with either phenyltrimethoxysilane (PhTMS) or phenylethyltrimethoxysilane (PhETMS) using a previously published method\(^{17}\). The grafting density was measured using size exclusion chromatography (SEC) coupled with an IR absorption detector and found to be about 1.5 molecules per nm\(^2\). The particle diameter and polydispersity were measured by small-angle X-ray scattering (SAXS). The volume fractions of NP ($\phi_{NP}$) in PS were 0, 0.2. The films were prepared in the same manner as the PMMA and PS systems containing the smaller ($d_n =12.8$ nm) silica NPs.
6.2.2 Tracer diffusion couple and processing

The tracer diffusion couples consisted of thick nanocomposite matrix film covered with a thin deuterated polymer film (tracer). The matrix film on the glass substrate was soaked in water, removed from the glass substrate, floated on water, and then picked up by a silicon substrate. This matrix film was dried overnight in air and preannealed at ~150 °C in vacuum for 3 days to age the film and remove any residual solvent. Deuterated PS (dPS) with molecular weights of 49,000 g mol\(^{-1}\) (PDI = 1.03), 168,000 g mol\(^{-1}\) (PDI = 1.03) and 532,000 g mol\(^{-1}\) (PDI = 1.05) was spin coated on silicon substrates to produce ~20 nm thick films as measured by ellipsometry. The dPS film was floated off in water and deposited on the matrix film attached to the silicon substrate. Deuterated PMMA (~20 nm) (dPMMA) with molecular weights of 93,000 g mol\(^{-1}\) (PDI = 1.03) and 281,000 g mol\(^{-1}\) (PDI = 1.02) was deposited on the PMMA nanocomposite matrix film. Because dPMMA film did not detach from the silicon substrate, a sacrificial layer of chitosan (~30 nm) was first deposited on the silicon substrate prior to spin coating the dPMMA from a toluene solution. Because chitosan dissolved in water, the dPMMA layer was readily floated off in water and transferred onto the PMMA matrix film. Fourier transform infrared spectroscopy (FTIR) indicated that chitosan did not remain attached to the dPMMA layer. The dPMMA/PMMA nanocomposite diffusion couple was dried in air overnight and annealed at 195 °C. Molecular weights and polydispersities of dPS and dPMMA were measured in tetrahydrofuran using SEC.
6.2.3 Elastic recoil detection (ERD)

The dPS or dPMMA concentration profile in the matrix was measured by elastic recoil detection (ERD) after thermal annealing. In ERD, 3MeV He\(^{2+}\) ion beam intersects the plane of the sample at 15\(^{\circ}\) and the recoiled \(^1\)H and \(^2\)D are collected by an ERD detector. A 10 \(\mu\)m Mylar film was placed in front of the ERD detector to prevent the signal from the forward scattered He from masking the H and D signal. The ERD spectra of counts versus channel are converted to a dPS volume fraction profile using the thin slab approach\(^{18}\). The instrumental resolution is presented by the Gaussian function,

\[
y = \frac{1}{p\sqrt{2\pi}} \exp\left(-\frac{x^2}{2p^2}\right), \quad \text{where} \quad p = 30 \text{ nm}.
\]

The depth resolution and accessible depth are 60 nm and \(~ 800 \text{ nm}\), respectively. Details of ERD have been reviewed elsewhere\(^{19}\). To reduce the ion beam damage on PMMA samples, a low beam current (< 2 nA) was used and total 10 \(\mu\)C was collected from 5 different spots on the PMMA samples. The tracer diffusion coefficients are obtained by fitting the concentration profile to a one-dimensional (1-D) solution to Fick’s second law equation\(^{20, 21}\). Diffusion coefficients were obtained from multiple measurements taken for each sample including those annealed at different times and only the profiles having a sufficient diffusion length were considered to obtain the diffusion coefficients.
6.3 Results and discussion

6.3.1 NP distribution in polymer nanocomposites

In chapter 4 and 5, both 28.8 nm and 12.8 nm diameter phenyl-grafted silica NPs are well dispersed in a PS matrix. Good dispersion of 12.8 nm silica NPs in a PMMA matrix is achieved without any surface treatment on silica NPs because of the attractive interaction between hydroxyl group on silica NPs and ester group in PMMA. Figure 6.1 shows cross-sectional TEM images of PS: $\phi_{NP} = 0.03$, PMMA: $\phi_{NP} = 0.035, 0.14, 0.25$ nanocomposite films and phenyl-terminated silica NPs and hydroxyl-terminated silica NPs are well dispersed in PS and PMMA matrices, respectively. Using RBS, the depth profiles of PS and PMMA nanocomposite films were obtained at the incident angle of 10° and compared with the results using XRUMP® simulation (not shown here), indicating that both silicon and oxygen elements are uniformly distributed at least at length scales probed by the diffusion studies (~ 1 µm) without any surface segregation or depletion.

Observation of NP dispersion using TEM and RBS demonstrates that phenyl-terminated silica NPs and hydroxyl-terminated silica NPs are well dispersed in PS and PMMA, respectively.

The NP diffusion coefficient in PS is calculated using PS viscosity and Stokes-Einstein equation\textsuperscript{23}. NP diffusion coefficient ($d = 12.8$ nm) in a 400k PS matrix at 170 °C is $\sim 10^{-17}$ cm$^2$ s$^{-1}$, similar to that ($d = 28.8$ nm) in a 265k PS matrix at 170 °C. These NP diffusion coefficients are much smaller than the diffusion coefficients of 49k, 168k, 532k at 170 °C ranging from $10^{-12}$ to $10^{-15}$ cm$^2$ s$^{-1}$, which shows that both NPs are immobile relative to the tracer molecules. NP diffusion coefficient ($d_{n} = 12.8$ nm) in a 390k
PMMA matrix at 190 °C and 203 °C is \( \sim 1 \times 10^{-18} \text{ cm}^2 \text{ s}^{-1} \) and \( \sim 6 \times 10^{-18} \text{ cm}^2 \text{ s}^{-1} \), respectively. NP diffusion coefficient \( (d_n = 12.8 \text{ nm}) \) in a 390k PMMA matrix at 195 °C will be much smaller than dPMMA diffusion coefficient \( (10^{-14} \sim 10^{-16}) \) in a 337k dPMMA matrix at 195 °C. Based on the TEM and RBS observation and calculation of NP diffusion coefficient, PS:phenyl-terminated silica (PS:Ph-NP) and PMMA:hydroxyl-terminated silica (PMMA:OH-NP) systems are an appropriate system for diffusion study.

The glass transition temperatures \( (T_g) \) of PMMA and the nanocomposites were measured using differential scanning calorimetry (DSC). Addition of NPs did not change \( T_g \) of PMMA significantly and therefore, changes in diffusion coefficient are not due to changes in \( T_g \).

### 6.3.2 Effect of polymer-NP interaction

Polymer diffusion in a polymer nanocomposite was investigated by obtaining the concentration profiles of a tracer in a polymer nanocomposite matrix as a function of depth using ERD. The tracer diffusion coefficient \( (D) \) was determined by fitting the experimental deuterated polymer volume fraction profiles, \( \phi(x) \), with the appropriate solution to Fick’s second law:

\[
\phi(x) = \frac{1}{2} \left[ \text{erf} \left( \frac{h - x}{\sqrt{4Dt}} \right) + \text{erf} \left( \frac{h + x}{\sqrt{4Dt}} \right) \right] (1)
\]

where \( \text{erf} \) denotes the error function, \( h \) is initial dPS film thickness, and \( t \) is annealing time. This equation was convoluted with a Gaussian function which represents the depth.
resolution. The depth resolution was 60 nm and least-square fitting was used to minimize the deviation between experimental result and eq. (1).

In chapter 5, the polymer diffusion in PS:Ph-NP was investigated. As volume fraction of NP ($\phi_{NP}$) in the PS matrix or the molecular weight of the tracer ($M$) increased, polymer diffusion slowed down. Here, we examine how the attractive interaction between PMMA and hydroxyl-terminated silica NP can affect this diffusion behavior. Attractive interaction between polymer and NP is expected to slow down polymer diffusion more than weak interaction. The volume fraction of silica NPs ($\phi_{NP}$) in a PMMA matrix is 0, 0.005, 0.035, 0.07, 0.14, 0.25 and the two different molecular weight of dPMMA ($M = 93k, 281k$) are used. Figures 6.2 (a) and (b) show the concentration profiles of dPMMA ($M = 93k$) into nanocomposite film containing $\phi_{NP} = 0.005$ and 0.25 after annealing at 195 °C for 24 and 120 h. At the low loading of NPs, the expected Fickian diffusion shape is observed as shown in Figure 6.2 (a) whereas at the higher loading, a surface peak is observed as shown in chapter 4 and 5. The surface peak is attributed to a reduced flux at the interface possibly caused by impenetrable NPs and is observed when tracer molecule is highly constrained. The solid lines in Figures 6.2 (a) and (b) represent fits of the experimental data with eq. (1) with $D = 5.7 \times 10^{-15}$ cm$^2$ s$^{-1}$ and $7.8 \times 10^{-16}$ cm$^2$ s$^{-1}$, respectively. The dashed line in Figure 6.2 (b) represents sum of a surface peak and the solid line. As NP volume fraction increases from 0.005 to 0.25, almost one order decrease in tracer diffusion coefficient is observed. Figures 6.2 (c) and (d) show the diffusion profiles of dPMMA ($M = 93k, 281k$) into nanocomposite film containing $\phi_{NP} = 0.14$ after annealing at 195 °C for 24 h and 659 h, respectively. Tracer
diffusion coefficient is obtained from fitting with a solid line as shown in Figures 6.2 (c) and (d) and decreases from $2.1 \times 10^{-15}$ cm$^2$ s$^{-1}$ to $1.2 \times 10^{-16}$ cm$^2$ s$^{-1}$ as tracer molecular weight increases from 93k to 281k. A surface peak is observed for both tracers probably due to the high constraint ($ID/2R_g < 1$).

Figure 6.3 shows tracer diffusion coefficient of dPS and dPMMA in composite relative to the pure PS ($D/D_0$) is against NP volume fraction ($\phi_{NP}$). As NP volume fraction or tracer molecular weight increases, reduced diffusion coefficient ($D/D_0$) decreases for both deuterated polymers. Also, dPMMA diffusion is slower than dPS diffusion at almost same NP volume fraction (e.g., $\phi_{NP} = 0.035$ and 0.03) for all tracer molecular weights and reduced diffusion coefficient of dPMMA with low molecular weight is smaller than that of dPS with high molecular weight (e.g, $D/D_0$ (93kdPMMA) < $D/D_0$ (168kdPS, 532kdPS) and $D/D_0$ (281kdPMMA) < $D/D_0$ (532kdPS)). This result indicates that the attractive interaction between a dPMMA segment and hydroxyl groups on the NP slows down diffusion more than the weaker interaction between a dPS segment and phenyl-groups on silica NPs. To compare diffusion of dPS and dPMMA at the same volume fraction of NPs, the $D/D_0$ values of dPS at $\phi_{NP} = 0.035$ and 0.14 are estimated by using the $D/D_0$ vs $ID/2R_g$ plot shown in Chapter 5. Figure 6.4 shows $D/D_0$ against the tracer molecular weights of dPS and dPMMA at $\phi_{NP} = 0.035$ (a) and 0.14 (b). At the same $\phi_{NP}$, $D/D_0$ of dPS is larger than that of dPMMA; moreover, as the NP volume fraction increases from 0.035 to 0.14, the difference between $D/D_0$ from dPMMA and dPS increases as shown in Figure 6.4. To compare the tracer diffusion results for the same molecular weight of dPS and dPMMA, $D/D_0$ is also estimated using the $D/D_0$ vs
ID/2R_g data from Chapter 5. At φ_{NP} = 0.035, the D/D_0 values for 93kdPS and 281kdPS are 0.60 and 0.49, respectively, whereas at φ_{NP} = 0.14, D/D_0 are 0.44 and 0.34, respectively. At φ_{NP} = 0.035, the average of \( \frac{(D/D_0)_{93kdPS}}{(D/D_0)_{93kdPMMA}} \) and \( \frac{(D/D_0)_{281kdPS}}{(D/D_0)_{281kdPMMA}} \) is ~ 1.2 whereas at φ_{NP} = 0.14, the average is ~ 2.6. At the same volume fraction of NPs, the reduced diffusion coefficients of dPS relative to that of dPMMA, \( \frac{(D/D_0)_{dPS}}{(D/D_0)_{dPMMA}} \), are similar for both tracer molecular weights. Note that as φ_{NP} increases from 0.035 to 0.14, \( \frac{(D/D_0)_{dPS}}{(D/D_0)_{dPMMA}} \) increases from 1.2 to 2.6. This result indicates that dPS diffusion increases faster than that of dPMMA by a factor of ~2 as the volume fraction of NP increased by a factor of ~4. This increase in diffusion of dPS relative to dPMMA may be attributed to an increase in interfacial area between the tracer molecules and NPs. Namely, as φ_{NP} increases, the number of contacts between dPMMA (dPS) segments and hydroxyl (phenyl) groups increases. These results also suggest that the tracer molecular weight has a secondary effect on slowing down by the increase of enthalpic energy. This observation is consistent with dPMMA adsorption studies on silica from trichloroethylene, where for M = 45k and 595k, the bound fraction of segments are nearly independent of molecular weight, 0.37 and 0.34, respectively. Thus, the enthalpic interaction energy between PS:Ph-NP and PMMA:OH-NP mainly depends on the interaction strength and interfacial area between polymer and NP, rather than tracer size.

