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Entangled Polymer Dynamics in Attractive Nanocomposite Melts

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ABSTRACT: We investigate single chain dynamics of an entangled linear poly(ethylene oxide) melt in the presence of well-dispersed attractive nanoparticles using high-resolution neutron spectroscopy at particle volume fractions as high as 0.53. The short-time dynamics shows a decrease of the Rouse rates with particle loading, yet the change remains within a factor of 2, with no evidence of segment immobilization as often hypothesized. The apparent reptation tube diameter shrinks by $\approx 10\%$ from the bulk at a 0.28 particle volume fraction when the face-to-face interparticle distance approaches the single chain size. The tube diameter is remarkably concentration-



independent at higher loadings where all chains are essentially bound to particle surfaces. These direct experimental observations on the microscopic chain dynamics in attractive nanocomposites are distinct from their nonattractive counterparts and account for some of the unusual dynamic behaviors of the nanoparticles as well as rheology in the composites.

INTRODUCTION

The effect of nanoparticles on polymer chain dynamics is an intriguing unresolved problem with many practical implications, e.g., in designing polymer nanocomposites (PNCs) with tailored rheological properties.¹ The complexity arises due to several reasons. On the nanoparticle side, formation of selfassembled superstructures or agglomerations in polymer matrices, especially in nonattractive systems, 2^{-5} makes it difficult to examine the true nanoparticle effect in nonuniform media. On the polymer side, distinct relaxation processes dominate at different structural levels in the melt state, whose study requires unconventional techniques with high spatiotemporal resolution. For example, at the monomeric level (\approx a few Å's), thermally driven fluctuations result in a multimodal Rouse motion of the connected units with an elementary relaxation rate, $W = (3k_{\rm B}T)/(\zeta_{\rm o}l^2)$, determined by the local friction coefficient, ζ_{0} , and the segment length, $l^{.6}$ At an intermediate length scale (on the order of nanometers), long polymer chains are forced to perform a curvilinear motion (reptation) along their backbone that is confined within a dynamic tube of diameter d due to topological constraints (entanglements) imposed by the surrounding chains.⁷ The bulk rheological properties, such as zero-shear viscosity and rubbery elastic modulus, are directly linked to these microscopic chain parameters (W and d) for linear polymer melts;8-10 however, such a direct link cannot be established for PNCs as their macroscopic viscoelasticity results from a complex interplay between nanoparticles, polymer matrix, and the interfaces in-between.¹¹ Therefore, the question of how nanoparticles alter these microscopic dynamical parameters (Rouse rates and tube diameter) in PNCs and the resulting effects on bulk rheology have yet remained unanswered.

Particularly interesting for PNCs is the high particle volume fraction (ϕ) , a range where the face-to-face interparticle distance (ID) can be comparable to or even smaller than the single chain size, creating a highly confined environment for polymers. Schneider et al.¹² showed on a repulsive polyethylene-alt-propylene (PEP)-SiO₂ PNCs that the apparent tube diameter, measured by neutron spin echo (NSE), decreases significantly at $\phi > 0.31$. Strong geometric confinement induced by the nanoparticles at high volume fractions leads to significant disentanglements of polymer chains without much affecting the local segmental relaxation. Later simulations by Li et al.¹³ and Kalathi et al.¹⁴ revealed a similar chain disentanglement in repulsive PNCs although segmental relaxation, W, gets slower at high loadings. So far, direct measurements of the entangled polymer dynamics in PNC melts were reported on either nonattractive system¹² or attractive PNCs involving short (unentangling) chains only.^{16,17} We hypothesized that the effects of the attractive nanoparticles on the entangled chain dynamics in PNCs would be significantly different since, unlike nonattractive systems, the favorable interaction between the polymer and particles often results in a surface-bound polymer layer whose structure and dynamics can significantly differ from those of the bulk polymer.^{18–20}

In this study, we performed quasielastic neutron scattering measurements (QENS), specifically using backscattering and

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spin echo spectrometers, on long linear poly(ethylene oxide) (PEO) filled with attractive SiO₂ nanoparticles that are dispersed individually at volume fractions as high as $\phi = 0.53$. The results reveal that the Rouse rates, *W*, decrease with ϕ at high particle loadings; however, the reduction remains within a factor of 2 even at the highest volume fraction. On a larger length scale, the apparent tube size slightly decreases (by $\approx 10\%$) at moderate particle loadings but remarkably becomes concentration-independent thereafter, where all chains are in direct contact with the nanoparticles. These new results on the microscopic confined polymer dynamics in attractive PNCs are distinct from the previously reported observations on non-attractive systems and shed light on the origin of the bulk rheological behavior of such PNCs.

