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Understanding Interfacial Block Copolymer Structure and Dynamics

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Abstract

Block copolymer (BCP) structure and dynamics were studied using small angle neutron scattering (SANS), neutron spin echo (NSE) spectroscopy, and molecular dynamics (MD) simulations to obtain fundamental understanding of the impact of an interfacial block on chain dynamics. A glassy block acted as the interface, and the dynamics of a rubbery block was studied. The rubbery block was protonated near the interface in one sample and near the chain end in another sample to observe the interfacial effect on the rubbery polymer. Analysis of the structure and dynamics revealed the interfacial rubbery block was confined in layered morphologies and exhibited much slower dynamics than the chain-end rubbery block that was dispersed in the rubbery matrix. The interfacial rubbery block showed weaker dynamical relaxation than that at the chain-end, and it also had critically important length scale dependence. Dynamical slowing was only observed at length scales significantly larger than the characteristic segmental length, and the disparity between interfacial and chain-end dynamics increased with increasing length.

Keywords

Confinement, Rouse Dynamics, Interface, Nanostructure, Neutron Scattering, Molecular Dynamic Simulation, Coarse Grain

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I. INTRODUCTION

With high-impact applications in drug delivery systems,¹ lithography² and polymer electrolytes,³⁻⁵ block copolymers (BCPs) have become recognized for exhibiting unique properties not present in homogeneous, single-component materials and are poised to play a crucial role in future materials design.⁶ BCPs possess a rich array of morphological nanostructures^{7,8} with fascinating dynamical behaviors that are of fundamental science interest.⁹ Specifically, diblock copolymers of poly(styrene-*b*-ethylene oxide), PS-PEO hereafter termed SEO, are of unique interest owing to their application as polymer electrolytes when mixed with an appropriate salt, for example, lithium bis(trifluoromethylsulfonyl)imide or lithium perchlorate.¹¹ Since ion and small molecule transport through rubbery polymers, such as PEO, is often coupled to the chain dynamics, it is of particular interest to examine the effect of nanostructure on chain dynamics. Moreover, the fact that lithium salt has been found to preferentially segregate toward the center of PEO lamella in SEO electrolytes¹² but distribute homogeneously upon change in architecture,^{13, 14} makes understanding the distribution of dynamics within the PEO microphase potentially relevant to batteries.

There have been multiple studies of SEO and other block copolymers to understand segmental mixing, chain stretching, confinement, and chain connectivity effects. Substantial amount of work has been done in synthesis and characterization of block copolymers and their applications.^{15, 16} Many studies on SEO block copolymer morphology can be credited to the SEO polymer electrolyte research in understanding the morphologies and dynamics of lithium (Li) ion transport through SEO block copolymers.^{17,18} Other relevant studies have investigated glass transition temperature in PS-poly(dimethyl siloxane) block copolymers.¹⁹⁻²¹ These and earlier works showed that the phase segregation in a BCP depends heavily on the interaction energy between chemically dissimilar segments and the molecular weight of individual blocks.²² At the lower limit of either property, a BCP is disordered, and the dynamics can be approximated as that of a homopolymer blend in which the glass transition temperature (T_g), and the dynamics, are expected to be a weighted average of the components.^{23, 24} As segregation strength increases (either by increasing molecular weight or increasing the role of interaction energy via reduction of temperature), concentration fluctuations occur that cause deviation from simple mixing principles.²⁵ Further increase in segregation strength from weak to intermediate segregation, leads to transition from Gaussian chain conformations to stretched conformations and ordering of the block copolymer.²⁶ Yet, there exists a large interfacial region which is described by a thickness (Δ) where the copolymer units interact with each other owing to the favorable entropy of mixing and low interfacial tension between the two blocks. In the strong segregation limit, the interphase between the two blocks is sharp and as such can be thought of as an interface. Strongly segregated BCPs are of particular interest not only due to the sharp interfaces formed between phases but also due to their mechanical robustness.

Polymer dynamics of the individual blocks of strongly segregated BCPs has parallels with polymers grafted to surfaces, in that the chains are covalently tethered to the interface and any reduction in dimensionality is normal to the interface (due to stretching) as opposed to adsorption on the surface (due to attractive interaction of many monomers along the chain). Due to this parallel and the larger number of studies of grafted polymer dynamics, they are briefly reviewed here. The “permanent crosslink” created by tethering to a surface would be expected to cause segments of the chain that are close to the tether (in curvilinear coordinates along the chain backbone) to be more localized and thus tethering to have a collective impact on local chain dynamics.²⁷ Molecular dynamic simulations support this assertion, where chains grafted to nanoparticles were found to be slowed more than free chains near the same nanoparticles.²⁸ Quasielastic neutron scattering and dielectric relaxation spectroscopy suggest that anchoring of a polymer chain can slow down its dynamics.^{29, 30} On the other hand, a thermodynamic-based approach to tethered and confined polymers, suggests that interfacial presence should have a far greater impact on dynamics than the tether itself.³¹ This must depend on specific interactions between the polymer and the interface, because PEO adsorption on silica nanoparticles has been shown to strongly slow PEO chains in the vicinity of nanoparticles,³² but alumina nanoparticles were found not to affect PEO dynamics at all in the absence of grafting.³³