Tracer diffusion coefficient in PS:Ph-NP nanocomposite relative to the pure PS (D/D_0) against the interparticle distance relative to probe size (i.e., ID/2R_g) collapses onto
a master curve for both 12.8 nm and 28.8 nm diameter NPs in chapter 5, demonstrating that interparticle spacing and tracer size are key parameters to decide polymer diffusion in a weakly interacting system. Tracer diffusion coefficient in PMMA:OH-NP nanocomposite relative to the pure PMMA \( (D/D_0) \) is also plotted against \( ID/2R_g \) with that in PS:Ph-NP nanocomposite relative to the pure PS in Figure 6.5 (a). Interparticle distance, \( ID \), is calculated under the assumption that NPs are randomly distributed in a polymer matrix and the NP diameter has a log-normal distribution. The interparticle distance is derived as a function of diameter \( (d_n) \), volume fraction of NPs \( (\phi_{NP}) \), and polydispersity of NP size \( (\sigma) \) in chapter 5:

\[
ID = d_n \left\{ \left( \frac{\pi}{6\phi} \right)^{1/3} \left[ \exp(\ln \sigma)^2 \right] - 1 \right\}
\]  

(2)

Both phenyl-terminated and hydroxyl-terminated silica NPs have same diameter and polydispersity of 12.8 nm and 1.39, respectively, measured using SAXS. As shown in Figure 6.5, the reduced diffusion coefficients \( (D/D_0) \) of dPS and dPMMA plotted against \( ID/2R_g \) collapse onto two master curves. Moreover, the reduced diffusion coefficient \( (D/D_0) \) of dPMMA is less than that of dPS. This result indicates that under similar geometric constraints (e.g., \( ID \) relative to \( 2R_g \)), the attractive interaction between dPMMA segments and the hydroxyl terminated NP slows down diffusion more than the weaker interaction expected for the dPS segments and phenyl-terminated NP. We can now better understand how the composite properties influence the thermodynamics that determine diffusivity. Namely, the enthalpic interaction energy will be proportional to
the interfacial area between tracer and NP, as mentioned above, whereas chain entropy loss depends on interparticle distance and tracer size as described in Chapter 5.

6.3.3 Effect of NP surface functional group

Tracer diffusion of dPS is studied in PS matrices containing phenyl-terminated and phenyl ethyl-terminated silica NPs (28.8 nm) in order to investigate the effect of NP surface functional groups on diffusion. The dPS molecular weights correspond to 49k, 168k, 532k and the NP volume fraction ($\phi_{NP}$) for both matrices are 0.2. Figure 6.6 shows the cross-sectional TEM images of PS matrices containing (a) phenyl-terminated silica NPs (PS:Ph-NP) and (b) phenyl ethyl-terminated silica NPs (PS:PhE-NP). The silica NPs are well dispersed in both polymer nanocomposites at $\phi_{NP} = 0.2$. Figure 6.7 shows the diffusion profiles of dPS (168k) into PS:Ph-NP (a) and PS:PhE-NP (b) after annealing at 156 °C for 14 h. The diffusion coefficients were obtained by fitting experimental data with eq. (1) (solid line) and found to be 5.3x10^{-15} \text{ cm}^2 \text{ s}^{-1} and 7.4x10^{-15} \text{ cm}^2 \text{ s}^{-1}, respectively. Upon changing the coupling agent from PhTMS to PhETMS, the dPS (168k) diffusion coefficient increases by ~40 %. Figure 6.8 shows the reduced diffusion coefficient of dPS ($D/D_0$) plotted against $ID/2R_g$. The closed diamonds represent data obtained from the PS:Ph-NP (28.8 nm) presented in chapter 4. The other closed and open symbols are data from PS:Ph-NP and PS:PhE-NP (28.8 nm), respectively, annealed in the same vacuum oven for the same time. Compared at the same $ID/2R_g$, the reduced diffusion coefficients of all dPS tracers in PS:PhE-NP are ~40% larger than those in PS:Ph-NP. The faster diffusion in the PS:PhE-NP system could result from a weaker interaction with PS segments.
6.3.4 Role of enthalpic interactions in polymer diffusion

The diffusion of linear, high molecular weight polymer chains in an entangled polymer matrix can be described by the reptation model\textsuperscript{26, 27} which predicts that the tracer diffusion coefficient is inversely proportional to the square of the tracer molecular weight ($M$) ($D \sim M^{-2}$). From the plots of $D/D_0$ versus $M$ for the dPS system in Figure 6.4, $D \sim M^{2.18}$ and $D \sim M^{2.25}$ at $\phi_{NP} = 0.035$ and 0.14, respectively. Also, from $D/D_0$ for dPS at $\phi_{NP} = 0.03$ and 0.1, $D \sim M^{2.17}$ and $D \sim M^{2.23}$. This scaling indicates that tracer diffusion in polymer nanocomposites is not solely described by reptation but rather confinement effects that increase with $M$ play a role in the mechanism. An analytical theory relating $D$ to $M$ is lacking.

In chapter 4, polymer diffusion in a weakly interacting system, such as PS:Ph-NP, slows down mainly due to a reduction of chain entropy which is captured by the entropy barrier model. However, in an attractive system, such as PMMA:OH-NP, polymer diffusion can depend on enthalpy. Previously, Muthukumar\textsuperscript{28} proposed that $D/D_0 \sim \exp(-\Delta F/k_b T)$ where $D_0$ is the diffusion coefficient of a single chain with no geometrical constraints, $\Delta F$ is free energy difference associated with partial confinement of a chain per each bottleneck, and $T$ is temperature. If polymer interactions with geometrical constraints (e.g., walls) are weak, $\Delta F$ is determined by chain entropy loss due to conformational restrictions. Because $\Delta F = \Delta H - T \Delta S$, $D/D_0 \sim \exp\left(-\frac{\Delta H - T \Delta S}{k_b T}\right)$ where $\Delta H$ and $\Delta S$ are the differences in enthalpy and entropy, respectively, of a polymer chain near a particle surface and in the bulk. Assuming that dPMMA and dPS with the same molecular weight (degree of
polymerization) in a polymer nanocomposite with same NP volume fraction experience
the same chain entropy change ($\Delta S_{dPS} \approx \Delta S_{dPMMA}$) and $\Delta H$ is independent of temperature
in this temperature range investigated, the reduced diffusion coefficient of dPS relative to
dPMMA can be given by

$$
\frac{(D/D_0)_{dPS}}{(D/D_0)_{dPMMA}} = \frac{\exp \left( \frac{\Delta S_{dPS}}{k_B} \right) \exp \left( \frac{-\Delta H_{dPS}}{k_B T} \right)}{\exp \left( \frac{\Delta S_{dPMMA}}{k_B} \right) \exp \left( \frac{-\Delta H_{dPMMA}}{k_B T} \right)} = \exp \left( \frac{\Delta H_{dPMMA} - \Delta H_{dPS}}{k_B T} \right)
$$

For dPS with $M = 93k$ and $281k$, $D/D_0$ at $\phi_{NP} = 0.035$ and 0.14 can be calculating using
the $D/D_0$ vs $ID/2R_g$ plot from Chapter 5. The values of $D/D_0$ are 0.60 and 0.49,
respectively, at $\phi_{NP} = 0.035$. Thus, for $M = 93k$, 
$$
\frac{(D/D_0)_{dPS}}{(D/D_0)_{dPMMA}} = 1.24
$$
and

$$
\Delta H_{dPMMA} - \Delta H_{dPS} = k_B T \ln(1.24) = 0.22k_B T ,
$$
and for $M = 281k$, 
$$
\frac{(D/D_0)_{dPS}}{(D/D_0)_{dPMMA}} = 1.22
$$
and

$$
\Delta H_{dPMMA} - \Delta H_{dPS} = k_B T \ln(1.22) = 0.19k_B T .
$$
Also, for dPS with $M = 93k$ and $281k$, $D/D_0$
are 0.44 and 0.34, respectively, at $\phi_{NP} = 0.14$. Thus, $\Delta H_{dPMMA} - \Delta H_{dPS} (M = 93k)$
$= k_B T \ln(2.5) = 0.91k_B T$ and $\Delta H_{dPMMA} - \Delta H_{dPS} (M = 281k) = k_B T \ln(2.78) = 1.02k_B T .
$From diffusion measurements in PMMA and PS systems, the enthalpy differences
between PMMA:OH-NP and PS:Ph-NP, $\Delta H_{dPMMA} - \Delta H_{dPS}$, are $\sim 0.21k_B T$ and $\sim 0.96k_B T$
at $\phi_{NP} = 0.035$ and 0.14, respectively. Namely, as the NP volume fraction increases from
0.035 to 0.14 (i.e., 4x), $\Delta H_{dPMMA} - \Delta H_{dPS}$ increases from $0.21k_B T$ to $0.96 k_B T$ (i.e., 4.6x).
Also, as NP volume fraction increases from 0.035 to 0.07 (i.e., 2x),
\( \Delta H_{dPMMA} - \Delta H_{dPS} \) increases from 0.2\( k_B T \) to 0.3\( k_B T \) (i.e., 1.5x). Because \( \Delta H_{dPMMA} - \Delta H_{dPS} \) is expected to be proportional to the NP volume fraction or interfacial area, the increase of \( \Delta H_{dPMMA} - \Delta H_{dPS} \) may be attributed simply to the increase in interfacial area between polymer and NPs. Tracer size has a negligible effect over the range of molecular weights studied, and \( \Delta H_{dPMMA} - \Delta H_{dPS} > 0 \) indicates that the interaction between PMMA segments and hydroxyl groups on silica is more favorable than that between PS and phenyl groups on silica.

For phenyl ethyl- and phenyl-terminated silica NPs \( (d_a = 28.8 \text{ nm}) \), \( \frac{(D/d_0)_{PhE}}{(D/d_0)_{Ph}} \) \( (\phi_{NP} = 0.2) \approx 1.4 \) for dPS molecular weights of 49k, 168k, 532k. Thus, \( \Delta H_{Ph} - \Delta H_{PhE} \approx 0.33 \ k_B T \). While the interfacial area in PMMA:OH-NP (or PS:Ph-NP) \( (12.8 \text{ nm}) \) at \( \phi_{NP} = 0.14 \) is 1.58 times greater than that in PS:PhE-NP (or PS:Ph-NP) \( (28.8 \text{ nm}) \) at \( \phi_{NP} = 0.2 \), \( \Delta H_{dPMMA} - \Delta H_{dPS} \) is 2.91 greater than \( \Delta H_{Ph} - \Delta H_{PhE} \). Also, the interfacial area in PMMA:OH-NP (or PS:Ph-NP) \( (12.8 \text{ nm}) \) at \( \phi_{NP} = 0.035 \) is 0.39 times smaller than that in PS:PhE-NP (or PS:Ph-NP) \( (28.8 \text{ nm}) \) at \( \phi_{NP} = 0.2 \), \( \Delta H_{dPMMA} - \Delta H_{dPS} \) is 0.61 times smaller than \( \Delta H_{Ph} - \Delta H_{PhE} \). Under the assumption that the enthalpic interaction energy is proportional to the interfacial area but not dependent of NP size, this indicates that the enthalpic interaction energy difference between PMMA:OH-NP and PS:Ph-NP is larger than that between PS:PhE-NP and PS:Ph-NP.

The difference in the change of enthalpic interaction energy near the silica NP and in bulk of PS and PMMA, \( \Delta H_{PMMA} - \Delta H_{PS} \) can be obtained from the polymer adsorption
experiment on the silica surface. Kawaguchi et al.\textsuperscript{25} investigated the adsorption of PS and PMMA onto 16 nm diameter silica particle in trichloroethylene at 25 °C using IR and UV spectroscopies. The adsorption energy parameter, $\chi_s$, for PS and PMMA is obtained by comparing three variables - the adsorbed amount of polymers, the fraction of the silanol groups occupied by polymer chains, and the fraction of the polymer repeating unit which is directly attached to surface silanol groups with the Scheutjens and Fleer theory based on a lattice model\textsuperscript{25,29}. The adsorption energy parameter $\chi_s$ is defined by\textsuperscript{25}

$$
\chi_s = \left[ \varepsilon_{2s} - \varepsilon_{1s} + \frac{1}{2}(\varepsilon_{11} - \varepsilon_{22}) \right] / k_BT
$$

where $k_B$ is the Boltzmann constant, $T$ is the absolute temperature, and the $\varepsilon$ terms are binary interaction energies among polymer segments (2), solvent molecules (l), and the adsorbent surface (s). For PS and PMMA,

$$
\chi_{s,PS}k_BT = \left[ \varepsilon_{PS,s} - \varepsilon_{1s} + \frac{1}{2}(\varepsilon_{11} - \varepsilon_{PS,PS}) \right]
$$

(3)

$$
\chi_{s,PMMA}k_BT = \left[ \varepsilon_{PMMA,s} - \varepsilon_{1s} + \frac{1}{2}(\varepsilon_{11} - \varepsilon_{PMMA,PMMA}) \right]
$$

(4)

By subtracting eq. (3) from eq. (4)

$$
(\chi_{s,PMMA} - \chi_{s,PS})k_BT = \left[ \varepsilon_{PMMA,s} - \varepsilon_{PS,s} - \frac{1}{2}\varepsilon_{PMMA,PMMA} \right] - \left[ \varepsilon_{PS,s} - \frac{1}{2}\varepsilon_{PS,PS} \right]
$$

(5)

Because

$$
\left[ \varepsilon_{PMMA,s} - \frac{1}{2}\varepsilon_{PMMA,PMMA} \right] - \left[ \varepsilon_{PS,s} - \frac{1}{2}\varepsilon_{PS,PS} \right] = \Delta H_{PMMA} - \Delta H_{PS}
$$

(6)
\[ \Delta H_{PMMA} - \Delta H_{PS} = (\chi_{s,PMMA} - \chi_{s,PS})k_B T \]  \hspace{1cm} (7)

By fitting the adsorption data with Scheutjens and Fleer theory\textsuperscript{29}, Kawaguchi et al.\textsuperscript{25} determined that $\chi_{s,PMMA} = 1.4$ and $\chi_{s,PS} = 0.42$, and thus $\Delta H_{PMMA} - \Delta H_{PS} = 0.98k_B T$. Although determined from solution adsorption studies, $\Delta H_{PMMA} - \Delta H_{PS} = 0.98k_B T$ is of the same order as determined from our diffusion studies. However, a quantitative comparison is not possible because (1) the bound fraction of segments in our composites and interfacial area in their work\textsuperscript{25} are unknown and (2) our PS studies involved phenyl-terminated silica whereas hydroxyl-terminated silica is used in ref. 25. Kawaguchi et al.\textsuperscript{25} also reports that preadsorbed PS chains on silica were displaced by PMMA, again supporting the strong attraction of PMMA segments towards hydroxyl groups\textsuperscript{25}.