EXPERIMENTAL DETAILS

Nanocomposite Preparation. We used hydrogenated and deuterated PEO of similar molar masses (*h*-PEO, $M_w = 35$ kg/mol, $M_w/M_n = 1.08$ and *d*-PEO, $M_w = 35$ kg/mol, $M_w/M_n = 1.08$, Polymer Source Inc.) well above the entanglement molar mass ($M_e = 2$ kg/mol). The colloidal silica nanoparticles (\approx 50 nm diameter with size polydispersity \approx 0.3) in 2-butanone were supplied by Nissan Chemicals America Corp. and used as received. The samples were prepared by mixing the desired ratios of *h*-PEO, *d*-PEO, and SiO₂ in acetonitrile followed by solvent casting, drying at reduced pressure at room temperature, and vacuum annealing at 90 °C for 2 days to remove the residual solvent. For neutron backscattering measurements, *h*-PEO was used as the matrix, whereas *h*-PEO and *d*-PEO were mixed at a 51/49 ratio to contrast-match the silica²¹ for the measurement of the single chain dynamics using NSE.

Small-Angle Neutron Scattering Experiments. Small-angle neutron scattering (SANS) was performed on the NG7 beamline at the National Institute of Standards and Technology Center for Neutron Research (NCNR). The samples were melted at 80 °C and loaded within the spaces of quartz windows with a 50 μ m Teflon ring spacer. The data were collected at 80 °C in the melt state of PEO in a vacuum chamber. Isotropic scattering patterns were background-subtracted and analyzed using Igor Pro based macros.²²

Dynamic Neutron Scattering Experiments. Neutron backscattering and spin echo experiments were performed using high-flux backscattering (HFBS) and neutron spin echo spectrometers at NCNR, respectively. The samples for the backscattering and NSE measurements were sealed in Al cans in a He environment; they were formed in an annular shape of 3 cm diameter, 3 cm height, and ≈ 0.1 and ≈ 0.5 mm thicknesses for the experiment using backscattering and NSE, respectively. The samples were equilibrated at 400 K for 1 h prior to the measurements. The data collected on an empty cell with the same geometry was used to subtract the background. The instrumental resolution function was determined using standard vanadium and carbon samples for the HFBS and NSE measurements, respectively. The data collected on the vanadium sample were also used for detector efficiency normalization on HFBS. For the backscattering measurements on HFBS, Doppler-shifted neutrons at a frequency of 15 Hz with an incident wavelength of 6.27 Å provided a dynamic range of $\pm 11 \ \mu eV$ (with a resolution of 0.8 μeV full width at half-maximum). The HFBS data was collected over a range of wave vectors Q = 2.5 to 17.5 nm⁻¹. Data fitting was performed using the DAVE software.²³ On NSE, two incoming wavelengths were used, namely, 6 and 11 Å, allowing maximum Fourier times of 20 and 100 ns, respectively, to be reached. In both cases, the wavelength spread was $\approx 20\%$. Three (for 6 Å) and four (for 11 Å) scattering angle configurations were employed to collect data at Q = 0.08 (for 11 Å only), 0.11, 0.15, and 0.20 Å⁻¹.

RESULTS AND DISCUSSION

Nanoparticle Dispersion and Polymer Conformation. The nanoparticle and polymer structures in PNCs were determined by small-angle neutron scattering (SANS) at T =353 K above the melting temperature of PEO. When the nanoparticles are dispersed in an isotopically homogeneous matrix, in this case hydrogenated PEO, the small scattering is solely due to the contrast between the silica and the polymer and reflects the structure and dispersion of the nanoparticles. The hydrogen bonding between the ether oxygen of PEO and hydroxyl groups on the surface of SiO₂ favors formation of an adsorbed polymer layer on particle surfaces, which provides steric protection against aggregation. The nanocomposites were prepared using dilute particle concentration in polymer solution where the average face-to-face distance was larger than 90 nm (more than 10 times bigger than the radius of gyration of the chains) at all concentrations. Therefore, the interparticle bridging was not favorable; the polymer is adsorbed on NP surfaces and provides an effective repulsion. Figure 1a shows



