Single Particle Tracking of Non-Sticky and Sticky Nanoparticles in Polymer Melts

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Abstract

We use single particle tracking (SPT) to explore the role of nanoparticles/polymer interactions and polymer molecular weight on nanoparticle (NP) diffusion in unentangled polymer melts. The very dilute NP concentrations (~10⁻⁷ wt%) in SPT measurements enables tuning NP/polymer interactions so that the systems with unfavorable or neutral NP/polymer interactions in polymer melts can be studied without nanoparticle aggregation. Here, the diffusion coefficients of weakly interacting (methyl capped, CH₃ QDs) and strongly interacting (carboxylic acid capped, COOH QDs) nanoparticles (radius = 6.6 nm) in poly(propylene glycol) (PPG) melts were measured via SPT. Mean-squared displacements and van Hove distributions of nanoparticle motion are consistent with Brownian motion of single nanoparticles in the long time diffusion regime. The effective COOH QDs size increases with PPG molecular weight as $Mw^{0.5}$, indicating a long-lived bound layer. However, for weakly interacting CH₃ QDs, the effective nanoparticle radius is independent of PPG M_w due to the absence of a bound layer. In contrast to ensemble average methods (i.e. X-ray photon correlation spectroscopy), SPT methods directly detect spatial and temporal diffusion behavior of individual nanoparticles and provide previously inaccessible information about nanoparticle diffusion in polymer melts.

Introduction

Nanoparticle diffusion in polymer nanocomposites (PNCs) is important to the fabrication and processing of PNCs materials to tune their mechanical, thermal, and electrical properties.^{1–3} It also serves as a model system of biological transport and dynamics in complex media such as drug delivery^{4,5} and intracellular particle motion^{6,7}. Although the generalized continuum Stokes-Einstein (SE) describes nanoparticle diffusion in simple liquids, several experimental,^{8–13} theoretical,^{14–16} and simulation^{16–19} studies have identified deviations from this SE relationship in polymer melts.

A few critical factors including length-scale related parameters (nanoparticle size and radius of gyration of polymer) and nanoparticles/polymer interactions (neutral/non-sticky and attractive/sticky) have been suggested as causes of SE deviations of nanoparticle (NP) diffusion in polymer melts.^{15,16} In unentangled polymers, the SE relation was predicted when the radius of the nanoparticle (R_{NP}) is larger than the order of polymer radius of gyration (R_g), $R_{NP} > \sim 1.5 R_g$.¹⁴ When NPs in polymer melts enter the $R_{NP} < R_g$ regime, nanoparticle diffusion faster than the SE relation was observed in slightly¹² and highly¹³ entangled polymer melts. On the other hand, strongly attractive large NPs ($R_{NP} > R_g$) showed slower dynamics than the SE prediction as the adsorbed polymer on the nanoparticle surface increases effective particle size, and this bound layer was the size of R_g .¹¹ The bound layer was proposed to exist when the desorption time of adsorbed polymers (τ_{des}) is longer than the chain relaxation time (τ_r) such that the τ_{des} is an important parameter in suppressing nanoparticle dynamics.¹⁶ Stronger attractive interactions between NPs and polymer are expected to extend τ_{des} . A simulation study on varying NP/polymer interaction at $R_{NP} > R_g$ showed that an increase of NP/polymer interaction results in increased effective viscosity near the NP due to the increased τ_{des} .¹⁸

The current understanding of how NP/polymer interactions impact nanoparticle diffusion in polymer melts is incomplete. For example, enhanced diffusion is expected for the both non-sticky and sticky NPs when $R_{NP} < R_g$, although it is unclear how the faster diffusion is related to the NP/polymer interactions.^{8,12,13} There are a variety of experimental challenges that limit the ability to isolate the role of