A number of studies have specifically examined segmental and chain dynamics in ordered BCPs. Dielectric spectroscopy has been used extensively to measure dynamics in polymers³⁴ and applied to, amongst other polymers, poly(ethylene oxide) due to the dipoles within the backbone giving rise to measurements of end-to-end vector reorientation.^{34, 35} Fluorescence spectroscopy has also been used to investigate confinement effects in polymer thin films and ordered BCPs.^{20, 21} From the context of T_g alone, no difference was found between polymer multilayers and lamellar BCPs,²¹ indicating that chain connectivity present in BCPs does not affect dynamics. However, in poly(*n*-butyl methacrylate-*b*-methyl methacrylate) (PBMA-PMMA) block copolymers, Christie et al.³⁶ showed that due to dominant contribution from covalent bonding there is a depression in T_g that is beyond the contribution that comes from confinement alone. Using fluorescent labels, they showed that the T_g of homopolymer PMMA confined within a BCP is depressed by ~5 K, but that it remains ~10 K higher than that of the PMMA block of the BCP itself. This could be due to slowing caused by chain stretching that has been observed in polymer brushes,³⁷ or it could perhaps be due to the BCP chain being slaved to interfacial reorientation dynamics, which Floudas and others have shown is a slow process that appears in dielectric spectroscopy measurements upon BCP ordering.^{38, 39} Fast, chain-end segmental dynamics remain detectable in the ordered state, but longer range (4-6 nm) end-to-end vector fluctuations are considerably slowed near the BCP interfaces

1 if the other block is glassy⁴⁰ or at least rigid.¹⁹ Additional experimental studies are clearly needed to determine if
2 there is a gradient of dynamics in BCPs and the length-scale dependence of such.
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5 Polyethylene oxide (PEO) has increasingly become an industrially and scientifically relevant polymer owing to its
6 ability to form solvated-salt complexes. Ion transport in the amorphous phase occurs via local segmental motion
7 of the chains as well as long-range diffusion of polymer chains.^{17, 18, 41-43} It is known that the former is molecular-
8 weight independent, however, the latter only contributes significantly to ionic conductivity when the chain length
9 is below the entanglement threshold of PEO, which is 2 kg/mol.^{44, 45} Reports from Maranas and others of
10 segmental dynamics of entangled PEO homopolymer using neutron and complementary techniques indicate that
11 PEO segmental dynamics quantitatively correlate with ion mobility.⁴⁶⁻⁴⁹ Thus, it is of interest to use similar
12 techniques to study local dynamics of PEO within SEO BCPs, which possesses dynamic asymmetry (PS T_g = 105
13 °C,⁵⁰ PEO T_g = -65 °C^{51, 52}).

14 In this work, we investigate the structure of the block copolymer interfaces using small angle neutron scattering
15 (SANS), and the effect of the interfaces on the dynamics at different length scales of the SEO using neutron spin
16 echo (NSE) spectroscopy and molecular dynamics (MD) simulations. We hypothesize that the interfacial dynamics
17 and chain-end dynamics strongly correlate to morphological arrangements of different blocks that give rise to
18 length scale dependencies of relaxation time. Using neutron scattering and MD simulations we demonstrate that
19 at certain length scale the structural and dynamical correlation ceases to exist. We synthesized two proton
20 labeled SEO samples precisely placing the protonated PEO block at the middle and end of the deuterated PEO
21 blocks attached to the deuterated PS block as shown schematically in Figure S1. The samples are called *dPS-hPEO-*
22 *dPEO* (Sample A) and *dPS-dPEO-hPEO* (Sample B), where 'd' stands for deuterated, and 'h' stands for protonated.
23 This was done to take advantage of the difference of the scattering length densities (SLD) between protons and
24 deuterium in neutron scattering experiments. While NSE detects the total scattering intensity, scattering from
25 individual polymer blocks was obtained from coarse-grained MD simulation studies, thus providing molecular
26 details capable of explaining the origin of complex relaxation dynamics.
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44 II. METHODS

45 *Experimental:* Two selectively deuterated block copolymer samples were synthesized by sequential anionic
46 polymerizations under high-vacuum conditions with custom-glass apparatus equipped with break-seals
47 techniques.^{53, 54} In brief, the PS block was synthesized first in benzene using sec-butyllithium as the initiator and
48 terminated with ethylene oxide. This hydroxyl functionalized PS (PS-OH) was thoroughly characterized. Then a
49 pre-determined amount of PS-OH was charged into another custom-made glass-apparatus equipped with
50 ampoules with the needed amounts of ethylene oxide-d4 and/or ethylene oxide monomers, diphenylmethyl
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potassium (DPMK) tetrahydrofuran (THF) solution. After PS-OH was fully dried under high vacuum, the desired amount of dry THF was distilled into the reactor and DPMK was introduced into the reactor. Then EO-d4 or EO monomer was added, and the polymerization continued at 50 °C for 24 to 48 hrs depending on the chain length of the EO. The polymerization was terminated with acidic methanol. The polymers were recovered by precipitating in ethyl ether and then dried under vacuum. Two controls were also synthesized in a similar manner, a fully deuterated block copolymer (termed Sample C) and a fully deuterated PEO homopolymer (referred to as Sample F). Each selectively deuterated BCP was composed of 20 kg/mol deuterated polystyrene (*d*PS), 6 kg/mol hydrogenated poly(ethylene oxide) (*h*PEO), and 44 kg/mol deuterated poly(ethene oxide) (*d*PEO). The total weight-averaged molecular weight, M_w , of each sample is about 70 kg/mol from size exclusion chromatography (SEC) in THF with light scattering and RI detectors ($\bar{M}_w < 1.1$ from SEC). As depicted in Figure S1 (and also bottom of Figures 2 and 3), the only difference between the two selectively deuterated samples is the relative position of the blocks along the chain. The fully deuterated BCP control (Sample C), was composed of 20 kg/mol *d*PS and 50 kg/mol *d*PEO. The homopolymer control was 44 kg/mol *d*PEO. The as-prepared polymers were purified by precipitation in hexanes (three times) and dried at 90 °C under vacuum overnight. The dried polymer (powder) was hot pressed in a dry room at 80 °C and 8000 psi to obtain 2 mm thick samples. The samples were loaded into niobium cells of 4 mm thickness with two 1 mm niobium spacers on each side and annealed for at least 24 hours at 120 °C.

