Dynamics in Polymer Nanocomposites Containing Fixed and Mobile Nanoparticles

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Abstract
This dissertation describes experimental studies on the dynamics of polymer nanocomposites (PNC), namely, center-of-mass (COM) polymer diffusion in PNCs, and COM nanoparticle (NP) diffusion in polymer melts. Elastic recoil detection (ERD) is used for polymer diffusion studies and Rutherford backscattering (RBS) is used for NP diffusion studies. Diffusion of the tracer polymer, deuterated poly(methyl methacrylate) (dPMMA) is slowed down in a PMMA matrix filled with hydroxyl-capped spherical silica nanoparticles. A confinement parameter, ID/2Rg, where ID is interparticle distance and 2Rg is probe size is defined to account for the NP crowding effect. For highly crowded region where ID < 2Rg, D decreases by up to 80% relative to the bulk value. Surprisingly, D is reduced by 15% relative to the bulk value even when ID is eight times larger than 2Rg in the weakly confined region. A comparison between the current PMMA and polystyrene nanocomposites indicates that attractive interactions in the PMMA system do not significantly alter the center of mass diffusion of macromolecules in polymer nanocomposites.

Diffusion of deuterated polystyrene (dPS) is probed in PS matrices containing string-like chained nanoparticles (cNP) grafted with PS. This investigation connects prior diffusion studies in model spherical and cylindrical NP systems, and provides insight for technological applications, which typically involve irregularly-shaped NPs such as carbon black. We report that the presence of chained NPs in PS matrices induces a minimum in the diffusion coefficient (D) with increasing cNP concentration when the key length scale, 2Rg/L ≤ 1.5, where Rg is the gyration radius of dPS and L is the mean length of the impenetrable core of the chained NPs. The diffusion minimum is attributed to anisotropic diffusion in the vicinity of the chained NPs and requires that the long dimension of the cNP be comparable to or longer than the tracer molecule. Two normalizations are explored to account for the brush effect on polymer diffusion. These studies show that the NPs not only act as impenetrable obstacles for polymer diffusion, but that the polymer brush grafted to the cNP provides an alternative pathway to control polymer dynamics.

The relative mobility of nanorods in PNC is shown to impact chain diffusion. Nanorod (NR) mobility was tuned by varying the molecular weight of the matrix and NR concentration. When the tracer polymer diffuses faster than the NRs, the tracer diffusion coefficient in the PNC decreases similarly to the immobile (fixed) NR case as NR concentration increases. However, when the tracer diffuses slower than the NRs, enhanced tracer diffusion is observed with respect to the fixed NR case below the overlap concentration for NRs. This enhancement is attributed to NR mobility which allows for removal of topological constraints present in PNCs with fixed NRs. At NR concentrations above the overlap concentration, where NR mobility is reduced by interactions with neighboring “overlapping” NRs, tracer diffusion becomes independent of matrix molecular weight. These experimental results establish criteria by which the mobility of NRs relative to long chains assists polymer diffusion and will motivate a broader inspection of the role of mobile nanoparticles on the properties of polymer nanocomposites.

We also study the diffusion of PMMA-grafted iron oxide nanoparticles (core diameter = 5 nm) in PMMA melts. Dry and wet brush architectures are obtained by tuning brush molecular weight (16 and 21 kg/mol), brush grafting density (0.17, 0.33 and 0.55 chains/nm2) and PMMA matrix molecular weight (4 – 50 kg/mol). The diffusion of nanoparticles is slowed down relative to the Stokes-Einstein relation prediction, suggesting that the interpenetration between the brush and matrix influences nanoparticle mobility. Self-consistent field theory is performed to predict the structure of brush and matrix in the vicinity of the particle
to quantify the effect of brush-matrix interpenetration on NP diffusion. These experiments demonstrate that the structure of the brush could affect nanoparticle center of mass diffusion and the brush-nanoparticle interpenetration should be considered.

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DYNAMICS IN POLYMER NANOCOMPOSITES
CONTAINING FIXED AND MOBILE NANOPARTICLES

Chia-Chun Lin

A DISSERTATION
in
Materials Science and Engineering
Presented to the Faculties of the University of Pennsylvania
in Partial Fulfillment of the Requirements for the Degree of Doctor of Philosophy
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It has been five years since I started this journey at Penn. I still remember how excited I was when I just arrived the U.S. because I, as an international student from Taiwan, was able to experience this entirely new environment and take new challenges every day. It is hard to imagine how fast the time flies, and how excited I am when I completed this thesis research. This work was performed at the Laboratory for Research on the Structure of Matter (LRSM), at the University of Pennsylvania, and funded by the National Science Foundation (NSF) and the Engineering and Physical Sciences Research Council (EPSRC) - Materials World Network (DMR-0908449 and EP/5065373/1), the NSF/MRSEC (DMR 11-20901), Polymer Programs (DMR 09-07493), and Dupont Central Research and Development.

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mentoring me while at Penn. He is always willing to teach me science when I have questions, give me precious suggestions when I get stuck, motivate me while I face challenge, and patiently help me on making progress especially regarding to elastic recoil detection (ERD), a critical technique that I heavily rely on to complete my work. In addition, he has improved my writing and presentation skills, which are critical in effective communication that can be used for life. Besides the scientific knowledge that I have gained from him, more importantly, I have learned the right attitude toward conducting a research, leading a group, and even sharing life with family members. All these are truly inspiring and this is one of the most precious experiences I ever had. I appreciate all the positive enlightenment he has provided. Thank you.

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Chia-Chun Lin
Philadelphia, PA
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spheres.
CHAPTER 1. INTRODUCTION

A polymer is a macromolecule that is composed of a large number of repeated units, or monomers. Polymer science has made a significant impact on the way we live, and until now in the 21st century, polymers continue to play an important role in technology developments, from commodity use such as films and packaging to high technology applications such as photovoltaic solar cells and reconfigurable materials. The unique viscoelastic properties that polymers possess allow for low cost processability into various shapes and sizes. In addition, various functional groups and chemical structures can be routinely synthesized at a large scale, thus providing the ability for mass production in industries.

Understanding polymer dynamics is critical in optimizing the condition used to process polymers. In this thesis, we first focus on polymer diffusion in polymer nanocomposites, and a good place to start is to understand the theoretical background of polymer dynamics. Polymer diffusion in an entangled matrix can be controlled by two
relaxation mechanisms, i.e., reptation\textsuperscript{1,2} and/or constraint release mechanism\textsuperscript{3,4}. Doi and Edwards developed a tube model of entangled polymer network describing that a polymer chain is confined in a tube-like region imposed by surrounding chains, where the lateral motion of the confined chain is restricted by the topological constraints. Reptation theory was then introduced by de Gennes\textsuperscript{1} in 1971 where polymer chains move predominantly along the tube. The time for the restricted chain to diffuse out of the original tube of the average length \( <L> \) is the reptation time, \( \tau_{\text{rep}} \). Theoretically, the reptation time is proportional to the cube of the molar mass (\( M \)) of the diffusing polymer while experimentally, the scaling exponent is greater than 3, i.e., \( \tau_{\text{rep}} \sim M^{3.4} \).

The stronger dependence of the reptation time on \( M \) is possibly due to tube length fluctuation. The reptation model also predicts the diffusion coefficients (\( D \)) of the confined chain that moves a distance of its own size in the reptation time as:

\[
D \sim M^{-2}
\]  

(1.1)
given that the constraints defining the tube are relatively immobile on the time scale of \( \tau_{\text{rep}} \). Using forward recoil spectrometry, Mills et al.\textsuperscript{5} measured tracer diffusion coefficients of deuterated polystyrene in entangled polystyrene matrix, and reported \( M^{-2} \) dependence in agreement with reptation model.

For matrix molecular weight (\( P \)) less than a characteristic molecular weight (\( P^* \)) and greater than entanglement molecular weight (\( M_e \)), constraint-release mechanism takes place in addition to reptation mechanism. Reptation and constraint-release are
independent mechanisms, and thus the diffusion coefficient of a given chain is the sum of two contributions:

\[ D^* = D_{\text{rep}}(M) + D_{\text{cr}}(M, P) \approx \frac{R^2}{\tau_{\text{rep}}(P)} + \frac{R^2}{\tau_{\text{tube}}} \]  

(1.2)

where \( D_{\text{rep}} \) is the diffusion coefficient of \( M \) chain contributed by reptation mechanism, \( D_{\text{cr}} \) is the contribution from constraint-release mechanism, \( R \) is chain size, \( \tau_{\text{rep}} \) is the reptation time of \( P \)-mer and \( \tau_{\text{tube}} \) is the Rouse relaxation time of the confining tube. The faster of the two types of mechanisms controls the diffusion of \( P \)-mer. Namely, reptation dominates for shorter \( P \)-mers since \( \tau_{\text{rep}} < \tau_{\text{tube}} \) whereas constraint-release mechanism dominates for longer \( P \)-mers where \( \tau_{\text{rep}} > \tau_{\text{tube}} \).

1.1 Polymer Nanocomposites

Introduced in 1990s, nanoparticles are combined with polymers to build polymer nanocomposites (PNC) that has made tremendous impact in science and technology. As opposed to traditional composites, the fillers are nanosized with dimensions below 100 nm and therefore the surface area dramatically increases as the nanofiller size decreases at a given volume fraction. Thus the addition of a small volume of nanofillers can produce great amount of interfacial area between polymer matrix and nanofillers, effectively impacting polymer properties without compromising the processability, light weight and optical transparency inherent to polymers.\(^6\)\(^-\)\(^8\) For example, Ramanathan et al.\(^9\) reported a significant shift in glass transition temperature (\( T_g \)) of \( \sim 30^\circ \text{C} \) upon adding only 0.05 w\% of functionalized graphene sheet into poly(methyl methacrylate) matrix.
In addition to achieving desired properties more efficiently, the addition of nanofillers to polymers also impart unique properties that traditional fillers are not able to achieve such as mechanical strength, flame resistance, thermal, optical and electrical properties. Specifically, tunable optical property is observed upon adding gold nanorods into polymers, and high-efficiency polymer-based photovoltaic can be prepared or created by adding TiO$_2$ nanoparticles. Furthermore, the addition of nanofiller also changes polymer viscosity, a key parameter that influences molecular transport and flow behavior. Therefore, polymer dynamics are typically impacted upon incorporating functional nanoparticles into polymer, understanding the dynamics in PNCs would provide insights into important issues such as optimizing processing conditions and manipulating assembly kinetics, and various applications including coatings, self-healing materials and membranes.

1.2 Dissertation Outline

The objective of this dissertation is to investigate the effect of confinement on polymer dynamics. We first focus on the effect of “fixed” obstacles in polymer nanocomposites. Namely, nanofillers are immobile on the time scale of polymer diffusion. Next we focus on nanoparticle dynamics in polymer melts, and finally we take the mobility of nanoparticles into account to investigate the effect of these “mobile” nanoparticles that are also diffusing on the same time scale of polymer diffusion.

In Chapter 2, recent studies of dynamics regarding either polymers or nanoparticles in polymer nanocomposites are introduced, including the effect of polymer-
nanoparticle interactions, polymer brush, and shape on center-of-mass polymer diffusion. In addition, polymer local dynamics and effects of nanoparticles on different length scales and confinement, i.e., nanoparticle vs. cylindrical confinements, are discussed. Finally, studies on dynamics of bare as well as hairy nanoparticles in polymer melts are explored, and deviation from the Stokes-Einstein relation is discussed. Chapter 3 presents studies of the effect of polymer-NP interactions on macromolecular diffusion using deuterated poly(methyl methacrylate), or dPMMA, as the tracer, and OH-capped Si NPs as the impenetrable and immobile nanofiller that has attractive interactions with PMMA. The result is compared with previously studied athermal systems. Chapter 4 explores the effect of polystyrene (PS)-grafted chained NPs (cNP) on the tracer diffusion of deuterated PS (dPS) in a homopolymer/cNP matrix. cNPs are technologically important because they mimic the fractal-like morphology of carbon black utilized in toughened polymers such as styrene-butadiene rubber (SBR). Chapter 5 addresses the question of how to take NP mobility into account when polymer diffusion is probed. Namely, dPS diffusion is measured in PNCs having mobile nanorods, and the results are compared with the fixed nanorod case. Chapter 6 looks into diffusion of PMMA-grafted iron oxide NPs in PMMA melts. The effects of brush molecular weight, brush grafting density and matrix molecular weight on NP diffusion are investigated. Finally, Chapter 7 summarizes the work in this thesis, and future work as well as outlook are suggested.
CHAPTER 2. DYNAMICS IN POLYMER NANOCOMPOSITES

In this Chapter, recent theoretical and experimental studies of polymer dynamics and NP dynamics in PNCs are reviewed. Polymer dynamics are first investigated by reviewing studies of the slowest relaxation mode represented by center of mass diffusion, to fast relaxation modes represented by segmental relaxations, in various confinements including PNCs and nanopores. Polymer dynamics are influenced by the polymer-NP interactions, NP shape, grafted polymer brushes and the pore size, and details will be discussed. In the second section of this chapter, NP dynamics are investigated by focusing on the NP diffusion in polymer melts compared with the classic Stokes-Einstein (SE) relation in a continuum medium. Enhanced NP diffusion relative to the SE prediction reported by experimental and simulation studies is reviewed. Furthermore, dynamics of polymer-grafted NPs are discussed where the brush relaxations and structures are correlated with NP dynamics. This review provides a clear picture of the
current studies on dynamics in PNCs, and a better understanding about the background of this thesis.

2.1 Effect of Spherical Nanofillers on Polymer Diffusion

Center-of-mass polymer (COM) diffusion is investigated in PNCs containing hard and soft spherical NPs are discussed. Namely, hard NPs functionalized with short ligands that can have an athermal interaction with the polymer matrix and tracers as well as an attractive interaction will be explored. By grafting a polymer brush to the hard NP, soft NPs are formed and their diffusion into homopolymer is described.

2.1.1 Polymer Diffusion through PNCs with Hard NPs with Athermal Interactions

To study the effect of geometric confinements on polymer center of mass diffusion, enthalpic interactions between nanoparticles and host polymer should be minimized. Semicrystalline polymers provide a non-interacting and complex environment containing amorphous region where polymer can diffuse and crystalline regions that confine the motion of the polymer. Using dynamic secondary ion mass spectroscopy (DSIMS), Segalman et al.\textsuperscript{37} investigated the diffusion of deuterated polystyrene in precrystallized isotactic polystyrene matrices, and reported that the tracer diffusion decreases with increasing molecular weight ($M$), i.e., $D \sim M^{-1}$. This $M^{-1}$ dependence of $D$ is consistent with the scaling suggested by Entropic Barrier Model (EBM). EBM is proposed by Muthukumar and Baumgartner,\textsuperscript{38, 39} and they modeled the diffusion of a self-avoiding polymer chain in arrays of cubic cavities connected by short
bottlenecks. The diffusion coefficient of the probed chain is determined based on how monomers of the probe chain are partitioned in the cavity and the connected bottleneck, and the scaling of the diffusion coefficient of the probed chain finally comes down to $D \sim M^1$. EBM is used to explain the slowdown of tracer diffusion in Segalman’s study. The entropic barrier in the context of polymer dynamics is the entropic difference that a polymer chain has to overcome when it diffuses from a region of large volume where the chain has more accessible configuration, or higher entropy, to a region of smaller volume where the chain has less entropy. Namely, these randomly distributed lamellae (crystalline region) serve as obstacles that form bottlenecks (space between crystalline regions) where dPS chains have to explore as they diffuse in the matrices (amorphous region). However, because spherulite size and dispersity are hard to control and the space available for diffusion is ill-defined in semicrystalline polymers, a well-defined model system is needed to rigorously test the applicability of the entropic barrier model for describing polymer diffusion through a matrix with obstacles.

Polymer nanocomposites are an ideal platform for testing diffusion in confined systems because the size and distribution of NPs can be controlled and thus the space available for the diffusion of the polymer chain can be well-defined. In addition, the surface of nanoparticles can be functionalized using short ligands so that the nanoparticle-polymer interaction is nearly athermal while maintains a sharp nanoparticle-polymer interface. Namely, “hard” nanoparticles whose surfaces are functionalized with short ligands instead of polymer brushes are expected to be compatible with the host polymer. Gam et al.\textsuperscript{40,41} investigated the diffusion of dPS ($M = 49, 168$ and $532$ kg/mol)
in PS nanocomposites containing non-interacting nanoparticles using elastic recoil detection (ERD). In these systems, silica nanoparticles with narrowly-distributed particle diameters \((d = 13\) and \(29\text{nm}\) with polydispersity, \(\rho = 1.39\) and \(1.12\), respectively) were prepared with a coupling agent, phenyltrimethoxysilane (PhTMS). The surface of these phenyl-capped silica nanoparticles are chemically identical to the host polymer, polystyrene, resulting in a non-interacting environment for polymer and nanoparticles. By rapid removing the solvent, the NPs are well-dispersed in polystyrene up to volume fraction, \(\phi_{NP} = 0.5\), suggesting that the polymer surface groups are able to minimize the repulsive interactions between remaining hydroxyl groups on silica and polystyrene. These studies show that the diffusion coefficient of dPS decreases significantly in the presence of nanoparticles (e.g., by 80 % at \(\phi_{NP} = 0.5\)). Furthermore, the normalized diffusion coefficients of dPS, \(D/D_0\), collapse onto a curve when plotted against a confinement parameter, \(ID/2R_g\), where \(R_g\) is the radius of gyration of the tracer polymer (dPS) and \(ID\) is interparticle distance defined by:

\[
ID = d_n \left\{ \left( \frac{2}{\pi \phi_{NP}} \right)^{1/2} \left[ \exp(ln\rho)^2 \right] - 1 \right\} \tag{2.1}
\]

where \(d_n\) is the number average NP diameter, \(\phi_{NP}\) is the volume fraction of the NPs in the PNC, and \(\rho\) is the NP diameter polydispersity, suggesting that the confinement parameter is able to capture the effect of nanoparticle dimension, nanoparticle size distribution and tracer molecular weights. Moreover, the scaling behavior of the tracer diffusion coefficient is in good agreement with the entropic barrier model which accounts for the loss in chain entropy caused by bottlenecks between nanoparticles. The agreement
suggests that the EBM is able to capture the slowdown in dPS diffusion due to confinements imposed by nanoparticles.

### 2.1.2 Polymer Diffusion through PNCs with Hard NPs with Attractive Interactions

The enthalpic interaction could be important in terms of improving nanoparticle dispersion in the host polymer, especially when the interactions between nanoparticles and polymer are attractive. This enthalpic contribution could further affect polymer dynamics compared to the athermal case. For example, Zheng et al.\textsuperscript{42} reported a long range effect on polymer diffusion as a function of distance from an attractive planar surface, and the diffusion of the probed chain is an order of magnitude slower than that in the bulk. Hu et al.\textsuperscript{43} also reported a slowdown in the diffusion of deuterated poly (methyl methacrylate) (dPMMA) by a factor of 3 in PMMA/clay nanocomposites at clay loading of ~ 5 vol\%. Simulation studies\textsuperscript{44} using molecular dynamics showed slower polymer diffusion in the presence of attractive nanoparticle-polymer interactions. Furthermore, using forward recoil elastic spectrometry, Lin et al.\textsuperscript{45} measured the center of mass diffusion of dPMMA, in PMMA matrices containing hydroxyl – terminated silica nanoparticles where attractive nanoparticle-polymer interactions are present. The diffusion of dPMMA is slowed down as a function of nanoparticle loadings and data collapse onto a curve when normalized diffusion coefficients ($D/D_0$) are plotted versus confinement parameters ($ID/2R_g$). Interestingly, when compared with the studies\textsuperscript{40, 41} of dPS diffusion into PS matrices containing phenyl-capped silica NP, i.e., athermal nanoparticle-polymer interactionst, the scaling of $D/D_0$ vs. $ID/2R_g$ is very similar in both
system, suggesting that attractive nanoparticle-polymer interactions are insufficiently alter COM polymer diffusion.

Theoretically, Meth et al.\textsuperscript{46} developed an analytical model to describe the slowdown of polymer diffusion in the presence of nanoparticles by modeling polymer chains as spheres diffusing through cylindrical pores and found that the reduction in diffusion can be attributed to excluded volume. The model is able to capture the experimental results of Gam et al.\textsuperscript{40, 41} and Lin et al.\textsuperscript{45} at low loadings for $ID/2R_g > 2$ where polymers can still maintain their Gaussian conformations whereas at high loadings, the model overestimates the experimental data, suggesting that other mechanisms are responsible for the reduction of polymer diffusion in highly crowded environments, such as altered chain conformations and entanglement densities. The local dynamics that these fundamental terms influence will be discussed in later chapters (Chapter 2.3).

2.1.3 Polymer Diffusion through PNCs with Soft Spherical Nanoparticles

To control NP/matrix interactions, nanoparticle surfaces can be modified by polymer brushes. As a result, the dispersion of NPs can be enhanced in polymer nanocomposites because the repulsive force between nanoparticle surfaces and the host polymer are reduced. In addition, various NP dispersion states can be achieved by tuning brush graft densities and the ratio of degree of polymerization between brush and the host polymer,\textsuperscript{47-49} and thus unique properties can be imparted. For example, optical absorption can be controlled by tuning NP-NP spacing,\textsuperscript{15, 16} and enhanced mechanical properties can be achieved by tuning nanoparticle morphologies in the matrix.\textsuperscript{50, 51} In terms of center of
mass dynamics, the presence of the brush provides a distinct particle-polymer interface because of the interpenetration between brush and host polymer, and the boundary between “hard” and “soft” nanoparticles becomes complicated by the interpenetration of the matrix chains and the polymer brush. To understand the effect of this tunable brush/matrix interface on center of mass polymer diffusion, the ratio of the degree of polymerization between grafted brush and polymer matrix can be varied to control the transition from hard NP to soft NP. Choi et al.\textsuperscript{52} investigated the diffusion of dPS in the presence of soft nanoparticles and compared the result with the hard nanoparticle case. Silica nanoparticles grafted with polystyrene brush (brush molecular weight, $N = 87$ kg/mol) were dispersed in PS matrix ($P = 160$ kg/mol) and the diffusion of dPS (23 to 532 kg/mol) was measured using ERD. The dPS penetration into brush varies depending on ratio between the molecular weights of dPS and the brush. Namely, larger tracers penetrate less deeply into brush than smaller tracers and the interface is sharper due to steric exclusion, and an effective particle diameter can be defined. Using self-consistent filed theory (SCFT) coupled with small-angle neutron scattering (SANS), effective particle diameters were quantified and thus effective interparticle distance can be determined using a diameter given by the hard NP plus dry brush.

The result showed that for larger dPS, interparticle distance is decreased because the dPS chains are partially excluded from the brush, whereas smaller dPS chains have more accessible interparticle spacing leading to smaller effective particle diameters. When normalized diffusion coefficients, $D/D_0$, are plotted against effective confinement parameters, both hard and soft NP systems show similar scaling behaviors, suggesting
that universal scaling of polymer diffusion also extend to soft nanoparticles. In addition, the bulk diffusion coefficients are recovered ($D/D_0 = 1$) only when nanoparticles are far apart, i.e., $ID/2R_g > 20$, indicating a long-range effect on polymer diffusion. This remarkable long-range effect was also observed in a planar surface system\textsuperscript{42} where the diffusion of dPS is slower than that in the bulk up to a distance of $10R_g$ from the surface, and the result is explained by a change in local structure in the vicinity of the surface due to attractive force, and the effect propagates to a greater distance. However, this long-range effect is still not well-understood, and models are required to accurately explain this observation.