NP/polymer interactions on dynamics in PNCs. When the NP/polymer interactions are varied by changing the polymer, other parameters such as τ_r and R_g also change, so comparisons are complicated.²⁰ Also, NPs readily aggregate during PNC fabrication when the mixing energy is thermodynamically unfavorable,⁸ so that changing the NP/polymer interaction at a fixed NP concentration also changes the NP dispersion. Poor NP dispersion, particularly for weakly interacting NPs, makes it challenging to meet the NP concentration required to utilize conventional experimental methods such as Rutherford backscattering spectrometry (RBS),²¹ X-ray photon correlation spectroscopy (XPCS),⁸ and dynamic light scattering (DLS).¹² If the NPs are aggregated, the dynamics measured through an ensemble average of the system will deviate significantly from the dynamics of single nanoparticles, because the isolated and aggregated nanoparticles are indistinguishable. In contrast, single particle tracking (SPT) is not an ensemble-averaging method, but rather tracks individual NPs directly. SPT has been employed to explore NP dynamics in polymer gels,²²⁻ ²⁴ showing heterogeneous NP dynamics and stick/unstick transitions of nanoparticles within a gel network (non-Fickian), and in polymer solutions^{25,26} that observed long-time Fickian diffusions.

In this paper, single particle tracking (SPT) was performed to directly observe the motion of isolated nanoparticles on large length scales (> $5R_{NP}$) and long timescales (>> τ_r) in polymer melts as a function of NP/polymer interactions and polymer molecular weights. Note that this is the first use of SPT to measure the NP dynamics in polymer melts. Specifically, the diffusion coefficients of methyl-capped quantum dots (CH₃ QDs, non-sticky) and carboxylic acid-capped quantum dots (COOH QDs, sticky) with $R_{NP} > R_g$ were measured as a function of molecular weight (400 - 8000 g/mol) of polypropylene glycol (PPG) melts. The SPT method was able to measure single nanoparticle dynamics of both CH₃ QDs and COOH QDs in PPG melts, thereby probing NP/polymer interactions by avoiding NP aggregation at extremely low NP concentration (~10⁻⁷ NPs wt%). By identifying single nanoparticles and tracking their motion, SPT gives dynamic information exclusively about individual nanoparticles unlike RBS, XPCS, and DLS. The diffusion coefficients obtained from the mean-squared-displacement of nanoparticle trajectories show that non-sticky NPs quantitatively follow the SE relationship in the regime of $R_{NP} > R_g$, while sticky NPs exhibit slower dynamics than SE relationship. This deviation was attributed to the increased effective

particle size of $R_{NP} + R_g$, demonstrating a long-lived PPG bound layer was formed on the COOH QDs, but not on the CH₃ QDs. These results establish SPT as a method to study NP diffusion in polymer melts and open the opportunity for more complete comparisons to theoretical and simulation studies by circumventing NP aggregation.

Experimental

Tetrahydrofuran (THF) and toluene were purchased from ThermoFisher. Propylene glycol (PG) was purchased from TCI America and poly(propylene glycol)s (PPG) with the M_n of 425 g/mol (PPG 1), 1000 g/mol (PPG 2), 2000 g/mol (PPG 3), 4000 g/mol (PPG 4) were purchased from Sigma-Aldrich. A PPG with M_n of 8000 g/mol (PPG 5) was purchased from Advanced Technology and Industrial. Polydispersity indices of PPG 1 – PPG 5 are 1.06, 1.04, 1.02, 1.01, and 1.01, respectively, as measured by gel permeation chromatography. Octadecylamine capped CdSe@ZnS quantum dots solution (CH₃ QDs, $R_{NP} = 6.55 \pm 0.12$ nm) and mercaptopropionic acid capped CdSe@ZnS quantum dots solution (COOH QDs, $R_{NP} = 6.64 \pm 0.13$ nm) were purchased from NNCrystal, USA. The reported particle size of QDs was measured from the SPT in PG and their measurements are in good agreement with X-ray scattering and transmission electron microscopy analysis. The methyl end groups on CH₃ QDs are neutral or non-sticky to PPG, whereas the carboxylic acid end groups on COOH QDs are attractive or sticky to PPG via hydrogen bonds (Figure 1).²⁷ Toluene and deionized water were used to dilute the concentration of CH₃ QDs and COOH QDs solutions, respectively, to 1µg/mL prior to use.

Poly(propylene glycol), PPG



Figure 1. For PNC samples, methyl (CH₃) and carboxylic acid (COOH) capped QDs were used for nonsticky and sticky nanoparticles in poly(propylene glycol) melts, respectively.