Small angle neutron scattering (SANS) experiments were carried out at Beamline 6 using the EQ-SANS instrument of the SNS at Oak Ridge National Laboratory.⁵⁵ Three sample-to-detector distance/minimum wavelength, λ , settings were used to collected SANS data: 4 m with a minimum wavelength setting of 10 Å, 4 m with a minimum wavelength setting of 2.5 Å and 1.3 m with a minimum wavelength setting of 2.5 Å, which provide a q -range of $\sim 0.004 \text{ \AA}^{-1} < q < \sim 1.4 \text{ \AA}^{-1}$, where $q = 4\pi \sin(\theta)/\lambda$ and 2θ is the scattering angle. Measurements were made at temperatures of 25, 80, 100, and 120 °C. SANS experiments were carried out on samples A and B both before and after annealing. The samples were annealed at 120 °C for 2 hours. Data reduction followed standard procedures using routines implemented in Mantid.

Neutron spin echo (NSE) experiments were carried out at Beamline 15 of the Spallation Neutron Source (SNS) at Oak Ridge National Laboratory⁵⁷ at 120 °C and then at 100 °C. Samples were allowed to equilibrate at each temperature for 30 minutes before beginning measurements. NSE spectroscopy is uniquely suited to study polymers due to its ability to measure dynamics on relevant length (10 – 100 Å) and time (0.01 – 100 ns) scales not accessible by other techniques.^{58, 59} It allows the direct determination of the normalized intermediate scattering function, $S(q,t)/S(q,0)$, as a function of scattering vector (q) and correlation time (t). Scattering

contrast is provided by the combination of protonated and deuterated regions within the chains. According to our calculations as well as previous reports, *d*PS and *d*PEO have negligible neutron scattering contrast.⁶⁰ The data were reduced with DrSPINE reduction software.⁶¹

Molecular Dynamics (MD) Simulations: Two block copolymers were built following the Kremer-Grest bead-spring model⁶² with lengths of 100 monomer beads (degree of polymerization) connected by Finitely Extendable Nonlinear Elastic (FENE) bonds. The number of beads in each of the 3 blocks were *d*PS = 30, *h*PEO = 10, and *d*PEO = 60. The monomer bead masses were normalized to ethylene oxide masses. The inter-chain interactions were modeled using Lennard-Jones (LJ) potentials, and the interaction strengths, ϵ_{ij} , between *i* and *j* blocks were obtained from the χ_{ij} parameters, normalized to χ_{SE} between PS and PEO. We simulated two different systems for MD simulations of 10 million LJ time steps each to equilibrate at a reduced temperature of $T^* = 1.0$. The reduced temperature $T^* = 1.0$, transferring to a coarse-grained atactic model having $e = 3.2$ kJ/mol, gives rise to a real unit temperature of $T \sim 110$ °C.^{63, 64} The temperature is in the range of experimental temperatures. All other dimensionless units are defined as follows, $\rho^* = \rho\sigma^3$, $U^* = U/k_B T$ and $r^* = r/\sigma$, $t^* = t/\sqrt{(m_i\sigma^2/\epsilon_R)}$, where ρ is the density, U is the energy, σ is the distance at which the interaction potential becomes zero, i.e., the monomer diameter, r is the distance, m_i is the monomer mass, and ϵ_R is the repulsive LJ interaction parameters. After equilibration, each of the samples was annealed for 5 million time steps at twice the equilibrium temperature and subsequently cooled down to $T^* = 1.0$ for 5 million time steps. All of these simulations are performed using LAMMPS molecular dynamics package developed at Sandia National Laboratory⁶⁵.