In competitive adsorption study of dPS and PS on silica substrate, preferential adsorption of dPS was observed, while the amount of surface excess of dPS and PS is almost same during noncompetitive adsorption in separate experiments\textsuperscript{30}. Also, although polymer diffusion and polymer adsorption are performed in a melt and a solvent, respectively, the difference in the change of enthalpic interaction energy near the silica NP and in bulk of PS and PMMA as shown in eq. (6), $\Delta H_{PMMA} - \Delta H_{PS}$ will not be largely influenced by the medium where a polymer chain moves. Thus, the comparison of diffusion study with adsorption study is reasonable. For better comparison of diffusion study with adsorption study, surface of silica NPs should be covered with PhTMS. Observation of polymer adsorption on the surface of silica NPs covered with PhTMS and
PhETMS will help to understand the effect of NP surface functional group on polymer diffusion.

6.4 Conclusions

In order to investigate the role of enthalpic interaction, polymer diffusion is investigated in three matrices including PMMA:hydroxyl-silica (PMMA:OH-NP), PS:phenyl-terminated silica (PS:Ph-NP), and PS:phenyl ethyl-terminated silica (PS:PhE-NP) composites. The strong attraction between PMMA segments and hydroxyl groups on the silica NPs slows down diffusion more than the weak interaction between PS segments and phenyl groups when compared at the extent of confinement (e.g., NP volume fraction and tracer molecular weight). For both the strongly (PMMA:OH-NP) and weakly (PS:Ph-NP) attraction systems, $D/D_0$ plotted against $ID/2R_g$ collapses on master curves. Compared to the phenyl-terminated NPs, tracer diffusion in NPs having phenyl ethyl termination is faster, indicating that the phenyl tethered to silica by an ethyl spacer is less favorable than the phenyl alone. From the diffusion coefficients, the enthalpic interaction energy difference between PMMA:OH-NP and PS:Ph-NP is calculated and found to $0.21k_BT$ and $0.96k_BT$ for 3.5 and 14 vol% NP. These values indicate that PMMA and silica are more strongly attractive than PS and phenyl-terminated silica. This difference in enthalpic energies increases as the NP volume fraction or interfacial area increases. To quantify the faster diffusion in phenyl ethyl-terminated silica, the adsorption of dPS on the silica substrates or NPs modified with the phenyl and phenyl ethyl brushes would be helpful. Experiments are underway to
measure dPMMA tracer diffusion in PMMA containing larger silica NPs \((d_n = 28.8 \text{ nm})\). These studies will provide a strong test for evaluating the invariance of NP size in systems where the NPs and polymers are attractive. Moreover, two complete sets of studies in the PS and PMMA systems will be completed for NPs having \(d_n = 12.8 \text{ nm}\) and 28.8 nm.
6.5 References


Figure 6.1  Cross-sectional TEM images of (a) PS:Ph-NP ($\phi_{NP} = 0.03$), (b) PMMA:OH-NP ($\phi_{NP} = 0.035$), (c) PMMA:OH-NP ($\phi_{NP} = 0.14$), and (d) PMMA:OH-NP ($\phi_{NP} = 0.25$). In all cases, the number average diameter is 12.8nm. The phenyl- and hydroxyl-terminated silica NPs are well dispersed in PS and PMMA, respectively. Scale bars are 100 nm.
Figure 6.2 Diffusion profiles of dPMMA in PMMA:OH-NP measured using ERD to investigate the effect of NP volume fraction and tracer molecular weight. Solid lines are fits of experimental data with eq. (1) using appropriate $D$ values. The dashed lines represent the sum of the solid line and a surface peak. The tracer diffusion coefficients are (a) $5.7\times10^{-15}$ cm$^2$ s$^{-1}$, (b) $7.8\times10^{-16}$ cm$^2$ s$^{-1}$, (c) $2.1\times10^{-15}$ cm$^2$ s$^{-1}$, (d) $1.2\times10^{-16}$ cm$^2$ s$^{-1}$ at 195 °C. Surface peaks are observed for profiles in (b), (c), (d) because polymers are more strongly confined by the matrix, namely $ID < 2R_g$. 
Figure 6.3 The reduced diffusion coefficients ($D/D_0$) of dPS and dPMMA are plotted against NP volume fraction. As NP volume fraction increases, the reduced diffusion coefficients for dPS and dPMMA decrease rapidly at low NP volume fractions and then more slowly as the NP volume fraction increases. The reduced diffusion coefficients of dPMMA are systematically below those of dPS.
Figure 6.4  $\ln\left(\frac{D}{D_0}\right)$ for (a) dPS in PS:Ph-NP and dPMMA in PMMA:OH-NP at $\phi_{NP} = 0.035$ and (b) dPS in a PS:Ph-NP and dPMMA in PMMA:OH-NP at $\phi_{NP} = 0.14$ plotted against $\ln(M)$, where $M$ is a tracer molecular weight (g mol$^{-1}$). Compared at the same volume fraction of NPs, the reduced diffusion coefficient of dPMMA is less than that of dPS. The dotted lines are guide to eye. The scaling of $D/D_0$ with $M$ is discussed in the text.
Figure 6.5 The reduced diffusion coefficients ($D/D_0$) of dPS and dPMMA plotted against $ID/2R_g$ falls on two curves. As $ID/2R_g$ decreases, $D/D_0$ decreases. The reduced diffusion coefficients ($D/D_0$) of dPMMA are systemically shifted to lower values than dPS. For both systems, the number average diameter of NP is 12.8 nm.
Figure 6.6 Cross-sectional TEM images of (a) PS:Ph-NP and (b) PS:PhE-NP silica at $\phi_{NP} = 0.2$. Scale bars are 200 nm. Both phenyl- and phenyl ethyl-terminated silica NPs are well dispersed in a PS matrix. The number average diameters are 28.8 nm for both systems.
Figure 6.7 Diffusion profiles of dPS in PS : NP containing (a) phenyl- (ph) and (b) phenyl ethyl-terminated silica (phE) at 156 °C. The tracer molecular weight ($M$) and NP volume fraction ($\phi_{NP}$) are denoted in the legends. Solid lines are best fits of experimental data with eq. (1) using (a) $D = 5.3 \times 10^{-15}$ cm$^2$ s$^{-1}$ and (b) $D = 7.4 \times 10^{-15}$ cm$^2$ s$^{-1}$. The dashed lines are the sum of the solid line and surface peak.
Figure 6.8  The reduced diffusion coefficients ($D/D_0$) plotted against $ID/2R_g$ for PS:Ph-NP systems (28.8 nm) from Chapter 4 (filled diamonds), and its fit to a master curve (solid line). New data include diffusion in PS:PhE-NP and PS:Ph-NP (28.8 nm) denoted by filled and open squares, circles and triangles, respectively. Faster diffusion is observed by ~ 40% in the phenyl ethyl versus phenyl grafted NPs.
Chapter 7
Polymer Diffusion into a Bicontinuous Polymer Blend Stabilized with Nanoparticles

7.1 Introduction

Bicontinuous morphologies produced from phase separated polymer blends are an ideal structural motif for creating novel functional materials that require high interfacial area including nanostructured organic solar cells, membranes, and catalysts. These bicontinuous structures can be produced by controlled solvent evaporation of homopolymers, block copolymers, and polymer blends. By incorporating inorganic nanoparticles (NP) into their structure, functionality, such as conductivity, photosensitivity, optical properties, and catalytic behavior, can be introduced. Additionally, incorporation of NPs can significantly impact the final morphology of polymer films. For example, Kim and co-workers utilized polymer-grafted gold NPs to produce morphologies ranging from spherical to lamellar. Si and co-workers reported that the addition of organoclay to polymer blends produced morphologies that depended on the polymer-clay interaction, clay concentration, and blend composition. Chung and co-workers showed that NPs that segregate to the interface between coexisting phases pinned the internal morphology via NP jamming, resulting in either bicontinuous or discrete structures. However, if the NPs partitioned into one of the coexisting phases, the dynamics of phase separation slowed down but pinning was not observed. In addition, the jamming of NPs at the interface was shown to prevent films
from dewetting during annealing\textsuperscript{38}. This ability to control and stabilize film morphology and domain size is an attractive property for thermoplastic materials because desired properties, such as transport, will not change during thermal annealing.

Phase separation has also been used to create bicontinuous emulsions\textsuperscript{39-41}. Analogous to polymer blends, low molecular weight liquids undergo demixing either by nucleation and growth or spinodal decomposition. Colloids dispersed in the mixed system (prior to quenching) can become trapped at the liquid/liquid interface to create an arrested state. Following initial studies of wetting/phase separation in nanocomposites by Ginzburg\textsuperscript{42}, Stratford\textsuperscript{43} performed computer simulations demonstrating that neutrally wetting colloids became trapped at the fluid/fluid interface, forced together as domains coarsen, and eventually jammed into a monolayer. Such jammed morphologies are not in thermodynamic equilibrium, but rather are metastable due to the large energy penalty associated with removing NPs from the interface and relocating them into one of the phases, as shown by Hore and Laradji\textsuperscript{44}. Both two dimensional\textsuperscript{39} and three dimensional\textsuperscript{40, 41} bicontinuous gels were formed by adding colloidal silica to binary fluids. For example, upon quenching a lutidine:water mixture at the critical composition from 25 °C to 40 °C, fluorescence confocal microscopy was used to image fluorescently labeled silica that partitioned to the interface of a spinodal structure\textsuperscript{40}. This approach allowed “slices” of the morphology to be viewed at various depths and then reconstructed as a three-dimensional (3D) image. However, because of the small domain and particle size, confocal microscopy is not a viable method for investigating phase evolution in polymer blend nanocomposites. Instead, the 3D structures of polymer systems, such as block copolymers and polymer blends with filler, are typically reconstructed using SEM,
transmission electron microscopy (TEM) or scanning force microscopy (SFM) after sequential plasma etching\textsuperscript{45-48} or microtoming\textsuperscript{49}. Previously, a method using focused ion beam (FIB) etching and scanning electron microscopy (SEM) was used to image and reconstruct the lamellar structure of poly(styrene-block-isoprene) block copolymer films.\textsuperscript{50} Here we apply FIB/SEM to determine the internal morphology of polymer blend nanocomposites. Relative to small molecule mixtures previously discussed, the rate of phase separation of polymer blends is relatively slow and therefore phase growth can be observed. Moreover, one phase can be selectively removed from a bicontinuous structure to produce a continuous pathway that can remain open (e.g. for low dielectric) or backfilled with a functional polymer or liquid (e.g. membrane).

The phase evolution of neat polymer blend films undergoing symmetric wetting is relatively well understood theoretically\textsuperscript{51-53} and experimentally\textsuperscript{13, 54-60}. In particular, systematic studies have been carried out on films of deuterated poly(methyl methacrylate) (dPMMA) and poly(styrene\textemdash ran\textemdash acrylonitrile) (SAN) over the past 10 years\textsuperscript{13, 58, 60}. Polymer blend films at the critical composition (50:50) (dPMMA:SAN) undergo early, intermediate, and late stages of phase evolution and wetting\textsuperscript{13, 53, 57-60}. The early stage is characterized by the simultaneous formation of a 3D bicontinuous structure of tubes as well as wetting of dPMMA at the surface and substrate. During the intermediate stage, the bicontinuous dPMMA domains reconfigure into two-dimensional (2D) discrete dPMMA domains, which grow within the continuous SAN-rich matrix sandwiched between the two wetting layers. A goal of the present study is to show that the addition of NPs can stabilize the morphology during either the early or intermediate stages, namely as a bicontinuous or discrete morphology, respectively. In the late stage,
interfacial fluctuations cause the films to become unstable, rupture, and dewet from the substrate. Thus, in addition to controlling morphology, the addition of NPs can stabilize the films against rupture resulting in robust films.

In the present study, we have investigated the morphological evolution of PMMA:SAN films with thicknesses from 140 nm to 2,500 nm and NP concentrations from 1 to 10 wt%. The silica NPs segregate to the interface between coexisting phases during phase separation and stabilize the morphology to produce either discrete or bicontinuous domains. By repeated ion beam etching and SEM imaging, FIB/SEM is used to construct 3D images of discrete and bicontinuous morphologies. Upon increasing the film thickness from 140 nm to 2,500 nm, the concentration of NPs required to arrest the bicontinuous morphology decreases from 10 wt% to 2 wt%. A jamming map is constructed to show the combinations of NP concentration and film thickness that produce discrete and bicontinuous morphologies. The delineation between these jammed morphologies agrees with a simple geometric model based on arranging spherical NPs at the polymer/polymer interface. Polymer diffusion into a bicontinuous structure demonstrated to be slower than diffusion into pure PMMA. Whereas the tortuous path would slow down diffusion, diffusion along the interphase could be faster because of a reduction in entanglement density or enthalpic interactions with the brush decorating the interface. Using SEM images, the path length increases by 30 % in the bicontinuous structure, relative to one-dimensional (1D) diffusion length measured by ERD. By modeling the total diffusion in terms of a bulk (unperturbed) diffusion and fast diffusion along the interphase region (∼2Rg), the “fast” diffusion coefficient is found to 2 times greater than the bulk diffusion. Thus, when one considers only the penetrable area, the
diffusion coefficient of dPMMA in a bicontinuous structure increases by 17% compared to the homopolymer case.