To make the polymer nanocomposites (PNCs), 0.1g of PPG was dissolved in 1mL of THF followed by the addition of 1µL of diluted QDs solutions under stirring. The solvent was quickly removed from the QD/polymer solution, at 50°C and then vacuum dried at room temperature for overnight. The resulting QDs concentration in PPG was approximately 10⁻⁷ wt%. This low concentration of QDs and fast removal of solvent prevented QD aggregation as demonstrated by the continuous blinking of QDs in optical microscopy. Linear viscoelastic measurements of pure PPG melts and QD/PPG PNCs were performed on an ARES G2 rheometer (TA instrument) in a cone and plate geometry (50mm diameter, 0.04rad cone) with a 10/s of shear rate. The viscosities of QD/PPG PNCs are identical with pure PPGs. Figure S1 plots $1/\eta$ vs M_w and slope decreases from -1 to -1.7 with increasing molecular weights. This indicates that all polymers are unentangled, which is consistent with $M_e = 2800$ g/mol. Prepared sets of QD/PPG PNCs were loaded and sealed into a glass chamber that is approximately 2cm×0.5cm×0.2mm. The QD/PG composites were prepared in the same procedure to measure the hydrodynamic size of QDs.

Single particle tracking experiments were performed (T = 21.8°C) on an inverted optical microscope (Nikon Eclipse Ti) using an oil immersion objective (×100, 1.49NA) and a 512×512 px detector (1 px ~ 106 nm). A 532-nm laser source was used for both types of QDs, which have an emission peak spanning 620-640 nm. Videos were recorded for 30sec with the frame rate of 33 fps. Representative frames are shown for the SPT of COOH QDs in PPG 1, Figure 2. The fluorescent signal emitted from QDs has enough signal-to-noise ratio to localize the center of QDs in the PPG background. In SPT measurements blinking QDs indicate single QDs in PPG melts, while optical intensity from aggregated QDs is constant.²⁸ Sufficient QD dispersion was achieved by using low QD concentrations (~10⁻⁷ wt%) and fast solvent removal. This was effective even for the CH₃ QD/PPG nanocomposites with weak NP/polymer interactions. Low NP concentrations are also necessary to localize QDs without connecting trajectories of nearby particles. The red circles in the frame images at 0s and 1.5s (Figure 2) show the movement of these NPs within the XY plane. In addition, some QDs disappear (blue circles) and other QDs appear (green circles) after 1.5s, most likely due to the diffusion of QDs along the Z-direction and blinking of QDs. Note that the depth of focus along the Z-direction is ~0.1µm and much smaller than the field of view in the XY plane

(54µm x 54µm). For in-plane movement, the X and Y coordinates of individual QDs in each frame are determined to create trajectories by connecting the XY positions between frames.



Figure 2. Frame images of recorded video at (a) 0s and (b) 1.5s for SPT measurement of COOH QDs in PPG 1. Red circles indicate three QDs diffusing in the XY plane. Blue circles in (a) indicate QDs lost after 1.5s of diffusion. Green circles in (b) indicate QDs that were not observed in (a).

Images were analyzed with Fluorescent Imaging Evaluation Software for Tracking and Analysis (FIESTA).²⁹ FIESTA localizes and connects the center of mass of QDs in X and Y positions by fitting the fluorescent intensity to a 2D Gaussian point spread function. The positional error is < 40nm although the FWHM of the fluorescent intensity is $\sim 600 - 700$ nm. In FIESTA, the criteria for usable trajectories includes a maximum speed of 15000nm/s, a maximum of four break frames to allow for blinking QDs, and a minimum of six frames per trajectory. These criteria can lead to connecting adjacent particles, so unrealistic trajectories were rejected by limiting the maximum jump distance to 1000nm (PG), 850nm (PPG 1), 750nm (PPG 2), 500nm (PPG 3), and 350nm (PPG 4), and 300nm (PPG 5). Longer maximum jump distances were allowed for NPs in less viscous PPG melts. Trajectories with an averaged positional error greater than 40nm (PG), 35nm (PPG 1), and 30nm (PPG 2 to PPG 5) were excluded. Larger positional errors were allowed for the trajectories in less viscous melts, because the fluorescent intensity of rapidly moving QDs diffuses more than the slowly moving QDs. Typically, ~20% of trajectories are rejected from these criteria and SPT measurements used >500 trajectories. Mean-squared-displacements (MSD) were calculated from the timeaveraged displacements of single particle trajectories. Ensemble-averaged MSDs were calculated by weight-averaging the MSD of trajectories, wherein weighting factors are inversely proportional to the trajectory lengths. For example, MSD of a 10 frames length of trajectory has a weighting factor of 9 for MSD at $\Delta t = 0.03$ s whereas the weighting factor of 1 is given for MSD at $\Delta t = 0.27$ s. The slope of the ensemble-averaged MSD curves were fit to determine the time-independent diffusion coefficient (D_{SPT}):