IV. RESULTS AND DISCUSSION

To obtain the structural information, Sample A (*d*PS-*h*PEO-*d*PEO) and Sample B (*d*PS-*d*PEO-*h*PEO) SANS data for 120 °C and 100 °C are shown in Figure 1. Refer to Figures S2 and S3 for SANS of all samples, including controls – Samples C and F – at all temperatures investigated. The SANS data in Figure 1 show more prominent diffraction peaks that arise from chain segregation after annealing at 120 °C than prior to it. The higher order peaks are at q values that are integer multiples of the primary scattering peak position, consistent with a lamellar structure. The annealed Sample A (magenta) has four diffraction peaks below $q = 0.10$ Å⁻¹, compared to two broader peaks prior to annealing. The scattering contrast within the layered lamellar morphology comes from the different SLDs of the various blocks. The protonated PEO block has an SLD of 0.566×10^{-6} Å², while those of the *d*PS and *d*PEO are 6.354×10^{-6} Å² and 6.799×10^{-6} Å², respectively. The primary scattering peak at 0.013 Å⁻¹ is apparent in both samples and corresponds to the overall block copolymer structure, as discussed in the Supporting Information. The diffraction peaks are less prominent in Sample B (Figure 1b), with the annealed sample having only two diffraction peaks after annealing. The different diffraction patterns may be attributed to the different pattern of scattering

length densities along the polymer chains, but Sample B also has the protonated block away from the dPS block in the chain, which likely causes it to be less well-segregated in the structure. The broad feature that is evident near $0.07 \text{ \AA}^{-1}$ in the SANS data of Sample B before and after annealing, which is not as evident in the data from Sample A due to the stronger diffraction peaks, is due to the more poorly ordered distribution of PEO in the dPEO matrix. Above $q \sim 0.1 \text{ \AA}^{-1}$, both Sample A and B show no substantial diffraction features. We will discuss the dynamics at the shorter length scales ($q > 0.1 \text{ \AA}^{-1}$) as it relates to the structure in Figure 1.

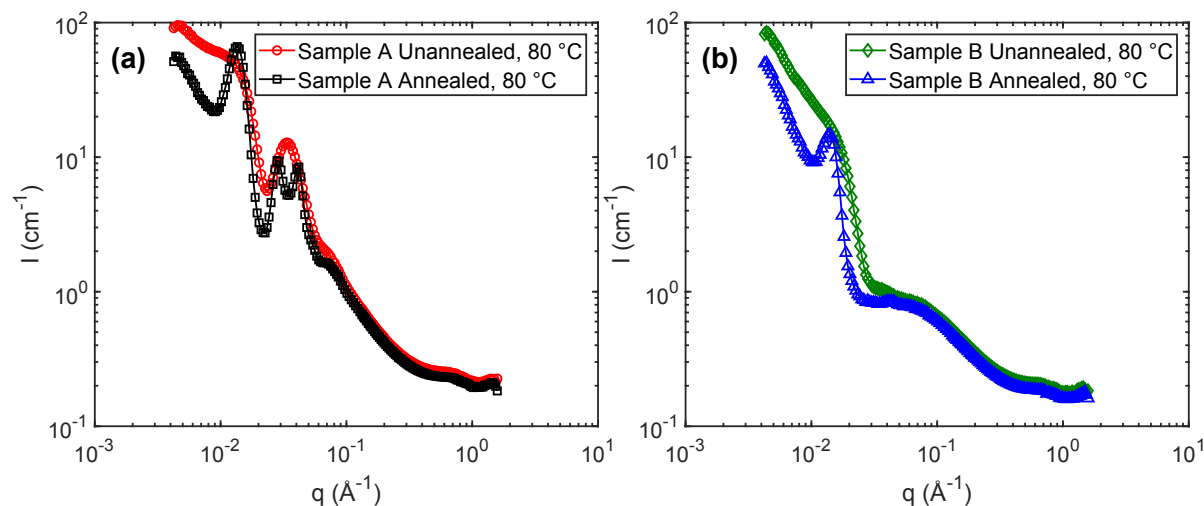


Figure 1. Small angle neutron scattering (SANS) data for, (a) sample A, and (b) sample B before and after annealing. Legends show color scheme of the before and after annealing curves.

The Sample A (*dPS-hPEO-dPEO*) and Sample B (*dPS-dPEO-hPEO*) NSE dynamics data for the q range $0.05 \leq q \leq 0.15 \text{ \AA}^{-1}$ at $120 \text{ }^{\circ}\text{C}$ are shown in Figure 2. The normalized intermediate scattering function does not start at unity as has been observed in studies of homopolymer PEO dynamics with several different neutron scattering techniques.^{45, 47, 66-68} For both samples, the decay rate of $S(q,t)$ increases with increasing q ($q=2\pi/d$), where ' d ' is the characteristic scattering length scale, therefore, high q -values correspond to shorter length scales, and hence faster relaxation. Sample A (Figure 2(a)), where the proton label is at the interface, exhibits a slower decay compared to Sample B (Figure 2(b)) for all q -values. The curves in Figures 2(a) and (b) are best fits of the Kohlrausch-Williams-Watts (KWW) stretched exponential model, which was used to obtain relaxation times, $\tau(q,T)$.

$$\frac{S(q,t)}{S(q,0)} = A(T) \cdot \exp\left[-\left(\frac{t}{\tau(q,T)}\right)^{\beta}\right] \quad (1)$$