7.2 Materials and experimental methods

7.2.1 Preparation of PMMA:SAN films containing silica NPs

The polymer blend consists of poly(methyl methacrylate) (PMMA) and poly(styrene-ran-acrylonitrile) (SAN) having an acrylonitrile content of 33 wt%. PMMA was purchased from Polymer Source \( (M_w = 82.4 \text{ kg/mol}, \text{PDI} = 1.07) \) and used in the 140 nm, 1 µm, and 2.5 µm thick films. For the 550 nm thick films, deuterated poly(methyl methacrylate) \( (dPMMA) \) \( (M_w = 106 \text{ kg/mol}, \text{PDI} = 1.20) \) was used. Because the quench depth is deep and molecular weights are similar, the small difference in the lower critical solution temperature between PMMA:SAN and dPMMA:SAN blends does not play a role in these studies. Namely, the cloud points for PMMA:SAN with PMMA \( M_w \)'s of 82k and 105k differ by only 0.44 °C according to the interaction parameter between PMMA and SAN, \( \chi_{PMMA/SAN} \) \(^{61,62} \). SAN was a gift from Monsanto \( (M_w = 118 \text{ kg/mol}, \text{PDI} = 2.24) \) and purified before use. The NPs have a silica core grafted with a PMMA brush and the total diameter is 18 nm. The \( M_w \) and grafting density of the PMMA brush are 1800 g/mol and 0.7 chains/nm\(^2\), respectively. PMMA brushes were synthesized using a surface-initiated atom transfer radical polymerization (ATRP) method and were terminated by chlorine. In previous studies\(^ {37,38} \), PMMA grafted silica NPs were found to locate in the PMMA phase, at the interface or both depending on brush length. Due to end group termination and the short brush length, the PMMA \( (1800 \text{ g/mol}) \) grafted silica was found to strongly segregate to the interface between phases.
The PMMA:SAN (50:50) and NPs were dissolved in methyl isobutyl ketone (MIBK) or methyl isoamyl ketone (MIAK) and spun-cast on a silicon wafer to produce films with thicknesses ranging from 140 nm to 2,500 nm. MIAK and MIBK were used to prepare dPMMA:SAN and PMMA:SAN films, respectively. To remove residual solvent, films were dried at 120 °C for 24 h in a vacuum oven. The thicknesses of these homogeneous films were measured by ellipsometry. To induce phase separation, films were annealed above the critical temperature, approximately 160 °C\textsuperscript{63}, on a hot stage at 195 °C in an argon atmosphere for up to 120 h. Under these conditions, each phase corresponds to nearly pure PMMA and SAN.

7.2.2 Characterization of PMMA:SAN films

The surface and interface morphologies of these films were examined using atomic force microscopy (AFM) (Agilent MAC III). To observe the interface or internal morphology, the PMMA phase was removed by first exposing the film to UV-ozone or ion beam irradiation and then immersing the film in an acetic acid bath to dissolve the PMMA. Cross-sectional and top view images of thick films ($h > 1 \mu m$) were observed using scanning electron microscopy (SEM) after focused ion beam (FIB) (FEI Strata DB235) etching. First, a Au/Pd coating was deposited on the films, which reduces sample charging. Ga$^+$ ions (30 kV; 100~300 pA) were used to lightly etch a surface area of 10 µm x 10 µm or 20 µm x 20 µm for top view images. The Ga$^+$ ion beam current was increased to 300-1000 pA to etch trenches that penetrated through the film and into the substrate. These samples were tilted at 52° for cross-sectional images.
7.2.3 Polymer diffusion into a bicontinuous structure

To prepare the tracer diffusion couples, deuterated PMMA, dPMMA, films ~20 nm thick with a molecular weight of 93,000 g mol⁻¹ (PDI = 1.03) are transferred onto PMMA:SAN films previously annealed to form a stable bicontinuous structure. Because the dPMMA adheres to silicon and is difficult to float off, a sacrificial layer of a water soluble polymer chitosan with a thickness of ~30 nm is first spin coated on silicon substrates. Then the dPMMA film is spin coated onto the chitosan layer, floated off in water and transferred onto the PMMA:SAN film attached to the silicon substrate. Using Fourier transform infrared spectroscopy (FTIR), no residual chitosan was detected on the dPMMA film after floated off in a water bath. The diffusion couples are annealed in a vacuum oven at 195 °C. Molecular weight and polydispersity of dPMMA are measured in tetrahydrofuran using SEC. Tracer diffusion is investigated using elastic recoil detection (ERD) and details are given in Chapters 4, 5, and 6.

7.3 Results and discussion

7.3.1 Morphology of PMMA:SAN films containing silica NPs

By locating NPs at an interface between phases, the morphology can be pinned if the NPs jam to create a metastable structure. Using silica NPs (15 nm) with a dPMMA brush, NPs were found to segregate and jam at the interface between SAN rich and dPMMA rich phases. Thermodynamically, these NPs locate at the dPMMA/SAN interface to reduce interfacial tension. Once located at the interface, the NPs are unlikely to be driven back into the dPMMA or the SAN phases because the energetic cost to move a particle from the interface to either phase is 74 and 11 k_BT, respectively, at 195 °C.
a prior study, we investigated NP jamming in polymer blends at a fixed film thickness of 550 nm$^{37}$. The effect of film thickness on phase behavior is not straightforward to predict. For example, the surface/substrate may interfere with partitioning of NPs for thinner films but this influence will weaken as film thickness increases. In this paper, we show that morphology quenching via NP jamming in polymer blend nanocomposites is applicable to a wide range of film thicknesses. Moreover, a simple geometric model can accurately predict whether the final morphology is discrete or bicontinuous.

The morphology of PMMA:SAN blends is pinned because NPs jam during phase separation. Figure 7.1 shows the surface (left) and internal (right) morphologies of 140 nm and 550 nm thick films with 5wt% (a,b) and 10 wt% (c,d) NP after annealing at 195 °C for 24 h. These morphologies were pinned during the intermediate and early stages, respectively, and remained unchanged upon further annealing. For comparison, films without NPs completely rupture after annealing for the same conditions (not shown). In Figure 7.1 (a), the surface image of the 140 nm thick film clearly shows discrete "hills" of PMMA domains, a characteristic of the intermediate stage$^{58}$. On the other hand, the surface image of the 550 nm film in Figure 7.1 (c) shows a bicontinuous network, indicating that the morphology is pinned during the early stage$^{13}$. To view the internal morphologies in Figures 7.1 (b) and 7.1 (d), the PMMA phases were removed by selective etching using acetic acid and appear as holes (dark) in AFM images. For the 140 nm thick film in Figure 7.1 (b), the PMMA domains (dark) appear as individual (round) or coarsened (irregularly shaped) domains (i.e., discrete), whereas the SAN phase is continuous. However, Figure 7.1 (d) shows that both phases are continuous in the 550 nm thick film. At 5wt% NP, the 550 nm thick films exhibit a discrete morphology (not
shown). For comparison, the addition of 10wt% NP is insufficient to pin the bicontinuous morphology of 140 nm thick films. This result clearly indicates that thinner films require a higher concentration of NP to stabilize the bicontinuous morphology than thicker films. We also note that the 140 nm thick film with 2wt% NP dewets the substrate and eventually ruptures after further annealing, whereas the addition of 5wt% and 10wt% NP stabilizes the morphology and prevents the film from rupturing even after 120 h of annealing. A detailed description of the film rupturing mechanism can be found elsewhere38.

For thicker films ($h > 550$ nm), a combination of FIB etching and SEM imaging of the top and cross-sectional views was used to identify the morphology. In particular, the surface morphology can be viewed from the top by lightly etching the surface with FIB and then imaging by SEM. The accuracy of the top view can be cross-checked with AFM images. The cross-section of the morphology can be observed by first etching a deep trench and then tilting the sample for SEM imaging37. The FIB/SEM method is particularly attractive for thicker films because the imaging dimensions are commensurate with the length scale of the morphology. For these films, AFM imaging of the internal morphology is not possible because the film detaches from the substrate during immersion in acetic acid (i.e., etching of PMMA). Another advantage of the FIB/SEM method is that the NP location in the polymer blend film can be readily identified.

After 24h of annealing, PMMA:SAN films with thicknesses of 1 µm and 2.5 µm were characterized using FIB/SEM. For 1 µm thick films, a bicontinuous structure at 5 and 10 wt% NP is apparent from top and side views as discussed later. AFM analysis of
the surface is also consistent with a bicontinuous morphology as noted by a fixed domain size after further annealing. At 2wt% NP, a mixed morphology of discrete and bicontinuous domains are observed. However, at 1wt% NP only a discrete morphology is observed as shown in Figure 7.2. Figure 7.2 (a) shows the surface after ion beam etching for 19 min and SEM imaging at 52° tilt. The PMMA domains appear as depressions because the ion beam degrades PMMA more rapidly than the continuous SAN phase. In prior AFM studies of the surface topography, PMMA phases were found to protrude slightly higher than the film surface, as illustrated in Figures 7.4 (a)-(f) of Chung’s paper. The cross-sectional image shown in Figure 7.2 (b) shows direct evidence that the PMMA domains are discrete and span nearly the entire cross-section, except for the thin wetting layers. The PMMA phases can be distinguished from SAN because PMMA wets both the surface and substrate. Moreover, this image shows that the NPs locate at the interface between the continuous SAN phase and discrete PMMA domains. Figure 7.2 (b) also shows that the correlation length is greater than the film thickness (i.e., domains are disk-like), characteristic of the intermediate stage.

A 1 µm thick PMMA:SAN film with 10 wt% NP exhibits a bicontinuous morphology after 24 h as shown in Figures 7.3 and 7.4. This interconnected morphology is in contrast to the discrete morphology shown in Figure 7.2 for a film with the same thickness but containing only 1 wt% NPs. A three dimensional (3D) image of the morphology can be created by sequential FIB etching of the surface (Figure 7.3) or sidewall (Figure 7.4) followed by SEM imaging. Sequential ion beam etching was used to remove the top surface to reveal a top-down view of the 3D bicontinuous structure shown in Figure 7.3. In Figure 7.3 (a), A, B, and C represent surface images after etching for 2,
3, and 5 minutes, respectively. Figure 7.3 (b) shows details of the morphologies corresponding to sections A, B, and C in Figure 7.3 (a). Region A shows the interconnected SAN domains (white) ~400 nm wide, whereas region B reveals the NPs decorating the interface between the SAN and PMMA phases. Region C shows that the interconnected morphology persists below the surface of the film. In region A, the top down image without tilt (0°) reveals the SAN domains (light) whereas the tilted image at 52° shows that the SAN phase is higher than PMMA. For the same film, sequential cross-sectional images were taken after etching and shown in Figure 7.4. Figure 7.4 (a) shows that the morphology of the sidewall exhibits a lacy pattern of NPs. After removing ~200 nm by ion etching, Figure 7.4 (b) shows that this lacy pattern is maintained. However, closer inspection reveals that the lateral arrangement of the NPs has changed slightly as indicated comparing the areas encircled by the dotted lines in Figures 7.4 (a) and (b). After removing another ~200 nm, new features appear inside the dotted area as shown in Figure 7.4 (c). A domain size of ~500 nm is observed for both the top down (Figure 7.3) and side-view (Figure 7.4) images.

The effect of NP loading on 2.5 µm thick films was also investigated. Figures 7.5 (a), (b), and (c) show that films containing 2, 5, and 10 wt% NP, respectively, exhibit a bicontinuous morphology. The domain size decreases from ~400 nm to ~200 nm as NP loading increases from 2 wt% to 10 wt%. Interestingly, the NP loading required to stabilize a bicontinuous structure decreases as film thickness increases. For example, a bicontinuous structure is not observed for 140 nm thick films even at 10 wt% NP. The NP loadings required to stabilize the bicontinuous morphology decreases from 10 wt% to 5 wt% to 2 wt% as thickness increases from 550 nm, to 1 µm, and to 2.5 µm, respectively.
The two morphologies observed for PMMA:SAN:NP films deduced from the AFM and FIB/SEM images are summarized in Figure 7.6. In Figure 7.6 (a), the top (left column) and cross-section (right column) views describe the discrete morphology, corresponding to the surface (Figures 7.1 (a), 7.1 (b), 7.2 (a)) and cross-sectional (Figure 7.2 (b)) images. On the other hand, Figure 7.6 (b) represents the top and cross-sectional views of a bicontinuous morphology, corresponding to the surface (Figures 7.1 (c), 7.1 (d), 7.3) and cross-sectional (Figures 7.4, 7.5) images. For both morphologies, the NPs segregate and jam at the interface between PMMA and SAN during phase separation, resulting in a pinned internal structure.