$$D_{SPT} = \frac{MSD}{2n\Delta t} \qquad (1)$$

where n is the dimensionality, and in these experiments n = 2. Using the diffusion coefficient, apparent QDs sizes (R_{SPT}) from the SPT measurements were recovered by using the Stokes-Einstein (SE) relationship:

$$R_{SPT} = \frac{k_B T}{6\pi\eta D_{SPT}}$$
(2)

where $k_{\rm B}$ is the Boltzmann constant, *T* is the temperature, and η is the temperature dependent bulk viscosity of polymer melts from linear viscoelastic measurements.

Results and Discussion

The trajectories of isolated CH₃ QDs in PPG 1 are plotted by shifting the initial positions to the origin (0µm, 0µm), <u>Figure 3a</u>. The isotropic trajectories indicate random motion of QDs within a homogeneous melt of PPG 1. Most QDs move \pm 500nm with < 35nm resolution and are densely packed near the origin, because QDs leaving the XY plane and blinking truncate the trajectories. Individual MSDs (colored, <u>Figure 3b</u>) are obtained by averaging the displacements of every Δt within a trajectory. Most MSD curves increase monotonically with Δt , implying no particle trapping within the polymer melt. A small fraction of MSD curves fall off sharply near the end of their trajectory, indicating the QDs diffused back toward the origin. The contribution of such MSDs is minimized by weight-averaging all MSDs to obtain the ensemble-averaged MSD curve (black, Figure 3b). MSD has a linear relationship with Δt on a log-log scale and a slope of 1 (Eq 1), which is the characteristic of Brownian motion. This shows that the ensemble-averaged MSD effectively captures NP diffusion from SPT measurements. In addition, SPT provides the ensemble average of diffusion dynamics (as does RBS, DLS, and XPCS) and also a plethora of dynamic information from the individual MSD of single nanoparticles.



Figure 3. (a) SPT trajectories of CH₃ QDs in PPG 1 (1790 tracks). The origins of all trajectories were shifted to $X = 0\mu m$ and $Y = 0\mu m$. (b) Mean-squared-displacements (colored) of individual trajectories and ensemble-averaged MSD (black) as a function of Δt . (c) One dimensional van Hove correlation functions of CH₃ QDs in PPG 1 at $\Delta t = 0.06s$, 0.15s, and 0.30s. Solid lines indicate Gaussian fits.

The van Hove correlation functions provide the distribution of distance that single nanoparticle can reach by the diffusion mechanism over time. Figure 3c shows the distribution of one-dimensional displacements of CH₃ QDs in PPG 1 at $\Delta t = 0.06s$, 0.15s, and 0.30s, and the distribution broadening with increasing Δt . These distributions are well-described by Gaussian distributions (R²=0.999), further indicating the random motion of non-aggregated QDs in a polymer melt. If the SPT measurements captured heterogeneous populations of aggregated and non-aggregated QDs, an exponential distribution would be expected due to the slower dynamics of aggregated QDs.³⁰ The mean values of distributions were nearly zero at all Δt and standard deviation (σ) of them were 194nm, 325nm, and 469nm at 0.06s, 0.15s, and 0.30s of Δt , respectively. The standard deviation of NP displacements is the characteristic length of NP diffusion, $\sigma = \sqrt{2D\Delta t}$, such that the MSD (= 4D\Delta t) corresponds to the $2\sigma^{2.31}$ The X and Y displacements distributions are also well-fit by Gaussian functions with standard deviations of 195nm and 193nm at $\Delta t = 0.06s$, respectively, as expected for Brownian diffusion of QDs. Thus, Figure 3c shows the distributions of both X and Y directional displacements. The SPT measurements of CH₃ QDs and COOH QDs for all PPG molecular weights are analyzed in a similar way and their van Hove correlation functions are given in Figure S2. The number of tracks, quality of Gaussian fit (\mathbb{R}^2), and σ are also provided in Table S1. The Gaussian distributions confirm isotropic NP displacements in all PNCs studied.