$S(q,t)/S(q,0)$ is the normalized intermediate scattering function. The inverse of the variance of the normalized intermediate scattering function was used to weight the KWW regressions. $A(T)$ is a temperature-dependent

pre-factor, and β is the stretching exponent. $\beta = 1$ corresponds to a single Debye process.⁶⁹ We follow previous analyses of PEO homopolymers by fixing $\beta = 1/2$,⁴⁷ which is predicted by the Rouse model.^{59, 70, 71} Although the BCPs used in this study are of sufficient molecular weight to be entangled, the length scales being probed in these NSE measurements range from less than two entanglements for PEO ($q > 0.1 \text{ \AA}$) to more than two entanglements ($q < 0.1 \text{ \AA}$). Thus, the Rouse model is appropriate to apply to the data at the largest q -values, where the intermediate scattering function decay is most significant, and therefore the most reliable relaxation times can be extracted. By inspection, the stretched exponential ($\beta = \frac{1}{2}$) yields better fits than a simple exponential decay ($\beta = 1$). Furthermore, allowing β to be an adjustable parameter resulted in β -values of approximately $1/2$ for both samples. β -values of Sample A were consistently lower than those of Sample B by about 10%. Since regression results were not improved by allowing β to be an adjustable parameter, all reported results are for β fixed at $1/2$. Faster dynamics are observed at $q > 0.1 \text{ \AA}$, shorter length scales, relative to longer length scales for both the samples as shown in Figure 2. The dynamics in Sample A remain considerably slower (note the log-scale of Figure 2a). At longer length scales, the difference in relaxation times may be due to the difference in structural arrangement of PEO blocks in these two samples as shown in Figure 1. From Figure S4(a), a simple extrapolation of the power law fit (straight lines) show that the relaxation times of Samples A and B cross at $q = 0.39 \text{ \AA}^{-1}$ or $d = 16 \text{ \AA}$. This means that at and below a length scale of 5 PEO segments ($N \cong (1.6/0.73)^2$) the block copolymer interface is free from slow PEO dynamics. This is in good agreement with a study of PEO confined in cylindrical pores of anodic alumina oxide, where only longer Rouse modes were impacted by confinement.⁷²

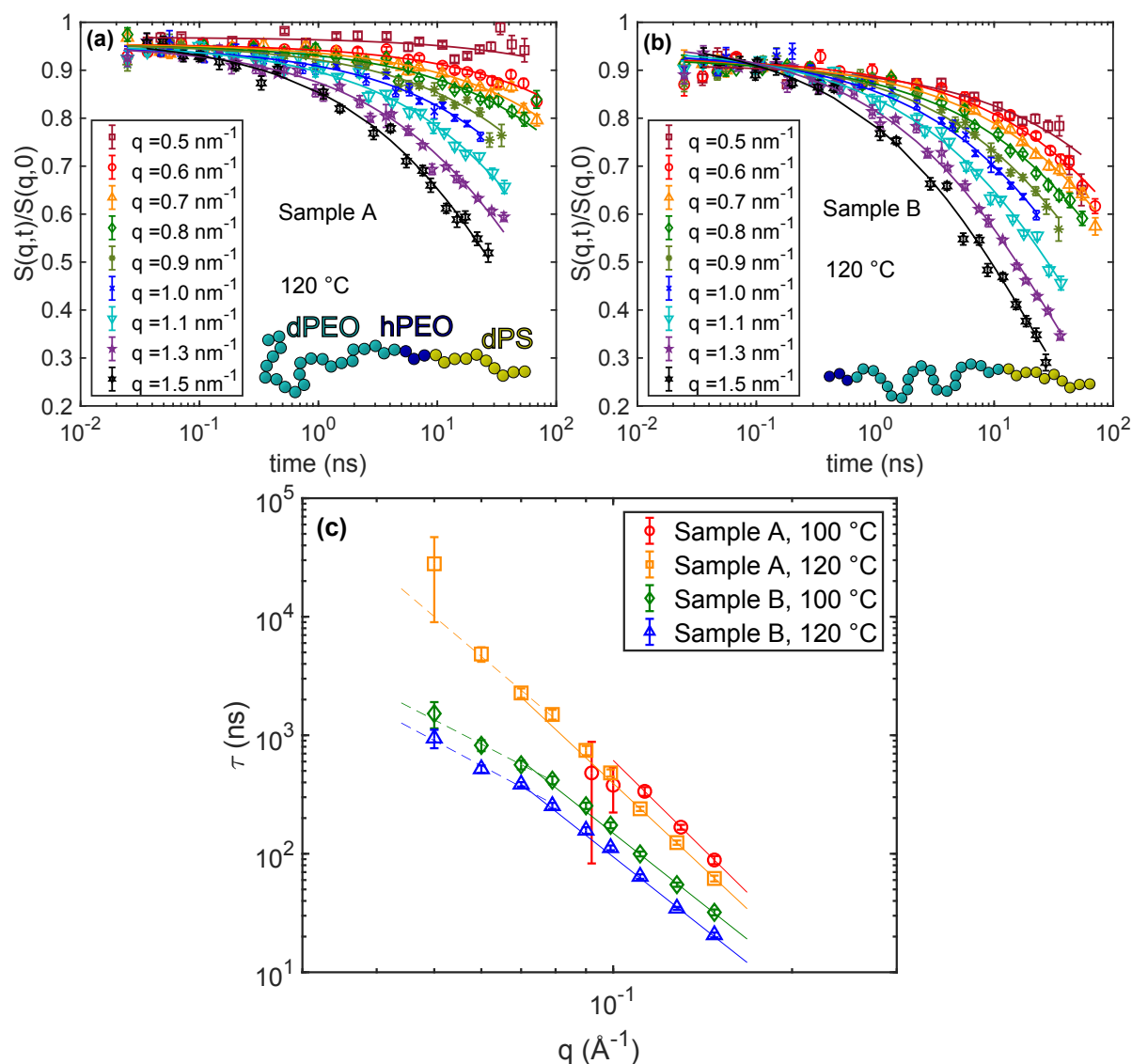


Figure 2. Semi-log plots of normalized intermediate scattering functions as a function of time at wavevector values designated in the legend for (a) Sample A: dPS-hPEO-dPEO and (b) Sample B: dPS-dPEO-hPEO, with BCP architecture represented schematically in the inset. Curves represent KWW fits to the experimental data. (c) Characteristic relaxation time as a function of scattering wave vector along with power law fits to the three highest- q data points (solid lines) and the four lowest- q data points where possible (dashed lines). The high- q data is in the Rouse regime. For Sample B, a change in slope is seen near $q = 0.08 \text{ \AA}^{-1}$, where entanglement effects begin to become apparent.