### 2.2. Polymer Diffusion through PNCs with Anisotropic Nanofillers

In this section we focus on the geometric factors that influence polymer diffusion in nanocomposites, specifically, anisotropically-shaped nanotube, nanorods, and chained nanoparticles.

#### 2.2.1 Minimum in Diffusion Coefficient in Polymer/Carbon Nanotube Systems

In contrast to polymer/spherical NPs systems where a monotonic decrease in polymer diffusion is observed, polymer diffusion in the presence of carbon nanotubes, initially slows down, reaches a minimum, and recovers with increasing carbon nanotube loading. For example, using ERD, Mu et al.\textsuperscript{53} investigated tracer (dPS) diffusion in PS matrices containing single-walled carbon nanotubes (SWCNT, diameter $\sim 9.6$ nm with
aspect ratio \( \sim 35 \) reported that tracer diffusion decreases initially with increasing SWCNT concentrations, and then recovers beyond a critical concentration, \( \phi_{\text{crit}} \sim 0.4 \) vol\% in a PS (480 kg/mol) matrix. The critical concentration is consistent with a dynamical percolation threshold measured using rheology, indicating that the diffusion minimum correlated with the formation of a percolated carbon nanotube network. A phenomenological trap model was proposed and simulated where polymer diffusion is anisotropic in the vicinity of nanoparticles. Namely, polymer diffusion is faster parallel to the CNT than perpendicular to the CNT, and thus beyond the critical concentration, polymer chains are able to diffuse fast along the CNT network resulting in the diffusion recovery. A further investigation by the same research group using multi-walled carbon nanotube (MWCNT) suggested that this diffusion minimum is a function of relative size between the tracer polymer chain and the nanofiller, i.e., the diffusing chain has to be larger than the carbon nanotube diameter to observe a minimum diffusion coefficient. Further studies of this geometric effect, i.e. relative size between tracer dimension and nanorod length, are introduced in the Chapter 3.

### 2.2.2 Geometric Criteria for Polymer Diffusion in PNCs

The studies of polymer/CNT systems indicate that a minimum in diffusion requires that (1) the size of the tracer chain (\( 2R_g \)) has to be larger than the nanorod diameter, and (2) the CNTs form a percolative network. However, the effect of the length \( L \) of the nanorod was not investigated because the CNTs’ are semi-infinite. Choi et al.\(^5\) investigated both geometric factors and systematically studied anisotropic polymer diffusion in the presence of nanorods by varying tracer molecular weight \( M = 168 \) –
3400 kg/mol), nanorod diameter \((d = 4.6 \text{ nm})\) and nanorod length (NR-short: \(L = 43.1 \text{ nm}\), and NR-long: \(L = 371 \text{ nm}\)). They observed non-monotonic diffusive behavior when the tracer size was larger than the nanorod diameter \((2R_g > d)\), but less than the nanorod length. On the contrary, monotonic diffusive behavior was observed when the tracer size was either larger or smaller than both the nanorod diameter and length.

In addition, at low NR loadings \((\varphi < \varphi_{\text{min}} = 0.04\) where \(\varphi_{\text{min}}\) is the NR concentration where diffusion minimum is observed), the scaling behavior for both short and long NRs follows \(D \sim M^{\nu}\) where \(\nu = 2\), in agreement with Doi-Edwards model of chain reptation,\(^{56}\) suggesting that chain conformation and local friction felt by the tracer chain are not perturbed by the NRs. At high NR-short loadings above \(\varphi_{\text{min}}\) \((\varphi = 0.1 > \varphi_{\text{min}})\), with dPS of \(M (168 – 3400 \text{ kg/mol})\) where \(L < 2R_g\), the exponent slightly increases from 2 to 2.3, suggesting that tracer diffusion is not influenced significantly by NR geometry. The diffusion mechanism is similar to the isotropic case where tracers see NRs as isotropic obstacles. The slightly greater exponent may be explained by entropic barriers imposed by stronger confinement (smaller NR network mesh size) compared to the NR-long systems. In contrast, for the PS/NR-long system, \(D \sim M^{1.1}\) scaling behavior is found. In this case, \(L > 2R_g\), indicating that anisotropic obstacles are felt by tracer chains. The much smaller \(\nu\) is attributed to monomer-NR friction as NRs are able to thread through polymer chains, and an expanded chain conformation which was recently observed suggested by Tung et al.\(^{57}\) for PS in the presence of SWCNT.
2.2.3 Polymer Dynamics in the Presence of Chained Nanoparticles

We have introduced the center of mass dynamics of polymer chains in the presence of isolated individual nanoparticles having well-defined dimensions, i.e., spherical and high aspect ratio cylindrical nanoparticles with a well-defined diameter and length. In this chapter, we focus on the dynamics in the presence of chained-nanoparticles (cNP) that mimic the widely used carbon black aggregates. Moreover, polymer diffusion in the presence of these stringy nanoparticles provide insight connecting dynamical behaviors previously reported in spherical NP\textsuperscript{40,41,45} as well as cylindrical NP systems.\textsuperscript{53,54,58}

Lin et al.\textsuperscript{59} probed center of mass tracer (dPS) diffusion in PS nanocomposites containing PS-grafted ($N = 132$ kg/mol, $\sigma = 0.19$ chains/nm$^2$), string-like chained-nanoparticles (cNP) using ERD. When the molecular weight of dPS is very large (1866 kg/mol), $D$ decreases monotonically with increasing loading, consistent with the results for the spherical NP systems. In contrast, when the molecular weights of dPS are small (49, 168 and 532 kg/mol), $D$ decreases with increasing NP core volume fraction ($\phi_{\text{NP}}$), reaches a minimum at $\phi_{\text{NP}} = 0.0025$, and recovers again as $\phi_{\text{NP}} > 0.0025$, which is consistent with the observation in the carbon nanotube systems and the nanorod systems. The importance of relative size between the tracer ($2R_g$) and cNP ($d$ and $L$) is evident in how these stringy NPs impose anisotropic polymer diffusion. In addition, the brush could also affect tracer diffusion because the dPS can penetrate into the brush region where the tracer is comparable (or lower) in molecular weight than the brush. For diffusion in a
heterogeneous two-phase medium, the effective tracer diffusion coefficient \((D_e)\) that captures both the diffusion in the brush and matrix regions are calculated using:

\[
\frac{D_1 - D_e}{D_1 + 2D_e} \phi_1 + \frac{D_0 - D_e}{D_0 + 2D_e} \phi_0 = 0
\]  

(2.2)

where \(D_0\) is the diffusion coefficient of dPS in the pure PS matrix (270 kg/mol), \(D_1\) is the diffusion coefficient of dPS in the pure brush (132 kg/mol), and \(\phi_0\) and \(\phi_1\) are the volume fractions of the PS matrix and PS brush regions, respectively. Thus, \(D\) can be normalized using \(D_0\) as done in prior systems, or \(D_e\), which accounts for the heterogeneity of the matrix. Namely, \(D/D_0\) does not account for the effect due to the brush, whereas \(D/D_e\) distinguishes between diffusion in the brush and matrix regions and incorporates the effect of polymer brush on tracer diffusion. When normalized diffusion coefficients are plotted against cNP loading, a sharp transition from a diffusion minimum to a monotonic decrease is observed for \(D/D_0\), whereas a gradual transition is observed for \(D/D_e\). The study demonstrates the importance of considering how the polymer brush influences polymer diffusion in heterogeneous matrices.

### 2.3. Local Dynamics

In the reptation model,\(^1\) the motion of an entangled chain is confined by surrounding chains which form a tube-like topological constraint. The entangled chain diffuses along the tube and its diffusion coefficient \((D_{\text{rep}})\) is determined as follows:

\[
D_{\text{rep}} \approx \frac{R^2 k_B T N_e}{\zeta b^2 N^3}
\]  

(2.3)
where $R$ is the size of the chain, $k_B$ is the Boltzmann constant, $T$ is temperature (K), $N_e$ is the number of monomers in an entanglement strand, $\zeta$ is monomeric friction coefficient, $b$ is monomer length, and $N$ is the number of monomers in a chain. A dimensionless prefactor is not shown in order to focus on the scaling behavior. $R$ determines the chain conformation, $N_e$ represents the distance between entanglements and thus determines tube diameter ($d_t$), and $\zeta$ determines the viscosity ($\eta$) of the melt. Therefore, at a given thermal energy, $R$, $N_e$, and $\zeta$ govern the diffusion of entangled chain in a melt.

### 2.3.1 The Polymer Chain Conformation in the PNCs

Upon adding nanoparticles into a polymer matrix, the chain conformation is altered depending on filler size and concentration. For PNCs containing spherical nanofillers, the radius of gyration of the chain is increased when $R_g$ (at $\phi_{NP} = 0$) is greater than the NP size, i.e., $2R_{g, \phi_{NP} = 0} > d$, whereas $R_g$ is not significantly affected when $2R_{g, \phi_{NP} = 0} < d$. For example, using SANS, Nakatani et al.\textsuperscript{60} investigated polydimethylsiloxane (PDMS) chain dimensions in the presence of trimethylsilyl-treated polysilicate and compared the result with Monte Carlo calculations. They reported that $R_g$ of larger chains relative to the filler is increased by 50% upon adding 20 w% of the polysilicate filler which has dimensions $\sim$ 2 nm. However, for PDMS chains that have similar dimensions as the filler, $R_g$ is slightly decreased with increasing polysilicate loadings. In addition, a similar increase in $R_g$ is observed in polystyrene matrices containing cross-linked PS NPs where $R_g$ of dPS chains is increased by up to 20% when 10 vol% of NPs ($d = 7$ nm) are added.\textsuperscript{61} Conversely, when phase separation occurs in the matrices, polymer chains are smaller than the aggregates and thus the effect of chain swelling is not observable.\textsuperscript{62-64}
Simulation studies also revealed an increased $R_g$ in the presence of small NPs (i.e., $d < 2R_g, \phi_{NP} = 0$) in various systems, and unaffected melt conformation when the NP sizes are comparable to the chain $R_g$. Furthermore, in polystyrene/carbon nanotube systems, Tung et al.\textsuperscript{57} reported a 30% increase of $R_g$ upon adding 10 w\% of single-walled carbon nanotubes ($d_{SWCNT}/2R_g \sim 0.4$), whereas a slight decrease in chain dimension occurs when 2 w\% of multi-walled carbon nanotubes are added ($d_{SWCNT}/2R_g \sim 1$).

On the contrary, in a Si/PS system, Crawford et al.\textsuperscript{68} reported that PS chain dimensions are not influenced by adding Si NP ($d = 13$nm) up to $\phi_{NP} = 32.7$ vol\%, regardless of the chain size relative to the NP diameter. Using Monte Carlo calculations, Vacatello\textsuperscript{69} also reported no change in chain dimensions when $2R_g$ is ~2.5x greater than the filler diameter at $\phi_{NP} = 20$ vol\%. Critical length scales that influence chain conformation still remains an open question, and other dimensions should be considered, e.g., particle size relative to tube diameter.

2.3.2 The Segmental Relaxation Time in PNCs

The monomeric friction coefficient ($\zeta$) is directly proportional to the shortest Rouse relaxation time ($\tau_0$) that is experimentally measurable. The time scale of the segmental relaxation is typically on the order of nanosecond, and thus neutron scattering and NMR spectroscopy techniques\textsuperscript{70} are usually adopted to observe chain motion. For systems with weak or neutral interactions between polymer and nanoparticles, experimental studies\textsuperscript{63, 71-73} showed that segmental relaxations are unaffected. For example, Schneider et al.\textsuperscript{71} investigated segmental dynamics in poly(ethylene-propylene)
(PEP) matrices containing silica NP ($d = 17$nm) coated with short hydrocarbons using neutron spin echo spectroscopy (NSE), and reported that the basic Rouse relaxation rate remains unaffected with increasing NP loadings. Conversely, simulation studies suggest enhanced segmental dynamics when NPs are added into polymer matrix, and Kalathi et al. pointed out the importance of NP size relative to entanglement mesh size using molecular dynamics simulations. Namely, in a PNC where NPs are smaller than the mesh size, NPs reduce the monomer friction and thus enhance segmental relaxation whereas for NPs larger than the mesh size, segmental relaxation times are not affected significantly even at high NP loadings, indicating that NP size is an important parameter in determining segmental dynamics in athermal systems, and possibly explains the divergent results from experiments.

For systems with favorable polymer-NP interactions, bound layers are reported in the vicinity of the nanoparticle, suggesting that attractive interactions can suppress the translational diffusion at the NP surface. On a shorter length scale, however, divergent segmental behaviors of adsorbed chains are observed, and there are primarily 3 observations: (i) glassy shell, (ii) slowed down segmental mobility and (iii) unaffected segmental motion. The glassy shell is a layer of highly immobilized segments attached on the surface of nanoparticles due to attractive interactions. Berriot et al. reported an immobilized polymer layer on colloidal silica ($d = 60$ nm) in a poly (ethyl acrylate) nanocomposite, and the thickness of this immobilized layer decreases with increasing temperature. In addition, studies suggest that the thickness of the immobilized layer increases with increasing nanoparticle size, or decreasing curvature. For example, Harton
et al.\textsuperscript{79} reported a 1-nm thick bound layer near a 15-nm diameter silica nanoparticles compared to a 5-nm thick bound layer at flat silica surfaces.

Estimations of the thickness of the glassy shell are based on the assumption that polymers in the shell are completely immobilized compared to bulk polymers whereas simulation and experimental studies of local dynamics found that chain mobility in the vicinity of the nanoparticles shows slowed dynamics relative to bulk polymer.\textsuperscript{76, 82-87} For example, using broadband dielectric spectroscopy (BDS) and SAXS, Holt et al.\textsuperscript{83} investigated segmental dynamics near the nanoparticle surface in poly(2-vinylpyridine)/silica nanocomposites, and showed that the interfacial region (4-6 nm) exhibits a gradient in segmental mobility, i.e., slower segmental relaxation near the NP surface that recovers to its bulk value near the interfacial region. In contrast, unaffected segmental relaxations are reported by Bogoslovov et al.\textsuperscript{88} and Glomann et al.\textsuperscript{72} by means of dielectric relaxation measurements and neutron spin echo spectroscopy, respectively. These divergent results raise the question about how to interpret data from different timescales and length scales probed by various techniques.\textsuperscript{89} Moreover, whether the relative size between the polymer entanglement and nanoparticle is an important parameter affecting local dynamics in PNCs remains an open question. Future studies are needed to address these issues.

2.3.3 The Entanglement Density in PNCs

The entanglement degree of polymerization, $N_e$, is a microscopic quantity that is usually calculated from the measured plateau modulus of a pure melt. However, in PNCs,
traditional viscoelastic measurements are confounded by the simultaneous dynamics due to polymer and NP relaxation. Neutron scattering and NMR techniques can directly measure such local dynamics using deuterium/proton labeling. Specifically, in a weakly interacting system, using neutron spin-echo spectroscopy (NSE), Schneider et al.\textsuperscript{71} reported that PEP chains undergo significant disentanglement in the presence of short hydrocarbon-coated silica NP ($d = 17$ nm) at high loadings, i.e., increased $N_e$. Simulation studies also showed that $N_e$ increases at high nanoparticle loadings,\textsuperscript{74, 90, 91} and that the nanoparticle size relative to tube diameter influences $N_e$. For example, Kalathi et al.\textsuperscript{76} investigated segmental dynamics using molecular dynamics simulation, and reported that an increase in $N_e$ is more pronounced in the presence of NPs smaller than tube diameter than that of NPs larger than the tube diameter. Namely, small NPs act akin to plasticizers that increase $N_e$ by 40% more than the value obtained with the addition of larger NPs, which leads to enhanced segmental relaxation which is discussed in Chapter 2.3.2. In contrast, a decrease in $N_e$ is reported in the presence of a neutral single-wall carbon nanotube\textsuperscript{92} and nanorods,\textsuperscript{93} and is explained by direct contact between fillers and polymers that increases entanglements when the nanorod diameter is less than tube diameter. Furthermore, $N_e$ decreases with favorable polymer – particle interactions\textsuperscript{94} because NPs are able to induce chain entanglements at their surfaces.

### 2.4. Cylindrical Nanoconfinement

Porous media coupled with polymeric materials have drawn tremendous interest because of their many technological and fundamental applications such as lubrication, filtration membrane and DNA mapping and separation, and understand transportation in
cells. When polymer chains are confined within these nanoscopic pores, polymer dynamics are perturbed and as a result mechanical relaxation and physical aging of polymer changes. Therefore, understanding how polymer dynamics are influenced by nanoconfinement is essential in the precise control of PNC properties.

Cylindrical confinement templates, such as anodic aluminum oxide (AAO) membranes, have received growing interest in recent years. Cylindrical pores provide 2-D channels where polymer chains are able to relax perpendicular and parallel to the pore wall. Thus, the system is simplified and the effect of nanoconfinements on polymer dynamics can be understood. Furthermore, with advances in chemistry, pore diameter and inter-pore distance can be well-controlled, so that the geometric parameters can be systematically tuned. Therefore, nanoconfinements, especially AAO membranes, are a model system to study polymer dynamics in 2-D nanoconfinement.

In this chapter, local dynamics under cylindrical confinements will be introduced, and the connection between local dynamics and polymer center of mass diffusion will be discussed.

**2.4.1 Local segmental dynamics in 2-D confinements**

Segmental dynamics in nanoconfinement have been probed using different techniques, such as inelastic neutron scattering, nuclear magnetic resonance (NMR), dielectric spectroscopy and calorimetry across various time and length scales. Here we focus on the effect of nanoconfinement on chain conformation, segmental relaxation time
and entanglement density because these three parameters can influence the reptation of polymers as noted in Eq. 5.

The conformation of polymer chains confined inside nanoscopic pores has been investigated using SANS. For example, Noirez et al.\textsuperscript{97} reported that the conformation of PS (38 to 310 kg/mol) does not change when confined in AAO templates having pore sizes comparable to the size of PS ($R_g$). Furthermore, when the pore size (15 nm diameter) is less than the PS chain dimension ($2R_g = 45$ nm), Shin et al.\textsuperscript{98} revealed that such strong confinement does not significantly influence chain conformation, consistent with theoretical and simulation studies.\textsuperscript{99,100}

Local segmental dynamics at short time ($t < 1$ ns) are found to be relatively unaffected with respect to the bulk behavior, while at intermediate times (Rouse time scale), dynamics are slowed down in nanoporous confinements.\textsuperscript{101-103} For example, using NSE, Martin et al.\textsuperscript{102} investigated dynamics of PEO chains confined in AAO templates, and revealed a slowdown in Rouse dynamics, consistent with studies using NMR techniques.\textsuperscript{103} The results also suggest that the slowdown at intermediate times is not due to an increase in monomeric friction because of the invariance of local segmental dynamics. The adsorption of PEO chains onto the AAO surface might be an possible explanation. On the other hand, using field-cycling NMR relaxometry, studies suggest that slowdown of rotational polymer segment dynamics could take place across confinement ranging from nano to micrometers.\textsuperscript{104,105} This observation is called the “corset effect” where the excluded volume of the polymer chain, low compressibility of
polymer melts, and impenetrability of the pore walls limit the lateral motion of polymer chains.\textsuperscript{106}

Even when $M < M_c$, the corset effect also revealed that chains could exhibit reptation dynamics in confinements as opposed to Rouse dynamics in bulk. Namely, unentangled chains show a crossover from Rouse dynamics to cooperative reptation behaviors as the capacity of free volume is reduced with stronger confinements, which also indicates a reduction of tube diameter of confined polymer chains, or a reduction of $N_e$.\textsuperscript{106-109} For example, using NMR, Fatkullin et al.\textsuperscript{108} reported a transition from Rouse dynamics in bulk to a slower dynamics having the same characteristics as reptation for perfluoropolyether (PFPE) chains ($R_g = 10$ nm) confined in SiO$_2$ porous glass ($d_{pore} = 4$ nm) where the confined PFPE chains show an effective tube diameter $\sim 2$ nm. In contrast, dilution of entanglement networks in nanoporous confinements is also observed.\textsuperscript{98-100, 102} Specifically, Martin et al.\textsuperscript{102} used NSE to show that the tube diameter of PEO in an AAO template increases by 15\% (5.3 to 6 nm) consistent with strongly confined polymer chains ($2R_g/d \sim 2$), consistent with simulations by Sussman et al.\textsuperscript{99} As shown in the reptation model (Eq. 5), chain diffusivity can be influenced by these microscopic quantities, and studies connecting these parameters with the center of mass diffusion of polymers are introduced in the next section.

2.4.2 Effect of Local Dynamics on Bulk Diffusivity

In this section, we will discuss center of mass polymer diffusion in cylindrical confinement and its relationship to changes in segmental dynamics. Using proton pulsed-
gradient NMR, Lange et al. investigated large-scale diffusion of entangled poly(butadiene) in cylindrical confinement (AAO template). In weak confinement (pore diameter ~ 60 nm, \( r_{\text{pore}}/R_g \sim 10 \)), chain diffusion is moderately reduced (~20%) with respect to the pure polymer case, whereas at stronger confinement (~ 20 nm, \( r_{\text{pore}}/R_g \sim 4 \)), chain diffusivity is reduced by 50%. In both cases, no significant dependence of polymer molecular weight (i.e. \( R_g \)) on the reduction of diffusivities is observed. Namely, pore diameter plays an important role in the slowing down of chain diffusion. This slowing down is explained by a short-range interaction on the length scale of molecular size at the polymer-wall interface where molecular friction increases by up to 10 fold.

A unified picture of the effect of cylindrical confinement on the local dynamics and polymer center of mass diffusion is reported. Using ERD coupled with molecular dynamics simulations, Tung et al. investigated how changes of local quantities, such as end-to-end distance (\( R_{ee} \)), Rouse relaxation time, and entanglement density influence polymer center of mass diffusion when polymer (PS) chains are confined in cylindrical confinement (AAO templates). Experimentally, chain diffusivity increases as confinement increases, consistent with MD simulation results where chain diffusivities are extracted by calculating the MSD of the chain along the cylindrical axis. In addition, simulations show anisotropic local dynamics, i.e., enhanced \( R_{ee} \), \( \tau \) and \( N_e \). Here chain diffusivity can be calculated from these parameters using the reptation model and shows an increase in polymer diffusion when confinement increases where pore size is comparable or even less than chain end-to-end distance, consistent with the MSD simulation results. Although the trend of fast diffusion with increasing confinement is
observed, the experimental measurements underestimate $D$ possibly because of favorable polymer-wall interactions. Here polymer segments adsorbed on the wall could further modify molecular friction and thus slow down polymer diffusion. Despite the difference in the enhancement of polymer diffusion, the study qualitatively connects local dynamics and long-range diffusion, and suggests that polymer chains are disentangled within strongly confined pores, leading to faster polymer center of mass diffusion compared to the bulk values.

