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Using neutron spin-echo spectroscopy, X-ray photon correlation spectroscopy and bulk rheology, we studied the effect of particle size on the single chain dynamics, particle mobility, and bulk viscosity in athermal polyethylene oxide-gold nanoparticle composites. The results reveal an $\approx$ 25 % increase in the reptation tube diameter with addition of nanoparticles smaller than the entanglement mesh size ($\approx$ 5 nm), at a volume fraction of 20 %. The tube diameter remains unchanged in the composite with larger (20 nm) nanoparticles at the same loading. In both cases, the Rouse dynamics is insensitive to particle size. These results provide a direct experimental observation of particle size driven disentanglements that can cause non-Einstein-like viscosity trends often observed in polymer nanocomposites.

Keywords:
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Addition of nanoparticles (NPs) into polymeric matrices causes remarkable changes in physical properties of the composites relative to the host polymer [1]. Particularly interesting and quite unexpected is the non-Einstein-like viscosity reduction often observed in composites with NPs of sizes comparable to the size of a single chain [2]. This is contrary to the classical models that always predict an increase in viscosity upon particle addition [3]. As the particle and polymer size become comparable, their motion is expected to be coupled. Understanding how the motion of one component is affected by the presence of the other is important for fundamental science as well as for optimization of nanocomposite properties for advanced materials applications.

The NP relaxation is commonly studied by X-ray photon correlation spectroscopy (XPCS) using tracer nanoparticles in polymeric liquids. [4-7] It is now understood that the motion of NPs smaller than the entanglement mesh size is dictated by local Rouse dynamics of the chains while larger particles are significantly slowed down by the entanglements resulting in a sub-diffusive motion [8,9]. The NP effect on the dynamics of the polymer in the nanocomposites has also been the focus of many experimental and theoretical works mostly considering large NPs [10-17]. A recent molecular dynamics simulation [17] and primitive path analysis [16] emphasizes the particle size effects on the local segmental dynamics in attractive and repulsive systems. Very rich dynamical effects, ranging from entanglement dilation to reduced local relaxation, have been predicted for NP sizes comparable to entanglement mesh. Experimentally, how the self and collective chain dynamics are affected by NPs that are as small as the entanglement spacing has not been clarified, mainly due to the lack of spatial and temporal resolution in conventional experimental techniques.

In this work, we apply neutron spin-echo spectroscopy (NSE) on athermal and isotopically labeled PEG (low M_w analog of PEO) functionalized gold (Au) NP filled PEO composites to evaluate the role of particle size on the single chain dynamics at a space-time resolution relevant to the segmental and the collective polymer motion in a melt. The results present experimental evidence of a significant tube dilation caused by particles smaller than the entanglement mesh size. No significant effect, however, is observed on the local relaxation. The slow NP motion was probed by XPCS, revealing a compressed and sub-diffusive relaxation behavior of small and large NPs, respectively. The effects of decreasing topological confinement on the bulk viscoelastic behavior of the nanocomposites are discussed along-with the rheological trends.

The hydrogenated PEO (hPEO) (M_w:35 kg/mol, M_w/M_n=1.08) and the deuterated PEO (dPEO) (M_w:35 kg/mol, M_w/M_n=1.09) samples, both well above the entanglement molecular weight, M_e=2 kg/mol, were supplied by Polymer Source Inc. and dried further under vacuum at 90 ^{o}C for 12 h. The synthesis and

characterization of PEG functionalized Au nanoparticles are described elsewhere [18].The PEG chains on the surface are too short (M_w=1 kg/mol) to entangle; their role is to provide steric repulsion between NPs. The nanocomposites with 3.5 ± 0.7 nm (PEG grafting density 2.43 molecules/nm^2) and 20.2 ± 4.3 nm (PEG grafting density 2.75 molecules/nm^2) diameter NPs were prepared by dissolving the particles and PEO separately in acetonitrile (Sigma Aldrich, anhydrous). (The uncertainties throughout this manuscript represent one standard-deviation). The *d/h* ratio of PEO was 74/26 that matches the scattering from Au nanoparticles. The NPs in acetonitrile were then added to the polymer solutions and cast in Teflon cups to result in a particle volume fraction of 20 % (ϕ_{part} = 0.20) in the final nanocomposite. The samples were dried overnight and vacuum annealed at 363 K for 2 days to ensure removal of any residual solvent (see Supplemental Material for composite structures [19]). The particle-free *d/h* PEO was prepared using an identical casting and annealing protocol. Additional dilute nanocomposite samples in *h*PEO (particles weight fraction of 1 %) were prepared for XPCS measurements.
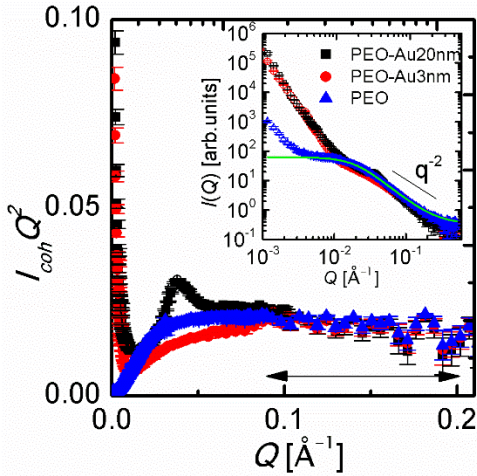