To elucidate the interplay between film thickness and NP concentration on morphology, a jamming map was constructed to show the conditions leading to stabilized discrete and bicontinuous structures. Figure 7.7 shows that thicker films form bicontinuous structures (solid squares) at lower loadings than thinner films which tend to form discrete domains (open squares). Although not captured in this map, the domain size also decreases as NP loading increases. The transition between bicontinuous and discrete structures can be understood from prior experimental studies which show that the duration of the early stage of spinodal decomposition increases with film thickness. Namely, thicker films display a bicontinuous morphology over a longer time than thinner ones which more quickly evolve into a discrete morphology. In other words, bicontinuous or discrete morphologies are determined by whether NPs jam during the early or intermediate stages, respectively (see Figure 7.6).

As we proposed in a prior study, the jamming transition can be predicted by a geometric argument by assuming that spherical NPs form a 2D hexagonal close-packed
structure upon jamming at the interface. We can relate the total interfacial area at jamming ($A_{NP}$) to the NP volume fraction ($\phi_{NP}$), radius ($R$), and film thickness ($h$). The parameter $n$ represents $A_{NP}$ normalized by film area ($A_{film}$) and is given by

$$n = \frac{A_{NP}}{A_{film}} = \frac{3\sqrt{3}h\phi_{NP}}{2\pi R}.$$  

Because the PMMA phase wets the substrate and free surface (symmetric wetting), a trilayer of PMMA/SAN/PMMA represents the idealized layered structure and defines the case where $n = 2$ (i.e., NPs at both interfaces). Because the discrete morphology (see Figure 7.6 (a)) has less interfacial area relative to the ideal layered structure, $n = 2$, and interfacial area decreases during the PMMA domain coarsening, the discrete morphology is stabilized by jamming for $n < 2$. On the other hand, for $n > 2$, the film has more interfacial area relative to the layered case and the bicontinuous morphology (see Figure 7.6 (b)) is stabilized. The volume fraction separating the bicontinuous and discrete structures is determined by the previous equation and plotted as a solid line in Figure 7.7. Thus, the model captures the experimental observation that thicker films require a lower concentration of NPs than thinner films to create a bicontinuous structure. Therefore, over the range of thicknesses and compositions investigated in this study, the morphologies are in excellent agreement with the jamming criterion predicting discrete and bicontinuous structures.

### 7.3.2 Polymer diffusion into a bicontinuous structure

A stable bicontinuous matrix is formed by adding NPs that jam at the interphase of a phase separating blend of PMMA and SAN. The matrix is 1 µm thick, contains 10 wt% NP, and forms a bicontinuous structure after annealing at 195 °C for 2 h. The
diffusion couple, a deuterated PMMA (dPMMA, $M = 93k$) layer deposited on the matrix, is annealed for ~ 22 hr at 195 °C. The bicontinuous structure does not change during diffusion because jamming stabilizes the structure and prevents further coarsening. For comparison, dPMMA is diffused into a pure PMMA matrix film. Figure 7.8 shows the diffusion of dPMMA into the much larger PMMA domain, as well as the NPs jamming at the interface and the SAN phase. Figures 7.9 (a) and 7.9 (b) are the AFM topography images of the surface and show that the correlation length is ~ 800 nm after 2 h and 24 h indicating that the morphology is jammed and does not evolve during diffusion. The SEM images in Figures 7.3 and 7.4 show that the domain size of the PMMA channel is ~ 400 nm.

The volume fraction profiles of dPMMA in pure PMMA and the bicontinuous structure are shown in Figures 7.10 (a) and 7.10 (b), respectively. Whereas the dPMMA profile into PMMA exhibits a typical Fickian shape (i.e., erf), a surface peak is observed for the dPMMA profile in the bicontinuous film. Solid lines in Figures 7.10 (a) and 7.10 (b) are the fits of experimental data with Fick’s second law equation with tracer diffusion coefficients ($D$), $7.8 \times 10^{-15}$ cm$^2$ s$^{-1}$ and $5.4 \times 10^{-15}$ cm$^2$ s$^{-1}$, respectively. The dashed line in Figure 7.10 (b) is the sum of the solid line and surface peak. Previously, a surface peak was observed for polymer diffusion into a highly confined system (e.g., high NP volume fraction or high tracer molecular weight)$^{65}$ and attributed to a reduced flux due to an impenetrable phase. The origin of this surface peak was previously described$^{65}$. Whereas the near-surface NPs perturbed the profile in polymer nanocomposites., the SAN phase in the middle layer accounts for ~50 % of the volume and acts as an impenetrable barrier for dPMMA diffusion. The SEM images in Figures 7.3 and 7.4 are
consistent with area fractions of PMMA and SAN in the middle layer which are nearly equal.

The diffusion of dPMMA in the bicontinuous matrix is \(~30\%\) slower than that in neat PMMA as shown in Figure 7.10. The flux of dPMMA is reduced at the interface because only \(\sim 50\) vol\% of the matrix is accessible. However, because the domain size (\(~400\) nm) of the PMMA is so much greater than the probe size, dPMMA is not confined as it diffuses along the PMMA channel. The slower diffusion is (partly) attributed to the tortuous path that dPMMA must circumvent the longer path length relative to a uniform diffusion front into the matrix. Green et al.\(^{66}\) found that the tracer diffusion coefficient in a nonequilibrium, symmetric (50:50) diblock copolymer (PS-b-PMMA) is reduced by more than 50\% relative to the homopolymer value because of the spatial orientation of the domains, limited accessible matrix, and tortuosity of the domain\(^{66}\). Another contribution to diffusion in a bicontinuous structure is that dPMMA diffusion near the interphase could be enhanced by several factors including a reduced entanglement density due to the short PMMA brush on NPs and a repulsive interaction due to the Cl-termination on the PMMA brush. dPMMA molecules diffusing along the interface will encounter the short PMMA brushes (i.e., less entangled) relative to those diffusing along the core that encounter the PMMA matrix chains. Unfavorable interactions between dPMMA and the Cl-terminated PMMA brush could also accelerate diffusion for enthalpic reasons. For example, using molecular dynamics simulations Kumar et al.\(^{67}\) predicted that polymer diffusion is enhanced if PMMA and NP have a repulsive interaction. In the present study, the tracer diffusion coefficient of dPMMA in a bicontinuous structure relative to that in neat PMMA \((D/D_0)\) is \(\sim 0.69\), indicating that the
increased path length due to the tortuosity of the matrix is more dominant than factors that speed up diffusion.

A model is proposed using a combination of bulk and interfacial diffusion to describe diffusion into the bicontinuous structure. We first define the area fraction of the interphase region ($A_{int}$) and the center PMMA region ($A_{c-PMMA}$) as shown in Figure 7.8. Because the domain size of PMMA ~ 400 nm is much greater than the dPMMA size, $2R_g$ ~ 16.7 nm, the area fraction of the interphase region, $A_{int}$, assuming a thickness of $\sim 2R_g$, is 0.16 for the bicontinuous structure in this study. Due to the tortuosity of the matrix, the real path length ($l_r$) that dPMMA diffuses will be longer than the diffusion length ($l$) into a homopolymer matrix. Thus, the actual diffusion coefficient in a bicontinuous structure will be faster than that measured by ERD because $D$ is proportional to the square of diffusion length. Assuming that diffusion in the center of PMMA phase is same as that in neat PMMA ($D_0$), the experimentally measured $D$ is given by

$$D = A_{int} \times \frac{1}{(l_r/l)^2} D_{int,r} + A_{c-PMMA} \times \frac{1}{(l_r/l)^2} D_0$$

(1)

where $D_{int,r}$ is the diffusion coefficient in the interphase region. $\frac{1}{(l_r/l)^2} D_{int,r}$ and $\frac{1}{(l_r/l)^2} D_0$ are diffusion coefficients in the interphase region and center of the PMMA phase, respectively, normalized by the tortuosity factor. If the polymer diffusion is faster along the interphase ($\frac{D_{int,r}}{D_0} > 1$) because of the factors previously described, $l_r/l$ must be larger than 1.2 according to the $D_0$ and $D$ values given in Figure 7.10. Assuming that the PMMA tortuous path length from the top view in Figure 7.3 reflects the cross-
sectional view in Figure 7.4, \( l_r/l \) is \( \approx 1.3 \), which is determined by averaging 10 tortuous PMMA paths and \( \frac{D_{int,r}}{D_0} \approx 2 \). This analysis is consistent with faster diffusion of dPMMA along the interphase relative to the center region of the PMMA domains.

Using \( D_r = A_{int}D_{int,r} + A_{bulk}D_0 = D(l_r/l)^2 \), the real diffusion coefficient of dPMMA (\( D_r \)) into the bicontinuous matrix is \( 9.1 \times 10^{-15} \text{ cm}^2 \text{ s}^{-1} \). Relative to the PMMA matrix, the experimentally measured diffusion coefficient of dPMMA into the bicontinuous matrix is reduced experimentally by 30\%, although the real diffusion coefficient (\( D_r \)) increases by 17\%. To test the proposed mechanism, more experiments are needed over a wider range of bicontinuous feature sizes. For example, if larger PMMA domains are produced at a constant volume fraction of PMMA, the interphase region (\( A_{int} \)) will be reduced and the diffusion coefficient of dPMMA (\( D \)) reduced for the same \( l_r/l \), as expected from eq. (1). On the other hand, if the PMMA domains are narrower, polymer diffusion would depend on the area fraction of interphase and center regions, as described by eq. (1), if the PMMA domain size is much larger than tracer size. However, if the PMMA domain size is similar to or smaller than the dPMMA size (c.f., Figure 7.8), the tracer will be elongated in the narrow PMMA channels, restricting conformational degrees of freedom. Moreover, the dPMMA will interact with the NPs at the interface where enthalpic interactions and entanglements can influence diffusion.

Our experimental results concerning the effect of film thickness and particle loading on the formation of a bicontinuous or discrete morphology are also supported by dissipative particle dynamics (DPD) simulations performed by Hore and Laradji\textsuperscript{44, 53}. When spherical NPs adsorb to the interface between two immiscible fluids in 3D, the
authors found that the pinned domain size decreased as the NP radius decreased or NP volume fraction increased, which lead to a crossover scaling function that can be used to predict the final domain size for a given NP size and loading\textsuperscript{44}. More recently, Hore and Laradji\textsuperscript{44, 53} simulated thin film spinodal decomposition using DPD. Their results are in agreement with experimental work performed by Chung, Wang, and Composto.\textsuperscript{56-59} In particular, they observed three distinct stages of spinodal decomposition. Interestingly, the crossover between the early and intermediate stages of spinodal decomposition was found to depend on the thickness of the film, with thicker films spending more time in the early stage than thinner films. This helps to corroborate our findings and provides a mechanism to explain why the bicontinuous morphology is favored in thicker films, and also why the domain size is smaller as the NP loading is increased. In addition, self-assembly of NPs at liquid/liquid interfaces has been controlled by changing the size and volume fraction of NPs and the type of the ligands grafted to the NPs\textsuperscript{68, 69}. For instance, Kutuzov and coworkers\textsuperscript{69} investigated the kinetics of NP self-assembly at an oil/water interface as a function of NP size using a pendant drop tensiometer. The rate of adsorption of the NPs at the oil/water interface increased with increasing NP size. These results suggest that the effect of NP size on the kinetics of phase separation and the morphology of polymer blend nanocomposite films would be interesting to pursue. The ability to control of the size of PMMA domain by increasing or decreasing the NP concentration as shown in Figure 7.5 can be used to investigate polymer diffusion in a bicontinuous structure having well defined channels. The interaction between PMMA and the Cl-terminated PMMA brush can be quantified by studying PMMA adsorption on silica substrates or NPs brush using IR and UV spectroscopies\textsuperscript{70, 71} or isothermal titration
calorimetry. Whereas the present morphology studies focused on one blend ratio, by changing the volume fraction of PMMA and SAN, the accessible volume that dPMMA diffuses into can be controlled. A jamming map for other compositions is necessary prior to studying dynamics into these bicontinuous structures.