### 2.5. Dynamics of Nanoparticles in Polymer Melts

The diffusion of a spherical particle in a continuous medium is described by the classic Stokes-Einstein (SE) relation:

$$D_{SE} = \frac{k_B T}{f \pi \eta R}$$

(2.4)

where $D_{SE}$ is the Stokes-Einstein diffusion coefficient, $k_B$ is the Boltzmann constant, $T$ is absolute temperature, $\eta$ is the pure solvent viscosity, and $R$ is the particle radius. The constant $f$ is 4 or 6 depending on whether there is slip or non-slip condition at the particle/medium interface, respectively. Particle diffusion follows the SE relation using the bulk polymer of the polymer melt, whereas for NPs smaller than the characteristic length, i.e., tube diameter in an entangled polymer melt, the SE relation could underestimate the diffusion of NPs. Brochard Wyart and de Gennes argued that the bulk viscosity does not capture the behavior of surrounding flows near NPs, and thus NP diffusion is decoupled from the SE relation. Namely, when NPs are smaller than the mesh size, the friction for the particle depends on the contact with monomers, resulting in a
length-scale dependent friction that is less than the bulk value. Such breakdown in SE relation when NP size is comparable to the characteristic length is reported in various studies.\textsuperscript{20, 112-118} For example, Grabowski et al.\textsuperscript{116} investigated the effect of NP size on diffusion in polymer melts, and showed that the diffusion coefficient ($D$) of gold NPs with a diameter of 5 nm, comparable to the poly(butyl methacrylate) mesh size (~ 6 nm) is ~ 200x faster than the SE prediction. On the other hand, these small NPs reduce the viscosity of polymer melts and the reduction in the melt viscosity is explained by an increase in free volume due to fast movement of NPs\textsuperscript{20} whereas the reduction in viscosity is attributed to a decrease in entanglement density ($N_e$).\textsuperscript{21}

Brochard Wyart and de Gennes\textsuperscript{111} also argued that when NP size increases and approaches the mesh size, there is a sharp crossover in friction “felt” by NPs, and at a large length scale, the viscosity is close to the bulk value where NP diffusion follows normal SE behavior. In contrast, theoretical studies\textsuperscript{119} show a continuous transition from NP diffusion determined by local viscosity to bulk SE behavior, which is recovered when $d$ is ~ 10x greater than the tube diameter, suggesting that other mechanisms might take place to affect NP dynamics in this transition zone. Yamamoto and Schweizer\textsuperscript{119} proposed a constraint-release type mechanism for NP diffusion. Namely, NPs are trapped by a polymer network as NP motions become gradually coupled to the entanglement network, and a slight density fluctuation results in the escape of NPs, resulting in faster NP diffusion. On the other hand, Cai et al.\textsuperscript{117, 120} proposed a NP hopping mechanism to explain the NP diffusion. For NPs moderately larger than $d_i$ in polymer melts, they are trapped in cages of the entanglement network. NPs have to overcome a hopping free
energy barrier while the entanglement strands are able to slip around the NPs, and subsequently hop to a neighboring cage.

To understand the size-dependent NP diffusion in polymer melts, a neutral interaction between NP and host polymer is required. One popular method to control NP-polymer interaction is grafting polymer brushes chemically identical to the matrix to the surface of the NP. In this case, the brush structure can be further controlled by varying the ratio of the brush to matrix degree of polymerization \((P/N)\).\textsuperscript{16, 48, 49} For example, studies\textsuperscript{48} of spherical NPs showed that when \(P/N < 3\), the brush is interdigitated with the matrix chain, resulting in a wet-brush condition, and when \(P/N > 3\), the brush excludes the relatively large matrix polymer, resulting in a dry-brush condition at fixed graft density. Accordingly, when the brush is wet by the matrix chains, NP diffusion requires that entangled chains drag along with the NP, whereas when the brush is dry, the brush collapses and thus an effective diameter determining NP diffusion. Studies showed dynamics is affected by the grafted polymer chain\textsuperscript{111} in both polymer solutions\textsuperscript{121, 122} and melts.\textsuperscript{123, 124} For instance, Kandar et al.\textsuperscript{124} investigated the effect of PS brush on the dynamics of hairy gold nanoparticles in PS matrices using XPCS, and reported an unusual dynamical arrest when grafting density is low (0.4 chains/nm\(^2\)), with a two-step relaxation, a fast mode corresponding to grafted chain relaxation and a slow mode corresponding to entire particle motion. In contrast, only liquid-like motion is observed when NPs have relatively higher grafting density (2.3 chains/nm\(^2\)). Simulation studies by Ghanbari et al.\textsuperscript{125} showed the mobility of grafted-NPs is \(\sim 10x\) slower than ungrafted-NPs in a polymer melt, which is attributed to larger hydrodynamic radius of grafted-NP,
resulting in slower center of mass diffusion. Accordingly, the above studies suggest that the dynamics of polymer-grafted chain in polymer melts can be influenced by brush-matrix interpenetration and brush grafting density.

In this chapter, recent simulation and experimental studies of polymer and nanoparticle dynamics are reviewed first by introducing center of mass polymer diffusion in PNCs containing various types of NPs including nanospheres, nanorods, carbon nanotubes and chained NPs. Local segmental dynamics of PNCs are discussed subsequently, and here we focus on how these key parameters ($R$, $N_c$, and $\zeta$) are altered by NPs and nanoconfinements because these key parameters could further influence reptation diffusion. Finally, new discovery of NP dynamics in polymer melts is introduced, including diffusion of NPs that is smaller than the mesh size, exhibiting enhanced NP diffusion relative to the SE relation, as well as diffusion of hairy NPs whose diffusion is influenced by the brush structure. In the following chapters, details of the effect of attractive polymer-NP interactions (Chap. 3) and PS-grafted chained NPs (Chap. 4) on COM polymer diffusion are discussed, and here the NPs are immobile on the time scale of tracer diffusion. Moving forward, studies about nanorod-assisted polymer diffusion in PNCs (Chap. 5) are investigated where nanorods are mobile on the time scale of tracer diffusion. This is the first systematic study about the effect of mobile NP on polymer diffusion. In addition to polymer dynamics, hairy NP dynamics are studied in detail (Chap. 6) where brush structure is correlated with NP diffusion. These studies provide insight and serve as guidance for future models and theories on polymer and NP dynamics in complex PNCs.
CHAPTER 3. DO ATTRACTIVE POLYMER-NANOPARTICLE INTERACTIONS RETARD POLYMER DIFFUSION IN NANOCOMPOSITES?

This work was accomplished in collaboration with Prof. Karen I. Winey at the University of Pennsylvania, and Prof. Nigel Clarke at the University of Sheffield, U.K. The contents of this chapter were adapted with permission from MACROMOLECULES, 2013, VOLUME 46, 4502-4509. Copyright (2013) American Chemical Society.

3.1 Introduction

Polymer nanocomposites (PNC) have drawn enormous interest because the addition of nanoparticles to polymers imparts unique properties. Specifically, inorganic
nanofillers such as clays have been shown to enhance thermal stability\textsuperscript{126} and mechanical strength,\textsuperscript{127} whereas noble metal nanoparticles and carbon nanotubes can impart polymers with tunable optical properties\textsuperscript{16} and electrical conductivity.\textsuperscript{12} Another advantage is that a very small loading of nanofiller can significantly affect properties because of the high interfacial area between matrix and nanofillers.\textsuperscript{6, 8} For example, 1 vol % of 10 nm-nanoparticles has 0.006 nm\textsuperscript{2} of surface area per nm\textsuperscript{2} of volume; thus interactions are expected to be very influential. The viscosity of polymers is also influenced by the addition of nanofillers and, correspondingly, the processability of PNCs differ from the pure polymer case.\textsuperscript{18, 112} Thus, understanding the dynamics of macromolecules in the presence of nanoparticles can provide important insight into understanding processing conditions and flow behavior\textsuperscript{2} of the PNC.

Experimental studies of polymer relaxation in PNCs provide conflicting results regarding the effect of nanofillers on polymer dynamics. Moreover, a comprehensive model that incorporates local segmental and long range center-of-mass relaxations (aka reptation model) is lacking. For example, Bogoslovov et al.\textsuperscript{88} investigated the effect of attractive interactions on local dynamics in PNCs containing poly(vinyl acetate) and silica nanoparticles (NPs), and found that the local segmental relaxations near the surface of the nanoparticles is unaffected. On the other hand, studies\textsuperscript{128-132} of the glass transition of PNCs having attractive interactions indicate that the mobility of the chains in the vicinity of the nanoparticles are slower than the bulk, thus altering the relaxation behavior. Bound layers immobilized around the NPs having attractive interaction with the matrix polymer have also been investigated.\textsuperscript{79, 133-135} For example, Harton et al.\textsuperscript{79} showed
1-nm thick bound layers near silica nanoparticles (15 nm) surrounded by poly(2-vinlypyridine) (P2VP) matrix, and the cooperative motion of those unbound P2VP is not strongly affected compared with bulk P2VP.

To describe the role of nanoparticles on the slowest relaxations times, a modified tube model,\textsuperscript{1} can be invoked where the topological constraints from neighboring chains in an entangled polymer melt are altered by the inclusion of nanoparticles. Simulation and experimental results show that the entanglement density decreases when nanoparticles are added.\textsuperscript{90,102} However, studies of the effect of nanofillers on the viscosity of polymers show different behaviors which crucially depend on nanofiller size relative to polymer radius of gyration ($R_g$). When the nanoparticles are smaller than $R_g$, the PNC viscosity decreases, relative to pure polymer, as filler is added.\textsuperscript{18-20,112} For example, Nusser et al.\textsuperscript{19} showed that the viscosity of polydimethylsiloxane (PDMS)/polyhedral oligomeric silsesquioxane (POSS) composites decreases by 15% as POSS content increases to 0.004, and explained this lowering of viscosity due to a constraint release mechanism resulting from the mobility of the nanoparticles. Namely, because of the small size of POSS (~2 nm), the relaxation of the NPs is faster than that of the topological constraint imposed by the polymer melt. When the nanoparticles are larger than $R_g$, Anderson et al.\textsuperscript{25} showed that the viscosity of poly(ethylene oxide) (PEO)/silica (44 nm) increases for PEO matrix polymers having $R_g$’s between 0.8 nm and 5.9 nm.

Polymer diffusion is slowed down by spherical nanoparticles that have nearly neutral or weak interactions with nearby polymer segments. In our previous study,\textsuperscript{40} elastic recoil detection (ERD) was used to investigate the tracer diffusion of deuterated
polystyrene (dPS) into polystyrene (PS) mixed with phenyl capped silica nanoparticles having a diameter of 29 nm. Because of the weak NP-PS interaction and immobile NPs, dispersions up to 50 vol % were achieved, allowing for a systematic investigation of tracer diffusion over a previously unexplored range of loading. These studies showed that (1) the normalized diffusion coefficients collapsed onto a master curve when plotted versus the confinement parameter defined as the interparticle distance divided by the tracer size ($ID/2R_g$), (2) the normalized diffusion coefficients decreased more rapidly for $ID$ values smaller than $\sim 2R_g$ suggesting a second mechanism for slowing down at high confinement, and (3) diffusion was reduced by 80% at 50 vol %. In a follow up study, tracer diffusion was studied in the same weakly-interacting polymer-NP system to evaluate the effect of NP diameter, 13 and 29 nm, and NP polydispersity. The normalized diffusion coefficients collapsed onto a master curve at the two NP sizes. The effect of polydispersity, although minor, was found to bring results into better agreement for the more polydisperse small NPs. These findings validate using the confinement parameter (ranging from 0.1 to 3) to produce a master curve for weak polymer-NP interactions.

Using molecular dynamics simulations, Kumar et al. showed that polymer diffusion slowed down if nanoparticles are attracted to the diffusing polymer. Experiments by Hu et al. found that the diffusion coefficients of poly(methyl methacrylate), dPMMA, decreased by a factor of 3 as clay concentration increased to 5 vol % in PMMA matrix, whereas slowing down was not observed in a non-attractive matrix of PS and clay.
In the present study, we probe tracer diffusion in a polymer composite having attractive interactions between spherical nanoparticles and the tracer (matrix) chains. The polymer nanocomposite contains a PMMA matrix mixed with hydroxyl functionalized silica nanoparticles with diameters of 12.8 nm, 28.8 nm and 49.3 nm, denoted as NP13, NP29 and NP50, respectively. Because of the attractive interaction between PMMA and silica, the NPs are well dispersed at volume fractions ranging from 0.05 vol % to 50 vol %. The tracer diffusion of dPMMA in PMMA/silica can be compared with prior studies in a weakly interacting system and thereby allow new insights about the role of interactions on polymer dynamics in PNCs. For the tracer diffusion of dPMMA in PMMA/silica, the normalized diffusion coefficients collapse on a master curve where diffusion occurs in highly confined (\( ID < 2R_g \)) and weakly confined (\( ID > 2R_g \)) regions. Furthermore, the normalized diffusion coefficients for the weakly interacting system are in good agreement with this master curve suggesting that interactions between polymer and nanoparticles do not significantly affect center of mass diffusion.

### 3.2 Experimental Section

#### 3.2.1 Materials

Poly(methyl methacrylate) (PMMA), (MW = 337,000 g mol\(^{-1}\), polydispersity (PDI) = 1.82; MW = 600,000 g mol\(^{-1}\), PDI = 3.3, Sigma Aldrich) and deuterated PMMA (dPMMA) (MW = 100,000 g mol\(^{-1}\), PDI = 1.06, ) were used as received. Molecular weight and PDI were determined by size exclusion chromatography (SEC) using tetrahydrofuran (THF) as the solvent. Three different nanoparticles were used in this
work, and they are referred as NP13, NP29 and NP50. The number average diameter ($d_n$) and the size polydispersity ($\sigma$) are summarized in Table 3.1. NP13 (Nissan Chemical) and NP29 (Ludox) were used as received. NP50 (Nissan Chemical) was solvent transferred from isopropanol (IPA) to N,N-dimethyl acetamide (DMAC). $d_n$ and $\sigma$ were determined using small angle x-ray scattering (SAXS) and dynamic light scattering (DLS) with log-normal distribution fitting:\textsuperscript{136}

$$f(d_i) = \frac{e^{-((\ln d_i - \ln d_m)^2 / 2(\ln \sigma)^2)}}{(\ln \sigma)^2 \sqrt{2\pi}}$$  \hspace{1cm} (3.1)

where $f(d_i)$ is the probability of finding a particle having diameter $d_i$, $d_m$ is the geometric mean diameter, and $\sigma$ is NP size polydispersity. Figure 3.1 shows the size distribution of NP13, NP29 and NP50. NP29 has the smallest $\sigma$ and thus has the narrowest distribution. As the size of the particle increases, the distribution could be wider at fixed $\sigma$. For example, the distribution of NP50 is across a wider range than that of NP13 observed on Figure 3.1 although its $\sigma$ is similar to the $\sigma$ of NP13. Zeta potential ($\zeta$) of NP13, NP29 and NP50 are -38.7±3, -38±6 and -88.6±3 mV respectively, determined by Delsa Nano C particle analyzer.

Table 3.1. **Silica nanoparticle characteristics. Number average diameter and size polydispersity.** ($\sigma$ is defined using the log-normal distribution, Eq. 3.1.)

<table>
<thead>
<tr>
<th>Name</th>
<th>$d_n$</th>
<th>$\sigma^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td>NP13</td>
<td>12.8 nm</td>
<td>1.39</td>
</tr>
<tr>
<td>NP29</td>
<td>28.8 nm</td>
<td>1.13</td>
</tr>
<tr>
<td>NP50</td>
<td>49.3 nm</td>
<td>1.30</td>
</tr>
</tbody>
</table>
**Figure 3.1.** The size distribution for NP13 (blue curve), NP29 (red curve) and NP50 (green curve) as determined from DLS. Arrows denote the number average diameters 12.8 nm, 28.8 nm and 49.3 nm, respectively. Using a log-normal distribution, the polydispersities are 1.39, 1.13 and 1.30, respectively.

### 3.2.2 Preparation and characterization of polymer nanocomposites

In this work, a polymer nanocomposite was composed of PMMA and silica NPs. We aimed to well-disperse the silica nanoparticles in the PMMA matrix. PMMA was dissolved in dimethylacetamide (DMAC) or dimethylformamide (DMF), and was stirred for 20 hours. Nanoparticles were dispersed in DMAC. The nanoparticle solution was sonicated overnight before being mixed with the PMMA solution. An appropriate amount
of the nanoparticle solution was mixed with the PMMA solution. Films were prepared by doctor blading the mixed solution on a heated (150 °C) glass substrate, which allows the solvent to evaporate rapidly. After doctor blading, the film was dried at 150 °C in a hood for 30 minutes, and then was dried under vacuum at 150 °C for 24 hours. The resulting thickness of the film was about 5 μm as determined by ellipsometry. The nanoparticle volume fractions were determined using thermal gravimetric analysis (TGA). The films were heated at 10 °C/min from 20 °C to 400 °C and held at 400 °C for 2 hours. The NP volume fractions for each nanocomposites are summarized in Table 3.2. The type of the nanocomposite is named as PMMA/NPx where x is 13, 29 and 50.

The distribution of the nanoparticles were observed using TEM after cross-sectioning the nanocomposite thin film using a microtome. Small angle x-ray scattering (SAXS) was also used to observe the distribution of the nanoparticles in the PMMA/NP29 nanocomposite. Glass transition temperatures were determined using differential scanning calorimetry (DSC). The nanocomposite films (~ 8 mg) were placed in an aluminum pan and heated from 20 °C to 160 °C at 10 °C/min.

Table 3.2. PMMA/silica nanocomposites.

<table>
<thead>
<tr>
<th>Nanocomposite</th>
<th>NP Volume Fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>PMMA/NP13</td>
<td>0.005, 0.035, 0.07, 0.14, 0.25</td>
</tr>
<tr>
<td>PMMA/NP29</td>
<td>0.01, 0.05, 0.10, 0.20, 0.40</td>
</tr>
<tr>
<td>PMMA/NP50</td>
<td>0.02, 0.05, 0.15, 0.25, 0.40</td>
</tr>
</tbody>
</table>
3.2.3 Diffusion couple preparation and annealing

The diffusion couple consisted of a thick (~ 5 μm) nanocomposite film covered with a layer of thin dPMMA film. The nanocomposite film was floated from the glass substrate in water and picked up using a silicon wafer. The nanocomposite film on the wafer was aged at 150 °C for three days in vacuo. The dPMMA tracer film was spin-coated on a silicon wafer and had a thickness ~20 nm as measured by ellipsometry. The tracer film was transferred from the silicon wafer to the top of the nanocomposite film, forming a diffusion couple. The diffusion couple was dried under ambient conditions overnight, and then annealed isothermally at 195 °C under a nitrogen purge on a Metler hot plate. The annealing time was chosen to allow sufficient penetration of the dPMMA into the matrix, typically ~ 300 nm. To ensure consistency of annealing condition, a control sample of dPMMA/PMMA was annealed adjacent to the sample.

3.2.4 Elastic Recoil Detection (ERD)

ERD was used to probe the dPMMA depth profile in the nanocomposite. Details of ERD have been reviewed elsewhere. The measurement was conducted under room temperature. The energy of the incident helium ion (He\(^{2+}\)) beam was ~3.022 MeV, and the ion beam intersected the plane of the sample at 15°. The energy of the recoiled atom was detected by a solid-state detector. A 10 μm Mylar film was placed in front of the detector in order to filter forward scattered helium that masked the hydrogen and deuterium signal. A low beam current (< 2 nA) was used, and total 10 μC was collected from 5 different spots on the diffusion couple sample. The ERD spectra of count versus
channel were converted to dPMMA depth profile of dPMMA volume fraction versus depth. The diffusion coefficient of the tracer was obtained by fitting the depth profile using the one-dimensional (1-D) solution of Fick’s second law for a finite source in a semi-infinite medium.\textsuperscript{139} The instrumental resolution ($\sigma$), or half of the full width at half maximum (FWHM) was captured by the Gaussian function,

$$y = \left[\frac{1}{\sigma (2\pi)^{1/2}}\right] \exp\left(-\frac{x^2}{2\sigma^2}\right),$$

where $y$ is the dPMMA fraction and $x$ is the depth. $\sigma$ is 40 nm and the accessible depth was ~800 nm. The diffusion coefficients obtained in this work were from multiple measurements. Only the depth profiles having a sufficient diffusion length (> 200 nm) were used.

3.3 Result and Discussion

3.3.1 Distribution of Nanoparticles in Polymer Nanocomposites

Before investigating polymer dynamics, the distribution of nanoparticles is studied. A good dispersion is required because nanoparticle aggregation results in an effective larger interparticle distance, which can increase polymer mobility. The cross-sectional TEM images shown in Figure 3.2 demonstrate that silica nanoparticles disperse in the PMMA matrix without aggregating. At low nanoparticle loadings (top row), individual NPs are observed. The volume fraction was increased from 0.5 to 2 vol % to partially compensate for the decrease in number density as NP size increases. At high NP loading (bottom row), the NPs are also well dispersed and the interparticle distance is on the length scale of $R_g$. Qualitatively, a comparison of the NP29 and NP50 at 40 vol % shows that the number density decreases as the NP size increases, as expected.
Theoretically, the number density should be about 5 times larger for the NP29 system. Because the image represents a ~100 nm thick cross-section of the film an accurate measure of distance and number density is challenging via TEM. Using SAXS and TEM, Meth et al.\textsuperscript{137} showed that the distribution of NP29 in a PMMA matrix prepared by the same method are well dispersed, in agreement with Figure 3.2 (center column). The effect of size polydispersity is also apparent at low loading. Namely, NP29 particles have very similar diameter consistent with its low polydispersity. Although having a similar polydispersity, NP50 appears to exhibit a larger range of diameters than NP13, likely because of the low number (~8) of imaged particles. Thus, these TEM results are in qualitative agreement with the polydispersities for NP13, NP29 and NP50 measured by DLS and shown in Figure 3.1.
Figure 3.2. Cross-sectional TEM images of PMMA matrices containing NP13, NP29 and NP50. Individual NPs are observed at the lowest volume fraction prepared (top row). At the highest volume fraction (bottom row), NP distribution remains uniform. The interparticle distance ($ID$) is much greater than the NP diameter in the top row whereas $ID << NP$ diameter in the bottom row for the crowded composite (cf. Figure 3.5). The scale bars are 100 nm.

In contrast to the polystyrene/phenyl-capped silica previously investigated, silica nanoparticles with surface hydroxyl groups (i.e., colloidal silica) have an attractive interaction with PMMA and this affinity drives the dispersion because PMMA chains preferentially wet silica. By studying adsorption from trichloroethylene, Kawaguchi et al. showed that PMMA strongly adsorbs to silica which prevents nanoparticles from aggregating. In the present studies, the high molecular weight of the PMMA matrix provides a highly viscous environment for the nanoparticles at low solvent
concentrations, further preventing aggregation during the casting of matrix films. In summary, the TEM studies show that the NP13, NP29 and NP50 are well-dispersed in PMMA across a wide range of volume fractions and therefore the PMMA:silica matrix provides a stable structure for subsequent diffusion studies.