FIG. 1. (Color online) Kratky plot of the contrast matched composites, ϕ_{part}=0.20 and h/d (74/26) PEO matrices. The arrow represents the spatial range used in NSE. The inset shows the SANS profiles and the Debye fitting to the neat polymer data.

Small-angle neutron scattering (SANS) experiments were performed on beam line NG-7 at the NIST Center for Neutron Research (NCNR, Gaithersburg, MD).. The *Q*-range covered was from $\approx$ 0.003 Å^{-1} to 0.5 Å^{-1}. All scattering profiles were corrected for background, empty cell and sample transmission to get 1-D isotropic scattering patterns. Collective PEO dynamics were obtained using the NGA Neutron Spin Echo Spectrometer at the NIST Center for Neutron Research (NCNR, Gaithersburg MD). The measurements were performed at 400 K using a wavelength of λ = 11 Å ($\Delta\lambda/\lambda$ = 0.15) for Fourier times up to 100 ns and a wave vector range of Q = 0.08 Å^{-1} to 0.2 Å^{-1}.

Additional measurements were performed at λ = 6 Å for Fourier times up to 15 ns. The samples were sealed in Al-cans in Helium environment. Charcoal was used to obtain the instrumental resolution. Data were corrected for background using an empty can measurement using the software DAVE [21]. Rheology experiments were performed on a strain-controlled ARES-G2 (TA instruments) rheometer equipped with 25 mm parallel plate fixtures. XPCS measurements were performed using a photon energy of 11 keV on beamline 8-ID-I at the Advanced Photon Source at Argonne National Laboratory. Samples were equilibrated at 400 K for 15 min prior to measurements. The normalized intensity-intensity auto-correlation function, g_2 (*Q,t*), was obtained over the wave vector range 0.003 Å^{-1} < *Q* < 0.02 Å^{-1} and analyzed at 36 discrete *Q* values.

Figure 1 inset shows the SANS profiles for the neat polymer and the composites with 20 nm and 3.5 nm NPs that are zero-average-contrast matched to the matrix. All profiles converge to give the scaling, $I(Q) \sim Q^{-2}$ at $Q >$ 0.04 Å^{-1} due to the single chain form factor of PEO in the mixture of *d*PEO and *h*PEO. Fitting the neat polymer profile for Q>0.008 Å^{-1} to the Debye form factor yields the coil size, $R_g \approx$ 7.5 nm, a value close to the predicted number [22]. The Kratky plots, $Q^2 I(Q)$ vs. Q, obtained after subtracting the incoherent background [19] show a well-defined plateau in this regime, suggesting that the Gaussian statistics of PEO is retained in both composites samples. The peak at $Q \approx$ 0.035 Å^{-1} in the 20 nm NP composite corresponds to a length scale $D \approx$ 18 nm, a number close to the individual particle size, and can be attributed to the correlation of the PEG chains attached to the particle surface. A similar correlation peak in the nanocomposite with 3.5 nm NPs appears at $Q \approx$ 0.1 Å^{-1}; its intensity is negligible compared to the signal from the PEO. The low-Q upturns are identical for nanocomposites with both NP sizes and it is present even in the homopolymer mixture, indicating that this feature is likely related to the excess scattering due to the large scale composition fluctuations in the matrix and slight scattering length density mismatch between the polymer and the particles [23]. Regardless, these effects become negligible in the spatial range of NSE, where the scattering is exclusively due to PEO chains.