7.4 Conclusions

Directed interfacial segregation of nanoparticle (NPs) at the interphase of phase-separated polymer blend film stabilizes the film in either bicontinuous (3D) or discrete (2D) structures. These structures were observed with AFM and FIB/SEM for thin \( h < 550 \text{ nm} \) and thick \( h > 550 \text{ nm} \) films, respectively. The FIB/SEM not only provides a direct method for identifying the morphology, but also for observing the 3D structure. Based on the observation of the morphology, a jamming map is created against film thickness and NP loading. This map indicates that stable bicontinuous structures can be formed at lower NP loading as a film thickness increases. In addition, the jamming transition between bicontinuous and discrete structures can be predicted by considering the geometry of each structure and such a prediction is well matched with our jamming map. The results of this study -- namely the tunability of the morphology of polymer blend nanocomposites -- could be used to create new polymeric electronic devices such as polymeric solar cells with controlled morphology and domain size utilizing, for example, blends of conductive polymers with quantum dot nanoparticles. The diffusion coefficient of dPMMA into a bicontinuous structure is found to be smaller than in neat PMMA, which is attributed to the tortuosity of the accessible PMMA phase. Interfacial interactions may increase diffusion due to repulsive interactions between tracer and the
Cl terminated NP brush and reduced entanglement density between tracer and short PMMA brush. By modeling diffusion in terms of real diffusion coefficients in the interphase and center regions of PMMA, a real polymer diffusion in a bicontinuous matrix is determined and found to be faster than the pure a homopolymer matrix. Results of these diffusion studies can be compared to rheology measurements to better understand the dynamics of polymer nanocomposites with complex morphologies.
7.5 References


49. Foster, B. American Laboratory 2005, 37, (10), 42-44.


Figure 7.1  AFM topography images (10×10 µm) of the (a) surface (Δz = 14 nm) and (b) internal morphology (Δz = 135 nm) for a 140 nm thick PMMA:SAN film containing 5 wt% NP annealed at 195 °C for 24 h. The corresponding images of the (c) surface (Δz = 30 nm) and (d) internal morphology (Δz = 200 nm) for a 550 nm thick film with 10 wt% NP. The thinner film jams during the intermediate stage, resulting in the discrete PMMA domains (dark in (b)), whereas the thicker film jams during the early stage, resulting in continuous PMMA domains (dark in (d)).
Figure 7.2  SEM images of a discrete morphology in 1 μm thick PMMA:SAN films containing 1 wt% NP annealed at 195 °C for 24 h. Image (a) is taken by tilting the sample at a glancing angle of 52 °, whereas image (b) represents a cross-section of the morphology after etching a trench through the film. In (a), the round PMMA domains are lower than the surrounding SAN domains because PMMA etches faster than SAN. In (b), the NPs are located at the interface between the SAN and PMMA domains. The top of the image shows the Au:Pd coating.
Figure 7.3  SEM images of a bicontinuous structure in 1 μm thick PMMA:SAN films with 10 wt% NP annealed at 195 °C for 24 h. (a) SEM of the surface at 0 ° (top down) for regions exposed to 2 min (A), 3 min (B) and 5 min (C) of ion beam etching. (b) Magnified images of regions A, B, C. For region A, etching has removed the PMMA wetting layer at the surface to reveal the SAN phase (light) and PMMA domains (dark with raster lines). A similar region was imaged at 52 ° to show that the SAN phase is higher than the PMMA domains. Regions A and B show that the NPs locate at the interface and that the bicontinuous morphology persists into the film.
Figure 7.4  Cross-sectional SEM images of 1 μm thick PMMA:SAN films containing 10 wt% NP after annealing at 195 °C for 24 h. Images (a), (b) and (c) are taken at a lateral position of 0 nm, 200 nm, and 400 nm with respect to the initial trench position. The NPs locate at the interface and organize into a lacy interconnected structure. The areas denoted by the dotted ovals show that the structure evolves with lateral position but the lacy structure persists.
Figure 7.5  Cross-sectional SEM images of 2.5 µm thick PMMA:SAN films with (a) 2 wt% NP, (b) 5 wt% NP and (c) 10 wt% NP. Films are annealed at 195 °C for 24 h and exhibit a bicontinuous structure. As loading increases, domain size decreases.
Figure 7.6  Cartoons of top (left) and cross-sectional (right) views of (a) discrete and (b) bicontinuous structures observed for PMMA:SAN films containing NPs. Depending on the film thickness and NP concentration, NPs locate at the interface and jam to stabilize these morphologies either during the (a) intermediate or (b) early stages of phase evolution, respectively.
Figure 7.7 A jamming map shows how film thickness ($h$) and NP loading ($\phi_{NP}$) determine the structure of PMMA:SAN films containing silica NPs. Films ranging from 140 nm to 2,500 nm exhibit either bicontinuous (filled square) or discrete (unfilled square) structures. The half filled symbol represents a mixed morphology. The solid line represents the predicted cross-over between morphologies from the equation $h = \frac{2\pi n R}{3\sqrt{3} \phi_{NP}}$ for $n = 2$. These results indicate that thicker films can stabilize into a bicontinuous structure at lower concentrations than thinner films, a result of practical importance for designing multi-phase materials.
Figure 7.8  A schematic showing the tracer molecule diffusing into a bicontinuous structure consisting of a penetrable PMMA phase (gray) and impenetrable SAN phase (black). Here, the bicontinuous structure represents a magnified image of the cross-section shown in Figure 7.6 (b). The dotted lines surrounding the nanoparticles at the interphase represents the “fast diffusion” region which is taken to have a thickness of $\sim 2R_g$. 
Figure 7.9  AFM topography images (40 µm x 40 µm, Δz = 20 nm) of PMMA:SAN films (1 µm thick) containing 10 wt% silica NPs after (a) 2 h and (b) 24 h annealing at 195°C. The correlation length is ~ 800 nm after both times indicating that phase evolution has stopped.
Figure 7.10 Diffusion profiles of dPMMA in (a) PMMA and (b) PMMA : SAN films with a bicontinuous morphology after 2 h annealing at 195°C measured using ERD. Solid line is a fit of experimental data with Fick’s second law equation using $D$ values of (a) $7.8 \times 10^{-15}$ cm$^2$ s$^{-1}$ and (b) $5.4 \times 10^{-15}$ cm$^2$ s$^{-1}$. The dashed line represents the sum of the solid line and surface peak. The matrix polymers are denoted in the legends. The surface peaks in Figure 7.10 (b) is attributed to the impenetrable SAN phase.
Chapter 8

Conclusions and Future Work

8.1 Conclusions

Polymer nanocomposites (PNCs) containing nano-sized fillers are attractive because the addition of nano-sized fillers can enhance properties including mechanical, optical, and barrier. As the size of the particles decreases, the area-to-volume ratio increases and thus, the interfacial region has a larger impact on properties. In this dissertation, we investigated macromolecular diffusion and morphology in PNCs containing spherical nanoparticles (NPs). The PNC matrices are polystyrene (PS) with phenyl-terminated silica and poly(methyl methacrylate) (PMMA) with hydroxyl-terminated silica NPs. Using a doctor blade method, PNCs were prepared with well dispersed NPs at concentrations up to 50 vol% and characterized using transmission electron microscopy and Rutherford backscattering spectrometry. As NP concentration increases, polymer diffusion slows down. Moreover, the diffusion coefficient in PNCs relative to the pure polymer matrix ($D/D_0$) plotted against the interparticle distance of NPs relative to the tracer radius of gyration ($ID/2R_g$) collapses onto a master curve. With decreasing $ID/2R_g$ ($< 1$), a polymer chain is highly constrained and $D/D_0$ decreases more rapidly. The slowing down of polymer diffusion with increasing confinement (e.g. at high volume fraction of NPs or large tracer molecular weight) is compatible with the entropic barrier model which describes the diffusion of a polymer chain in a random
array of impenetrable barriers. In this model, a polymer chain must stretch to diffuse through a bottleneck, resulting in a loss of conformational entropy.

The tracer diffusion coefficient was found to decrease as the diameter of particles decreases compared at constant volume fraction (\(\phi_{NP}\)). As the number average diameter of phenyl-terminated silica NPs decreases from 28.8 nm to 12.8 nm in a PS matrix, the interparticle distance decreases by 66% and therefore tracer chains are more highly confined in the smaller NP system at a given \(\phi_{NP}\). In addition to the number average diameter, the effect of size polydispersity on the interparticle distance is investigated for a log-normal distribution of diameters. By including size polydispersity or using volume average diameters, the interparticle distance increases compared to its value using the number average value and thus, provides a better master curve in a plot of \(D/D_0\) against \(ID/2R_g\) for 28.8 nm and 12.8 nm NPs. The interparticle distance is also calculated to include the distribution of interparticle spacing between randomly arranged NPs in one-dimension (\(x\)). Upon plotting \(D/D_0\) against \(\sqrt{\left(\frac{x}{2R_g}\right)^2}\), the data collapse onto a master curve but not as well as plotting vs \(ID (d_n, \sigma)\) or \(ID (d_i)\).

The effect of polymer-NP interaction on polymer diffusion in nanocomposites was also investigated by comparing transport through PS:phenyl-terminated silica and PMMA:hydroxyl-terminated silica nanocomposites. While there is a weak attractive interaction between PS and the phenyl-terminated silica, the latter system represents an attractive interaction due to the hydrogen bonding between PMMA ester side groups and hydroxyl units on silica surface. As the volume fraction of NPs or tracer molecular
weight increases, polymer diffusion slows down in both nanocomposites. However, the slowing down of dPMMA in PMMA nanocomposites is larger than that of dPS in PS nanocomposites at the same volume fraction of NPs and tracer molecular weight. This diffusion behavior is attributed to an increase in the enthalpic interaction between polymer and particle.

We also studied tracer diffusion in a bicontinuous structure prepared from a PMMA: poly(styrene-ran-acrylonitrile) (SAN) film containing silica NPs. The addition of NPs that segregate and jam at the interphase produces discrete or bicontinuous structures of the PMMA:SAN films. Using atomic force microscopy or scanning electron microscopy after focused ion beam etching to identify morphologies, a morphology jamming map was constructed as a function of NP concentration and film thickness. The transition from discrete to bicontinuous morphologies can be predicted by a simple geometric model based on arranging spherical NPs at the PMMA/SAN interface. The tracer diffusion coefficient of dPMMA into the bicontinuous structure relative to pure PMMA \(D/D_0\) was \(~0.7\), indicating slowing down of dPMMA diffusion. The slowing down of polymer diffusion in a bicontinuous structure is maybe attributed to the tortuosity of the continuous PMMA matrix phase.
8.2 Future work

8.2.1 Effect of diameter and diameter distribution of NPs on polymer diffusion

A significant finding in this thesis is that tracer diffusion coefficient of dPS in a nanocomposite relative to that of pure PS plotted against the interparticle distance relative to the size of tracer molecule (i.e., $ID/2R_g$) produces a master curve. The collapse of the diffusion data is somewhat surprising because $ID$ can be determined using a variety of definition for diameter such as the number or volume average as well as including the polydispersity of the diameters in a real system. Using small angle X-ray scattering, the diameter distribution for large and small silica NPs was found to follow a log-normal distribution. The master curve is found to slightly improve when polydispersity is included to calculate $ID$. However, because the polydispersity of the NPs is close to 1, the effect of diameter polydispersity on $ID$ is small. Because many real composites such as rubber toughened polymers have a much wider distribution, future studies should investigate PNCs containing a broad distribution of NP diameters (e.g. $\sigma = 2$). By investigating polymer diffusion in a polymer nanocomposite containing polydisperse NPs and including this polydispersity in calculating $ID$, we could clarify whether $ID$ can be captured by only the number average diameter or if the log-normal distribution is needed.

In Chapters 4, 5, 6, a plot of $D/D_0$ against $ID/2R_g$ collapses onto a master curve for PNCs containing small and large NPs. It would be interesting to investigate much larger NPs. As NP diameter increases from 10 ~ 30 nm, the size in this thesis, to 100 nm, interparticle distance increases more than 3 times and thus, polymer diffusion may not be perturbed at high NP loading. On the other hand, if the interparticle distance is the same
for small \((d = 10 \sim 30 \text{ nm})\) and very large \((d > 100 \text{ nm})\) particles, the number density of small particles is much larger than that of larger particles. However, the confined path length between large particles will be larger than that between small particles as shown in Figure 8.1. It would also be interesting to investigate NPs that are smaller than those investigated in this thesis, namely \(d < 10 \text{ nm}\). When particles smaller than 10 nm or star polymers are used as fillers, opposite results to particles larger than 100 nm could be expected but additional effects could be observed because smaller NPs will not be immobile relative to a polymer chain. This study will help us to understand the tracer diffusion in nanocomposites containing spherical particles with a wide range of size.

8.2.2 Effect of polymer-NP interaction on polymer diffusion

In Chapter 6, effect of polymer-NP interaction on polymer diffusion was investigated in matrices of PS:phenyl (or phenyl ethyl)-terminated silica and PMMA:hydroxyl-terminated silica. Upon comparing diffusion in matrices with silica modified by phenyltrimethoxysilane (PhTMS) or phenyltriethoxysilane (PhETMS), we observed that tracer diffusion was faster for functionalized NP with the extra ethyl tether. This difference may be due to an enthalphic energy change. To evaluate the effect of coupling agent, polymer adsorption on planar silica or silica particle modified by PhTMS and PhETMS can be studied using IR and UV spectroscopies\(^1,^2\) or isothermal titration calorimetry\(^3,^4\). A larger adsorption of polymer on the surface implies a more favorable interaction between polymer and the silica surface and thus, slower diffusion of polymer.
near the surface. This study will be helpful to investigate the polymer-NP interaction and thus, to understand polymer diffusion in a polymer nanocomposite.

In this thesis, dPMMA tracer diffusion into PMMA containing 12.8 nm hydroxyl-terminated silica was studied. It would be interesting to investigate larger NPs, particularly 28.8 nm. As the diameter of NPs increases from 12.8 nm to 28.8 nm, total interfacial area between PMMA and NP decreases more than twice at the same volume fraction of NPs. If polymer diffusion in PMMA:silica nanocomposite containing 28.8 nm diameter is investigated, effect of contact area between polymer and NP can be understood for attractive interaction between polymer and NP.

8.2.3 Diffusion into a bicontinuous structure

In Chapter 7, a bicontinuous structure was fabricated from polymer blend containing NPs at the interphase. We found that polymer diffusion in a bicontinuous structure slows down compared with that in a pure PMMA possibly because of the tortuous diffusion path length. As a future work, polymer diffusion into a bicontinuous structure with larger domain size of PMMA is suggested to elucidate the mechanism of polymer diffusion in a bicontinuous structure. If increase in the domain size of PMMA at same volume fraction of PMMA will slow down polymer diffusion compared to the result in Chapter 7, it could result from the smaller interfacial area which decreases the contact of short Cl-terminated PMMA brush on NPs at the interphase with dPMMA. However, for smaller PMMA domains, it will be more complex to estimate the polymer
diffusion. If the PMMA domain size is smaller than tracer size, geometric confinement for a chain motion should be also considered in addition to the effect of interfacial area. Large or smaller domain size can be achieved by decreasing or increasing NP concentration to polymer blend film, respectively. This study will be useful to understand the mechanism of the polymer diffusion in a bicontinuous structure.