3.3.2 Tracer Diffusion in Nanocomposites

Using ERD, the tracer diffusion coefficients of dPMMA (100 kg/mol) in PMMA/NPx were determined as a function of the nanoparticle size ($d_n$) and volume fraction ($\phi_{NP}$). The dPMMA volume fraction profile was obtained after annealing the diffusion couple. This profile can be described by the 1-D solution to Fick’s second law for a finite source in a semi-infinite medium. The deuterated volume fraction, $\phi(x)$, is given by:\textsuperscript{139}

$$\phi(x) = \frac{1}{2} \left[ \text{erf} \left( \frac{h-x}{\sqrt{4Dt}} \right) + \text{erf} \left( \frac{h+x}{\sqrt{4Dt}} \right) \right]$$ (3.2)

where $x$ is depth, $h$ is original dPMMA film thickness, $t$ is diffusion time, and $D$ is the diffusion coefficient of dPMMA. An experimental depth profile was fitted by $\phi(x)$ convoluted with the Gaussian instrumental resolution function. Quality fits were obtained by minimizing $\chi^2$ using least-squares fitting. Figure 3.3 shows representative depth profiles (solid circles) and their fits (solid lines) for dPMMA diffusion into (a, d) PMMA/NP13, (b, e) PMMA/NP29, and (c, f) PMMA/NP50 at the lowest (top row) and the highest (bottom row) volume fractions of nanoparticles. The depth profiles follow Fickian diffusion, Eq. 3.2, at low volume fractions. At high volume fractions, surface peaks are observed for tracer diffusion. As previously described,\textsuperscript{40} this surface peak is
attributed to an initial reduction in flux at the interface between the tracer layer and the nanocomposite due to the impenetrable silica nanoparticles. A Gaussian function was used to fit the surface peak and then added to the Fickian diffusion profiles (dashed lines in e and f). Consistent with our prior study, the magnitude of the peak decays with time as more of the dPMMA is able to penetrate into the matrix. For dPMMA diffusion into PMMA/NP13, PMMA/NP29 and PMMA/NP50, the tracer diffusion coefficients decrease by more than a factor of 2 as NP loading increases from its minimum to maximum values. This demonstrates that nanoparticles slow down center of mass diffusion of dPMMA in PMMA/silica nanoparticle systems. Before addressing the key question about the role of interfacial interactions, we first address the issue of the glass transition.
Figure 3.3. Volume fraction profiles of dPMMA in PMMA/NP13 (a, d), PMMA/NP29 (b, e) and PMMA/NP50 (c, f) at 195 °C. (a – c) and (d – f) corresponding to the lowest and highest values of $\phi_{NP}$, respectively. Solid curves represent fits using Equation 2 convoluted with a Gaussian instrumental resolution function. In (e) and (f) the dashed curves represent the sum of the solid curves and surface peaks. Annealing times of (a) 7.8 hr, (b) 7.95 hr, (c) 7.95 hr (d) 15 hr, (e) 33.37 hr and (f) 20 hr were chosen to provide an optimum diffusion length $\sim$ 350 nm.

Diffusion coefficients are very sensitive to temperature, so it is most appropriate to compare $D$ at fixed $T - T_g$, where $T$ is the annealing temperature and $T_g$ is the glass transition temperature of the composites. The glass transition temperatures of the PMMA/NPx matrices are summarized in Table 3.3. Whereas the $T_g$’s of PMMA/NP13 and PMMA/NP29 are relatively constant; the $T_g$ of PMMA/NP50 increases at high volume fractions. At $\phi_{NP} = 0.40$ in PMMA/NP50, the $T_g$ is 4.6 K higher than that of the pure PMMA matrix. This increase in the glass transition temperature is attributed to the
attractive interaction between the hydroxyl-capped surface of silica and PMMA. For a PMMA/silica nanocomposite containing 62.5 wt % silica, Moll et al.\textsuperscript{135} observed a $T_g$ increase of $\sim 7$ K, in good agreement with our findings. The question then becomes why the glass transition temperature increases for PMMA/NP50 but remains nearly constant for the PMMA/NP13 and PMMA/NP29 matrices. Because $T_g$ depends on the interaction between surface groups on the NP and the surrounding polymer, the surfaces of NP13, NP29 and NP50 may contain different areal densities of hydroxyl groups. To test this hypothesis, the zeta potential ($\zeta$) of NP13, NP29 and NP50 were determined in DMAC, the same solvent used to cast the PMMA/NP$x$ nanocomposite films. The $\zeta$ of NP13 and NP29 are similar, whereas the $\zeta$ of NP50 is twice that of NP13 and NP29, as summarized in Table 3.1. Because the $\zeta$ reflects the surface charge,\textsuperscript{141} NP50 has a higher concentration of hydroxyl groups which in turn allows for more attractive interactions with PMMA segments and a corresponding increase in $T_g$. Thus, even within the PMMA/silica NP system, we have a range of interfacial attractions. To account for the higher glass transition temperature in the PMMA/NP50 matrices, the diffusion coefficients were shifted using the Williams-Landel-Ferry (WLF) equation:\textsuperscript{142}

$$\log \frac{D(T_0)}{D(T_f)} = \frac{-C_1(T-T_0)}{C_2 + T - T_0}$$

(3.3)

where $T_0$ is the reference temperature, here the glass transition temperature, 393 K, is used, $T_f$ is the shifted temperature, $T$ is the annealing temperature, $C_1 = 11.9$ and, $C_2 = 69$ K.\textsuperscript{143} Thus, all values are compared at $T - T_g = 75$ K, where $T_g$ is the glass transition temperature of the nanocomposite. For example, for the PMMA/NP50 system with $\phi_{NP} =$
0.40, the diffusion coefficient should be determined at 199.6 °C to account for the 4.6 °C increase in $T_g$. By comparing at $T - T_g =$ constant, differences in the diffusion coefficient of dPMMA can be attributed to the NP volume fraction, NP size and NP spacing.

**Table 3.3.** Summary of the $T_g$ changes for different nanoparticle volume fractions in NP13, NP29 and NP50 nanocomposites. Values of the zeta potential ($\zeta$) of nanoparticles in DMAC are in the far right column.

<table>
<thead>
<tr>
<th>$\phi_{NP13}$</th>
<th>0.005</th>
<th>0.07</th>
<th>0.14</th>
<th>0.25</th>
<th>$\zeta$ (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta T_g$ (°C)</td>
<td>-1</td>
<td>-0.1</td>
<td>-0.8</td>
<td>-0.1</td>
<td>-38.7 ± 3</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>$\phi_{NP29}$</th>
<th>0.01</th>
<th>0.05</th>
<th>0.10</th>
<th>0.20</th>
<th>0.40</th>
<th>$\zeta$ (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta T_g$ (°C)</td>
<td>-1</td>
<td>-0.3</td>
<td>-0.8</td>
<td>0.1</td>
<td>1.7</td>
<td>-38 ± 6</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>$\phi_{NP50}$</th>
<th>0.02</th>
<th>0.05</th>
<th>0.15</th>
<th>0.25</th>
<th>0.40</th>
<th>$\zeta$ (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta T_g$ (°C)</td>
<td>0.65</td>
<td>-0.25</td>
<td>1.4</td>
<td>4</td>
<td>4.65</td>
<td>-88.6 ± 3</td>
</tr>
</tbody>
</table>

$\Delta T_g = T_{g, PMMA/NP_x} - T_{g, PMMA}$, where $T_{g, PMMA} = 120$ °C

The normalized diffusion coefficients ($D/D_0$) are plotted against the nanoparticle volume fraction in Figure 3.4. At low nanoparticle loading, the diffusion coefficient decreases sharply as loading increases. For example, the diffusion coefficient decreases ~25% upon adding only 0.005 of NP13 to the PMMA matrix. The diffusion coefficient continues to decrease, although less sharply, at high NP loadings. Plotting $D/D_0$ at a fixed
$T - T_s$ as a function of nanoparticle volume fraction does not collapse the three sets of data representing the PMMA/NP13, PMMA/NP29 and PMMA/NP50 matrices. Namely, compared at the same volume fraction, the diffusion coefficient decreases as the NP size decreases from 50 to 29 to 13 nm. This result may be attributed to the increase in the number of obstacles to diffusion as size decreases. However, when plotted versus the number density of NPs, $D/D_0$ does not collapse on a master curve (not shown). As a reference we include the prediction of the Maxwell model,\cite{144} showing, as in our previous studies that tortuosity along does not account for the slowing down of diffusion in the presence of immobile silica nanoparticles.
Figure 3.4. Normalized diffusion coefficients versus NP volume fraction for dPMMA diffusion in PMMA/NP50 (green triangles), PMMA/NP29 (red squares) and PMMA/NP13 (blue circles). The black dotted line is the calculation from the Maxwell model.

3.3.3 Confinement Parameter

For diffusion into a system with weak polymer-NP interactions, the normalized diffusion coefficient was shown to collapse on a master curve when plotted against the confinement parameter.$^{40}$ The confinement parameter is defined as the ratio of the interparticle distance ($ID$) relative to the probe size, $2R_g$, where $R_g$ is the radius of
gyration of the dPMMA tracer chain. Thus, $ID/2R_g$ represents the melt region available for polymer chains to diffuse between a fixed array of randomly placed nanoparticles.

Given that the nanoparticles are well-dispersed in the PMMA matrix, $ID$ in 3D can be calculated\textsuperscript{41,145} under the assumption that nanoparticles are randomly distributed:

$$ID = d_n \left[ \left( \frac{2}{\phi_{NP} \pi} \right)^{1/3} \times e^{ln(\sigma^2)} - 1 \right]$$ (3.4)

Thus, $ID$ depends on nanoparticle size ($d_n$), nanoparticle volume fraction ($\phi_{NP}$), and nanoparticle size polydispersity ($\sigma$). Figure 3.5 shows how $ID$ decreases as the nanoparticle volume fraction increases up to 0.40. For NP13, NP29 and NP50, $ID$ drops dramatically at low $\phi_{NP}$; for NP13, $ID$ decreases by $\sim$150 nm when $\phi_{NP}$ increases from 0 to 0.01. In contrast, $ID$ decreases relatively weakly at higher $\phi_{NP}$ (i.e., $\phi_{NP} > \sim 0.1$; for NP13, $ID$ decreases by only 13 nm as $\phi_{NP}$ increases from 0.05 to 0.25.) Furthermore, at the same $\phi_{NP}$, $ID$ increases as the nanoparticle diameter increases. For example, at 10 vol $\%$, the $ID$ of PMMA/NP50 is 43.6 nm, which is more than 3 times larger than the $ID$ value in the PMMA/NP13, 13.6 nm. This difference reflects the lower number density of NP50.
Figure 3.5. The average interparticle distance ($ID$) as a function of nanoparticle volume fraction ($\phi_{NP}$) using Eq. 4, which assumes randomly distributed NPs. $ID$ decreases rapidly at low nanoparticles loadings. At fixed $\phi_{NP}$, $ID$ also decrease as NP size decreases when compared at same $\phi_{NP}$.

The probe size is described by the radius of gyration ($R_g$) of dPMMA, assuming that chains obey Gaussian statistics, and given by: $^{146}$

$$R_g = \frac{a\sqrt{N}}{\sqrt{6}} = \frac{a\sqrt{M_w/M_0}}{\sqrt{6}} \quad (3.5)$$
where \( a \) is the monomer length (0.66 nm), \( N \) is the degree of polymerization, \( M_w \) is the weight-averaged molecular weight and \( M_0 \) is the molar mass of a monomer unit (108.12 g/mol). For \( M_w = 100 \) kg/mol, \( R_g = 8.2 \) nm.

When the confinement parameter is greater than 1, the diffusion of dPMMA between the immobile particles is reduced. However, when the confinement parameter is less than 1, the dPMMA chain is larger than the average space between particles. In this crowded regime, either the tracer must be patient, probe its surroundings and find a path between particles with a large spacing or suffer the loss of configurational entropy by squeezing between closely spaced particles. The competition between the former case, which corresponds to a limited number of broad pathways, and the latter case, which corresponds to the greater number of narrow pathways is likely to dictate the magnitude of diffusion. At present, there are no models that relate the materials parameters \( \phi_{NP}, d_n \) and \( ID \) to the tracer diffusion coefficient in a polymer nanocomposite.

Figure 3.6 shows that the normalized diffusion coefficients fall on a master curve when plotted against the confinement parameter for the PMMA/NP13, PMMA/NP29 and PMMA/NP50 systems. Whereas prior studies investigated confinement parameters up to \(~3,^{40,41}\) the present system extends this range out to \( ID/2R_g \sim 8 \). These studies show that even when the spacing between nanoparticles is about 8 times greater than the size of the tracer molecule the diffusion coefficient is reduced by 15%. Similar to prior studies,\(^{40}\) as the confinement parameter decreases, \( D/D_0 \) decreases weakly as \( ID/2R_g \) varies from \(~8\) to \(~2\). However, for \( ID/2R_g < \sim 2\), \( D/D_0 \) decreases very strongly with a much steeper
slope than at low $ID/2R_g$. In this highly confined regime, for example, at $ID/2R_g \sim 0.4$, the diffusion coefficient is reduced by 80%.

![Graph showing normalized diffusion coefficients ($D/D_0$) plotted against the confinement parameter ($ID/2R_g$). Data points represent $D/D_0$ in the attractive system (PMMA/hydroxyl-capped silica): PMMA/NP13 (blue circle), PMMA/NP29 (red square), and PMMA/NP50 (green triangle). The solid black line is the best fit from a weakly interacting system (PS/phenyl-capped silica) from a previous study. The dashed line shows that the extrapolation of the weakly interacting system is also in good agreement with the measured values at higher $ID/2R_g$ of the weakly interacting system.](image-url)

**Figure 3.6.** Normalized diffusion coefficients ($D/D_0$) plotted against the confinement parameter ($ID/2R_g$). Data points represent $D/D_0$ in the attractive system (PMMA/hydroxyl-capped silica): PMMA/NP13 (blue circle), PMMA/NP29 (red square), and PMMA/NP50 (green triangle). The solid black line is the best fit from a weakly interacting system (PS/phenyl-capped silica) from a previous study. The dashed line shows that the extrapolation of the weakly interacting system is also in good agreement with the measured values at higher $ID/2R_g$ of the weakly interacting system.

The empirical relationship between $D/D_0$ and $ID/2R_g$ indicates that the center of mass diffusion of macromolecules slows down as the particle spacing relative to the tracer chain size decreases. However, the mechanism of this slowing down is not well
understood. According to a modified reptation model proposed by Richter et al.,\textsuperscript{71} the local dynamics of polymer chains are not altered by the presence of NPs, but rather add to the physical constraints due to entanglements resulting in a reduced entanglement density. Thus, the additional geometric constraint provided by the nanoparticles reduces the apparent tube diameter, and thus slows down polymer dynamics. This model seemed to capture the dynamics of poly(ethylene-alt-propylene) containing hydrophobically modified silica (diameter = 17 nm). Using PRISM theory,\textsuperscript{113} Yamamoto and Schweizer showed that the addition of nanoparticles changes how polymer chains can pack in a nanocomposite, altering the friction in the melt. In addition, Harton et al.\textsuperscript{79} found nanoparticles with a favorable attraction towards the polymer results in an immobilized layer around the nanoparticles. This immobilized layer exhibits slower segmental motion, and thus larger friction, a possible explanation for the slowing down of tracer diffusion.

To determine if attractive interactions between PMMA and silica NPs slow down diffusion, we compare the dPMMA tracer diffusion studies in Figure 3.6 with results from our previous study\textsuperscript{40} of deuterated polystyrene (dPS) diffusing into a matrix of PS and phenyl capped silica, which is the same core particle as NP29 in the present study. Because PS only weakly interacts with the hydrophobic silica, the diffusion of dPS would be faster relative to the PMMA/NPx studies if attractions slow down diffusion. However, as seen in figure 3.6, $D/D_0$ for the PS/NP29 system (solid curve) is very similar to the PMMA/NPx case (symbols), particularly for $(ID/2R_g) > \sim 2$. In the highly confined regime, the PS data fall slightly above the PMMA results indicating slower diffusion. Because the PS studies were performed at 145 to 170 $^\circ$C and scaled to $T - T_g = 66$ $^\circ$C,
systematic studies of the temperature dependence of diffusion are needed before further comment about this small difference with the PMMA/NPx results, measured at 195 °C and scaled to $T - T_g = 75$ K, can be made. Whereas the $T_g$ of PMMA/NP50 increased at high NP loading, the $T_g$ for the PS nanocomposites remained constant. Thus, although attractive interactions can affect local relaxations, these favorable interactions do not appear to slow down macroscopic diffusion. One possible explanation is that each new interaction between a dPMMA segment and silica is off-set by a loss of a PMMA segment/silica interaction resulting in no net enthalpic change. To address the possibility that the PMMA matrix chains form an immobilized layer that masks the interaction between dPMMA and silanol groups on the NPs, we performed the following experiment. A tracer film of dPMMA/NP13 (1 vol%) was deposited over a PMMA matrix. For comparison, a control bilayer of dPMMA:PMMA was prepared. After annealing for 9.5 hours, at 195°C, the volume fraction profiles of dPMMA from the nanocomposite tracer and pure tracer were compared and found to overlap. These experiments indicate that the exchange between matrix PMMA and dPMMA adjacent to the NPs occurs on the time scale of these diffusion studies. Regardless of the reason, our experimental studies demonstrate that diffusion in polymer nanocomposites having weak and attractive interactions can both be described by a confinement parameter that reflects the spacing between nanoparticles, which depends on volume fraction and diameter, relative to the tracer size.
3.4 Conclusion

In this study, we present the first systematic experimental studies of tracer diffusion in a polymer nanocomposite having attractive interactions. Macromolecular diffusion in polymer nanocomposites having a strong segment/nanoparticle interaction is probed by tracer diffusion using ERD. Nanoparticles are uniformly dispersed in PMMA matrix, even up to very high loadings, $\phi_{NP} = 0.4$ for PMMA/NP29 and PMMA/NP50, such that these nanocomposites are ideal matrices for tracer diffusion studies. The glass transition temperature for PMMA/NP50 is found to increase by $\sim 5$ K, consistent with the literature. The enhancement of $T_g$ is attributed to the high surface charge of NP50 resulting in strong segmental/nanoparticle attraction (higher surface potential). Upon comparing at the same $T - T_g$, the normalized diffusion coefficients decrease as $\phi_{NP}$ increases, implying that nanoparticles hinder center of mass diffusion. This slowing down increases as the size of the NP decreases (i.e., compared at same $\phi_{NP}$).

The confinement parameter, $ID/2R_g$, which captured the effect of $\phi_{NP}$ and NP size on diffusion in a weakly interacting system, is tested for a strongly interacting system. When $D/D_0$ is plotted against the confinement parameter, all data collapse onto a master curve, suggesting that the confinement parameter is able to capture the effect of $\phi_{NP}$ and NP size on the diffusion even for systems with attractive or weak interactions. For $ID/2R_g$ between $\sim 8$ and $\sim 2$, the diffusion coefficients decrease slowly as $ID/2R_g$ decreases. For example, the diffusion coefficient is found to decrease by 15% even when $ID$ is much larger than the probe size, $2R_g$, by a factor of 8. This result shows that the presence of even very dilute concentrations of NPs have a large effect on polymer dynamics. For
$ID/2R_g < \sim 2$, the diffusion coefficients decrease sharply as $\phi_{NP}$ decreases. For example, the diffusion coefficient decreases by 80% at $ID/2R_g = 0.25$.

Furthermore, the tracer diffusion of dPMMA in PMMA/NPx is compared to prior studies in the weakly interacting polymer nanocomposite, and found to be in reasonable agreement. Namely, the reduced diffusion coefficients from both systems nearly collapse on the same master curve, suggesting that the confinement parameter captures slowing down independent of segment/nanoparticle interactions. At present, the mechanism of polymer diffusion in the presence of immobile, impenetrable nanoparticles is lacking. Clearly any theory would need to capture the behavior in the confined regime ($ID/2R_g > \sim 2$) and highly confined regime where nanoparticle spacing, on average, is less than the size of the tracer. These studies, combined with prior ones on weakly interacting systems, provide guidance for testing future models and theories describing polymer dynamics in polymer nanocomposites with immobile, impenetrable nanoparticles.
CHAPTER 4. MACROMOLECULAR DIFFUSION THROUGH A POLYMER MATRIX WITH POLYMER-GRAFTED CHAINED NANOPARTICLES

This work was accomplished in collaboration with Prof. Karen I. Winey at the University of Pennsylvania, Prof. Nigel Clarke at the University of Sheffield, U.K, and Prof. Kohji Ohno at Kyoto University, Japan. The contents of this chapter were adapted with permission from MACROMOLECULES, 2014, VOLUME 47, 5357-5364. Copyright (2014) American Chemical Society.
4.1 Introduction

Polymer nanocomposites (PNC), a combination of nanosized fillers and polymer, are promising hybrids for various applications because they exhibit unique properties while maintaining processability inherent to polymers. For example, gold nanorods impart tunable optical properties to polymers,\textsuperscript{16} whereas nanoclays improve flammability resistance.\textsuperscript{11} Organic nanofillers, such as carbon nanotubes and graphene, can enhance thermal, electrical and mechanical properties when they are blended with polymers.\textsuperscript{10, 14, 147, 148} For example, Thomassin \textit{et al.}\textsuperscript{148} reported that upon adding 0.2 wt % graphene oxide sheet (GO) to PMMA, the electrical conductivity of the nanocomposite approaches $1.2 \times 10^{-3}$ S/m. In addition, even very low loadings of nanofillers can produce high interfacial area between nanofillers and matrix, effectively influencing polymer properties and dynamics.\textsuperscript{6-8} The addition of nanofillers also alters polymer viscosity, a critical fundamental parameter that determines flow behavior and phase separation kinetics in PNCs.\textsuperscript{18, 20, 149, 150} Therefore, by understanding polymer dynamics in PNCs, we gain insight into important issues such as optimizing processing conditions, and applications such as drug delivery, self-healing materials, and membranes.\textsuperscript{34, 35, 151} Recent studies of polymer diffusion in polymer nanocomposites have focused on spherical and high-aspect-ratio cylindrical nanoparticles, while this study explores string-like chains of spherical nanoparticles. Our chained nanoparticles (cNPs) mimic the widely-used carbon black filler and provide an insightful intermediate between the divergent behaviors previously reported for diffusion in nanocomposites containing spherical or cylindrical nanoparticles.
For PNCs with spherical NPs, using elastic recoil detection (ERD), Gam et al.\textsuperscript{40,41} studied tracer diffusion (deuterated polystyrene, dPS) in polystyrene (PS)/silica NP, where the silica NP (13nm and 28nm in diameter) is grafted with phenyl groups having a nearly neutral interactions with the PS matrix. A monotonic decrease in the tracer diffusion coefficients ($D$) with increasing NP loading ($\phi_{NP} = 0 - 50$ vol %) is found. In addition, when normalized diffusion coefficients, $D/D_0$, are plotted against the confinement parameter, $ID/2R_g$, where $D_0$ is the tracer diffusion coefficients in the pure matrix ($\phi_{NP} = 0$), $ID$ is the interparticle distance, and $R_g$ is the radius of gyration of the tracer molecule, they collapse onto a master curve, suggesting that the confinement parameter is able to capture the effect of dPS molecular weights, NP diameters, and NP loadings on tracer diffusion. Furthermore, in the case when there are favorable interactions between matrix, poly (methyl methacrylate) (PMMA), and nanofiller, hydroxyl-capped silica NP (13nm – 50nm), studies\textsuperscript{45} found that polymer diffusion is not significantly influenced by these attractive interactions compared to the PS/silica NP system when $D/D_0$ is plotted against $ID/2R_g$. Theoretically, Meth et al.\textsuperscript{46} developed an excluded volume model that captures the slowdown in tracer diffusion at low NP loadings for $ID/2R_g > 2$. This model overestimates the reduction in diffusion at high loadings where tracer size is much larger than $ID$, suggesting that other relaxation mechanisms might occur in highly crowded PNCs. For example, experiments and simulations indicate a decrease in entanglement density when NPs are added to polymer.\textsuperscript{102,152} Moreover, the viscosity can depend on NP size and polymer-NP interactions and therefore these materials parameters can influence polymer dynamics in PNCs. When NPs are smaller than $R_g$, studies\textsuperscript{18-20,112} showed that the viscosity of the
PNC decreases compared to the pure matrix case; in contrast, the viscosity of poly(ethylene oxide) (PEO)/silica (44 nm) is observed to increase because the silica NP size is larger than $R_g$ of PEO (0.8 and 5.9 nm). Using nonequilibrium molecular dynamics simulations, Kalathi et al.\textsuperscript{21} observed a significant reduction in the viscosity of polymer melts when the NPs are smaller than the entanglement mesh size for a neutral NP-matrix interaction, whereas viscosity increases relative to the pure polymer melt for an attractive polymer-NP interaction.