The characteristic relaxation time, τ , obtained from KWW fits of the $S(q,t)$ of Figure 2(a) and 2(b) are shown in Figure 2(c) as a function of wavevector, q . Intermediate scattering functions were also measured for each sample at 100 °C, and the relaxation times obtained from KWW fits are shown in Figure 2(c). A power law,

$$\tau = Aq^B \quad (2)$$

was regressed to the data in Figure 2(c), weighted with the inverse of the variance of τ . As shown in Table S1, the power-law exponent of Sample B regressions is close to the 4th power predicted by Rouse theory (see SI for more detail).^{59, 73} This scaling has also been observed with time-of-flight (ToF) spectroscopy of *d*PEO.⁶⁷ The power of the q -dependence of τ does not change with temperature except for the prefactor, which is also predicted by Rouse theory.⁵⁹ In other words, the absolute values of the relaxation times slow with decreasing temperature, as expected, but the spatial dependence of the relaxation times of the PEO chain end is not affected by temperature. Although the investigated temperature range is quite narrow, it does span the glass transition temperature of PS, which is not significantly affected by the presence of PEO in strongly segregated SEO and has been reported as 105 °C in SEO.⁷⁴

For reference, characteristic length scale ($d = 2\pi/q$) is reported on the secondary horizontal axis of Figure S4. Using PEO monomer molecular weight (M_{mon}) of 44 g/mol and segment length (b) of 0.73 nm (interpolated to the temperatures of interest),⁷⁵ the random coil size of the 6,000 g/mol protonated segment of PEO would be 70 Å, calculated as follows:

$$2R_g = \frac{2}{\sqrt{6}}bN^{1/2} = \frac{2}{\sqrt{6}}b\left(\frac{6000}{M_{mon}}\right)^{1/2} \quad (3) \text{The NSE measurements}$$

span from almost four times the Gaussian R_g of the protonated segment to nearly half. As shown in the SI, the end-to-end distance of 2 entanglement strands is $R_c = 64$ Å, which corresponds to $q_c = \frac{2\pi}{R_c} = 0.10$ Å⁻¹. Thus all data at $q > q_c$ is expected to exhibit Rouse-like dynamics exemplified by the ½ stretching exponent of the KWW regressions and the 4th power q -dependence of τ that is observed for Sample B. If entanglements were dominant, the stretching exponent would be expected to be ¼,⁷⁶⁻⁷⁸ and a plateau observed in the intermediate scattering function at long times.⁵⁹ We suspect that the measurements are at sufficiently high temperature that the Rouse dynamics do not overlap with reptation, which is significantly slowed by the strong segregation of the block copolymer. Using the Flory-Huggins interaction parameter between protonated PS and PEO ($\chi = -7.05 \times 10^{-3} + 21.3/T$),⁷⁹ we estimate the strength of segregation (χN) of our block copolymers to be 75, greater than the value of 60 at which sharp interfaces are expected and chain diffusion orthogonal to the domain interfaces is strongly suppressed.⁸⁰ The power law fit to the high- q data in Figure 2(c) is limited to the three highest- q data points so that it can be applied to all samples, including Sample A at 100 °C for which there was insufficient statistics at lower q -values due to beam time limitations. For the other 3 data sets, parameter values from power law fits to the entire data set agree well with the regressions to the 3 highest- q data points as shown in Table S1. On the other hand, the power law fits to the 4 lowest- q data points in Figure 2(c) should be considered guides for the eye to identify that a slope change occurs at approximately 0.08 Å⁻¹ for Sample B. This slope change is most

likely due to entanglement effects that occur at these length scales that are longer than 2 PEO entanglement lengths. It is worth noting that the confinement/tethering of hPEO to the PS interface in Sample A dominates the observed relaxation times and their q -dependence, such that a slope change is not apparent. Further analysis of NSE results is focused on high- q results in order to examine confinement/tethering effects without needing to consider entanglement effects.