Figure 4a plots the ensemble-averaged MSD curves from the SPT measurements of CH₃ (solid line) and COOH QDs (dashed line) in PG monomer and PPG polymers to quantitatively compare the dependence of MSD on the surface chemistry of QDs and molecular weight of PPG melts. First, the MSD of CH₃ and COOH QDs in the PG monomer (green) are the same within the experimental uncertainty, as expected in the absence of polymer. Second, the MSD of CH₃ QDs are higher than COOH QDs in all PPG melts. This is also evident in their van Hove correlation functions (Figure S2). Third, in PPG melts, increasing the molecular weight of PPG reduces the MSDs in both CH₃ and COOH QDs, as expected from the increasing viscosity with PPG molecular weights. Finally, the relative MSD differences between the two types of QDs increase with increasing PPG molecular weights at all Δt . These data suggest that the viscosity is not the sole factor determining the dynamics of nanoparticles in these polymer melts, implying

the importance of NP/polymer interactions. The time-dependent diffusion coefficient, D_{SPT} , was obtained by fitting the MSD curves to Eq 1 across the range with MSD ~ Δt , corresponding to Brownian diffusion. For example, the MSD curves of QDs in PPG 4 and PPG 5 have slopes less than one at $\Delta t < 0.5$ s, and thus fitting started from $\Delta t \sim 0.5$ s. The time-dependent diffusion coefficients (D(Δt) = MSD/(4 Δt)) are given (Figure 4b) and independent of Δt , thus confirming MSD ~ Δt^1 . Therefore, the time-independent diffusion coefficient (D_{SPT}) is defined from the average of D(Δt).



Figure 4. (a) Ensemble-averaged MSD versus Δt from the SPT measurements of CH₃ QDs (solid lines) and COOH QDs (dashed lines) in PG monomer and PPG polymer melts. (b) Time-dependent diffusion coefficient (D(Δt) = MSD/(4 Δt)) for Δt = 0.5s - 1s. The average D(Δt) defines the time-independent diffusion coefficient from the SPT measurements, D_{SPT}, as presented in Figure 5.

Although the apparent subdiffusive behaviors in PPG 4 and PPG 5 can be a reminiscent of nanoparticle hopping as predicted in well-entangled polymer liquid (melts or solutions), which has been proposed as the reason for intermediate subdiffusion with longtime normal diffusion,^{26,32} it is likely a result of the inevitable positional error. Since our PNCs are comprised of large nanoparticles (~13 nm) relative to the tube diameter (d_T , ~4.9 nm) and the correlation length of chain segments of ~0.9 nm³³ in mostly unentangled PPG melts, the hopping will be less than 10nm if it is present. From the D_{SPT} of CH₃ and COOH QDs in PPG 4, jump distance for the 0.03s of delays are found as 29nm and 25nm, respectively, which are within the positional error of 30nm. Thus, Fickian diffusion of NP is observed in all the PNCs studied here at a long-time diffusion (~1s) and D_{SPT} is obatained.

Note that recent XPCS measurements with poly(ethylene glycol) grafted SiO₂ NPs in poly(methyl methacrylate), polystyrene grafted SiO₂ NPs in polystyrene, and poly(styrene-b-vinylpyridine) grafted CdS NPs in polystyrene, have observed a transition from Fickian to hyperdiffusive NP dynamics at $R_{NP} > R_g$ when the probing temperature becomes lower than ~1.25T_g in unentangled polymer melts or the polymer matrix becomes well-entangled.^{34–36} Hyperdiffusive NP dynamics have been explained by the local stress and/or thermal gradient in elastic polymer networks that cause ballistic NP motion.³⁷ Our SPT measurements exhibit Fickian diffusion in all cases to long diffusion times with no indication of a transition to hyperdiffusion, and this is in good agreement with the XPCS measurements since our polymer melts are unentangled and measuring temperature is ~1.45T_g.³⁸