In a PNC containing high aspect ratio, cylindrical NPs, namely single-walled carbon nanotube (SWCNT) bundles (aspect ratio > 30) in PS matrices, Mu et al.\textsuperscript{53} reported a minimum in $D$ with increasing NP concentration. Specifically, the tracer diffusion coefficient of dPS ($M = 75$, 140, and 680 kg/mol where $M$ is the molecular weight of dPS) initially decreases as $\phi_{SWCNT}$ increases, reaches a minimum at a critical SWCNT concentration, $\phi_{crit} \sim 0.4$ vol\%, and then increases approaching the $D$ for the pure PS case for $\phi_{SWCNT} > \phi_{crit}$. The recovery at $\phi_{SWCNT} > \phi_{crit}$ is attributed to anisotropic diffusion in the vicinity of the SWCNT; namely, because diffusion parallel to the nanotube is faster than that perpendicular to the nanotube, the percolated SWCNTs provide a fast continuous pathway parallel to the nanotube. Simulations conducted in the same study imposed anisotropic diffusion in the vicinity of cylindrical nanoparticles and found a minimum in the diffusion coefficient with increasing nanoparticle concentration in agreement with the experimental data. Using multi-walled carbon nanotubes (MWCNT), follow-up studies\textsuperscript{54, 58} showed that a diffusion minimum only occurs when the tracer molecule (dPS) is larger than the diameter of the carbon nanotubes. This
finding further supports the hypothesis of local anisotropy in polymer diffusion near cylindrical nanoparticles.

In the present study, we investigate tracer diffusion in polymer nanocomposites with irregularly-shaped NPs. Our interest in these complex NPs is motivated by their practical importance and their potential to reconcile the disparate $D$ versus $\phi_{NP}$ behaviors established for spherical and high-aspect-ratio cylindrical NPs. Here the irregularly-shaped aggregates contain individual nanoparticles that form short chains prior to functionalization, and then become covered with the grafted PS brush. Compared to the well-defined PNCs with isolated NPs, the systems more realistically mimic commercial nanocomposites. For example, a common nanofiller added into polymer matrices is carbon black which has a fractal shape consisting of linear aggregates of spherical NPs. The addition of carbon black improves abrasion resistance,\textsuperscript{153} fracture toughness,\textsuperscript{154} and tensile strength,\textsuperscript{155} and imparts electrical conductivity to normally insulating polymers.\textsuperscript{156,157} With respect to rubbers, carbon black is one of the most important and prevalent additives improving many important tire properties such as wear resistance, rolling resistance, and durability to achieve greater fuel efficiency.\textsuperscript{158}

The nanocomposites studied here contain a PS matrix mixed with PS-grafted chained nanoparticles (cNP), wherein each cNP consists of ~ 5 spherical iron oxide (Fe$_3$O$_4$) nanoparticles (5 nm diameter) fused together to form string-like aggregates. These cNPs are well-dispersed in PS matrices at Fe$_3$O$_4$ core volume fractions ($\phi_{cNP}$) from 0.0005 to 0.024, or corresponding to 2 to 100 wt % of the grafted NPs. For dPS (49, 168, and 532 kg/mol), $D$ exhibits a minimum at $\phi_{cNP} \sim 0.25$ vol %; however for dPS (1866
kg/mol), $D$ monotonically decreases when plotted versus $\phi_{cNP}$. This system of chained NPs of modest aspect ratio and a wide range of tracer molecular weights provides the means to explore the origins of the contrasting tracer diffusion behavior between spherical and high aspect ratio cylindrical nanoparticles. Moreover, these PNCs with PS-grafted cNPs establish that the polymer brush participates in tracer diffusion and provides a diffusive pathway distinct from the PS matrix. This insight provides a novel method to control polymer diffusion, for instance, by changing the size of the brush relative to the matrix.

4.2 Experimental Section

4.2.1 Materials

The matrix in the PNCs is polystyrene (PS) ($P = 270$ kg mol$^{-1}$, polydispersity (PDI) = 1.06, Polymer Source). The tracer polymers are deuterated PS (dPS) ($M = 49$ kg mol$^{-1}$, PDI = 1.03, Polymer Laboratories; $M = 168$ kg mol$^{-1}$, PDI = 1.02, Polymer Laboratories; $M = 532$ kg mol$^{-1}$, PDI = 1.09, Polymer Source; $M = 1866$ kg mol$^{-1}$, PDI = 1.3, Polymer Source). To implement the two-phase model, additional tracer diffusion experiments were performed using a matrix PS ($P = 130$ kg mol$^{-1}$, PDI = 1.08, Pressure Chemical) that mimicked the grafted polymer brush. The polymers and toluene (Sigma Aldrich) were used as received. Molecular weights and PDIs were determined by size exclusion chromatography (SEC) using tetrahydrofuran (THF) as the solvent.
4.2.2 Synthesis of chained nanoparticles

Iron(III) acetylacetonate (17.7 g) was mixed in trioctylamine (500 mL) with 1,2-hexadecanediol (64.6 g), oleic acid (42.4 g), and oleylamine (40.1 g) under nitrogen. The mixture was heated at a rate of 10 °C/min to 260 °C and held at this temperature for 30 min. After cooled down to room temperature, the dark-brown mixture was poured into a large excess of ethanol, and the resultant precipitate was collected by centrifugation at 3000 rpm and redispersed in THF. The precipitation/redispersion cycle was repeated twice.

4.2.3 Fixation of atom transfer radical polymerization (ATRP)-initiator on chained nanoparticles

A 500 mL round-bottom flask equipped with a magnetic stirring bar was charged with a suspension of chained nanoparticles (2 g) in THF (167 g). A mixture of 28% NH₃ (3.3 g) and THF (50 g) and then a mixture of a fixable ATRP-initiator, (2-bromo-2-methyl)propionyloxypropyl triethoxysilane (BPE),¹⁵⁹ (1.5 g) and THF (50 g) were added to the nanoparticle solution, in that order. The reaction mixture was stirred magnetically for 5 days at room temperature along with occasional sonication in a bath sonicator. The modified chained nanoparticles were washed by consecutive centrifugation and redispersion in THF to obtain a THF stock suspension.
4.2.4 Synthesis of polymer brush-afforded chained nanoparticles by surface-initiated ATRP

Polymerization was carried out using the initiator-BPE-fixed chained nanoparticles following our previous report.\textsuperscript{160,161} A Pyrex glass tube was charged with Cu(I)Cl (143 mg) as a catalyst (solid). A mixture of the initiator-fixed chained nanoparticle suspension in THF (6.3 wt\%, 1.19 g) containing styrene (15 g), ethyl 2-bromoisobutyrate (9.4 mg) as a free initiator, and 4,4’-dinonyl-2,2’-bipyridine (1.18 g) as a ligand for complexation with copper was quickly added to the Pyrex glass tube. The tube was immediately degassed by three freeze–pump–thaw cycles and sealed off under vacuum. The polymerization was carried out in a shaking oil bath (TAITEC Corp., Saitama, Japan, Personal H-10) thermostated at 100 °C for 48 h and quenched to room temperature. The reaction mixture was diluted by THF and centrifuged to collect the polymer-grafted chained nanoparticles. The cycle of centrifugation and redispersion in THF was repeated five times to obtain polymer-grafted chained nanoparticles that were perfectly free of unbound (free) polymer. To determine the molecular weight of the graft polymer, polystyrene chains were cleaved from the surface as follows: the polymer-grafted chained nanoparticles (50 mg) and tetraoctylammonium bromide (50 mg), as a phase transfer catalyst, were dissolved in toluene (5 mL), to which a 10\% HF aqueous solution (5 mL) was added. The mixture was vigorously stirred for 3 h. The cleaved polymer in the organic layer was subjected to a GPC measurement. The polymerization gave a graft polymer with a $M_n$ of 132 kg/mol and a $M_w/M_n = 1.20$; $M_n$ and $M_w$ are the number- and weight-average molecular weight, respectively, and $M_w/M_n$ is the
polydispersity index. The grafting density is ~0.19 chains/nm$^2$ determined by thermalgravimetric analysis (TGA). The final product of the PS-grafted chained nanoparticle (cNP) is shown in Figure 4.1a. To be clear, nanoparticles form aggregates before grafting the PS brush, and thus the brush is grafted around the periphery of the aggregate. There are ~5 individual Fe$_3$O$_4$ nanoparticles per cNP according to image analysis (Figure 4.1b). A single batch of PS-grafted NPs was used for all the work reported here.

Figure 4.1. (a) Chained nanoparticles (cNP) drop-cast on a TEM grid. The scale bar is 100 nm. (b) Distribution of spherical Fe$_3$O$_4$ nanoparticles per cNP. The solid line is a fit using a log-normal distribution having an average of 5 nanoparticles per cNP. The inset shows a schematic illustration of a cNP grafted with PS brushes (blue) where the core dimensions are $d = 5$ nm and $L = 25$ nm.

4.2.5 Preparation and characterization of polymer nanocomposites

In this work, a polymer nanocomposite is composed of PS and cNP. We aimed to well-disperse the cNPs in the PS matrix. PS and cNPs were dissolved in toluene separately by stirring for 24 hours. An appropriate amount of the cNP solution was mixed
with the PS solution to produce the desired PNC composition, and the mixed solution was stirred for 24 hours. Films were prepared by doctor blading the mixed solution on a heated (100 °C) glass substrate, which allows the solvent to evaporate rapidly. After doctor blading, the film was dried at 100 °C in a hood for 10 minutes, and then was dried under vacuum at ambient temperature for 24 hours. The resulting thickness of the film was about 3 μm as determined by ellipsometry. The sample compositions are reported in volume fraction of iron oxide nanoparticle ($\phi_{cNP}$) and vary from 0 to 0.024. Given the grafting density and molecular weight of the PS brushes on the cNP, the sample with $\phi_{cNP} = 0.024$ corresponds to 100% PS-grafted cNP in the absence of PS matrix. The distribution of the nanoparticles was observed using transmission electron microscope (JEOL 2100) after cross-sectioning the nanocomposite thin film using a microtome.

4.2.6 Diffusion couple preparation and annealing

The diffusion couple consisted of a thick (~ 3 μm) nanocomposite film covered with a layer of thin dPS film. The nanocomposite film was floated from the glass substrate in water and picked up using a silicon wafer. The nanocomposite film on the wafer was aged at 150 °C for three days in vacuo. The dPS tracer film was spin-coated on a silicon wafer and had a thickness ~25 nm as measured by ellipsometry. The tracer film was transferred from the silicon wafer to the top of the nanocomposite film, forming a diffusion couple. The diffusion couple was dried under ambient conditions overnight, and then annealed isothermally at 170 ± 1°C in a vacuum oven. The annealing time was chosen to allow sufficient penetration of the dPS into the matrix, typically ~300 nm. To
ensure consistency of annealing condition, a control sample of dPS/PS was annealed adjacent to the sample.

**4.2.7 Elastic Recoil Detection (ERD)**

ERD was used to probe the dPS depth profile in the nanocomposite. Details of ERD have been reviewed elsewhere.\(^{138}\) The measurement was conducted under room temperature. The energy of the incident helium ion (He\(^{2+}\)) beam was \(~3.022\) MeV, and the ion beam intersected the plane of the sample at \(15^0\). The energy of the recoiled atom was detected by a solid-state detector. A 10 \(\mu\)m Mylar film was placed in front of the detector in order to filter forward scattered helium that masked the hydrogen and deuterium signal. A low beam current (\(<2\) nA) was used, and total 10 \(\mu\)C was collected. The ERD spectra of count versus channel were converted to dPS depth profile of dPS volume fraction versus depth. The diffusion coefficient of the tracer was obtained by fitting the depth profile using the one-dimensional (1-D) solution of Fick’s second law for a finite source in a semi-infinite medium.\(^{139}\) The instrumental resolution (\(\sigma\)), or half of the full width at half maximum (FWHM) was captured by the Gaussian function, \(y = \left[1/\sigma (2\pi)^{1/2}\right] \exp(-x^2/2\sigma^2)\), where \(y\) is the dPS fraction and \(x\) is the depth. \(\sigma\) is 40 nm and the accessible depth was \(~800\) nm. The diffusion coefficients obtained in this work were from multiple measurements. Only the depth profiles having a sufficient diffusion length (\(>300\) nm) were used.
4.3 Results and Discussion

4.3.1 Distribution of Nanoparticles in Polymer Nanocomposites

The PNCs contain a PS matrix (270 kg/mol) with PS-grafted cNPs having $\phi_{cNP} = 0.0005 \sim 0.024$, where $\phi_{cNP}$ corresponds to the volume fraction of Fe$_3$O$_4$ in the PNC. A good dispersion of the cNPs is required for diffusion studies because agglomeration leads to a larger distance between cNPs, which can increase polymer mobility. Figure 4.2 shows cross-sectional TEM images for PNCs and in all cases the cNPs are well-dispersed in the PS matrices without agglomerating. Note that the average number of spherical Fe$_3$O$_4$ nanoparticles per cNP (~5, see Figure 4.1) is constant as cNP loading increases. In the absence of PS matrix at $\phi_{cNP} = 0.024$, the grafted PS brushes of neighboring cNPs interdigitate with each other and form a robust bulk film. At lower $\phi_{cNP}$ the PS brushes grafted to the Fe$_3$O$_4$ NP aggregates act to stabilize and disperse the cNPs within the matrix PS. Because the brush and matrix are chemically identical, the dispersion of cNPs can be controlled by depletion – attraction forces that depend on brush grafting density and degrees of polymerization of the brush and matrix.$^{162-165}$ For example, polymer-grafted spherical nanoparticles and nanorods are well-dispersed in the polymer matrix as the degree of polymerization of the brush is at least twice as large as the degree of polymerization of the matrix, namely $P/N < 4$ for spheres$^{48, 166}$ and $P/N < 2$ for nanorods$^{15, 16}$. In this study, the PS brush ($N = 132$ kg/mol) is “wet” by the PS matrix ($P = 270$ kg/mol) because $P/N \sim 2$ and thus the well-dispersed cNPs are stable due to their repulsive brush-brush interactions. Therefore, not only is good dispersion of cNP observed in the as-prepared films, this dispersion is maintained throughout the diffusion
studies described in the next section. This invariance of the cNPs and the PNC morphology leads to well-defined and reproducible tracer diffusion studies.

Figure 4.2. Cross-sectional TEM images of PS/cNP nanocomposites with increasing Fe$_3$O$_4$ core volume fraction, $\phi_{cNP}$: (a) $\phi_{cNP} = 0.0005$, (b) $\phi_{cNP} = 0.001$, (c) $\phi_{cNP} = 0.0025$, (d) $\phi_{cNP} = 0.005$, (e) $\phi_{cNP} = 0.01$, (f) $\phi_{cNP} = 0.024$. The scale bar is 100nm.

4.3.2 Tracer Diffusion in Nanocomposites

After annealing the diffusion couple, the tracer diffusion coefficients of dPS in PS/cNP were determined as a function of Fe$_3$O$_4$ NP core volume fraction using ERD. The profile is described by the 1-D solution to Fick’s second law for a finite source in a semi-infinite medium. The dPS volume fraction, $\phi(\chi)$, is given by.\textsuperscript{139}
\[
\phi(x) = \frac{1}{2} \left[ \text{erf} \left( \frac{h-x}{\sqrt{4Dt}} \right) + \text{erf} \left( \frac{h+x}{\sqrt{4Dt}} \right) \right]
\]

where \( x \) is depth, \( h \) is original dPS film thickness, \( t \) is diffusion time, and \( D \) is the diffusion coefficient of dPS. An experimental depth profile was fitted by \( \phi(x) \) convoluted with the Gaussian instrumental resolution function. Quality fits were obtained by minimizing \( \chi^2 \) using least-squares fitting. Figure 4.3a-d shows representative diffusion profiles for dPS (solid circles) with \( M = 49, 168, 532 \) and 1866 kg/mol, respectively, into PNCs at \( \phi_{cNP} = 0.0025 \) and their fits (solid lines) after annealing for 0.1 h, 1 h, 7 h, and 40 h, respectively. In all cases the depth profiles agree with Fickian behavior (Eq. 4.1); \( D \) systematically decreases as \( M \) increases. Figure 4.4 shows the diffusion coefficients of dPS(\( M \)) plotted against \( \phi_{cNP} \). At low loadings, \( D \) decreases strongly as \( \phi_{cNP} \) increases for all dPS. For example, for dPS (168 kg/mol) \( D \) decreases by \( \sim 35\% \), from \( 1.6 \times 10^{-15} \) cm\(^2\)/s to \( 1.1 \times 10^{-15} \) cm\(^2\)/s, as \( \phi_{cNP} \) increases from 0 (pure PS) to only 0.0025, respectively. For dPS (49, 168, and 532 kg/mol), \( D \) then increases as \( \phi_{cNP} \) increases for \( \phi_{cNP} > 0.0025 \), resulting in a minimum \( D \) near \( \phi_{cNP} = 0.0025 \). In contrast, for the highest \( M \) tracer, namely dPS (1866 kg/mol), \( D \) monotonically decreases as \( \phi_{cNP} \) increases. Moreover, at the highest loading, \( \phi_{cNP} = 0.024 \), corresponding to pure cNP, dPS (1866 kg/mol) tracer molecules are unable to diffuse through the PS brush for annealing times up to 72 h. This novel observation suggests that these PNCs with PS-grafted cNPs could effectively separate high molecular weight macromolecules and that the molecular weight sensitivity could be tuned by changing the brush molecular weight and matrix content.
In the dilute regime, the slowing down of diffusion with increasing NP loading is consistent with our prior studies of PNCs with spherical NPs where a decrease in $D$ is observed even when NPs are separated on average by a distance ($ID$, interparticle distance) 10 times larger than the tracer size, i.e. $ID/2R_g > 10$. (Unfortunately, in this study of PNCs with cNPs the parameter $ID$ cannot be adopted, because the spacing between these cNPs is ill-defined due to their anisotropic shape.) Using secondary ion mass spectrometry, Zheng et al. reported a similar long-range effect on polymer diffusion where dPS diffusion is an order of magnitude slower than in the bulk at a

Figure 4.3. Volume fraction profiles of dPS (a) 49 kg/mol, (b) 168 kg/mol, (c) 532 kg/mol, and (d) 1866 kg/mol, in PS/cNP nanocomposites at $\phi_{cNP} = 0.0025$ and 170°C. Solid curves represent fits using Equation 1 convoluted with a Gaussian instrumental resolution function. Annealing times of (a) 0.1 hr, (b) 1 hr, (c) 7 hr and (d) 40 hr were chosen to provide an optimum diffusion length ~ 400 nm.
distance of ~ $10R_g$ from a bare planar interface. The long-range effect is attributed to a change in local chain packing near the interface where interlocking loops decrease the entanglement length ($N_e$), and therefore, the resulting reduction in the tube diameter causes a slowing down of diffusion. Because the NPs in our system that provide the interface are grafted with a polymer brush, direct contact between matrix chains and the NP surface is blocked, and the adsorption of matrix chain is not possible. Self-consistent field theory (SCFT) calculations of the matrix chain penetration into the brush at similar conditions support this statement.\textsuperscript{49} Therefore, slowing down in this PS/cNP nanocomposite is unlikely due to a decrease in $N_e$ adjacent to the interface. Clearly, further experimental and theoretical studies are required to understand the mechanism underlying the slowing down of polymer diffusion when the interface is far from the tracer chain.

The presence or absence of a minimum in the tracer diffusion coefficient with increasing $\phi_{cNP}$ depends on the relative sizes of tracer molecule and cNP. Mu \textit{et al.}\textsuperscript{54} investigated polymer diffusion in a multiwall carbon nanotube (MWCNT)/PS system, and found that when the size of the tracer molecule, $2R_g$, is greater than the diameter of MWCNT, a minimum in the diffusion coefficient is observed. Anisotropic diffusion adjacent to the MWCNT with faster diffusion along the nanotubes than perpendicular to the nanotubes was hypothesized. Consequently, the tracer molecule can rapidly diffuse through a continuous path adjacent to the percolated nanotubes, thereby producing a minimum in the diffusion coefficient near the percolation threshold of the nanoparticle. Note that the nanotubes are bare, namely without grafted polymer brushes. In the present
study, the tracer molecule sizes ($2R_g$) are greater than the diameter of cNPs ($d \sim 5$ nm) as shown in Table 4.1, where $R_g$ is calculated assuming Gaussian chain statistics:146

$$R_g = \frac{a\sqrt{M_w/M_0}}{\sqrt{6}}$$

(4.2)

where $a$ is the monomer length (0.67 nm),167 $M_w$ is the weight-averaged molecular weight and $M_0$ is the molar mass of a monomer unit (112 g/mol). The tracer molecule size relative to the length of cNPs ($L \sim 25$ nm), $2R_g/L$, is a critical value for determining the observation of a diffusion minimum. When dPS molecular weight is 49, 168 and 532 kg/mol and $2R_g/L < \sim1.5$, a diffusion minimum is observed, Figure 4.4, suggesting that the tracer molecules diffuse anisotropically near the cNPs. However, when $2R_g$ is greater than $L$ by a factor of $\sim3$ corresponding to a dPS molecular weight of 1866 kg/mol, the monotonic decrease in the diffusion coefficient with increasing $\phi_{NP}$ is consistent with isotropic diffusion near the cNPs.