To further confirm the Rouse dynamics measurement, the relaxation times of homopolymer PEO from literature are compared with Sample B results. As shown in Fig S4(b), the reported measurements span length scales of more than 1.5 orders of magnitude, and relaxation times range over 7 orders of magnitude. Considering this large range, the agreement between block copolymer chain-end dynamics (from Sample B) and homopolymer PEO dynamics (from literature) is remarkable. These studies considered varieties of molecular weights of PEO and deuteration levels. Saboungi and coworkers⁶⁶ used 40 kg/mol hPEO and dPEO, and Brodeck et al.⁶⁷ used 36 kg/mol dPEO for coherent scattering. Niedzweidz et al. performed NSE on a blend of 10% hPEO (81 kg/mol) in dPEO⁴⁵, and Do et al. conducted NSE on a 19 kg/mol random copolymer of 9% hPEO and dPEO⁶⁸. Mongcopa et al. studied 35 kg/mol hPEO with QENS⁴⁷. Excluding the NSE and MD results from Saboungi et al. that used unconstrained Bayesian fitting of data on dPEO, there is quantitative agreement between our measurements of SEO and those on PEO, particularly the data of coherent time-of-flight (ToF) experiment and our ToF NSE experiments that match exactly. In particular, extrapolation of the power-law fit for Sample B down to the length scale of a monomer (7.3 Å) is validated by the data from Brodeck et al.⁶⁷

Turning to Sample A data in Figure 2(a), dynamics of the protonated label near the d PS interface is much slower over the range of our measurements compared to Sample B (Figure 2(b)), and the q -dependence of τ is stronger (Figure 2(c)). The deviation from Rouse behavior was ascribed to the dynamical asymmetry of confined PEO as observed in earlier work on miscible blends of unentangled PEO and poly(methylmethacrylate) (PMMA).⁸¹ Due to the large differences in glass transition temperature between PS and PEO, dynamical asymmetry is also present in SEO.

To this end, the length-scale dependence and effect of confinement and tethering on PEO dynamics was investigated further with molecular dynamics (MD) simulations. The structural and dynamical behavior of individual blocks of the BCP were investigated using coarse-grained MD simulations. The advantage of MD simulations is that it can examine each individual block's structure and dynamics at different length-scales separately. To be consistent with the experiments, we refer to the samples as Sample A (dPS-PEO-dPEO) and Sample B (dPS-dPEO-PEO), and the different blocks as dPS, dPEO and PEO, although the CG bead-spring simulations are representations of coarse-grained monomer beads only.

The structural details from MD simulations of the annealed samples are shown in Fig 3. The peaks of all the plots are shown in the inset of Figure 3a. The inter-block radial distribution function (RDF) in Fig 3(a) shows a peak followed by an amorphous broad peak (red dashed line) representing agglomeration of the amorphous PEO domain at the dPS of Sample A, while no short-range agglomeration or structure is observed at the interface in Sample B (red solid line). In other words, PEO is preferentially found at longer length scale away from the dPS interface ($r^* > 20$). The snapshots in Figure 3(c) and (d) show interfacial PEO in Sample A and dispersed chain-end PEO domains within the dPEO domain in Sample B. As there is no structural correlation between dPS and dPEO in Sample A due to interfacial PEO alignment, the inter-RDF curve (black dashed line) does not show any short-range structure. However, the Sample B inter-RDF (black solid line) shows short range structure due to the absence of an interfacial PEO domain driving the matrix to form dPS-dPEO interface (also seen in snapshot (d)). The PEO-dPEO inter-RDFs (blue lines) show short range structure for both Sample A and B, due to the PEO-dPEO connected architecture of the BCP. In addition, a broad peak is observed in Sample B at larger length scale that is representative of distributed PEO domains within the dPEO matrix, as postulated in our discussion of Figure 1. The intra PEO structural details can also be obtained from MD simulations as shown in Figure 3(b). Sample A (blue lines) show higher agglomeration peak followed by layered structure. In Sample B (red lines), more liquid-like structure is observed as evident from short peaks at short distances followed steady decay of the peaks at longer length scales, representative of highly distributed PEO domains within the matrix. The structural studies from MD simulations corroborate our hypothesis from experimental observations that the slow dynamics of Sample A (Figure 2) is the result of the formation of layered interfaces between PEO and dPS (Figure 1). Whereas the single, broad, higher-order SANS peak of Sample B in Fig 2 is the result of dispersion of PEO within the dPEO matrix in a less well-ordered fashion. Based on the 3D structure presented in Figure S6, both samples exhibit similar curvature with roughly cylindrical PS inclusions in the dPEO/PEO matrix, such that curvature is unlikely to play a role in slower dynamics being observed near the PS interface.