The effect of particle size on chain dynamics is measured by NSE using a mixture of deuterated and hydrogenated PEO chains. The single chain dynamic structure factor, $S(Q,t)$, is obtained at the spatio-temporal range relevant to a local reptation motion. Figure 2a shows the data for *t* <15 ns corresponding to the initial unrestricted Rouse motions. The profiles are identical; there is no significant effect of particle size on the segmental relaxation rates. This is consistent with previous finding on nanocomposites with neutral polymer-NP interactions [24]. The lines in Figure 2a are the predicted Rouse decays in the absence of

entanglements [25]. The dynamics is slowed down as soon as t ≈ 10 ns due to entanglements; the reptation motion dominates the dynamics in the intermediate time scale. The collective dynamics within the confining tube is well described by de Gennes' model [26] as

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

(3)

Where $S_{local}(Q,t) = \exp\left(\frac{t}{\tau_o}\right)erfc(\sqrt{t/\tau_o})$ is the local reptation within the tube with characteristic time-scale $\tau_o = 36/(Wl^4 Q^4)$. $S_{esc}(Q,t)$ is the long-time creeping of the chain out of its original tube and $S_{esc}(Q,t) = 1$ for the motions probed by NSE in this work as $t_{NSE} \ll \tau_R (\approx 1\mu s)$. The long time plateau level is determined by $\exp(-\frac{Q^2 d^2}{36})$.

Using $Wl^4 = 1.51$ nm^4/ns for PEO at 400 K [27], the only free parameter, the reptation tube diameter, d, was obtained from global-fitting of eq. 3 to the data. Since eq.3 does not account for the initial unrestricted Rouse motion at short times, fitting was applied for t > 50 ns (Figure 2b and 2c). The tube size in nanocomposites with large NPs ($d_{PEO-20nmAu}$ = 5.17 ± 0.19 nm) (Figure 2b) is practically identical to that for the particle free matrix (d_{PEO} = 5.03 ± 0.10 nm). This is in contrast to the increase of the nanocomposite tube diameter with small NPs ($d_{PEO-3nmAu}$ = 6.11±0.13 nm), revealed by the remarkable decrease of the long time plateau level with respect to the neat PEO (Figure 2c). To our knowledge, these results provide the first direct experimental evidence of tube dilation in polymer nanocomposites in the small particle limit.

The NP size driven increase of the reptation tube size leads to a decrease in entanglement density in the composites without significantly changing the local dynamics. The implications of these results on the nanoparticle motion as well as on the macroscopic properties are very appealing as the level of entanglements largely determines and may influence the transport properties of NPs in melts.

We measured the slow nanoparticle motion in melts on dilute samples using XPCS. The intensity-intensity autocorrelation function is related to the intermediate scattering function (ISF), $f(Q,t)$, as $g_2(Q,t) \sim 1 + A.[f(Q,t)]^2$, with A and t being the Siegert factor of the instrument and the delay time, respectively. ISF is fit to the stretched/compressed exponential functions, $f(Q,t) = \exp[-(t/\tau)^\beta]$, with relaxation time τ and stretching exponent β (representative profiles are given in Figure 3a inset). The NP relaxation in the composites are very different. The large NPs exhibit slightly stretched

exponential relaxation with $\beta \approx 0.8$, in agreement with the theoretical predictions for large particles in an entangled polymeric medium [8].
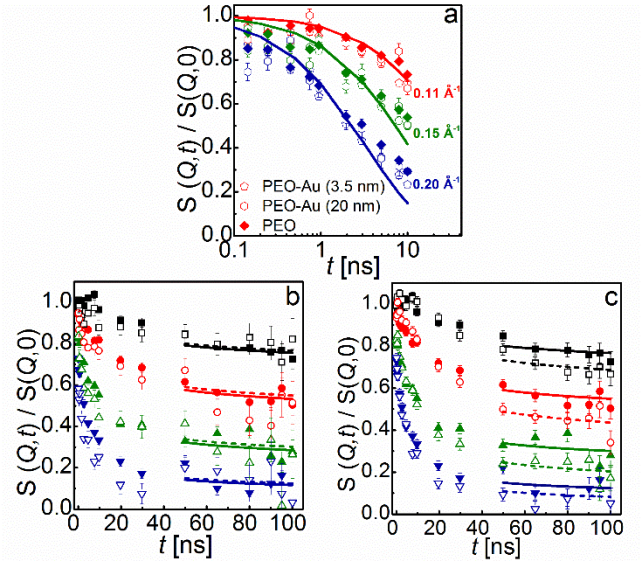