8.2.4 NP diffusion in a polymer nanocomposite

In our study, diffusion coefficient of NPs in a polymer matrix was calculated using Stokes-Einstein (SE) relation\(^5\) and the viscosity of a polymer matrix\(^6,7\). The NP diffusion was not considered because it was immobile relative to polymer diffusion. However, as NP size decreases, their mobility increases and thus, they no longer act as immobile constraints. Thus, it is important to measure the diffusion coefficient of spherical particles in a melt and compare it with SE relation. NP diffusion in a polymer matrix can be investigated using Rutherford backscattering spectrometry (RBS). A bilayer for NP diffusion study consists of a polymer film with NPs and another without NPs and is annealed at high temperature. By controlling the size of NPs, molecular weight of a polymer matrix, and annealing temperature, we can measure the diffusion coefficient of NPs at each condition, obtain the relation among them, and compare it with SE relation. Also, effect of polymer-NP interaction on NP diffusion in a polymer melt can be studied using different polymer-NP systems. If NP diffusion slows down in a different polymer-NP system, polymer-NP interaction will be more attractive than that in the original polymer-NP one. This study will help us not only to find the relation among
diffusion coefficient, the size of NPs, molecular weight of a polymer matrix, and annealing temperature in different polymer-NP system but also to evaluate the polymer-NP interaction.
8.3 References


Figure 8.1 Small (a) and large NPs (b) can have same interparticle distance (double arrow) but different confined path length between NPs.
Appendix I

Morphology Mapping of Phase Separated Polymer Films using Nano-Thermal Analysis

A.1 Introduction

Polymer thin films are utilized in many present day technologies\textsuperscript{1,2} because they exhibit attractive physico-chemical properties. By combing mixtures of polymers, new combinations of properties can be achieved that impart the materials with functionality, improved processability and lower cost. However, the targeted properties of polymer mixtures can be perturbed because of phase separation, phase coarsening, and interfacial segregation under exposure to environmental conditions such as heat, moisture, and pressure.\textsuperscript{3} Monitoring the spatial distribution of the glass transition temperatures across a sample can be used to identify the coexisting phases. Conventional methods for determining the glass transition temperature in phase separated systems require large samples, \textasciitilde{}milligrams, and large domains.\textsuperscript{4,5} Moreover, these methods are typically not appropriate for thin films, particularly those having phases with sizes on the order of tens of nanometers. Although several methods with sub-micron spatial resolution are available, such as Transition Temperature Microscopy (TTM)\textsuperscript{6,7} and NEXAFS microscopy,\textsuperscript{8} these methods are either lacking resolution for characterization of sub-micron domain size in multiphase systems (e.g., TTM) or requiring expensive equipment (e.g., NEXAFS). Recent experiments suggest that nano-confinement of the polymer near
interfaces, such as vacuum – polymer, substrate – polymer, results in a change of structural relaxation and the local glass transition temperature. The glass transition in polymers is associated with a large change in mechanical properties. Atomic force microscopy (AFM) is an attractive platform for investigating the glass transition in polymer films by mapping the mechanical properties with high resolution and spatial distribution at sub-100 nm resolution, a routine exercise for AFM. Although attempts have been made, the mechanical properties of polymers as a function of temperature have not been mapped at high resolution. Local measurements of the mechanical properties of polymers as a function of temperature have only been recently demonstrated. Here, we show that AFM based band excitation nano-thermal analysis (BE-NanoTA) can be used to measure the mechanical properties and glass transition temperature in the near surface region with a point-to-point lateral resolution of 50 nm. Specifically, BE-NanoTA analysis confirms the results from prior experiments showing that poly(methyl methacrylate) (PMMA) : poly(styrene-ran-acrylonitrile) (SAN) films undergo an early and intermediate stage of phase separation. Moreover, BE-NanoTA provided new observations including PMMA and SAN rich channels near the surface at early times, as well as SAN-rich domains trapped within PMMA domains that span the film during intermediate times.
A.2 Materials and methods

A.2.1 Implementation of BE-NanoTA

BE-NanoTA technique consists of four main components: Veeco Multimode Atomic Force Microscope (AFM) equipped with a Nanonis controller; an in-house developed MATLAB/LABVIEW data acquisition and control system; tip heating protocol and nano-heater placed on the AFM tip. Anasys Instruments heated probes (AN2-300) were used for the experiments (cantilever spring constant ~ 0.5 N/m). Heating of the probe was done using MATLAB/LABVIEW control system. The heating protocol is a sum of two heating signals DC heating and AC heating. AC heating excitation band spanning approximately 100-500 kHz (increasing chirp)\(^{16}\) with an amplitude 0.2 – 0.5 V was used to generate temperature modulations of the tip. Constant 10 °C temperature amplitude of AC heating was maintained by changing amplitude of AC heating voltage. A tip experiences periodic (AC) heating, while in contact with the surface, resulting in the periodic thermal expansion of the underlying material (Figures A.1(a), A.1(b)). Usual length of AC heating wave is ~ 1s. The linear expansion coefficients (\(\alpha\)) for SAN and PMMA are 2-6·10\(^{-4}\) K\(^{-1}\) \(^{17}\) and 1-2·10\(^{-4}\) K\(^{-1}\) \(^{18,19}\), respectively. Thermal expansion of the polymer under the tip causes displacement of the tip normal to the surface plane. Assuming the AC heat wave propagates ~ 20 nm below the surface and \(\Delta T \sim 10^\circ\text{C}\), the amplitude of induced tip oscillations is on the order of 100 pm (within detection range of AFM photodetector). Thermal expansion of the material is measured using vertical displacement signal from VEECO Multimode AFM, when tip is heated and pushed on the surface with a force of hundreds of nN. The heating waveform contains band of\(^\ldots\)
frequencies centered at the contact resonance of tip – sample system (100 – 500 kHz). The mechanical response of the system is recorded by measuring and digitally storing the motion of the tip, taking the Fourier transform of the response. The amplitude, resonance frequency, and quality factor were extracted using a simple harmonic oscillator model at regular intervals during the tip heating process. The resonance frequency of the tip oscillations is proportional to the stiffness of the tip – surface contact. We probed resonance behavior of the mechanical response of tip – surface junction by changing the temperature of the tip with 10 °C amplitude in oscillatory fashion (for more details see ref. 20). This approach allows us to probe the tip resonance– surface contact as a function of temperature (Figure A.1 (c)). The mechanical response of the tip while in contact with the surface was probed by applying dc heating with a temperature step of ~ 4 °C, simultaneously with the periodic ac heating.

A.2.2 Temperature calibration of the heated probe

Due to the difference thermal impedance between the cantilever and tip, the temperature of the tip may be different from the temperature of the cantilever. In this work we use the standard polymeric samples (polycarbolactone (PCL), high density polyethylene (HDPE), and polyethylene terephthalate (PET)) with known melting temperatures to calibrate the temperature at the tip under static excitation.20 This approach for calibrating the dynamic transfer function was pioneered by Lee et al.21.
A.2.3 Mathematical analysis of the data

Glass transition temperature maps were created from temperature dependencies of resonance frequency. Global maximum on the resonance frequency curve was found after interpolation of the temperature dependence of resonance frequency by 4\textsuperscript{th} order polynomial using MATLAB routine.

A.2.4 Sample preparation

Individual polymers poly(methyl methacrylate) (PMMA) and poly(styrene-ran-acrylonitrile) (SAN) having an AN content of 33 wt\% were purchased from Polymer Source and Monsanto. PMMA was used as received and SAN was purified before use. During purification SAN transparent pellets were dissolved in chloroform and the SAN-chloroform solution was added drop by drop into methanol for precipitation. The SAN precipitate was dried at room temperature under the vacuum for 24 hours. The weight average molecular weights and polydispersities of PMMA and SAN are 82.4 kg/mol and 1.07, and 118 kg/mol and 2.24, respectively. A blend of PMMA and SAN with 1:1 weight ratio (50 wt\% of SAN) was investigated. The mixture of PMMA and SAN powder (1:1 weight ratio) was dissolved in methyl isobutyl ketone (MIBK), spin-cast on a silicon wafer, and dried at 120 °C in a vacuum for 24 hours to evaporate the MIBK. The thickness of spin-cast films was measured using an ellipsometer. The films were annealed on a hot stage (Mettler FP-82, Mettler Toledo) at 195 °C in an argon atmosphere and quenched to room temperature, far below the glass transition temperature of PMMA and 201
SAN. PMMA:SAN blend used has a lower critical solution temperature of ~160 °C and upon annealing at 195 °C separates into nearly pure PMMA and SAN phases.\textsuperscript{30} Quenching below $T_g$ is rapid relative to re-mixing kinetics and therefore the morphology observed at room temperature is representative of the phase separated structure. Surface morphologies of these films were measured using tapping mode AFM.

A.2.5 DSC analysis

DSC analysis of pure polymer components was performed using TA instruments Q2000 in He atmosphere. Approximately 3 mg of pure polymer component (SAN or PMMA) was placed in an aluminum pan. The scanning temperature range was 30 °C to 200 °C with a temperature ramp of 10 °C/min.

A.3 Results and discussion

Previous studies showed that PMMA:SAN blends undergoes early, intermediate and late stages of phase evolution.\textsuperscript{22-25} BE-NanoTA was applied to study PMMA:SAN phase separation by mapping the temperature dependence of mechanical properties and determine the glass transition temperature in the near surface region of the coating. BE-NanoTA is an extension of scanning thermal expansion microscopy (SThEM), where periodic heating of the tip surface junction results in periodic local thermal expansion of the substrate.\textsuperscript{26} BE-NanoTA periodically heats the tip and determines the mechanical
properties of the material (Young's modulus and viscoelasticity) as a function of temperature by measuring changes in the resonance frequency, amplitude, and quality factor of the AFM cantilever in contact with the surface. As shown in Figure A.1, BE-NanoTA uses an AFM probe with a heater that contacts the surface (Figure A.1 (a)). The contact resonance parameters, such as frequency, are measured locally (i.e., at tip – surface interface; Figure A.1 (b) presents typical frequency response of tip oscillation amplitude to temperature excitation) as a function of temperature (Figure A.1 (c)). Next, the glass transition temperature is determined as a maximum on temperature dependence of resonance frequency.

Based on the theory of contact mechanics, the contact stiffness changes if the contact area and/or Young’s modulus change during heating. The glass transition due to local relaxations of the polymer chain correlates with a change from a solid-to-melt state upon heating and a corresponding decrease of Young’s modulus by approximately 3 orders of magnitude over a fairly narrow temperature range. Thus, the decrease of Young’s modulus (i.e., decrease in the resonance frequency) can be used to determine the glass transition temperature of the polymer or phase adjacent to the tip. The initial increase in resonance frequency (Figure A.1 (c)) results from an increase in tip – surface contact area associated with the thermal expansion of the glassy polymer. As shown in Figure A.1 (c) a sharp decrease in resonance frequency occurs when the surface region under the tip undergoes a solid to melt transition. Figure A.2 shows the relationship between the resonant frequency and modulus.
Theoretical modeling of the contact mechanics at the tip–surface junction is required to understand how the contact resonance frequency depends on temperature. Initially as the tip approaches the surface, the contact radius \( R_{\text{contact}} \) is determined by the Hertzian model (eq. (1))\(^{27}\):

\[
R_{\text{contact}} = \left( \frac{3FR_{\text{tip}}}{4E(T)} \right)^{1/3}
\]

where \( R_{\text{tip}} \) is the tip radius (50 nm), \( F \) is the indentation force (1,000 nN), and \( E(T) \) is Young’s modulus (~ 1GPa for PMMA at 20°C). During heating, the force between the tip and surface is constant and the polymer creeps. Previous studies\(^{29}\) quantified the creep in PMMA using an irreversible deformation model:

\[
h^2 = \frac{F}{K_{\text{ir}}} + \frac{FM_{\text{ir}}}{t_1K_{\text{ir}}^2} \left[ \exp \left( -\frac{tK_{\text{ir}}}{M_{\text{ir}}} \right) - \exp \left( -\frac{(t-t_1)K_{\text{ir}}}{M_{\text{ir}}} \right) \right] + \frac{F}{2Qt_1} t^2 - \frac{F}{2Qt_1} (t-t_1)^2
\]

where \( h \) is indentation depth, \( t_1 \) is time when force stops increasing (1s), \( K_{\text{ir}} \) is the stiffness in the Kelvin model (18.3 GPa), \( M_{\text{ir}} \) is the dashpot parameter (109 GPa/s), and \( Q \) is the dashpot parameter (711 GPa/s).\(^ {29}\) Creep \( h(t) \) was calculated using the Kelvin model in series with the dashpot (Figure A.2 (b)). From \( h(t) \), the change in contact radius \( (R_{\text{contact}}) \) as a function of time can be calculated assuming a spherical tip with radius, \( R = 50 \text{ nm} \) (Figure A.2). For simplicity we assumed that contact radius is the sum of Herzian contact radius (eq. (1)) and contact radius due to creep. The change in the Young’s modulus of polymer was modeled using the sigmoidal shaped function with transition temperature ~180 °C and the change in Young’s modulus from 1 GPa to 100 MPa to
illustrate the change in contact resonance frequency as a function of Young’s modulus and temperature. Resonance frequency \( f_{\text{res}} \) was calculated following Ref.\textsuperscript{14, 20}:

\[
f_{\text{res}} = \left(1 - 7.7 \frac{k_{\text{tip}}}{k_{\text{cont}}} \right) f_{\text{bound}}
\]

(3)

where \( k_{\text{tip}} \) is the spring constant of the tip (1 N/m), and \( k_{\text{cont}} \) the contact stiffness, \( k_{\text{cont}} = 2 \cdot R_{\text{contact}} \cdot E \). The modeling (Figure A.2) is consistent with the behavior of the resonance frequency as a function of temperature. Initially, the resonance frequency increases due to the thermal expansion of the glassy polymer that increases the tip – surface contact area. As the polymer undergoes a glass to rubber transition, the contact resonance frequency decreases sharply (50 – 200 Hz/K) as the modulus decreases in the region around the tip-surface contact area.