The time-independent diffusion coefficients, D_{SPT} , decrease with increasing PPG molecular weight and the D_{SPT} of COOH QDs are smaller than CH₃ QDs (Figure 5a). To highlight this difference between the two types of QDs, the radius of QDs determined by SPT measurements (R_{SPT}) is calculated from D_{SPT} and Stokes-Einstein relationship (Eq.2), thereby accounting for the dominant factor of viscosity (Figure 5b). The radius of QDs are defined as R_{NP} , which is obtained from the D_{SPT} of QDs in PG monomer and Eq.2 ($R_{NP}(CH_3 QDs) = 6.55$ nm, $R_{NP}(COOH QDs) = 6.64$ nm). In Figure 5b, the R_{SPT} of CH₃ QDs is independent of molecular weight and equal to R_{NP} , indicating the PPG melts do not form a long-lived bound layer due to the neutral interaction with CH₃ QDs and the D_{SPT} simply scales with the viscosity factor in the SE relationship, $R_{SPT} \approx R_{NP}$. Because the methyl-capped QDs only interact via weak van der Walls force, PPG chains do not adsorb on the CH₃ QDs surfaces for an extended period of time, a so-called non-sticky NP/polymer system. This follows the theory and simulation results of non-sticky nanoparticle diffusion in unentangled polymer melts.^{12,14,39} In particular, a self-consistent generalized Langevin-based theory of single hard-sphere diffusion in polymer melts predicts the recovery of SE relationship (D/D_{SE} \approx 1) at R_{NP}/R_g $> \sim 1.5$ for unentangled polymer melts.¹⁵ This prediction agrees with our SPT measurement of CH₃ QDs in unentangled PPG melts wherein R_{NP}/R_g $\approx 2.4 - 10$.

In contrast, the R_{SPT} of COOH QDs is larger than R_{NP} and increases with PPG molecular weight (Figure 5b). Moreover, the differences between R_{SPT} and R_{NP} scale as $M_w^{1/2}$ (inset of Figure 5b). The deviation of R_{SPT}/R_{NP} from unity indicates the breakdown of the SE relationship in COOH QDs/PPG systems with attractive NP/polymer interactions. Previous reports of PNCs with attractive interactions, SiO₂/P2VP and SiO₂/PPG systems, in the regime of R_{NP} >> R_g reported similar nanoparticle diffusion behavior.^{11,12} This diffusion mechanism involves a core-shell object in which nanoparticles diffuse with a polymer bound layer, increasing the effective nanoparticle size (R_{eff}) by the radius of gyration of polymer chains, R_{eff} ~ R_{NP} + R_g.^{16,40} In this study, the radius of COOH QDs (R_{NP} ~ 6.6nm) is larger than the radius of gyration of all PPG molecular weights (R_g = 0.6 - 2.8nm)³³ and (R_{SPT} - R_{NP}) ~ M_w^{1/2}, indicating our observed M_w dependency of COOH QDs is a result of a PPG bound layer. Attractive interactions in COOH QD/PPG PNCs result in desorption times that are long relative to the time over which diffusion is observed, and the polymer bound layer sticks to the surface of the nanoparticles.



Figure 5. (a) D_{SPT} of CH₃ QDs (black) and COOH QDs (red) from the MSD curves as a function of PPG molecular weight. (b) Nanoparticle radius (R_{SPT}) recovered from D_{SPT} in SE relationship for CH₃ QDs and COOH QDs. R_{NP} is the NP radius measured in propylene glycol (monomer). Error bars of R_{SPT} are smaller than the symbol size. Inset shows the thickness of bound layer ($R_{SPT} - R_{NP}$) and its $M_w^{1/2}$ scaling.