FIG. 2. (Color online) Dynamic structure factor of the neat PEO (filled symbols) and the PEO nanocomposites with Au nanoparticles (open symbols) at T = 400 K showing (a) identical initial Rouse decays at short times and (b) identical long-time plateau for large NP composite and (c) reptation tube dilation of small NP composite. The symbols in b) and c) are for Q=0.08 Å^{-1} (square), 0.11 Å^{-1} (circle), 0.15 Å^{-1} (triangle), 0.20 Å^{-1} (inverse triangle). The lines in a) are the Rouse model predictions [27]; the lines in b) and c) are the global fit results from de Gennes equation [26] with elementary Rouse rate, Wl^4 = 1.51 nm^4/ns.

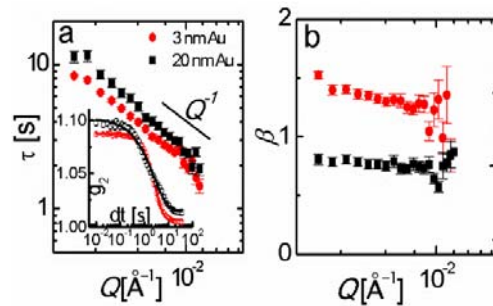FIG. 3. (Color online) (a) Relaxation time (τ) and (b) stretching exponent factor (β) versus Q for PEO composites with weight fraction of 1 % Au nanoparticles. The inset shows a representative autocorrelation function at Q=0.01 Å^{-1}.

The relaxation of small NPs is hyperdiffusive with compressed exponent $\beta \approx 1.2 - 1.5$ and $\tau \propto Q^{-1}$ as hypothesized for small particles hopping between the entanglement cages [28]. Given the fact that the segmental

chain dynamics remain unchanged in the composites, the difference in relaxation types is primarily due to different topological effects imposed by the chains on different sized particles, i.e. trapping *vs* caging. The terminal relaxation time of 35 kg/mol PEO at the XPCS temperature (353K) is $\approx$ 1 msec [24], which is smaller than the XPCS time scale ($\approx$10 millisec to $\approx$ 100 sec). Therefore, the center of mass motion of PEO dominates the bulk flow of the matrix and might cause a drift-like motion of the large particles, resulting in $\tau \propto Q^{-1}$ dependence. The viscosity experienced by the large particles of diameter a_{NP} estimated from $kT/a_{NP} = 6\pi a_{NP}\eta_{XPCS}v_{XPCS}$ [29], where $v_{XPCS} = (\tau Q)^{-1}$ is the particle velocity and η_{XPCS} is the local viscosity of the medium, is found to be $\approx$180 Pa-s that is close to the zero-shear viscosity estimated from the rheology. The motion of small particles confined within the entanglement tubes cannot be explained in the same way by a drift type of motion as they are too small.

Lastly, the linear viscoelastic moduli at 353 K are compared in Fig 4. The terminal relaxation time at this temperature ($\tau_d \approx$ 1 ms) is well below the time-scale of the rheology; the center-of-mass motion of matrix chains directs a liquid-like response with typical Rouse model scaling for elastic and viscous moduli, $G' \propto \omega^2$ and $G'' \propto \omega^1$, respectively. The NPs larger than d result in a strong reinforcement at intermediate and low frequency with $G' \propto \omega^0$ -a gel-like response commonly observed for large interacting particles at such high volume fractions. [30,31] The small NP composite at the same volume fraction remains liquid-like with viscosity ($\approx$ 90 Pa-s) $\approx$56 % of the viscosity of the particle-free matrix ($\approx$ 160 Pa-s) (Fig 4 inset). As $\eta_{bulk} \propto \tau_d = \dfrac{3N^3}{W\pi^2}(\dfrac{l}{d})^2$ and W remains unchanged in the composites, the effect of tube dilation on the bulk viscosity can be estimated as $\eta_{bulk,Au-3nm}/\eta_{bulk,PEO} = (d_{PEO}/d_{PEO-3nmAu})^2 \approx 0.67 \pm 0.23$ - a reasonable agreement is found. Similar dramatic viscosity reductions were observed by Tuteja et al. [32,33] on athermal nanocomposites with small polystyrene NPs dispersed in polystyrene matrix. It was hypothesized from indirect measurements that the accelerated motion of NPs in entangled melt and free volume effects results in reduced viscosities. Our measurements of the single chain dynamics reveal that the NPs smaller than the entanglement mesh size decrease the number of entanglements per chain. As $d \propto \sqrt{M_{ent}/M} \propto \sqrt{1/G_N^0}$ where M is the molar mass of the chain, M_{ent} is the molar mass between two entanglement points and G_N^0 is the equilibrium plateau modulus, we observed $\approx$ 50 % increase in the entanglement molar mass (and expect $\approx$ 50 % decrease of rubbery moduli) in the