Figure 1. (a) SANS profiles (shifted vertically for clarity) from PNCs in *h*-PEO at various concentrations. The nanoparticle form factor was obtained from dilute solution in acetonitrile. An interference peak appears for high concentration at the Q value matching the interparticle distance due to uniform dispersion. The lack of low-Q excess scattering indicates good particle dispersion in PNCs. (b) SANS profiles of the PEO chains in the neat form and PNCs with neutron-contrast-matched SiO₂ nanoparticles. The profiles of PNCs merge with the neat Gaussian coil profiles of PEO. Excess scattering at the low-Q regime is a result of a contrast mismatch between nanoparticles and the matrix (see the text), which vanishes at the length scales of the NSE experiments. The dashed line is the Debye fit to the neat PEO data. (c) Kratky representation of the SANS data shown in panel (b). The arrow shows the NSE Q range employed.

the intensity profiles at different particle volume fractions. The interference peak at intermediate wave vectors, Q, shifts to higher values at larger concentrations, consistent with decreasing interparticle separation $(2\pi/Q)$. Most importantly, the absence of an excess intensity at low Q suggests the aggregate-free nanoparticle dispersion in the polymer matrix. (Note that the slight low-Q uprise with Q dependence ($I \sim Q^{-0.22}$) for the sample with $\phi = 0.34$ is attributed to a more nonuniform interparticle separation at this sample rather than a large-scale agglomeration that often results in an exponent between -2 and -4 depending on the fractal dimension of the aggregation.²⁴) The corresponding average face-to-face particle

distance (ID) of the randomly distributed nanoparticles is calculated using ID = $2R_{\rm NP}[(2/\phi\pi)^{1/3} - 1]$, where $R_{\rm NP}$ is the radius of the nanoparticle.²⁵ For the compositions studied here, ID ranges from \approx 50 to \approx 3 nm, and the corresponding chain confinement parameter, ID/ $2R_{\rm gr}$, decreases from 3.46 (unconfined) to 0.22 (strongly confined) with increasing particle loading (see Table 1).

Table 1. Nanocomposite Characteristics, Mass and Volume Fractions of NPs, Face-to-Face Interparticle Spacing, the Confinement Parameter, Rouse Parameter, and the Apparent Tube Diameter Obtained from NSE

NP % mass	ID^{a}	ID/		
(volume)	[nm]	$2R_{g}$	$Wl^4 [nm^4/ns]$	<i>d</i> [nm]
0.00 (0.00)			0.92 ± 0.01	5.47 ± 0.05
0.15 (0.08)	49	3.46	0.96 ± 0.01	5.59 ± 0.07
0.30 (0.17)	26	1.89	0.78 ± 0.01	5.13 ± 0.05
0.45 (0.28)	15	1.07	0.76 ± 0.01	4.94 ± 0.05
0.52 (0.34)	11	0.79	0.73 ± 0.01	4.99 ± 0.05
0.60 (0.42)	7.2	0.51	0.65 ± 0.01	4.94 ± 0.05
0.70 (0.53)	3.1	0.22	0.520 ± 0.02	4.92 ± 0.07
a Face-to-face average interparticle distance calculated using				
ID = $2R_{\rm NP}\left[\left(\frac{2}{\pi\phi}\right)^{1/3} - 1\right]$ for randomly distributed spheres of				
diameter $2R_{ m NP}$ and volume fraction ϕ .				

In the contrast-matched NSE samples, the PEO single chains are visible in SANS. Figure 1b shows the intensity profiles at intermediate- and low-Q regimes, with the Debye form factor (dashed line) fit to the neat PEO data. R_{r} is found to be ≈ 7 nm as expected.²⁶ All profiles merge at Q larger than 0.05 A^{-1} , signifying the Gaussian nature of the polymer chains at all particle concentrations. In the low-Q regime, excess scattering in the PNCs compared to the neat PEO is noticeable. In zero-average contrast-matched samples, the low-Q excess scattering is the norm for PNC samples and has been the topic of many recent studies. Possible explanations include polymer voids,²⁷ scattering length density (SLD) mismatch between the polymer and nanoparticles,²⁸ large-scale composition fluctuations of d/h chain mixtures,²⁹ and particle aggregation.²⁴ More recently, Jouault et al.³⁰ showed that the excess scattering at the low-Q regime could result from the SLD difference in the bound polymer and the matrix chains. In our work, the SANS profiles from the particles (Figure 1a) rule out the aggregation explanation. Also, note that this system was structurally characterized using SAXS in our earlier work;³¹ no sign of aggregation was found at any composition. Regardless, in the length scale of the NSE experiments (see Figure 1b), the scattering is predominantly due to the PEO chains. The SANS profiles from the zero-average contrast-matched samples can be further analyzed in a Kratky representation, which is $I_{\text{coherent}}Q^2$ vs Q (the coherent intensity, I_{coherent} , is calculated by subtracting the background intensity from the total intensity). Figure 1c shows the profiles in the intermediate-Q regime, which give a clear plateau characteristic of the Gaussian coils.