**Table 4.1.** The radius of gyration of the tracer polymer relative to the nanoparticle dimensions.

<table>
<thead>
<tr>
<th>dPS MW (kg/mol)</th>
<th>$2R_g$ (nm)</th>
<th>$2R_g/d$</th>
<th>$2R_g/L$</th>
</tr>
</thead>
<tbody>
<tr>
<td>49</td>
<td>11.4</td>
<td>2.30</td>
<td>0.46</td>
</tr>
<tr>
<td>168</td>
<td>21.2</td>
<td>4.24</td>
<td>0.85</td>
</tr>
<tr>
<td>532</td>
<td>37.7</td>
<td>7.54</td>
<td>1.51</td>
</tr>
<tr>
<td>1866</td>
<td>70.6</td>
<td>14.12</td>
<td>2.82</td>
</tr>
</tbody>
</table>
Figure 4.4. dPS tracer diffusion coefficients in PS/cNP nanocomposites as a function of Fe$_3$O$_4$ core volume fraction (\(\phi_{cNP}\)) at 170°C. dPS molecular weights are 49 kg/mol (black), 168 kg/mol (red), 532 kg/mol (green), and 1866 kg/mol (blue). A minimum in \(D\) is observed at \(\phi_{cNP} = 0.0025\).

4.3.3 Effect of Polymer Brush on Tracer Diffusion

In addition to enhancing dispersion, the polymer brushes grafted to the NPs form a region around the NPs that is distinct from the bulk. In the absence of NPs, polystyrene tracer molecules diffuse by reptation when the matrix molecular weight, \(P\), is above a critical value, \(P_{crit} = 35\) kg/mol, and in this regime tracer diffusion is independent of \(P\).\(^{168}\)
However, when the matrix chains are short, the tracer molecule can diffuse by the constraint release mechanism as well as by reptation, because the relaxation time of the matrix chain is comparable to that of the tracer molecules. Namely, the tube can relax before the tracer chain leaves the tube formed by the entanglements by reptation. In our PS/cNP nanocomposites, there are three molecular weights of interest: matrix (270 kg/mol), tracer (49 – 1866 kg/mol) and brush (132 kg/mol). Two normalization schemes are considered for the tracer diffusion coefficient.

First, we normalize $D$ by the tracer diffusion coefficient in a pure matrix ($D_0$), as we have done previously and which neglects any differences between diffusion in the matrix and the brush. When $D/D_0$ is plotted against $\phi_{cNP}$, a minimum in $D/D_0$ is clearly observed near $\phi_{cNP} = 0.0025$ for three dPS tracers (49, 168, and 532 kg/mol), Figure 4.5. Moreover, there is a sharp transition from the nearly overlapping values of $D/D_0$ at the three smaller dPS tracers to the monotonic decrease in $D/D_0$ for the largest dPS tracer at $M = 1866$ kg/mol. Note that given the length and areal density of the PS-grafted brushes on the cNPs a significant fraction of the matrix is composed of the PS brush, so we propose an alternative approach for normalizing $D$. 
For these PNCs, diffusion of the tracer in the matrix may differ from the brush region, because the PS matrix chains are about 2x longer than the brush chains. This difference is likely to be most pronounced for the dPS with intermediate molecular weights, namely 168 and 532 kg/mol, due to the competition between the constraint release and reptation mechanisms. For example when dPS of 532 kg/mol diffuses into PS, $D$ is about 3x greater in $P = 132$ kg/mol than in $P = 270$ kg/mol. Sridharan et al.\textsuperscript{169} defined an effective diffusion coefficient ($D_e$) in a two-phase material. This model

\begin{figure}[h]
  \centering
  \includegraphics[width=0.5\textwidth]{figure4.pdf}
  \caption{Normalized diffusion coefficients $D/D_0$ plotted as a function of $\phi_{cNP}$. dPS molecular weights are 49 kg/mol (black), 168 kg/mol (red), 532 kg/mol (green), and 1866 kg/mol (blue). A minimum in $D/D_0$ is observed for the three smaller dPS tracers near $\phi_{cNP} = 0.0025$.}
\end{figure}
assumes penetrable spherical inclusions in a continuous matrix, which when applied to our PNCs corresponds to the PS brush and PS matrix, respectively, and yields the relationship:

\[
\frac{D_1 - D_e}{D_1 + 2D_e} \phi_1 + \frac{D_0 - D_e}{D_0 + 2D_e} \phi_0 = 0
\]  

(4.3)

where \(D_0\) is the diffusion coefficient of dPS in the pure PS matrix (270 kg/mol), \(D_1\) is the diffusion coefficient of dPS in the pure brush (132 kg/mol), and \(\phi_0\) and \(\phi_1\) are the volume fractions of the PS matrix and PS brush regions, respectively. Note that for \(\phi_1 = 0\) and 1, \(D_e\) is \(D_0\) and \(D_1\), respectively. For dPS (49, 168, 532 and 1866 kg/mol), \(D_1\) is measured in a PS matrix with a molecular weight that matches the PS brush. The normalized tracer diffusion coefficient relative to \(D_e\) is plotted against \(\phi_{cNP}\), Figure 4.6. Similar to \(D/D_0\) in Figure 4.5, \(D/D_e\) values overlap nicely in the dilute region, i.e. \(\phi_{cNP} < \sim 0.0025\). However, unlike \(D/D_0\), the molecular dependence of \(D/D_e\) at higher \(\phi_{cNP}\) is more evident.

Interestingly, while \(D/D_0\) exhibits a minimum when the dPS tracer is 532 kg/mol, when normalized by \(D_e\) to account for the PS brushes, \(D/D_e\) exhibits a monotonic decrease.

Using the two methods for normalizing the tracer diffusion coefficient, we establish that the critical normalized length scale required to exhibit a diffusion coefficient minimum is

\[2R_g/L = 0.85 - 1.5\]

which is consistent with the CNT system\(^{53}\) where the diffusion minimum occurs at \(2R_g/L \sim 1\).

These results indicate that the effective length of the cNPs is greater than the core length \(L\), because relatively large tracer molecules can be excluded from the brush regimes at the ends of the cNPs. Therefore, an accurate model of polymer diffusion
which captures the penetration depth of tracer into the brush domain is needed. Moreover, brush dynamics should differ from free chain dynamics because a brush is end-grafted to the NP. For example, Lai and Binder\textsuperscript{170} found that the relaxation time ($\tau$) of a polymer brush with chain length $N$ in solution at the Theta condition scales as $\tau \sim N^3$, whereas in entangled polymer melts, brush chains have to retract from entanglements, and thus $\tau$ scales as in star polymers where $\tau \sim e^N$, much slower than the relaxation time of a free chain.\textsuperscript{146, 171} In addition, the local mobility of monomers may increase as the distance from the NP surface increases; namely, the local mobility near the grafting site is expected to be slower than near the free end.\textsuperscript{172} This inhomogeneity in brush dynamics may result in a gradient in diffusivity of tracer molecules adjacent to the brush, and could influence the tracer diffusion in the 100% cNP sample relative to the PS/cNP nanocomposite. Furthermore, the effective dimensions of the cNP’s can be changed by varying the molecular weight of the brush and doing so is likely to result in different values of $\phi_{cNP}$. Regardless of the exact range of brush dynamics, a topic that requires future understanding, we demonstrate here that the tracer diffusion coefficients normalized by two limiting cases results in different trends in the diffusion minimum.
Figure 4.6. Normalized diffusion coefficients, $D/D_e$, plotted as a function of $\phi_{cNP}$. dPS molecular weights are 49 kg/mol (black), 168 kg/mol (red), 532 kg/mol (green), and 1866 kg/mol (blue). Solid lines are guide to the eye. A minimum in $D/D_e$ is observed for the two smaller dPS tracers near $\phi_{cNP} = 0.0025$.

4.4 Conclusion

We measure the tracer diffusion coefficient ($D$) in polymer nanocomposites having chained nanoparticles (aspect ratio ~5) grafted with PS brushes. When the dPS tracer molecular weight is large (1866 kg/mol), $D$ decreases monotonically with increasing nanoparticle concentration consistent with previous studies with monodisperse spherical nanoparticles. In contrast, when the dPS molecular weight is smaller (49, 168 or 532 kg/mol), $D$ exhibits a minimum at $\phi_{cNP} = 0.0025$, which has been previously reported.
in PNCs with carbon nanotubes when the tracer molecule is larger relative to the nanotube diameter ($2R_g/d > 1$). All the PS/cNP nanocomposites have $2R_g/d > 1$, but the minimum in the tracer diffusion is found only when the tracer molecule is also small relative to the cNP length ($2R_g/L < 1.5$). We are encouraged that the recent studies on PNCs with well-defined spherical and cylindrical nanoparticles have proven valuable in understanding the diffusion in these PNCs with string-like, anisotropic nanoparticles. In particular, the importance of tracer size relative to nanoparticle size ($d$ and $L$) is established, as well as the propensity of anisotropic nanoparticles to impose anisotropic diffusion coefficients near the nanoparticles.

In contrast to many model systems, these novel PS/cNP nanocomposites have significantly more PS brush relative to PS matrix, because these cNP have both high grafting density and high brush molecular weight. Thus, we explore two methods for normalizing the tracer diffusion coefficient: the tracer diffusion in PS ($D_0$) and the effective tracer diffusion ($D_e$) based on a two-phase system that distinguishes between diffusion in the matrix and the PS brush regions. Normalizing with the effective diffusion coefficient ($D/D_e$) clarifies the effect of the tracer molecular weight at higher cNP concentrations and highlights the importance of polymer brush dynamics on polymer diffusion. We hope these studies provide guidance for future models and theories on polymer dynamics in PNCs with complex nanoparticles and nanoparticles with extensive brushes.
CHAPTER 5. MOBILE-NANOROD-ASSISTED POLYMER DIFFUSION IN POLYMER NANOCOMPOSITES

This work was accomplished in collaboration with Prof. Karen I. Winey, Prof. Christopher B. Murray at the University of Pennsylvania, and Prof. Nigel Clarke at the University of Sheffield, U.K. The contents of this chapter were submitted to ACS Macro Letters in a modified version.

5.1 Introduction

By combining nanoparticles with polymers to form polymer nanocomposites (PNCs), coatings and bulk materials with unique functions, such as responsive optical, electrical and magnetic properties, can be prepared. Enhanced mechanical properties can also be achieved in PNCs while retaining the viscoelasticity of the host
polymer, preserving a significant advantage, namely the ease of polymer processing. In addition to adding functionality, nanoparticles can influence fundamental polymer properties including the diffusion of macromolecules. Therefore, by understanding how polymer dynamics are influenced by nanofillers, one can better optimize the processing conditions of these multicomponent materials consisting of hard, impenetrable and discrete particles embedded in a relatively soft and flexible matrix.\textsuperscript{71, 112} The center of mass (COM) diffusion of polymers is also partly responsible for determining whether a thermodynamically unstable polymer/NP system undergoes aggregation during processing/use or remains quenched in a metastable state.\textsuperscript{52} For example, in processing photovoltaic films,\textsuperscript{176} the dispersion of quantum dots and therefore the efficiency of conversion is directly related to the mobility of particles and polymer during processing. Further, because of heating during radiation exposure, the particles can aggregate resulting in reduced quantum efficiency. Whereas polymer diffusion in the presence of immobile NPs has received much attention,\textsuperscript{40, 45, 52, 53, 55, 59} studies of polymer diffusion in PNCs containing nanoparticles that diffuse on the time scale as the polymer has not yet been reported.

Recent studies of diffusion have focused on polymer diffusing in PNCs containing spherical and cylindrical nanoparticles (NPs). For spherical NPs, polymer diffusion decreases monotonically as the NP concentration increases. For example, Gam et al.\textsuperscript{40} reported that the tracer diffusion coefficient of deuterated polystyrene (dPS) decreases by 80\%, relative to a pure polymer matrix, when diffusing in a matrix containing 50 vol\% of phenyl-capped silica NPs (diameter, $d = 28$ nm) and PS. The
dPS/PS:phenyl-NP system is ideal for studying the effect of NPs on polymer diffusion, because data analysis isn’t confounded by changes in the glass transition, which is constant up to 50 vol%, and the interactions between dPS and phenyl-NP can be considered neutral. Nevertheless, subsequent studies showed that tracer diffusion of deuterated poly(methyl methacrylate), or dPMMA, in a PMMA:silica-OH matrix which has weakly attractive polymer-NP interactions follows the same scaling behavior as the neutral system.\textsuperscript{45} In contrast, in the presence of anisotropic NPs, polymer diffusion initially slows down at low NP concentration, reaches a minimum near a concentration where the NPs form a percolative network, and increases as concentration further increases.\textsuperscript{53-55, 59} In all of these studies, the spherical and anisotropic NPs are “immobile” on the time scale of polymer diffusion. Here “immobile” NPs are defined as those moving a distance of less than a NP diameter. For example, the Stokes-Einstein (SE) diffusivity of a 28 nm-silica NP is about 4 orders of magnitude slower than a polymer with molecular weight = 265 kg/mol in an entangled polymer melt. Because recent studies indicate that nanoparticles diffuse faster than the classical SE prediction,\textsuperscript{116, 118, 119, 177} comparison between NP and polymer diffusion is an approximation. For example, using fluctuation correlation spectroscopy (FCS), Grabowski and Mukhopadhyay\textsuperscript{116} reported that diffusion of Au NPs in poly(n-butyl methacrylate) is 2 orders of magnitude faster than the SE prediction when the NP diameter and tube diameter ($d_t$) are similar, $\sim$ 5 nm.

Small mobile nanoparticles can influence the dynamics of the host polymer if the transient nature of the NP location influences the topological constraints surrounding the
diffusing polymer. For example, simulation studies\textsuperscript{21, 74} showed that the number of monomers in an entanglement strand ($N_e$) increases when nanoparticles are added, whereas Mackay et al.\textsuperscript{20} reported that $N_e$ of PS matrix ($d_t \sim 8$ nm) is not affected upon adding intramolecularly cross-linked PS nanoparticles ($d = 6$ to 10 nm). Viscosities of PNCs containing small spherical NPs are generally found to decrease at low NP concentrations; however, above a critical concentration, PNCs can be reinforced due to the formation of a NP network or jammed NPs.\textsuperscript{19-21, 74} In addition, using molecular dynamics simulations (MD), Kalathi et al.\textsuperscript{118} reported that polymer diffusion in the presence of small NPs can be 40\% faster than in the neat polymer case, indicating that mobile NPs speed up the slowest relaxation mechanism (e.g., reptation time).

In this letter, we investigate polymer diffusion in the presence of mobile nanorods (NR). The diffusion coefficients of these NRs are known and vary from $10^{-12}$ to nearly $10^{-15}$ cm$^2$/s upon increasing the matrix molecular weight ($P$) from 60k to 2000k, respectively, at 190 °C.\textsuperscript{178} Compared to spheres of similar diameter, NR diffusion is particularly sensitive to matrix molecular weight because lateral diffusion is coupled to the matrix chain dynamics. In the present paper, we increase NR diffusion relative to polymer tracer diffusion, by decreasing $P$. Furthermore, because the tracer diffusion coefficient ($D$) of entangled polymers scales with molecular weight ($M$) as $D \sim M^{-2}$,\textsuperscript{2, 146} polymer and nanoparticle diffusion coefficients can be independently controlled by varying $M$ and $P$, respectively. In this way, NP diffusion, which is typically slow in polymer melts, can become faster than polymer diffusion. Here we show that the initial slowing down of polymer diffusion as NP concentration increases is weaker when $P$ is
small and NPs are mobile. We attribute this enhanced dPS diffusion to a reduction in topological constraints when NPs are mobile. However, above an overlap concentration, the NRs become immobile relative to the time scale of polymer diffusion, regardless of $P$ and become independent of matrix molecular weight.

### 5.2 Experimental Section

Phenyl-capped TiO$_2$ nanorods with diameter ($d$) = 4.5 nm, and length ($L$) = 31 nm were prepared using a nonaqueous surfactant-assisted synthesis method.$^{179, 180}$ The NR surface was functionalized with (chloromethyl)dimethyl phenylsilane to prepare phenyl-capped NRs that disperse in the hydrophobic matrix, polystyrene (PS; $P_n$ = 650 and 2000 kg/mol). NRs were dispersed in both PS matrices (650 and 2000 kg/mol) for NR volume fractions, $\varphi_{NR} = 0.004 - 0.08$ determined using thermal gravimetric analysis (TGA). The PNCs were preannealed at 150 °C for 72 h to relax the matrix. The glass transition temperatures ($T_g$) of the PNCs were 104 ± 1 °C, similar to the pure PS matrix, and consistent with our prior studies for phenyl-capped silica NP/PS,$^{40}$ suggesting that surface grafting results in a nearly neutral PS segment-NR interaction. Diffusion couples were prepared by depositing a deuterated polystyrene film (dPS; $M = 800, 1800$ and 3200 kg/mol) with a thickness of 20 nm on the top of a thick PNC film (> 2 μm). The diffusion couples were annealed in a vacuum oven at $T = 190$ °C for times (hours to days) that allow sufficient penetration of the dPS into the matrix, typically ~ 350 nm. The dPS volume fraction profiles were measured using elastic recoil detection (ERD)$^{138}$ as shown in Figure 5.1(a), and a representative dPS volume fraction profile is shown in Figure 5.1(b). The profile can be described using the 1-D solution of Fick’s second law for a
finite source in a semi-infinite medium. The deuterium volume fraction, \( \phi_{dPS} \), is given by:

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

(5.1)

where \( x \) is depth, \( h \) is original dPMMA film thickness, \( t \) is diffusion time, and \( D \) is the diffusion coefficient of dPS. \( D \) is extracted by fitting an experimental depth profile using Equation 1 convoluted with the Gaussian instrumental resolution function (red curve).

Figure 5.1. (a) Elastic recoil detection (ERD) geometry showing 3 MeV He\(^{2+} \) impinging on the dPS(red)/PNC diffusion couple. The energy of the recoiled deuterium from dPS is measured by a solid state detector. (b) Representative volume fraction profile of dPS (800 kg/mol) that diffused into the PNC, PS(650 kg/mol):NR(\( \phi_{NR} = 0.065 \)) , after annealing at 190°C for 3h (closed symbol). For comparison, the profile for an unannealed couple (open symbol) is shown and exhibits a Gaussian peak representing the instrumental resolution. The solid line represents a best fit of Eq. 1 convoluted with the instrumental resolution function resulting in \( D = 3.1 \times 10^{-14} \) cm\(^2\)/s. The dashed line is the sum of a “surface peak” that has the same FWHM as the unannealed profile and the solid line. The surface peak has been described elsewhere.\(^{37, 40} \)
5.3 Results and Discussion

5.3.1 Nanorod Dispersion

A good dispersion of NRs is necessary because NR aggregation will confound data analysis; for example, aggregation would cause time dependent dPS diffusion. Also, because NR bundles have a larger size than individual NRs, NR mobility will decrease upon aggregation. In the present study, it is important to know and control the diffusion coefficient of NRs to ensure that they are mobile on the time scale of polymer diffusion. The cross-sectional TEM images shown in Figure 5.2 demonstrate that NRs are well-dispersed in PS matrices having $P = 650$ and 2000 kg/mol for $\varphi_{NR}$ values from 0.004 to 0.08. At dilute $\varphi_{NR}$, individually dispersed NRs are able to freely diffuse. To estimate the concentration for NR overlap, we first estimate the volume that a NR explores by rotation ($V_{rot}$) to be the volume of a sphere having diameter = $L$, and then set the volume fraction for overlap of these effective spheres to 0.74, which corresponds to hexagonal close packing. Thus, the critical NR concentration for overlap ($\varphi_c$) equals $(0.74)\frac{V_{NR}}{V_{rot}}$, where $V_{NR}$ is the volume of the nanorod and for our nanorods $\varphi_c = 0.022$. This calculation suggests that NRs exhibit: (1) free diffusion at $\varphi_{NR} < 0.022$, where individual NR dynamics is dictated solely by (local) viscosity and (2) hindered NR diffusion, $\varphi_{NR} > 0.022$, where NRs impede the motion of one another. These two regimes in NR mobility are evident in our polymer tracer diffusion results. The transition from individual NPs to hindered NPs has been observed in other studies.\textsuperscript{74,114} Therefore, in addition to varying the NR mobility by changing the PS matrix viscosity, the accessible $\varphi_{NR}$ range enables
the tracer diffusion to be studied when NRs are well-separated (i.e., mobile) and jammed (i.e., immobile).

![Figure 5.2](image)

**Figure 5.2.** Cross-sectional TEM images depicting the morphology of PS(P)/NR matrices. (a) $P = 2000$ kg/mol, $\varphi_{NR} = 0.004$; (b) $P = 2000$ kg/mol, $\varphi_{NR} = 0.06$; (c) $P = 650$ kg/mol, $\varphi_{NR} = 0.065$; (d) $P = 650$ kg/mol, $\varphi_{NR} = 0.08$. Scale bars are 100 nm.

### 5.3.2 Tracer Diffusion in the Presence of Mobile Nanorods

The diffusion of dPS in PNC matrices containing mobile and immobile NRs was measured. Figure 5.3 shows that the diffusion coefficients $D_{dPS}$ of dPS (800, 1800 and 3200 kg/mol) decrease monotonically as $\varphi_{NR}$ increases from 0.004 to 0.08. This behavior
is consistent with previous studies of polymer diffusion when the polymer dimensions ($2R_g$) are greater than $d$ and $L$ of the nanoparticles.\textsuperscript{55} Compared at the same $\varphi_{NR}$, dPS (800 kg/mol) exhibits the fastest diffusion, namely $D_{dPS(800\text{kg/mol})} > D_{dPS(1800\text{kg/mol})}$ and $D_{dPS(800\text{kg/mol})} > D_{dPS(3200\text{kg/mol})}$, also consistent with other studies.\textsuperscript{40, 52, 55} A significant finding is that for $\varphi_{NR} < 0.022$, the diffusion of dPS (1800 and 3200 kg/mol) is faster in the lower molecular weight matrix ($P = 650$ kg/mol) than the higher molecular weight matrix ($P = 2000$ kg/mol) as shown in Figure 5.3. For example, dPS (3200 kg/mol) diffusion is ~25\% greater in the lower molecular weight matrix at $\varphi_{NR} = 0.01$. On the other hand, dPS (800 kg/mol) diffusion is independent of matrix molecular weight. Note that constraint release by matrix chains does not significantly affect dPS diffusion because at this molecular weights, both tracer and matrix chains are well-entangled.\textsuperscript{168} For example, dPS (3200 kg/mol) diffusion in a PS matrix with $P = 650$ kg/mol is predicted to be about 10\% faster than in a matrix with $P = 2000$ kg/mol. Importantly, dPS (3200 kg/mol) diffusion is observed to be nearly identical for both $P$’s (closed and open circles) at $\varphi_{NR} = 0$ as shown in Figure 5.3b by nearly overlapping points. Thus, the significant difference in dPS diffusion in the 650 and 2000 kg/mol matrices can not be attributed to constraint release of the polymers.
Figure 5.3. Tracer diffusion coefficients of dPS at $T = 190 \, ^\circ C$ for $M = 800$ kg/mol (squares), 1800 kg/mol (triangles) and 3200 kg/mol (circle) in PS(P):NR where $P = 650$ kg/mol (closed symbol) and $P = 2000$ kg/mol (open symbol), as a function of NR loadings. Stars represent NR diffusion coefficients when $\phi_{NR} > 0$ in melts with $P = 650$ kg/mol (closed) and $P = 2000$ kg/mol (open). Representative error bars are shown.