To further demonstrate the presence of a bound polymer layer with a thickness equal to R_g in COOH QD/PPG nanocomposites, the normalized D_{SPT} (symbols) and D_{eff} (dashed lines) are presented in Figure 6. Here, D_{eff} is the SE prediction of diffusion coefficient calculated using $R_{eff} = R_{NP}$ for CH₃ QDs and $R_{eff} = R_{NP} + R_g$ for COOH QDs. The diffusion coefficient D_{SPT} and D_{eff} are normalized by D_{NP} , which is obtained from SE relationship using R_{NP} (QD radius in PG monomer). The normalized D_{SPT} values for COOH QDs are less than one and decrease as PPG molecular weight increases, which is the observed PPG molecular weight dependency in Figure 5b for an attractive system. Moreover, the value of D_{SPT}/D_{NP} (symbols) are well-described by D_{eff}/D_{NP} (lines), thereby meaning $R_{SPT} = R_{NP} + R_g$ in COOH QDs/PPG systems. This demonstrates that the attractive interactions in the COOH QDs/PPG PNCs result in long-lived PPG bound layers on NPs that effectively increase the NP size by R_g . In the case of non-sticky CH₃ QDs in PPG, the normalized D_{SPT} values for CH₃ QDs are approximately unity and independent of PPG molecular weight so that the SPT measurements are consistent with the Stokes-Einstein behavior where $R_{SPT} = R_{NP}$, namely no bound layer.



Figure 6. Normalized D_{SPT} (symbols) and D_{eff} (lines) as a function of PPG M_w . D_{eff} represents the SE predicted diffusion coefficients of CH₃ QDs and COOH QDs in PPG melts, calculated using R_{eff} values of R_{NP} for CH₃ QDs and $R_{NP} + R_g$ for COOH QDs. D_{NP} is obtained from the R_{NP} (QD radius in PG monomer).

Through the quantitative analysis on the effective particle size of CH₃ QDs and COOH QDs, we demonstrate that the SPT method can experimentally measure the nanoparticle diffusion dynamics in polymer melts. Importantly, this method accesses weakly interacting NP/polymer systems and enables systematic studies of NP dynamics with varying NP/polymer interactions without the complication of NP aggregation. While this study explored NP/polymer systems that exhibit very short (non-sticky NP) and very long (sticky NP) desorption times relative to our particle tracking timescales, SPT methods provide an opportunity to explore NP motion on timescales comparable to the desorption time. SPT methods are also very well suited to more complex PNCs, including heterogeneous environments. For example, hopping of nanoparticles in entangled polymer melts,³² anomalous diffusion of nanoparticles in jammed environments,³⁷ and NP/polymer composites with strong ionic attraction⁴¹ can be extensively explored via single particle tracking.

Conclusion

Single particle tracking (SPT) has been employed to reveal and isolate the influence of nanoparticle/polymer interactions on the motion of nanoparticles in polymer melts. The motion of individual non-sticky (CH₃ QDs) and sticky (COOH QDs) nanoparticles ($R_{NP} \approx 6.6nm$) in PPG melts (R_{g} = 0.6 - 2.8nm) is tracked to obtain the NP diffusion coefficients. Particle trajectories, mean-squareddisplacements, and van Hove distributions uniformly validate that single nanoparticles in PPG exhibit Brownian motion. Further analysis shows that CH3 QDs in PPG follow Stokes-Einstein (SE) relationship, whereas COOH QDs in PPG have slower dynamics. A bound layer of PPG chains on the COOH QDs effectively increases the size of the nanoparticles by the PPG radius of gyration. The SPT method for measuring nanoparticle diffusion has several benefits. First, the exceptionally low NP concentrations used in SPT facilitate NP dispersion even when the NP/polymer interactions are weak. Second, SPT directly observes the motion of single nanoparticles to provide broad spatial- and temporal-dynamic information, in addition to the ensemble-averaged dynamics accessible by many methods. Thus, SPT methods can identify the motion of nanoparticles to reveal the characteristics of NP dynamics, both Fickian and non-Fickian, in a variety of environments (i.e. changing NP/polymer interactions). In the future, SPT methods can provide a deeper understanding of nanoparticle diffusion in complex media with dynamic heterogeneity such as polymer blends.

Supporting Information

Linear viscoelastic measurements with varying PPG molecular weight. van Hove distributions of SPT measurements for CH₃ QDs/PPGs and COOH QDs/PPGs with varying PPG molecular weight.

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