Self-dynamics from Neutron Backscattering. A typical dynamic neutron scattering experiment measures the probability that neutrons are scattered into a solid angle with an energy exchange (also called the double differential scattering cross section), which is related to the incoherent and coherent dynamic structure factors, $S_{inc}(Q,\omega)$ and $S_{coh}(Q,\omega)$; here, Q denotes the exchanged wave vector and indicates an inverse

length scale of observation, while $\hbar\omega$ is the energy exchanged by the neutron with the sample in the scattering event. $S_{\rm inc}(Q,\omega)$, typically measured by backscattering in the energy domain, relates the spatial correlations of the same atom at different times and gives the self-motion. $S_{\rm coh}(Q,\omega)$ is due to spatial correlations between different atoms at different times, therefore providing information on the collective dynamics, commonly measured by neutron spin echo in the time domain as the intermediate scattering function (ISF), the Fourier transform of the dynamic structure factor.

In fully hydrogenated samples, backscattering measures the self-motion of H-atoms over timescales ranging from 100 ps to \approx 2 ns. The Rouse dynamics of PEO is the dominant process creating a broadening of the elastic line, i.e., quasielastic broadening, at Q values up to 6 nm^{-1} , as shown by Brodeck et al.³² At 400 K, the dynamics of PEO at $Q > 5 \text{ nm}^{-1}$ becomes too fast to analyze reliably, and at lower Q values, the selfdynamics is interfered by coherent contributions;³³ therefore, we report only the analysis of the data taken at $Q = 4.7 \text{ nm}^{-1}$. The data were fit in the energy domain to the Fourier transform of a stretched exponential function, with the stretching exponent set to 0.5 for Rouse motion.⁶ The employed model is necessarily a simplification, which does not account for heterogeneity in the dynamics; however, it provides an effective relaxation timescale reflecting the average dynamics in the sample. The obtained relaxation times for the self-motions of the segments, $au_{ ext{self}}$ are related to Rouse rates by $W l_{self}^4 = 9\pi/(Q^4 \tau_{self})$,³⁴ where l = 0.56 nm is the segment length of PEO.⁸ Figure 2a shows the spectra at $Q = 4.7 \text{ nm}^{-1}$, together with the elastic line (obtained from vanadium). The + symbols overlapping with the elastic line represent the spectra for the bare SiO₂ nanoparticles only, suggesting that the nanoparticles or any surface ligands do not contribute to the quasielastic broadening. All PNC spectra are, therefore, fit to the Fourier transformed KWW (FT-KWW) function together with delta and a constant background to account for the broadening due to segmental relaxation, the elastic effect of the nanoparticles, and the fast vibration type of dynamics that falls outside of the instrument energy window.

 Wl^4 decreases with increasing ϕ at intermediate and high concentrations, but we did not observe any change in the trend due to geometric confinement. The Rouse parameter is reduced only by half of that of the neat polymer, even at the highest $\phi \approx 0.53$. This suggests that the bound polymer layer on nanoparticles, at least in our polymer-nanoparticle system, is still mobile at the segmental level, in contrast to the previously reported "frozen/glassy chain" hypothesis based on mechanical/dielectric relaxation spectra and NMR³⁵⁻³⁸ but in agreement with more recent and direct measurements of the segmental dynamics at the interfaces.^{19,39} As *Wl*⁴ is determined by the local friction at the monomeric level, increasing ϕ imposes more friction due to attractive surfaces and, thus, decreases overall segmental mobility. No change in the trend, however, was noticeable when transitioning from the unconfined to the confined regimes, in parallel with the segmental diffusion in P2VP-SiO2 nanocomposites reported by Bailey et al.³⁹ Since the spacing between nanoparticles remains much larger than the monomer length (l = 0.56 nm), the effect of the confinement parameter based on $R_{\rm g}$ of the chain has no noticeable effect on Wl⁴. Note that this is different from the center-of-mass diffusion of chains as reported by Winey and co-workers²⁵ in attractive PNCs where $ID/2R_{\sigma}$ is found to be the main parameter for the whole chain diffusion.