The diffusion coefficients of the NRs, $D_{NR}$, in pure PS matrixes ($P = 650$ and 2000 kg/mol) are plotted in Figure 5.3 (closed and open stars, respectively) and compared with dPS diffusion coefficients. For both matrices ($P = 650$ and 2000 kg/mol), dPS (800 kg/mol) diffusion is faster than NR diffusion across the dilute region ($\phi_{NR} = 0 - 0.04$). Namely, as $\phi_{NR} \to 0$, $D_{dPS}$ (squares) is about 3x and 10x greater than $D_{NR}$ (stars) for $P = 650$ and 2000 kg/mol, respectively. In addition, all dPS (800 kg/mol) data points collapse onto one curve, signifying that NR diffusion does not influence dPS diffusion, and accordingly these NRs are relatively immobile on the time scale of dPS (800 kg/mol) diffusion. On the other hand, for dPS (1800 and 3200 kg/mol) in dilute PNCs, dPS diffuses faster than NRs in a matrix with $P = 2000$ kg/mol, but slower than the NRs for $P = 650$ kg/mol. When NRs diffuse faster than dPS, enhanced tracer diffusion of dPS is
observed. For example, at $\phi_{NR} = 0.01$, dPS (3200 kg/mol) diffusion is $\sim 25\%$ faster in the lower $P$ matrix (filled circles) relative to the higher $P$ matrix (open circles). This suggests that NRs that are mobile on the time scale of polymer diffusion have a weaker effect on slowing polymer diffusion than immobile NRs. To further examine this interplay, we need to define NR mobility more exactly. At $P = 650$ kg/mol and $\phi_{NR} \to 0$, NR diffusivity is $\sim 4$ times greater than dPS (3200 kg/mol). Namely, when dPS diffuses by a distance of about $R_g$, NRs diffuse about $2R_g$ according to the characteristic diffusion relation (diffusion distance is proportional to $D^{-0.5}$), suggesting that NRs are able to migrate away from the entangled dPS. This is the same for the dPS (1800 kg/mol) case where $D_{NR} \sim 2.5 \ D_{dPS}$ at $\phi_{NR} \to 0$. On the other hand, when NR diffusion is slightly slower than dPS diffusion, i.e., NRs move $\sim 0.8 \ R_g$ as dPS (3200 kg/mol) moves by $R_g$, dPS diffusion is dominated by nominally immobile NRs. Accordingly, for the system in this study, when $D_{NR} > 2.5 \ D_{dPS}$, enhanced dPS diffusion relative to the fixed NR case can be achieved.

5.3.3 Jammed Nanorods above Overlap Concentration

Although dPS diffusion is enhanced at dilute concentrations, diffusion in PNCs at concentrations above 0.022 appears independent of matrix molecular weight. To highlight the difference in behavior below and above the overlap concentration, Figure 5.4 shows the reduced diffusion coefficient, $D/D_0$ where $D_0$ is the diffusion coefficient in PS, versus $\phi_{NR}$. The dotted line at the overlap concentration $\phi_{NR} = 0.03$ separates free NR diffusion from the more concentrated regime where NRs overlap. Note that dPS (800 kg/mol) diffusion in both regimes is independent of matrix molecular weight because
NRs are nominally fixed or jammed on the time scale of polymer diffusion. On the other hand, for dPS (1800 and 3200 kg/mol), NRs are mobile on the time scale of dPS diffusion when \( P = 650 \text{ kg/mol} \) (filled symbols) and thus dPS diffusion is enhanced relative to fixed NR case \( (P = 2000 \text{ kg/mol}; \text{ open symbols}) \) at \( \phi_{\text{NR}} < 0.022 \). This enhancement in dPS diffusion is absent above \( \phi_{\text{NR}} = 0.022 \), because NR motion is slowed or quenched due to network formation. Moreover, Figure 5.4 shows that the enhancement in \( D/D_0 \) increases as \( M \) increases because dPS is further slowed down RELATIVE to the NRs as \( M \) increases. Namely, the enhancement is more significant for dPS (3200 kg/mol) compared to dPS (1800 kg/mol), which further supports the concept that the relative difference between polymer and NR diffusion is responsible for the observed enhanced polymer diffusion at \( \phi_{\text{NR}} < 0.022 \).
Figure 5.4. Normalized tracer diffusion coefficients of dPS for $M = (a) 800$ kg/mol, (b) $1800$ kg/mol, and (c) $3200$ kg/mol, in PS(P)/NR where $P = 650$ kg/mol (closed symbol) and $P = 2000$ kg/mol (open symbol), as a function of NR volume fraction. The cartoon shows free diffusion of NRs (top left) at $\phi_{NR} < 0.022$ (dotted line) and jammed NRs (top right) at $\phi_{NR} > 0.022$. 
5.3.4 Discussion

This is the first experimental study showing that polymer diffusion is faster when nanoparticles in the matrix are mobile. To date, theories capturing this behavior are lacking. Simulation studies of PNCs\cite{92, 93, 181} provide some insight into the underlying mechanism for mobile-nanoparticle-assisted polymer diffusion by investigating how entanglements between polymers and nanorods reinforce mechanical properties. Using dissipative particle dynamics (DPD), Karatrantos et al.\cite{181} reported that the addition of NRs with a radius smaller than the polymer radius of gyration increases the entanglement density because NR anisotropy introduces entanglements between polymer and NR.\cite{74} New theories will also have to capture the importance of NP shape (e.g. nanorod versus sphere) on the mechanism of polymer diffusion.

When NRs are mobile on the time scale of tracer diffusion, polymer/NR entanglements can relax faster than the diffusing polymer chain, resulting in an effective dilution of the entanglement network with time, analogous to the mechanism of tube dilation. Namely, entanglements exist but relax by the NR moving out of the way before the polymer feels the effect of the NR on its own motion. Using MD simulation and primitive path analysis, Toepperwein et al.\cite{93} reported an increase in entanglement density in the presence of thin ($d < d_i$) nanorods that are intentionally fixed in the system (frozen particle limit). However, the entanglement density recovers to the bulk polymer value after the initially fixed NRs are removed, which may represent the case of extremely mobile NRs (phantom particle limit).
5.4 Summary

In this letter, the effect of mobile NRs on polymer diffusion is examined experimentally. The diffusivities of NRs were tuned by varying matrix molecular weight (\(P = 650\) and \(2000\) kg/mol) and by \(\varphi_{\text{NR}}\). We point out the fact that it is the relative diffusivities between polymer and nanoparticles that determine how mobile the nanoparticles are on the time scale of interest, i.e., the time scale of polymer diffusion. NRs are relatively fixed in the dPS (800 kg/mol):PS(\(P\)):NR systems because of the fast diffusion of the tracer, and thus no effect is observed when \(P\) is varied. On the other hand, we observed an enhanced dPS (1800 and 3200 kg/mol) diffusion when \(P = 650\) kg/mol compared to that when \(P = 2000\) kg/mol at \(\varphi_{\text{NR}} < 0.022\), indicating mobile NRs influence polymer dynamics in these PNCs. In addition, a tracer molecular weight dependence on enhanced diffusivity is observed, which further supports the effect of mobile NRs on tracer diffusion. On the other hand, this enhancement in \(D\) is only seen when \(\varphi_{\text{NR}} < 0.022\), consistent with the defined free NR diffusion regime composed of individual NRs that do not overlap. The enhancement in \(D\) arises from faster polymer/NR relaxation relative to the diffusing polymer chain. This foundational study establishes the criteria as to when polymer diffusion is enhanced by mobile nanorods and will motivate theories and simulations to account for mobile nanoparticles when probing the dynamics of PNCs.
CHAPTER 6. DYNAMICS OF BRUSH-GRAFTED NANOPARTICLES IN POLYMER MELTS

This work was accomplished in collaboration with Prof. Michael J. Hore at Case Western Reserve University, Prof. Karen I. Winey at the University of Pennsylvania, Prof. Nigel Clarke at the University of Sheffield, U.K, and Prof. Kohji Ohno at Kyoto University, Japan.

6.1 Introduction

When combined with polymers, nanoparticles impart polymer nanocomposites (PNC) with unique functionalities such as optical properties that can be tuned by controlling the dispersion of gold nanorods, and enhanced electrical conductivity at relatively low loadings (e.g., 0.2 w%) of graphene oxide. Moreover, improved
mechanical properties and flammability have been achieved by adding nanoparticles that impart strength and limit combustion, respectively, to the host polymer. Importantly, these functionalities can be achieved without sacrificing the inherent viscoelasticity of the host polymers, and thus the processability of these functional PNCs can be maintained. Besides adding functionality to the host polymer, nanoparticle mobility is an important consideration because particle dynamics influences fundamental properties such as melt flow and viscosity, as well as potential applications such as self-healing materials. Therefore, the transport properties of nanoparticles in polymer matrices requires fundamental understanding.

The classic Stokes-Einstein (SE) relation describes the diffusion of a sphere in a continuous medium as follows:

$$D_{SE} = \frac{k_B T}{f \pi \eta R}$$

(6.1)

where $D_{SE}$ is the Stokes-Einstein diffusion coefficient, $k_B$ is the Boltzmann constant, $T$ is absolute temperature, $\eta$ is the pure solvent viscosity, and $R$ is the NP radius. The constant $f$ is 4 or 6 depending on whether there is slip or non-slip condition at the particle/medium interface, respectively. In a polymer-particle mixture containing large NPs (e.g., colloidal), NP diffusion behavior follows the SE relation using the bulk viscosity of the polymer matrix. However, for NPs smaller than a characteristic length, i.e., tube diameter in an entangled polymer melt, particle diffusion is faster than predicted by SE relation. For this condition, Brochard Wyart and de Gennes argued that particle diffusion deviates from the SE prediction because the flow surrounding the NP is no longer
captured by bulk viscosity. Namely, when NPs are smaller than the mesh size, the particle friction depends on the number of monomers in contact with the particle, which leads to a length-scale dependent friction smaller than the bulk value. Experimental and theoretical studies have shown that the SE relation fails when NP size is comparable to the mesh size. For example, Grabowski et al. reported that the diffusion coefficient \( D \) of gold NPs in poly(butyl methacrylate) matrices is about 200 times faster than \( D_{SE} \) when the NP diameter \( d = 5 \text{ nm} \) is similar to the matrix mesh size \( 6 \text{ nm} \). In addition, these small NPs reduce the viscosity of polymer melts, acting akin to plasticizers. This reduction of melt viscosity can be attributed to an increase in free volume due to the fast movement of NPs, whereas simulation studies suggest that the reduction in viscosity is due to a decrease in the entanglement density \( N_e \). Using a scaling approach, Brochard Wyart and de Gennes reported a sharp transition from local friction to bulk friction felt by the NP as the NP size increases, i.e., NP diffusion recovers to the SE prediction as soon as the NP size approaches the mesh size. However, theoretical studies show that the transition is gradual. Namely, NP motion is coupled with entanglements gradually as NP size increases, and the SE diffusion is not recovered until \( d \) is \( \sim 10x \) greater relative to the tube diameter. This is attributed to a constraint-release type mechanism for NP diffusion due to local density fluctuations. On the other hand, in the same transition zone where the NP size is comparable to the mesh size, Cai et al. proposed a NP hopping mechanism that explains the gradual recovery for NP diffusion. That is to say, trapped NPs have to overcome an energy barrier to hop to a neighboring mesh, which only happens when the
entanglement strands are able to slip around the NPs. Note that the length scale of this mechanism is on the order of mesh size. When the NP size is much larger than the mesh size, NP motion is no longer coupled with the entanglement strands, and thus the SE behavior is recovered.

Preventing NP aggregation before and during NP diffusion studies is critically important because a well-defined NP size is required to test prevailing models of theories. One popular method to control the distribution of nanoparticles is to graft polymer brushes onto the surface of nanoparticles. Studies show that dispersion can be controlled by varying the ratio of the brush to matrix molecular weight ($P/N$) which determines the wet to dry brush transition.\textsuperscript{16,48,49} In this case, particle dynamics might be affected by the conformation of grafted polymer\textsuperscript{111} in both polymer solutions\textsuperscript{121,122} and melts.\textsuperscript{123,124} For instance, Hoshino et al.\textsuperscript{123} investigated the dynamics of polystyrene (PS)-grafted silica nanoparticles (110 nm) in unentangled PS melts, and found that these nanoparticles behave subdiffusively when the temperature is above $1.25T_g$, where $T_g$ is the glass transition of the matrix PS. Because the matrix chain itself is not entangled, the subdiffusive behavior is attributed to the interpenetration of short matrix chains and grafted brush. Kandar et al.\textsuperscript{124} further investigated the effect of grafting density on the dynamics of PS-grafted Au nanoparticles ($d = 2.4$ nm) in PS matrices. Using X-ray photon correlation spectroscopy (XPCS), they observed an unusual dynamical arrest at low grafting density ($\sigma = 0.4$ chains/nm$^2$), characterized by fast and slow modes corresponding to grafted chain relaxation and entire particle motion, respectively, whereas at high grafting density ($\sigma = 2.3$ chains/nm$^2$) only liquid-like motion is observed.
The above studies suggest that the diffusion of “hairy” NPs can depend on the dynamics of polymer brushes which in turn depend on the interpenetration between the brush and matrix chains. However, how these two factors affect center of mass diffusion of the nanoparticles is not well understood.

In the present study, we investigate the poly(methyl methacrylate)-grafted NP diffusion in poly(methyl methacrylate), or PMMA, matrices as a function of brush grafting density, brush molecular weight, and matrix molecular weight. The PMMA-grafted NPs with Fe$_3$O$_4$ core ($d = 5$ nm) are denoted as: IO21L ($N = 21$ kg/mol, $\sigma = 0.17$ chains/nm$^2$), IO21M ($N = 21$ kg/mol, $\sigma = 0.33$ chains/nm$^2$) and IO16H ($N = 16$ kg/mol, $\sigma = 0.55$ chains/nm$^2$). Brush and matrix density profiles were first calculated using self-consistent field theory (SCFT) and the result shows that grafting density has the strongest effect on the profiles. i.e., greater grafting density results in a more extended brush. The diffusion coefficients of PMMA-grafted NPs diffuse into PMMA matrices ($P = 4$ to 52 kg/mol) were measured and were found to be independent of annealing time, suggesting that NPs do not form aggregates when diffusing in the matrix, consistent with TEM analysis. $D$ decreases monotonically with increasing $P$ for three NPs. When the brushes are wet by the matrix chain, i.e., $P/N < 1$, IO21L and IO21M exhibit similar diffusion coefficients because the dragging of matrix chains dictates the effective size of the NP. On the other hand, IO16H exhibits the fastest diffusion because matrix chains weakly penetrate the brush due to the high grafting density. When the brushes are dry, i.e., $P/N > 1$, IO21L diffuse faster than IO21M due to its low grafting density resulting in a smaller effective diameter. Furthermore, IO16H exhibits the fastest diffusion among the three
because of a combined effect of its high grafting density and short brush, resulting in a smaller effective diameter and weak dragging of matrix chains. Effective NP diameters were extracted from the SCFT brush density profile, and were used to calculate the SE diffusion coefficients, $D_{\text{SCFT}}$. By plotting $D/D_{\text{SCFT}}$ vs. $P$, a transition from soft NP diffusion dictated by the dragging of matrix chains that slows down NP diffusion, to effective hard sphere diffusion similar to the SE prediction. These results are consistent with the SCFT prediction of the brush profile, namely, wet and dry brush conditions. This study underlines the importance of the effect of polymer brush structure on NP center of mass diffusion in polymer melts.

### 6.2 Experimental Section

#### 6.2.1 Materials

Poly(methyl methacrylate) (PMMA) was used as received and the molecular weight ($P$), polydispersity indices (PDI), glass transition temperature ($T_g$), and suppliers are shown in Table 6.1.

<table>
<thead>
<tr>
<th>$P$ (kg/mol)</th>
<th>PDI</th>
<th>$T_g$ (K)</th>
<th>Supplier</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>1.1</td>
<td>369</td>
<td>Polymer Laboratories</td>
</tr>
<tr>
<td>8</td>
<td>1.1</td>
<td>368</td>
<td>Polymer Source</td>
</tr>
<tr>
<td>14</td>
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<td>377</td>
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<td>Polymer Source</td>
</tr>
<tr>
<td>34</td>
<td>1.06</td>
<td>393</td>
<td>Polymer Laboratories</td>
</tr>
<tr>
<td>52</td>
<td>1.09</td>
<td>397</td>
<td>Pressure Chemical</td>
</tr>
</tbody>
</table>
PMMA-grafted iron oxide nanoparticles were synthesized using methods described elsewhere.\textsuperscript{182} The core diameter is 5 nm for all three NPs. Table 6.2 gives the brush molecular weight ($N$) and brush grafting density ($\sigma$) for IO16H, IO21M and IO21L, respectively.

**Table 6.2. Characteristics of PMMA-Grafted Fe$_3$O$_4$ NPs**

<table>
<thead>
<tr>
<th></th>
<th>IO16H</th>
<th>IO21M</th>
<th>IO21L</th>
</tr>
</thead>
<tbody>
<tr>
<td>$N$ (kg/mol)</td>
<td>16</td>
<td>21</td>
<td>20.7</td>
</tr>
<tr>
<td>$\sigma$ (chains/nm$^2$)</td>
<td>0.55</td>
<td>0.33</td>
<td>0.17</td>
</tr>
</tbody>
</table>

### 6.2.2 Diffusion Couple Preparation and Annealing

The diffusion couple consisted of a thick PMMA film covered with thin polymer nanocomposite (PNC) film. PMMA was dissolved in dimethylacetamide (DMAc) and stirred for $\sim$ 20 h, and the solution was doctor bladed on a heated (120$^\circ$C) glass substrate. The PMMA film ($\sim$ 5 $\mu$m, determined by ellipsometry) was floated from the glass substrate in water and picked up using a silicon wafer, and was aged for $\sim$ 3 days in vacuo before applying the top PNC film. The PNC film was a mixture of PMMA-grafted NPs and PMMA had the same degree of polymerization as the PMMA matrix. For PNC films, PMMA and NPs were both dissolved in toluene in separate vials and stirred for $\sim$ 20 h. An appropriate amount of NP solution was mixed with the PMMA solution and stirred for another 20 h. The PNC film was prepared by spin-coating the PMMA/NP solution onto a silicon wafer previously treated with a water soluble chitosan sacrificial layer. The PNC film thickness was $\sim$ 50 nm as measured by ellipsometry and contained 2.5 vol% of iron oxide core determined using thermal gravimetric analysis (TGA). The
film was floated in water by dissolving the sacrificial layer and picked up by the thick PMMA film/silicon wafer, and dried under ambient conditions for ~ 20 h before annealing. The diffusion couple was annealed isothermally at $T_g + 75$ K. The annealing time was chosen to allow sufficient penetration (~ 300 nm) of the PMMA-grafted NP into the PMMA film.

6.2.3 Rutherford Backscattering (RBS)

RBS was used to depth profile the NPs in the PMMA film under room temperature. Details of RBS have been reviewed elsewhere. The incident helium ion (He$^+$) beam was ~ 2.024 MeV. The incident beam is normal to the plane of the sample, and the energy of the recoiled He$^+$ was detected by a solid-state detector that intersected the incident beam at 10°. The amount of electric charge, typically ~ 30 μC, was collected until the yield near the maximum NP concentration reaches ~ 100. The RBS spectra of yield versus channel were converted to the NP depth profile, namely, the iron volume fraction versus depth into the matrix. The diffusion coefficient of the NP was obtained by fitting the depth profile using the one-dimensional solution of Fick’s second law for a finite source in a semi-infinite medium as follows:

$$\phi(x) = \frac{1}{2} \left[ \text{erf} \left( \frac{h-x}{\sqrt{4Dt}} \right) + \text{erf} \left( \frac{h+x}{\sqrt{4Dt}} \right) \right] \quad (6.2)$$

where $x$ is depth, $h$ is original dPS film thickness, $t$ is diffusion time, and $D$ is the diffusion coefficient of dPS. An experimental depth profile was fitted by $\phi(x)$ convoluted with the Gaussian instrumental resolution function, $y = \left[ 1/\alpha (2\pi)^{1/2} \right] \exp(-x^2/2\alpha^2)$, where $y$ is the iron fraction and $x$ is the depth. $\alpha$ is the instrumental resolution (~35 nm)
and the accessible depth was ~1000 nm. The diffusion coefficients obtained in this work were from multiple measurements. Only the depth profiles having a sufficient diffusion length (> 200 nm) were used.

6.2.4 Self-consistent field theory (SCFT)

SCFT is a mean field approach that has been successfully adopted to calculate various quantities in polymeric systems, e.g., block copolymer morphology. In this study, SCFT calculations were conducted to probe the structure of brush in polymer matrix with various $P$ and to further bridge the brush structure and bulk particle dynamics. The nanoparticle is modeled as a sphere grafted with polymer chains at a reduced grafting density of $s^* = (sN)/(\rho_0R_g)$, where $s$ is the experimentally determined grafting density (in nm$^{-2}$), $1/\rho_0 = 0.158$ nm$^3$ is the monomer volume for PMMA, and $R_g$ is the Gaussian radius of gyration of a polymer chain with degree of polymerization $N$. For samples IO16H, IO21M, and IO21L, the reduced grafting densities used were 3.85, 2.64, and 1.36, respectively. The theory is solved self-consistently until the error in the calculation is below $10^{-6}$, after which the brush and matrix density profiles were radially averaged. All length scales are normalized by the Gaussian radius of gyration of a brush chain. A more detailed description of the Hamiltonian for the theory and numerical methods for solving can be found elsewhere.
6.3 RESULTS AND DISCUSSION

6.3.1 Nanoparticle Dispersion

Figure 6.1 shows representative TEM images of the top PNC layer before annealing as grafting density decreases from 0.55 (top row, IO16H) to 0.17 (bottom row, IO21L). For this range of grafting density, the NPs are well-dispersed in PMMA matrices even up to $P/N \sim 6$, where NP aggregation is expected due to depletion-attraction forces.\textsuperscript{48} This could be attributed to the large curvature of the NP resulting in more penetration of matrix chains, or a kinetically trapped state that is not thermally stable. To investigate that the dispersion of NPs in the top PMC layer are whether NP dispersion thermodynamically stable, the diffusion coefficients can be measured at different annealing times. If NPs are stable and remain as isolated NPs, the diffusion coefficients should be independent of annealing time. If NPs grow with further annealing, the increase in NP size will result in a diffusion coefficient that is time-dependent, namely, diffusion slows down. Figure 6.2 shows representative diffusion profiles demonstrating the time-independent diffusion for IO21M in PMMA ($P = 52 \text{ kg/mol}$, $P/N = 2.5$) at annealing times ($t$) of 0 h (black circles), 30 h (dark grey circles) and 60 h (light grey circles) at $T = 472$ K. For $t = 0$ h, the Gaussian profile (black curve) is due to instrumental resolution (full width at half maximum = 35 nm). For $t = 30$ h and 60 h, a single diffusion coefficient ($1.9 \times 10^{-15} \text{ cm}^2/\text{s}$) can be used to provide best fits for both times (dark grey and light grey curves, respectively). For IO21L(M) and IO16H, the diffusion coefficients are independent of time for $P/N$ values up to 2.4 and 2.1, respectively, consistent with individual NP diffusion and a stable dispersion of NPs, attributed to “wet brush”
condition. By contrast, for systems with $P/N > 3$, the NPs are arrested near the surface and do not diffuse deeply into the PMMA, suggesting an aggregation-limited diffusion correlated with the thermodynamic stability of polymer brush grafted NPs. In this study, only NP systems displaying time independent diffusion are presented.