composite with small NPs at $\phi_{part} \approx 0.2$. It is commonly thought that NPs smaller than d act similar to solvent molecules in athermal polymer melts. [17,34] The analogy which appears to reasonably estimate the increase in d with $\phi_{Pol} \approx 0.8$ (since $d(\phi_{Pol}) = d(\phi_{Pol} = 1)\phi_{Pol}^{-0.76}$ [35]), cannot account for the unchanged Rouse dynamics at short times; the effect of particle size is rather complicated. We also performed NSE experiments (shown in Supplemental Material [19]) on blends of 1 kg/mol PEG chains (17 % volume fraction) in d/h PEO (a composition equivalent to PEG/PEO ratio in PNC with small Au NPs). In such case, the Rouse decay in the blends is significantly faster compared to neat PEO matrix. This is clearly different than the PNC with small NPs where the short time decay remained unchanged up to $\approx$ 30 ns.
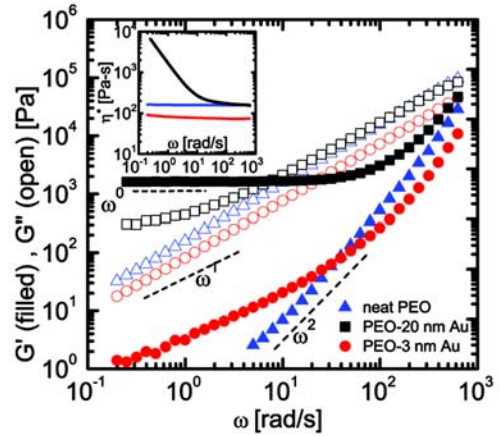

FIG. 4. (Color online) Linear elastic (G', filled symbols) and viscous (G'', open symbols) moduli of the neat matrix and the composites with ϕ_{part}=0.20 NP of different sizes. Complex viscosities, η^*, are plotted in the inset.

In addition to the nanoparticle size, the nanoparticle volume fraction and the polymer-surface interaction play a critical role in determining the chain dynamics. Kalathi et al.[17] reported unchanged Rouse dynamics with reduced entanglements in the presence of weakly interacting well-dispersed large particles. They predict slower dynamics at very high particle concentrations when the chains are highly confined, consistent with findings by Schneider et al. [14] suggesting a decrease of the apparent tube diameter due to geometric confinement. Composto and coworkers [36] reported reduced center of mass diffusion of chains in athermal PS-Silica nanocomposites with 13 nm and 29 nm diameter particles and attributed this to confinement effect of particles. Note that these particle sizes are above the tube diameter of PS ($\approx$ 8.5 nm) [22]. In their simulation work on a repulsive system, Li et al. [16] found that the proposed geometric confinement effect on tube diameter is negligible below the percolation threshold of the spherical particles ($\phi_c \approx 0.31$). Our study considers composites with $\phi_{part} < \phi_c$, where geometric confinement on entanglement spacing is

negligible. In the case of attractive polymer-surface interactions, recent neutron scattering experiments on composites with large silica nanoparticles and polymers in cylindrical pores suggest decreasing local relaxation rates [24,37]. We conjecture that the competing effects of particle-size induced disentanglements, chain confinement and slowing down/unchanged segmental dynamics may result in different macroscopic behavior of attractive nanocomposites.

In summary, the effects of nanoparticle sizes on the single chain dynamics, nanoparticle mobility and macroscopic rheology are investigated in athermal polymer nanocomposites using NSE, XPCS and rheology. The relaxation of large and small NPs is found to exhibit stretched and compressed exponential correlation function, respectively. The NSE results on the isotopically labeled chains reveal a significant increase of reptation tube size in the presence of small NPs while no effect is seen for the large NPs. The first direct experimental observation of NP size driven disentanglements together with the unchanged Rouse dynamics have immediate implications on the bulk rheology and helps to explain unusual viscosity reduction in polymer nanocomposites.

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