Figure 2. (a) QENS spectra of the neat PEO and PEO-SiO₂ nanoparticles at several particle volume fractions, showing decreasing broadening with increasing nanoparticle volume fraction. The instrument resolution was obtained using a vanadium sample (shown as the gray line). The lines are the fits to the Fourier transformed KWW function with background and delta (see the text). Purple (+) symbols are those for SiO₂ nanoparticles, which show no broadening. (b) The Rouse rates, Wl^4 , obtained from the QENS spectra (self-dynamics) and from NSE (coherent). The star symbol is the Rouse parameter obtained from a clustered sample for comparison. The error bars represent one standard deviation throughout this paper.

The discrepancy between these studies originates from the fact that different techniques measure polymer dynamics at different length scales. Elastic recoil detection, by Winey and co-workers,²⁵ measures long-time center-of-mass diffusion of the chains. The length scale of interest is, thus, the size of a single chain $(2R_{\sigma})$; the geometric confinement becomes effective when interparticle separation ID is smaller than a single chain. This technique does not however measure the segmental level relaxation. A chain can be pinned to the surface via direct contact of some segments, and the center-of-mass diffusion can be completely suppressed, while a significant portion of the segments (loops and tails) can still be highly mobile as explicitely shown by Krutyeva et al. using neutron spin echo.¹⁹ Similarly, complete freezing of the interfacial polymer was hypothesized based on the rheological behavior of the composites with an assumption of a T_g gradient from the particle surface to the bulk.³⁵ On the other hand, highresolution neutron backscattering provides a relaxation at the time (on the order of nanoseconds) and length (on the order of Å's) scales on the segmental level; therefore, it provides direct information on the internal dynamics of the polymer.

Overall, our QENS results show that, unlike nonattractive or repulsive systems, the attractive nanoparticles reduce the elementary Rouse rate of the polymers by increasing local friction at intermediate and high particle loadings.

Single Chain Dynamics from Neutron Spin Echo. We then investigated the large-scale chain dynamics using neutron spin echo (NSE). NSE measures the normalized intermediate scattering function, S(Q, t)/S(Q,0), directly in the time domain. In PNCs with a matrix formed by an opportune mixture of d/h-PEO chains, the scattering from the NPs is eliminated, and the contrast between d- and h-polymers yields a scattering signal arising from individual PEO chains (see also Figure 1b). The measured dynamics up to 100 ns for long (entangling) PEO at T = 400 K involves two distinct regimes. At short times, the chain segments exhibit an unrestricted coherent Rouse motion until the time (τ_e) is long enough to explore a distance comparable to an entanglement strand. The entanglement time, τ_{e} , is defined by $\tau_{e} = \frac{N_{e}^{2l^{4}}}{\pi^{2}W^{4}}$.⁸ Using $N_{e} = 45$ for the entanglement degree of polymerization of PEO, $Wl^{4} \approx 0.05$ m⁴/₂ (T_{e}) and T_{e}) of PEO, $Wl^{4} \approx 0.05$ m⁴/₂ (T_{e}) and T_{e}) of PEO, $Wl^{4} \approx 0.05$ m⁴/₂ (T_{e}) and T_{e}) of PEO, $Wl^{4} \approx 0.05$ m⁴/₂ (T_{e}) and T_{e}) of PEO, $Wl^{4} \approx 0.05$ m⁴/₂ (T_{e}) and T_{e}) of PEO, $Wl^{4} \approx 0.05$ m⁴/₂ (T_{e}) and T_{e}) of PEO, $Wl^{4} \approx 0.05$ m⁴/₂ (T_{e}) and T_{e} (T_{e}) and T_{e} (T_{e}) and T_{e} (T_{e}) and T_{e} (T_{e}) and T_{e} (T_{e} 0.95 nm⁴/ns (Figure 2b), and l = 0.56 nm,⁸ we obtain $\tau_e \approx 21$ ns. At $t > \tau_{e}$, the chains exhibit a confined motion within a reptation tube formed by the surrounding entangling chains. We, therefore, estimated the coherent Rouse rates from single chain dynamic structure factors up to 10 ns ($t < \tau_e$) (see Figure S3 for the effect of the time interval used in analysis) and the confining tube sizes for the long-time tails above 50 ns ($t > \tau_e$). Since τ_e is inversely proportional to Wl^4 , the value is expected to shift to longer times for the PNCs. For the highest particle concentration, Wl^4 decreased to 0.52 nm⁴/ns; thus, τ_e (ϕ = $(0.53) \approx 37$ ns, which is still below 50 ns. We confirmed that using different intervals such as t > 60 ns, t > 80 ns, and t > 90ns gives a practically identical tube diameter (see also Figure S4 for the obtained plateau levels).