**Figure 6.1.** Top-view TEM images of the PNC layers (~ 50 nm) containing NPs with graft densities of 0.55, 0.33 and 0.17 chains/nm², and matrix to brush molecular weight ratios from 0.2 to 2.5. The NP core diameter is 5 nm. Scale bar is 100 nm.
Figure 6.2. Representative Fe volume fraction profiles for IO21M in a PMMA (52 kg/mol). Annealing times are 0 h (black circles), 30 h (dark grey circles) and 60 h (light grey circles). The black solid curve represents a Gaussian profile with a FWHM of 35 nm which is the instrumental resolution. Dark and light grey curves represent best fits using Eq. 1 for \( t = 30 \) h and 60 h, respectively. The best fit is \( D = 1.9 \times 10^{-15} \text{ cm}^2/\text{s} \) for both times. The inset illustrates 2MeV He\(^+\) ions impinging on the diffusion couple and the profiles of brush grafted iron oxide NPs (circle with halo) in the matrix.

6.3.2 Polymer Brush Volume Fraction Profile

The volume fractions of the brush and matrix chains are calculated using self-consistent field theory. The brush and matrix profiles as well as the interpenetration between them provide a quantitative understanding of the interplay between wetting conditions and NP diffusion. Figure 3a and 3b show brush (solid lines) and matrix
(dashed lines) profiles for IO16H (green), IO21M (blue) and IO21L (black) at $P = 4$ and $34$ kg/mol, respectively. For all three values of $N$, the polymer volume fraction near the surface increases as the grafting density increases from 0.17 to 0.55. For example, when $P = 4$ kg/mol and $N = 21$ kg/mol, the polymer volume fraction of IO21M at the surface is $\sim 50\%$ greater than that of IO21L. Even for IO16H which has the shortest brush but highest grafting density, the polymer volume fraction near the surface is $\sim 30\%$ greater than that of IO21M, suggesting that grafting density affects brush profiles more strongly than the small difference in brush length (16 vs. 21 kg/mol). In addition, Figure 6.3 shows that the IO21M brush (blue) is more extended than IO21L brush (black) due to its larger grafting density. By comparison, the IO16H brush thickness is similar to the IO21M case because the larger grafting density and shorter $N$ compensate for each other. For matrix profiles, the penetration into the brush domain also depends mainly on brush grafting density. Namely, at low brush grafting density, the matrix chains penetrate more deeply into the brush. In the case of $P = 4$ kg/mol and IO21L (Figure 6.3a and black lines), the matrix chain volume fraction is $\sim 60\%$ near the NP surface whereas the matrix chain volume fraction decreases to $\sim 20\%$ for IO16H (Figure 6.3a and green lines). As $P$ increases, brushes become “drier”, and the polymer volume fractions near the NP surface increase relative to the wet brush case. For example, the polymer volume fraction of IO21L (black) at the NP surface increases by $25\%$ as $P$ increases from 4 to 34 kg/mol as shown by comparing Figure 6.3a and Figure 6.3b, respectively. Because they are dry, brushes on IO21L do not extend into the matrix as much as those in IO21M. On the other hand, IO16H has a similar brush thickness as IO21M when the brushes are dry. This
could be attributed to the high grafting density in IO16H that limits matrix chain penetration (Figure 6.3b, green dashed line).

**Figure 6.3.** Self-consistent field theory calculation of the polymer volume fraction as a function of distance from the center of the NP. Solid lines represent brush profiles of IO21L (black), IO21M (blue) and IO16H (green) in PMMA with (a) \( P = 4 \) kg/mol and (b) \( P = 34 \) kg/mol. Dotted lines represent corresponding matrix chain profiles.

### 6.3.3 Effect of Brush Structure on NP Diffusion

NP diffusion was measured as a function of matrix molecular weight as shown in Figure 6.4. For all three NPs, the diffusion coefficients decrease significantly as \( P \) increases. Namely, \( D \) decreases by nearly 3 orders of magnitude as \( P \) increases by a factor of 12 (from 4 to 50 kg/mol), qualitatively consistent with Eq. 6.1 where \( D \) decreases as viscosity (or \( P \)) increases. First, the effect of grafting density is evaluated for IO21L and IO21M because both NPs have the same value of \( P \) (21 kg/mol), while the grafting density increases from 0.17 to 0.33. In the wet brush region, i.e., \( P/N < 1 \), the
diffusion coefficients of IO21L (solid black circles) and IO21M (solid blue circles) are nearly identical. This is contradictory to the anticipation that IO21L would diffuse slower than IO21M due to more significant interpenetration between the brush and matrix chains. The similar diffusion of IO21L and IO21M suggests that the dragging force due to the wetting of matrix chains is dominant and thus the particles slow down similarly because the drag is similar.

Figure 6.4. Diffusion coefficients of IO21L (black), IO21M (blue) and IO16H (green) in PMMA matrices ($P = 4 \sim 52$ kg/mol) at $T = T_g + 75$ K. Solid symbols represent the wet brush regime, i.e., $P/N < 1$, and open symbols represent the dry brush regime, i.e., $P/N > 1$. Error bars represent the standard deviation from multiple samples.
The effect of brush/matrix interpenetration can be incorporated into the SE relation, Eq. 6.1. First, an effective NP diameter can be defined that includes the core diameter and the brush thickness from SCFT. This thickness is defined by the inflection of the polymer volume fraction near the brush height as shown in Figure 6.3. The SE diffusion coefficients can be calculated using this effective diameter and the measured bulk viscosity. Figure 6.5 shows the NP diffusion coefficient ($D$) normalized by the SE diffusion coefficient using the effective diameter obtained from SCFT ($D_{SCFT}$) as a function of $P$. For $P/N < 1$ (solid circles) where brush is wet, $D$ is more than 80% slower than $D_{SCFT}$, suggesting that dragging of the matrix chains slows down NP diffusion significantly for both IO21L (black solid circles) and IO21M (blue solid circles). This observation suggests that the difference in grafting densities (0.17 vs. 0.33 chains/nm$^2$) does not significantly influence NP diffusion when the brush is wet.

In the dry brush region where $P/N > 1$ (open symbols), the dragging effect should be less important because the brush chains are collapsed and the brush/matrix interface are sharper. Thus, the grafted NPs can behave more like “hard spheres” whose diffusions are dominated by effective diameters. If these hairy NPs behave as hard spheres, the diffusion should increase relative to the wet brush case. Figure 6.5 shows that $D/D_{SCFT}$ is $\sim 0.2$ up to $P = 20$ kg/mol and then increases sharply above 40 kg/mol, resulting in the grafted NPs behaving more like hard spheres. On the other hand, the diffusion coefficients of IO21L (black open circles) are greater than that of IO21M (blue open circles) when brushes are dry. This difference can be attributed to the smaller effective
diameter of IO21L, e.g., $d_{\text{eff, IO21L}} = 9.3$ nm and $d_{\text{eff, IO21M}} = 11.4$ nm at $P = 52$ kg/mol, which results in faster diffusion for IO21L, $D \sim d_{\text{eff}}^{-1}$.

**Figure 6.5.** NP diffusion coefficient normalized by the SE prediction using effective diameters for IO21L (black), IO21M (blue) and IO16H (green) as a function of $P$, $4 \sim 52$ kg/mol. The effective diameter used in Eq. 6.1 was determined from SCFT simulations of the brush profile. Solid and dotted lines are guide to the eye. Error bars represent the standard deviation from multiple samples. The cartoon depicts the transition from the wet brush case where matrix chains are “dragged” during NP diffusion and the dry brush case when the brush/matrix interface is sharper and NPs diffuse more like hard spheres.
Next, we compare the normalized diffusion of IO16H with IO21L and IO21M, both of which have longer brushes and lower grafting densities. At each $P$, $D/D_{SCFT}$ of IO16H is greater than IO21L and IO21M. For $P < 20$ kg/mol, $D/D_{SCFT}$ of IO16H is slightly, but not significantly, greater than that for IO21L and IO21M. Even when $P = 17.5$ kg/mol ($P/N = 1.1$) where the brush becomes drier, matrix dragging still takes effect on reducing the NP diffusion significantly. For $P > 34$ kg/mol where brushes become much drier, a strong increase in $D/D_{SCFT}$ is seen for all three cases as shown on Figure 6.5. This suggests that NPs behave as hard spheres, and thus $D$ approaches the predictions using the effective diameter from SCFT, i.e., for $P = 34$ kg/mol, $D/D_{SCFT} = 1.2$, 0.81 and 2.4, for IO21L, IO21M and IO16H, respectively. Interestingly, $D/D_{SCFT}$ of IO16H is much larger than the other two cases, i.e., at $P = 34$ kg/mol, $D/D_{SCFT}$ of IO16H is 2 and 3x greater than the IO21L and IO21M cases, respectively. This can be attributed to the fact that the brush of IO16H is retracted more from the matrix chains than IO21M and IO21L due to its greater grafting density and shorter brush, and thus it behaves as hard spheres without the effect of dragging by matrix chains. In addition, the diffusion coefficient of IO16H is 2.4x greater than $D_{SCFT}$ at $P = 34$ kg/mol, consistent with studies of enhanced NP diffusion relative to $D_{SE}$ as NP diameter approaches the tube diameter.\textsuperscript{116}

For $P = 52$ kg/mol, IO16H diffusion is not observed because the particles are aggregated. On the other hand, for IO21L and IO21M, NP diffusions are faster than the prediction, suggesting that both NPs are effective hard spheres, with effective diameters close to the tube diameter, diffusing in the PMMA matrices. Furthermore, $D/D_{SCFT}$ of IO21L is greater than IO21M at $P = 34$ and 52 kg/mol, which can be attributed to the smaller effective diameter that IO21L has, i.e., $d_{eff} = 18$ nm and 21 nm for IO21L and

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IO21M, respectively, at $P = 52$ kg/mol. Using the normalized diffusion coefficient, $D/D_{SCFT}$, we demonstrate that brush structure could have significant effect on the NP diffusion, which could be insightful for future studies on bare NP diffusion in the presence of strong attractive polymer-NP interactions. Namely, if the attractive interaction is strong between the polymer and the NP such that chains adsorb onto the NP, and are dragged along as NPs move. In this case we would expect that the bare NPs have a greater effective diameter, and behave more like NPs with grafted brush at $P/N = 1$.

6.4 Conclusion

In this study, we have investigated the effect of brush grafting density, brush molecular weight ($N$) and matrix molecular weight ($P$) on NP diffusion. We measure the diffusion coefficients ($D$) of PMMA-grafted iron oxide NPs (core $d = 5$ nm), IO21L ($N = 21$ kg/mol, $\sigma = 0.17$ chains/nm$^2$), IO21M ($N = 21$ kg/mol, $\sigma = 0.33$ chains/nm$^2$) and IO16H ($N = 16$ kg/mol, $\sigma = 0.55$ chains/nm$^2$) in various $P$ ranging from 4 to 50 kg/mol. $D$ does not change with varying annealing time, suggesting that NPs do not aggregate when diffusing in the matrix, consistent with TEM analysis. Self-consistent field theory is used to determine the matrix/brush volume fraction profiles and interpenetration. The SCFT results show that grafting density has the strongest effect on brush and matrix chain profiles. Namely, at high grafting density, brushes are more extended, and thus it is harder for matrix chains to penetrate into brush domain. RBS measurements show that $D$ decreases monotonically with increasing $P$ for all three NPs. When brushes are wet, i.e., $P/N < 1$, IO21L and IO21M have similar diffusion coefficients because dragging of the
matrix chains is dominant. When brushes are dry, i.e., $P/N > 1$, IO21L diffuses faster than IO21M, which can be attributed to the smaller effective diameter due to the lower grafting density. However, IO16H has the largest diffusion coefficients at $P = 4 - 34 \text{ kg/mol}$ because high grafting density results in less brush-matrix interpenetration and weaker dragging of the matrix chains. The SE diffusion coefficient can be calculated using the effective diameter from SCFT brush profile. When brush is wet, i.e., $P/N < 1$, $D$ is more than 80% slower than $D_{\text{SCFT}}$, further supporting that dragging of the matrix chains slows down NP diffusion significantly. When brushes are dry, a strong increase in $D/D_{\text{SCFT}}$ is seen, indicating that NPs’ behavior approaches hard spheres; the observation that $D/D_{\text{SCFT}} > 1$ is consistent with studies of enhanced NP diffusion relative to $D_{\text{SE}}$. IO16H has the greatest $D/D_{\text{SCFT}}$ among the three cases, which is attributed to highest grafting density and shortest brush, while IO21L having greater $D/D_{\text{SCFT}}$ over IO21M suggests that smaller grafting density leads to smaller effective diameter, and thus faster NP diffusion. This study highlights the importance of how brush structure could affect NP center of mass diffusion in polymer melts, and provides an insightful dynamical picture of both the polymer-grafted NP case, and the hard adsorbing sphere case. We hope this serves as guidance for future models on the dynamics of complex NPs in polymer nanocomposites.
CHAPTER 7. SUMMARY AND FUTURE DIRECTIONS

Polymer nanocomposites combine polymers and nanoparticles to create novel functional materials that play a significant role in various applications and technologies. PNCs take advantage of traditional polymer properties such as low cost, light weight and distinct viscoelasticity while nanoparticles impart unique properties that improve, for example, thermal stability, electric conductivity and optical properties. Despite the properties incorporated into polymers for different purposes, the addition of nanoparticles also influences polymer dynamics that provides insights in altered mechanical properties and glass transition, and serve as an important parameter in controlling material processability. In this dissertation, we have discussed the fundamental polymer dynamics in PNC and focused on polymer and nanoparticle center of mass diffusion on a macroscopic length scale ($10^2$ nm).
7.1 Summary

Nanoparticles are impenetrable obstacles that impede polymer center of mass diffusion. For hard spherical nanofillers with neutral polymer-particle interaction, a more significant slowdown in polymer diffusion compared to the prediction of Maxwell model suggests that effect of simple tortuosity is not applicable while reduction of the number of chain conformations and consequently the presence of entropic barrier might explain the slowdown.

In Chapter 3, we have discussed the effect of attractive polymer-particle interaction on polymer diffusion by introducing OH-capped spherical silica NPs (from 13 to 50 nm in diameter) to PMMA matrices at loadings up to 40 vol%. The normalized diffusion coefficients ($D/D_0$) collapse onto a master curve when plotted against the confinement parameter ($ID/2R_g$), suggesting that the confinement parameter is able to capture the effect of nanoparticle size, size polydispersity, and volume fraction on center-of-mass polymer diffusion. $D/D_0$ falls moderately by 15% when $ID > 2R_g$, and $D/D_0$ is slightly reduced even when $ID$ is 8 times greater than $2R_g$ whereas $D/D_0$ drops drastically by up to 80% as $ID < 2R_g$. Comparing the master curve of this thermally interacting PMMA/Si system to the neutral PS/phenyl-capped Si system, we conclude that polymer-nanoparticle interactions do not significantly influence polymer center-of-mass diffusion.

To connect prior diffusion studies in model spherical and cylindrical NP systems, and provide insight for technological applications such as irregularly shaped carbon black aggregates, diffusion of dPS is probed in PS matrices having string-like chained
nanoparticles (cNP) grafted with polystyrene brush. Chapter 4 has discussed the experimental details and results; the presence of chained NPs in PS matrices induces a minimum in dPS diffusion coefficient with increasing cNP loadings when $2R_g$ is less than 1.5x the mean length of the impenetrable core of the chained NPs ($L$). In contrast, when $2R_g > L$, dPS diffusion coefficients decrease monotonically with increasing cNP loadings. The minimum in diffusion coefficient is attributed to anisotropic diffusion near the chained NPs, and requires tracer size ($2R_g$) to be comparable or smaller than the long dimension of the chained NPs. Two normalizations on diffusion coefficient are explored to further investigate the diffusion mechanism: $D/D_0$ where $D_0$ is the diffusion coefficient in a pure homopolymer matrix, and $D/D_e$ where $D_e$ is an effective diffusion coefficient that accounts for the dynamics in both PS matrix and brush domains. For $D/D_0$, a sharp transition from a diffusion minimum to monotonic decrease is observed with increasing dPS molecular mass whereas a gradual transition is observed for $D/D_e$. This study provides insights of dynamics in technological important polymer nanocomposites and points out that polymer brush provides an alternative pathway to control polymer dynamics.

Recent studies on polymer dynamics in PNCs, nanoparticles are assumed “immobile” on the time scale of polymer diffusion. Chapter 5 has introduced “mobile” nanorods into PNC systems where nanorods are mobile on the time scale of dPS diffusion. We have shown how varying the relative mobility of nanorods impacts chain diffusion in PNCs, and the mobility of nanorods can be tuned by varying matrix molecular weight ($P = 650$ and 2000 kg/mol). When the tracer (dPS) is 800 kg/mol and
diffuses faster than the NRs in both matrices such that the NRs are nominally fixed, tracer
diffusion in both matrices and across all NR compositions are the same. In contrast, at
low NR concentration when the dPS tracer is 1800 or 3200 kg/mol, the tracer diffusion is
slower when the matrix is 650 kg/mol relative to 2000 kg/mol and thus NRs are
nominally mobile, such that the PNCs with more mobile NRs have less constraints on
polymer diffusion as NRs move away faster than the probed chain, and thereby enhance
tracer diffusion. On the other hand, above NR overlap concentration, NR mobility is
hampered by their proximity to other NRs, and thus NRs become immobile on the time
scale of polymer diffusion. This study establishes criteria by which the mobility of NRs
relative to polymers assists polymer diffusion and will motivate broader investigations
that incorporate of the role of mobile nanoparticles on the dynamics in polymer
nanocomposites.

To gain a complete picture of dynamics in polymer nanocomposites,
nanoparticles diffusion in polymer melts is studied. In Chapter 6, I have investigated the
diffusion of PMMA-grafted Fe₃O₄ nanoparticles (core diameter = 5 nm) in PMMA
matrices. Different brush architectures are obtained by tuning brush molecular weight and
brush graft densities of nanoparticles, i.e., IO16H (N = 16 kg/mol, σ = 0.55 chains/nm²),
IO21M (N = 21 kg/mol, σ = 0.33 chains/nm²), and IO21L (N = 21 kg/mol, σ = 0.17
chains/nm²), and PMMA matrix molecular weights (P = 4 – 52 kg/mol). The diffusion of
this hairy nanoparticle is slower than predicted by Stokes-Einstein relation using a 5-nm-
diameter sphere, suggesting that the brush-matrix interpenetration affects nanoparticle
mobility. When brushes are wet, i.e., P/N < 1, IO21L and IO21M have similar diffusion
coefficients because brushes are significantly penetrated by matrix chains and thus dragging force dominates, whereas IO16H has the greatest diffusion coefficients because of less brush-matrix interpenetration resulting in weaker dragging force. In the dry brush region, i.e., $P/N > 1$, brush is less significantly interpenetrated by matrix chains and thus particle diffusion is dominated by effective diameter. In this case, IO21L diffuses faster than IO21M, which can be attributed to the smaller effective diameter that IO21L has due to smaller graft density. On the other hand, IO16H has the fastest diffusion behavior because of its high graft density and short brush resulting in smaller effective diameter and dragging. Self-consistent field theory is performed to predict the structure of brush and matrix near the particle to quantify the effect of brush-matrix interpenetration and the simulated brush/matrix profiles further support the structure-dynamics effect observed in the experiments. This study highlights the effect of brush structure on nanoparticle center-of-mass diffusion serving as a guidance for future studies on the nanoparticle dynamics in polymer nanocomposites.

### 7.2 Future Directions

Going forward, several experiments can be pursued to further explore the dynamics in polymer nanocomposites, and thus some unsolved problems can be answered.

#### 7.2.1 Long Range Effect on Polymer Diffusion

In Chapter 3, dPMMA diffusion is slower in PNCs than bulk values even when interparticle distance is 8 times greater than $2R_g$, a long range effect also observed in
systems composed of spherical NPs and functionalized planar Si surface, explained by a series of interlocking loops between adsorbed chains and free chains at the interface resulting in greater entanglement density which propagates the influence to long distance. To examine the effect of surface adsorption, changing the surface chemistry such that polymer-particle interactions can be precisely quantified is a possible solution, e.g., precisely tuning the graft density of the silane molecules on the particle surface, or using various silane molecules that have different length of backbones.

7.2.2 Effect of Aspect Ratio of Mobile NRs on Polymer Diffusion

Chapter 5 has introduced nanorod as the mobile nanofiller in PNCs. Other than varying matrix molecular weight, tuning NR aspect ratio (AR) could be another method to change its mobility because NR length affects the motion perpendicular to the rod axis. As the nanorod length becomes smaller with \( d < d_c \), NR has less lateral confinements, and thus faster diffusion relative to long NRs is expected. It is also very interesting to reduce NRs to spherical nanoparticles which are not confined by the near polymer chains if the spherical NP diameters are smaller than the entanglement network. Much faster dynamics of spherical NPs in polymer melts relative to Stokes-Einstein relation prediction provides a significant impact to polymer dynamics. However, nanoparticle-polymer compatibility remains a critical problem to be solved. Carefully choosing compatible materials and/or tuning surface chemistry of the NP are needed to achieve good dispersion.
### 7.3.3 Star Polymer Arm Structure Effect on Particle Diffusion

The studies introduced in Chapter 6 have provided insights in how brush structure affects NP diffusion. It would be interesting using star polymers and investigate the effect of arm numbers on star polymer diffusion in comparison with the grafted NP system. When arm number is large, e.g., $f > 100$, the structure is similar to hard sphere due to arm crowding, so arm retraction could possibly be ignored such that it would act as hard sphere diffusing in polymer melts. Using star polymer is beneficial because (1) chemical structures are identical to the host polymer so star polymer is comparable with the matrix (2) It does not have the core nanoparticle so the size can be maintained small, and (3) it is a good analogue with the grafted NP, i.e., low arm number = low graft density and thus larger dragging by matrix chains; large arm number = high graft density that exclude matrix chains. Experimentally, deuterated PS star polymer can be synthesized routinely with controllable arm length, and tracer diffusion of dPS star polymer can be conducted using a similar set-up as the grafted NP system, so a direct comparison can be done. Therefore, star polymers are promising for the future experiments.
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