Before testing heterogeneous films, BE-NanoTA was used to determine the glass transition temperature of homogeneous SAN and PMMA films. The \( T_g \) values are 147 °C and 177 °C, respectively, and provide the minimum and maximum values expected for the heterogeneous system. These limits are noted as dashed lines in Figure A.3 (d). For a heating rate of 10 °C/min, the DSC values of bulk SAN and PMMA are 114 °C and 131 °C, respectively. Because BE-NanoTA uses a much higher heating rate \( \sim 100,000 \degree \text{C/s} \), the \( T_g \) values are much greater than those from DSC. Using the standard deviation of several measurements over a 10 \( \mu \text{m} \times 10 \mu \text{m} \) area, the \( T_g \) values determined by BE-NanoTA are reproducible to within 3 °C. Moynihan et al. showed that the glass transition temperature \( T_g \) is related to the heating or cooling rate \(|q|\) by:

\[
d\ln|q|/dT_g = \frac{\Delta h}{RT_r^2}
\]

(4)
where $T_r$ is a temperature in the middle of the transition range and $\Delta h$ is the activation enthalpy for the relaxation times controlling the structural enthalpy or volume relaxation. Activation enthalpies for glass transition process were calculated for PMMA and SAN materials using eq. (4) and the experimental glass transition temperatures (Table A.1). The activation enthalpy for PMMA is 469 kJ/mol, in agreement with literature values which range from ~350 – 800 kJ/mol. This agreement suggests that the transition temperatures from the BE-NanoTA method are consistent with the glass transition temperatures of the respective polymers at high frequency. No literature values for SAN were found.

The spatial distribution of glass transition temperatures was measured across the surface of a phase separated poly(methyl methacrylate) (PMMA): poly(styrene-ran-acrylonitrile) (SAN) blend film with a thickness of 350 nm. The surface morphology of was determined by BE-NanoTA as well as by conventional (topography and phase) AFM. Films were annealed at 195°C and quenched to room temperature, far below the glass transition temperature of PMMA and SAN (see Materials and Methods for more details). At 195°C, this blend separates into coexisting phases of nearly pure PMMA and SAN because this temperature is about 35°C above the lower critical solution temperature of PMMA:SAN mixture. For the as-cast (0 h) film, the glass transition map showed almost no spatial variation of $T_g$ (image not shown) and an average value of 150°C ± 3°C (3 µm x 3 µm). This observation is consistent with a homogeneous surface, where the softening temperature of the material is determined by the lowest softening temperature of the components. After annealing for 0.5 h the PMMA:SAN blend undergoes phase
separation with the formation of irregularly shaped PMMA domains (red) with widths ranging from 500–1000 nm (Figure A.3 (a)). As described in previous studies\textsuperscript{22-25,35} the topographical variation reflects the domains near the outermost ~200 nm of the surface. Qualitatively, the glass transition temperature map in Figure A.3 (a) correlates with the topography and phase maps. Namely, the high and low regions in the topography image correspond to the PMMA-rich (high $T_g$) and the SAN-rich (low $T_g$) regions in Figure A.3 (b). As expected, with further annealing (Figures A.3 (b) and A.3 (c)), the domain size of PMMA increases from ~600 nm to ~1500 nm. Thus, the BE-NanoTA measurements support the proposed mechanism for phase separation during the intermediate stage characterized by growth of PMMA domains.

Upon comparing films annealed for 0.5 h and 2 h, a map of the glass transition temperature across the surface of the phase separated films shows that the $T_g$ contrast increases as the phase size increases and becomes more discrete. To understand this behavior, the $T_g$ variations across all three samples are presented in Figure A.3 (d). Whereas the $T_g$ distribution for 0 (not shown), 0.5, 2h are monomodal with average temperatures 150 °C, 152 °C, 157 °C, respectively, the distribution after 5 h is bi-modal with average temperatures of 155 °C and 165 °C. The observation of a biphasic $T_g$ at longer times indicates that the phase size is large enough to be easily distinguished when plotted in this manner. According to the phase separation model for PMMA:SAN, the SAN domains in the mid layer are covered with wetting layer of PMMA, which reaches a maximum thickness of about 100 nm at the end of the early stage and steadily thins during the intermediate stage as PMMA flows from the wetting layer into the PMMA.
domains below. Because our technique is sensitive to the outer surface region (~200 nm), this wetting layer limits our ability to correlate the $T_g$'s from the blend with those of the pure components. Nevertheless, Figures A.3 (a) – (c) clearly show PMMA rich (high $T_g$/ red) and SAN rich (low $T_g$/ blue) regions and that these regions become larger and more circular with annealing.

Two new details of phase separation in PMMA:SAN films were uncovered by BE-NanoTA. After 2 h and 5 h of annealing, the SAN phase (blue) is continuous whereas after 0.5 h the SAN phase is highly elongated and possibly discrete. This latter observation may reflect that the bicontinuous structure characteristic of the early stage has not completely transformed into the perpendicular tubes associated with the PMMA domains thus signifying the beginning of the intermediate stage. In previous studies of PMMA:SAN films annealed for 0.5 h, AFM topographic measurements combined with PMMA etching was unable to directly observe PMMA tubes near the surface whereas Figure A.3 (a) shows tubes near the surface (red). A second new observation is apparent in the map of the sample annealed for 5 h which is well into the intermediate stage. Here, the morphology is dominated by PMMA domains (red) that span the film surface as previously determined by etching/topography mapping. However, BE-NanoTA imaging shows that small SAN rich domains appear trapped inside the larger PMMA domains. Neither the topography map taken before etching or after etching revealed these trapped SAN domains. These two results point out the main disadvantage of the etching/topography approach, namely, the inability to directly image the PMMA phase and trapped SAN within the larger PMMA domains.
Figure A.4 shows how the spatial resolution and sensitivity of BE-NanoTA compares with various techniques used in mechanical analysis including local thermal analysis (LTA) with Wollaston probe\(^5\) and silicon heater; \(^6\) local thermal analysis with silicon heater and band excitation detection, BE-NanoTA; and dynamic mechanical analysis, DMA.\(^4\) Regions on spatial resolution/ sensitivity map corresponding to different techniques are presented as a stack and arranged in an order of an area increase when techniques with larger spatial resolution – sensitivity range located at the bottom of the stack. The spatial resolution is either limited by the probe size in probe-based methods or the sample size in all other methods. Measurement of the displacement is a key component of all methods listed above, in Figure A.4 we compared the sensitivities of all techniques in displacement measurements. Figure A.4 also shows the spatial resolution and displacement sensitivity required for practical problems found in industrial applications, including analysis of pharmaceuticals, organic layers in OLEDs, lithography masks, mechanical properties of the surfaces (auto, optics etc.) (marked with blue/dark grey rectangle) as well as for basic scientific problems such as thermo-mechanical motion of single molecules (white/light ellipse). The spatial resolution and the sensitivity of Nano-TA is determined below. Recently, the spatial resolution for the local thermo-mechanical and \(T_g\) measurements is limited by the tip – surface contact radius, \(\sim 10\) nm.\(^15\) The vertical sensitivity level in static AFM (e.g., contact mode) is estimated as \(\sim 0.1\) nm, which is mainly determined by the experimental noise limit for conventional photodetectors. For \(ac\)-detection methods based on amplitude or frequency detection, the vertical sensitivity as limited by the thermo-mechanical noise\(^36\) is

\[
\delta l_{lm} \approx \sqrt{2 k_B T B / k_\omega r}, \quad \text{where } k_B \text{ is the Boltzman constant, } T \text{ is temperature, } B \text{ is the}
\]
bandwidth, $k$ is the cantilever spring constant, and $\omega_r$ is the cantilever resonant frequency. This yields the relationship between resolution and sensitivity as

$$\frac{\delta l}{R_{\text{contact}}} \approx -(1 + \nu) \alpha \delta T$$

(5)

where $\delta l$ – tip displacement due to thermal expansion of the material, $R_{\text{contact}}$ – radius of tip – surface contact, $\nu$ – Poisson ratio for surface material, $\alpha$ – linear thermal expansion coefficient. The linear expansion coefficient ($\alpha$) for SAN and PMMA are $6 \cdot 10^{-4}$ K$^{-1}$ (17) and $1 - 2 \cdot 10^{-4}$ K$^{-1}$ (18, 19), whereas the Poisson's ratio for polymers is about 0.34. For the typical cantilever parameters $k \sim 1$ N/m, $\omega_r \sim 2 \pi$ 300 kHz (contact resonance frequency), and $B \sim 1$ kHz (typical experimental bandwidth). Thus, for the temperature range 300 – 1000 K, the thermo-mechanical noise will be on the order of 3 – 10 pm.

### A.4 Conclusions

We demonstrate a non-destructive method, BE-NanoTA, that uses local thermal analysis of the polymer surface to measure the glass transition temperature with 50 nm lateral resolution. Moreover, BE-NanoTA provided insight into the early and intermediate stages of phases separation of SAN:PMMA films that was overlooked using an etching/topography mapping method. Because BE-NanoTA is non-destructive, phase evolution can be followed without chemical$^{23}$ or plasma$^{37}$ etching, which allows for in-situ studies of polymer dynamics. Overlaying the capabilities of the mechanical analysis
methods with industrial requirements (Figure A.4) demonstrates that local thermal analysis with a silicon heater and band excitation detection, namely BE-NanoTA, significantly widens the applicability of local thermal analysis techniques. The theoretical spatial resolution of BE-NanoTA\(^{20}\) approaches the length scale of the Kuhn segment length and therefore new understanding of the relationship between local segmental dynamics and mechanical properties may evolve from further studies. Thus, this chapter demonstrates the potential of high-resolution mapping of thermal properties for investigating a range of technologically important areas ranging from quality control of coatings in drug delivery systems to characterizing new resists for semiconductor industry as well as fundamental issues such as single molecule thermo-mechanical analysis.

Table A.1  Glass transition temperatures of PMMA and SAN measured using DSC and BE-NanoTA. Activation enthalpy of the glass transition calculated from $\Delta T_g$.

<table>
<thead>
<tr>
<th></th>
<th>$T_g(0.17 \text{ Hz}), ^\circ \text{C}$ (DSC)</th>
<th>$T_g(300 \text{ kHz}), ^\circ \text{C}$ (BE-NanoTA)</th>
<th>$\Delta T_g, ^\circ \text{C}$</th>
<th>$T_r, ^\circ \text{C}$</th>
<th>Activation enthalpy (kJ/mol)</th>
</tr>
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<tbody>
<tr>
<td>PMMA</td>
<td>131</td>
<td>177</td>
<td>46</td>
<td>154</td>
<td>469</td>
</tr>
<tr>
<td>SAN</td>
<td>114</td>
<td>147</td>
<td>33</td>
<td>131</td>
<td>582</td>
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A.5 References


7. Anasys Instruments.


Figure A.1 Cantilever schematic and analysis used in BE-NanoTA. (a) A heated tip locally heats the near surface of the film. The inset shows the contact mechanics model used for contact resonance frequency, contact area and Young’s modulus. (b) Amplitude of tip oscillations in vertical plane as a function of frequency caused by thermal expansion of the material under the tip. Simple harmonic oscillator (SHO) model fits contact resonance behavior well (black line is SHO fit). SHO model was used for determination of contact resonance frequency. (c) Contact resonance frequency as a function of temperature for pure PMMA and SAN films. The resonance frequency decreases as the polymer softens signifying that the near surface glass transition has been observed.
Figure A.2  (a) Dependence of contact resonance frequency on temperature and Young’s modulus was modeled according to the Hertzian + creep model described in the text. Initial slow increase in the contact radius is due to creep of polymer (after ref. 29), sharp increase at temperature higher than 180 °C is due to decrease in Young’s modulus (Hertzian model). (b) Mechanical model used for description of polymer creep.
Figure A.3  Maps of the glass transition temperature across the surface of PMMA:SAN films during the early and intermediate stages of phase separation represented by (a) 0.5 h, and (b) 2 h, (c) 5 h, respectively. The PMMA-rich and SAN rich domains are denoted as red and blue corresponding to high and low glass transition temperature regions. Initially, the PMMA domains are elongated (early stage) and evolve into circular domains at 2 and 5 h (intermediate state). The scan size is 4.1 µm x 3.8 µm. (d) Histograms of the glass transition temperatures extracted from the spatially resolved
maps in Figures A.3 (a) - (c). The dashed lines represent the glass transition temperatures measured for pure SAN and pure PMMA films. After 5 h, the phases have sufficiently evolved so that two separate glass transition temperatures appear. The wetting layer of PMMA (100 nm and less) confounds an exact mapping of the measured $T_g$ with the corresponding phase. The shape of glass transition temperature distribution histograms is similar for samples annealed at 0.5 h and 2 h, when the difference in domain structure of these samples is substantial (Figures A.3 (a), A.3 (b)). This illustrates the importance of high resolution $T_g$ mapping and added benefits of BE-NanoTA comparing with bulk methods of thermal analysis for studies of polymer phase separation.
Figure A.4  Comparison of thermo-mechanical analysis methods and potential applications. The sensitivity in displacement measurements and spatial resolution for DMA, LTA: Wollaston Probe, LTA: Silicon Probe, and BE-NanoTA. The accuracy in displacement measurements and spatial resolution required for different applications, including the mechanical properties of the surfaces, analysis of pharmaceuticals, lithography masks, organic layers in OLEDs (blue/dark grey rectangle). Fundamental studies include the mechanics of single molecules (white/light ellipse); ferroelectric transitions and thermal expansion of the materials (red/light grey rectangle).