The single chain dynamic structure factors at four *Q* values were obtained for neat PEO and all PNCs (Figure 3). We first



Figure 3. Comparison of the normalized intermediate scattering function (ISF) obtained from NSE (with a neutron wavelength of 6 Å and Fourier times up to 20 ns) for the neat PEO (open symbols) and the PNC with (a) 0.08 and (b) 0.42 volume fractions of nanoparticles (filled symbols) drawn in Rouse scaling, Q^4t . The dashed and the solid lines are the fitting results (of eq 1) for the neat PEO and the PNCs for data up to 10 ns, respectively. Deviation from the fitting at longer times is indicative of the confined motion of the chains in PNCs. For other compositions, see the Supporting Information.

investigate the short-time (t < 10 ns) behavior where the chain segments exhibit Rouse-like motion within a confining tube. For $\phi \approx 0.28$, the Rouse dynamics slows down very slightly compared to the neat PEO, whereas for $\phi \approx 0.42$, the difference is significant. The coherent Rouse dynamics is described by the equation³⁴



Figure 4. Comparison of the normalized intermediate scattering function (ISF) obtained from NSE for the neat PEO (open symbols) and the PNCs at all compositions studied (filled symbols). The lines are the global fit results of de Gennes' formulation⁴⁰ for the local reptation motion (see the text).

$$\frac{S_{\text{chain}}(Q, t)}{S_{\text{chain}}(Q)} = \int_{0}^{\infty} \exp\left\{-u - \frac{2}{\pi}\sqrt{\Omega_{R}t}\right\} \left[\sqrt{\pi} e^{u^{2}/4\Omega_{R}t} + \frac{1}{2}\pi \frac{u}{\sqrt{\Omega_{R}t}} \left(1 - \exp\left(\frac{u}{2\sqrt{\Omega_{R}t}}\right)\right)\right]\right\}$$
(1)

Here, the only variable in the equation is $\Omega_{\rm R}t = \frac{Wt^4}{36}Q^4t$. This allows construction of a master curve of the data taken at different Q values. The resulting normalized intermediate scattering functions at $\lambda = 6$ Å (up to a Fourier time of 20 ns) are displayed as a function of the scaling variable, Q^4t , as shown in Figure 3, which shows the comparison of the data for the neat (open symbols) and the PNC with 0.08 (a) and 0.42 (b) particle volume fractions (filled symbols). Results for the other compositions are given in the Supporting Information. A systematic slowdown upon particle addition is clearly seen. To obtain Wl^4 for each sample, we fit the above equation to the scaled data up to 10 ns, where $t < \tau_e$ (entanglement time). The corresponding fit results are displayed in Table 1. The Rouse parameters obtained from self- and coherent motions (see Figure 2b for comparison) are in very good agreement.

At longer times, the confined chain dynamics due to chain entanglements or geometric confinement results in a long-time plateau (Figure 4). The higher plateau for the PNCs relative to that for the neat polymer is the signature of a decreasing confinement length. However, since the Rouse dynamics is slowed down by particles (unlike the repulsive PNCs reported by Schneider et al.¹²), a direct assessment of the tube diameter simply from the plateau level may not be quite accurate. Instead, in this regime, the intermediate scattering function, S(Q,t), is well described by de Gennes' formulation⁴⁰

$$\frac{S(Q, t)}{S(Q, 0)} = [1 - \exp(-Q^2 d^2/36)]S_{\text{local}}(Q, t) + \exp(-Q^2 d^2/36)S_{\text{esc}}(Q, t)$$
(2)

where $S_{\text{local}}(Q, t) = \exp(t/\tau_{\text{o}})\operatorname{erfc}(\sqrt{t/\tau_{\text{o}}})$ is the local reptation within the tube with a characteristic timescale $\tau_{\text{o}} = 36/(Wl^4Q^4)$. $S_{\text{esc}}(Q, t)$ is the long-time creeping of a chain out of its original tube and is ≈ 1 as the timescale of NSE ($t_{\text{NSE}} \leq 100$ ns) is much shorter than the reptation time of PEO at T = 400 K ($\approx 100 \ \mu$ s). The term $\exp(-Q^2d^2/36)$ is the cross-sectional form factor of the tube with diameter d and determines, together with the long time tail of $S_{\text{local}}(Q,t)$, the long-time plateau level. With the experimentally determined Wl^4 values, the only free parameter, the tube diameter d, is obtained by global fitting the data to all Q's for each sample. The lines in Figure 4 are the resulting fits.

The remarkable concentration dependence of the apparent tube diameter, d, is shown in Figure 5 (see also the Supporting



Figure 5. Apparent reptation tube size as a function of particle volume fraction, ϕ . The star symbol is the tube diameter obtained from a clustered sample for comparison (see the text for details).

Information for the exact numbers). As ID is decreased down to $ID/2R_{\sigma} \approx 1$, d shrinks by about 10%. Increasing ϕ further into the confining regime, $ID/2R_g < 1$, does not further change d, and even at the highest ϕ , the tube diameter remains ≈ 4.9 nm. Both experiments by Schneider et al.¹² and simulations by Li et al.¹³ found an unchanged apparent tube diameter at moderate particle concentrations but a monotonic decrease at particle volume fractions above 0.31. They attributed this behavior to the competing effects of chain disentanglements and the geometric confinement imposed by nanoparticles at high ϕ . We explain the different behaviors in our attractive PNC by the presence of a bound polymer layer on nanoparticles, which, in the timescale of the experiments (up to 100 ns), essentially remains on the particle surfaces. When $ID/2R_{\sigma} > 1$, the composite consists of both free chains and the bound polymer; therefore, the dynamics is due to the contributions from both chain populations. However, when $ID/2R_{\sigma} \leq 1$, all chains are essentially interfacial; thus, the dynamics of the bound polymer layer on nanoparticles dominate at large ϕ . The \approx 4.9 nm confinement length scale measured in NSE is, therefore, the confinement felt by the bound polymer layer due to surface adsorption. This value is smaller than the bulk reptation tube size of the neat polymer but larger than the apparent tube diameter measured¹³ in the nonattractive system at similar loadings. To the best of our knowledge, this is the first experimental observation of the single chain dynamics of the bound polymer on nanoparticle surfaces.

In their study, Krutyeva et al.¹⁹ used a two-component model on unentangling poly(dimethylsiloxane) chains confined in alumina nanopores and revealed an interphase layer between the free and interfacial polymers. This confined layer had an apparent length scale of ≈ 3.1 nm that is much smaller than the reptation tube size of the neat polymer (≈ 8 nm). The formation of the transition phase was attributed to the looptail-train conformation of the surface-bound polymer and its interaction with the bulk. A two-component model, one representing the bulk and the other for the confined dynamics, was applied with essentially two free parameters: the bulk fraction and number of suppressed Rouse modes. In the entangled system we study here, a similar two-component model could also be used; however, this would require additional free parameters (specifically the tube diameter of the interfacial chains and the thickness of the interphase layer) with further assumptions that cannot be justified immediately. Instead, we present the apparent confinement length scale, d_i which is an average between the bulk reptation dynamics (dominating at small ϕ) and the dynamics of the interfacial polymer (effective at large ϕ). In addition, our analysis follows the procedure used for the repulsive system by Schneider et al.,¹² thus allowing for direct comparison between the two systems. Nevertheless, our results clearly show that the attractive polymer-nanoparticle interaction in PNCs opposes the effect of geometric confinement by the nanoparticle cores, leading to a lower limit for *d* at large ϕ .

These results on the microscopic polymer dynamics in attractive PNCs shed light on the unusual bulk rheological behaviors of these materials as well as the anomalous nanoparticle diffusion therein. In a previous study,⁴¹ the slow nanoscale particle relaxation measured by X-ray photon correlation spectroscopy interestingly reached a plateau at high concentrations (ID/ $2R_g < 1$), while the elastic moduli of the bulk composites increased orders of magnitude in the same

regime. Since the local viscoelastic media near the interfaces govern the nanoparticle motion, the concentration-independent relaxation regime for nanoparticles at high loadings matches very well with the trend of the tube diameter we measured here since both are controlled by the interfacial bound polymer layer, which displays the same viscoelastic behavior regardless of ϕ . The bulk rheological behavior of the PNCs, on the other hand, is due to a combined effect of the polymer, nanoparticle, and the interfaces. On a model attractive system of P2VP-silica, Baeza et al.⁴² used bulk rheology and thermal and dielectric spectroscopy and inferred the rubbery dynamics of the PNC transition from a reptation controlled regime to an adsorbed polymer controlled regime at $\phi \approx 0.31$. Our NSE results provide direct evidence of such a transition and helps to understand the complex network dynamics of highly filled attractive PNCs. We anticipate that our distinct experimental results on the Rouse and reptation dynamics of a long linear polymer in attractive PNCs at a wide range of nanoparticle concentrations will inspire new theoretical and experimental studies aiming at a microscopic level understanding of the complex relaxation processes and bulk reinforcement mechanisms in nanoparticle-polymer systems.

Finally, NP dispersion has a significant influence on microscopic polymer dynamics. We stress that our attractive PNC system consists of individually dispersed NPs in the polymer matrix (Figure 1a), allowing us to systematically study the interfacial and confinement effects. To compare the dispersed case to a clustered state, we prepared a PNC sample with a 0.28 particle volume fraction by using a binary mixture of dichloromethane and acetonitrile as a casting solvent. In a previous study, the SAXS results on these samples showed a clear low-Q intensity upturn, a clear indication of aggregation. The resulting Rouse parameter (coherent) and the apparent tube diameter from the clustered sample are presented as star symbols in Figures 2b and 5 (comparison of the dynamic structure factors is given in the Supporting Information). Wl^4 decreased further by $\approx 35\%$ for the aggregated nanoparticles compared to the dispersed state at the same particle volume fraction of 0.28. The tube diameter, on the other hand, goes from \approx 4.9 back to \approx 5.3 nm, a value that is close to the tube diameter obtained in PNC with NPs dispersed at a volume fraction of 0.18. An increase of the tube diameter is expected since less (uniform) confinement is induced on the polymer chains as particles cluster. The decrease of the Rouse parameter is rather unintuitive. In the case of mixed solvents, it is likely that the polymer can bridge nanoparticles in the presence of dichloromethane and cause loose aggregates where more polymer segments are in direct contact with surfaces, which restricts greatly the segment mobility. In fact, Akcora et al.⁴³ showed a slight decrease of segmental mobility in PNCs with PMMA-graft-silica nanoparticles upon aggregation of nanoparticles that are initially dispersed. While further experiments are needed to elucidate this unprecedented effect of particle aggregation on segmental mobility, this study clearly shows the importance of particle dispersion for understanding the microscopic polymer dynamics. In particular, good NP dispersion is highly unlikely for nonattractive and repulsive bare NP-polymer systems; special care must be taken.

CONCLUSIONS

In summary, we applied neutron backscattering and neutron spin echo spectroscopy on attractive PEO-silica nanocomposites at a wide range of particle concentrations to directly observe large-scale dynamics of polymer chains confined by nanoparticles. The Rouse dynamics of the chains monotonically slows down with nanoparticle addition, yet the decrease was limited to 50% even at the largest reachable nanoparticle volume fraction of $\phi \approx 0.53$, where all polymer chains are interfacial. The bound polymer layer, therefore, is not glassy in the timescale of the experiments, which is on the order of nanoseconds. More importantly, the large-scale dynamics at longer timescales show that the length scale of the confinements felt by the polymer chains is decreased by about 10% from the bulk at moderate particle concentrations up to $\phi \approx$ 0.31, where the face-to-face interparticle distance is equal to $2R_{\sigma}$ of the bulk chains. Above this concentration (at the strong confinement regime), the apparent reptation tube diameter does not further decrease. These experimental results on the Rouse and reptation dynamics are distinct from the previously observed dynamics on the nonattractive polymer nanocomposite systems where the Rouse dynamics is not significantly altered by nanoparticles, while the apparent tube size is greatly reduced in the strongly confined regime.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.macromol.9b02545.

Additional analysis of the spin echo and backscattering data (PDF)

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Notes

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