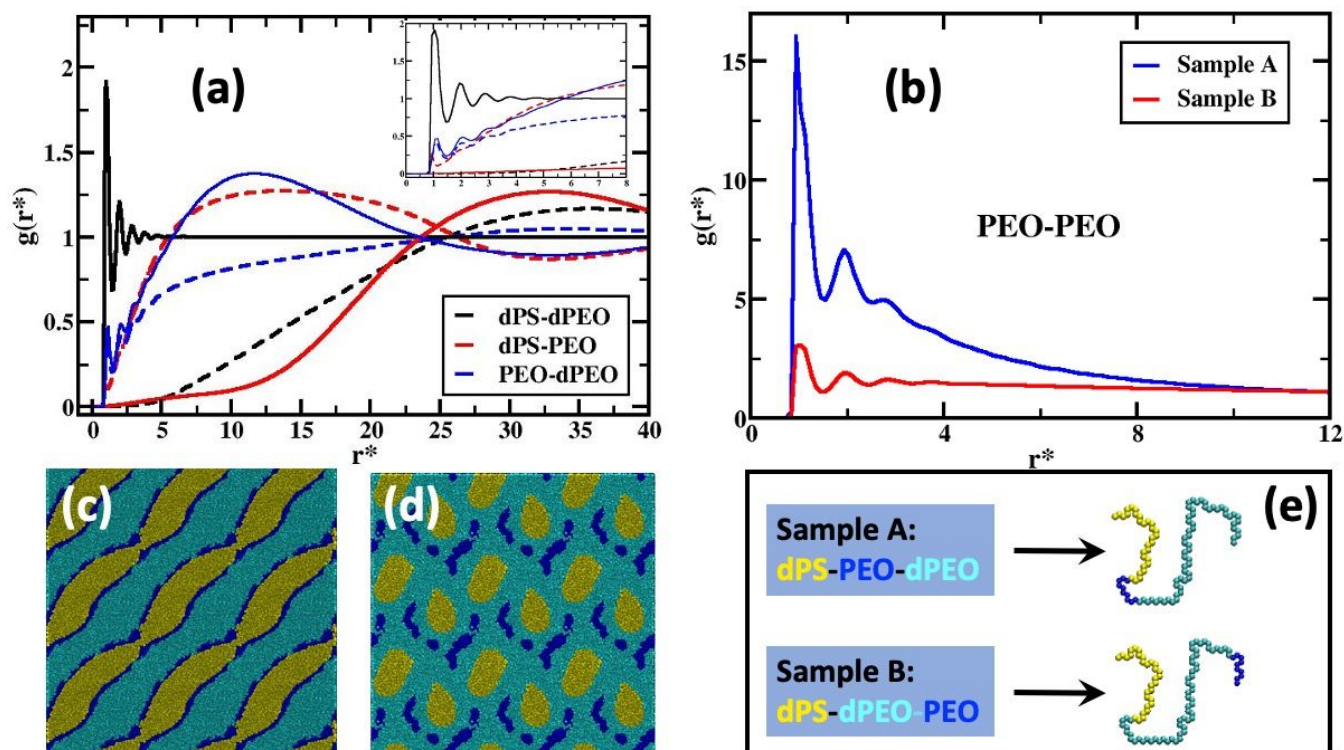


Figure 3. Intermolecular radial distribution function, $g(r)$, is shown in (a) and (b). In (a), Sample A is represented by dashed curves and Sample B is represented by solid curves. The inter-block RDF is plotted as shown in the legends. The intra-block PEO-PEO RDF is shown in (b). Higher agglomeration and layering is observed in Sample A (blue) and liquid-like small number of short-distance weaker peaks are observed followed by steady decay to $g(r) = 1.0$ at longer distances. The inset in (a) show peak heights and peak positions at small r^* values. The simulation snapshots after annealing are shown in (c) for Sample A and (d) for Sample B. Yellow represents dPS, blue represents PEO and cyan represents dPEO blocks. 3D snapshots are shown in Figure S6. The layered PEO structures are observed in Sample A, and dispersed PEO is observed in Sample B. (e) Schematic architecture of Sample A and Sample B.

The relaxation times of the individual blocks obtained from the MD simulations are shown in Figure 4. The advantage of MD simulations is that it can distinguish between individual relaxation dynamics and hence can provide a more detailed molecular level understanding of the relaxation dynamics. The relaxation time, τ^* , was obtained from the KWW (Equation 1) fit of $S(q,t)$ data shown in Figure S7. While the β values were fixed to 0.5 in the experimental fit, both the prefactor (A) and β values are adjustable parameters in the $S(q,t)$ fit from MD simulations. It should be noted that adjustable β as a parameter resulted in $\beta \sim 0.5$ in experiments. As there is flexibility in fitting of simulation data β parameters can be varied. The $S(q,t)$ fits and simulation β values are shown in Figure S7 and S8, respectively. In Figure S8, it can be seen that β values vary with wavevector, q . In MD simulations the relaxation time, τ^* , is calculated separately for three different blocks as shown in Figure 4. In

Figure 4(a), the dPEO and dPS dynamics is comparable, especially at longer length scales (small q) due to the fact that both dPS and dPEO forms matrix on different side of the hPEO interface. The coarse-grained simulations are performed at temperature higher than T_g , therefore, both the dynamics show similar bulk phase dynamical behavior, however, the PS dynamics is a little weaker at shorter length scales. PEO (hPEO) relaxation dynamics is slower in Sample A compared to Sample B until $q = 1.0 \sigma^{-1}$, approximately 5 monomer length scales (6.3σ). Beyond that PEO dynamics is faster in Sample A than Sample B (see Figure S9). This means that below the 5 PEO monomer length scale, the dPS-PEO interface does not slow the PEO chain dynamics. This is in good agreement with our NSE data (Figure 2(c)) of confined and tethered dynamics as well as with results for PEO in cylindrical pores.⁷² Moreover, the PEO dynamics is about two orders of magnitude slower in Sample A than Sample B for longer length scales due to the interfacial confinement and tethering of PEO blocks to the roughly cylindrical PS phase of Sample A (Figure S9), while dPS and dPEO dynamics (red square and blue circle) do not show considerable difference between Sample A and Sample B. This once again confirms our NSE and SANS findings that the slow dynamics in Sample A is a result of slow dynamics of PEO that is confined by and tethered to the PS phase (Figure 1 and 3) between dPS and dPEO domains. For Sample B, the dynamics is similar for all the blocks, with the exception that dPS (red square) dynamics is the slowest followed by dPEO and PEO. This means that, at shorter length scales, the interface between dPS and dPEO in the matrix slows down the dynamics of these two blocks, while the chain-end PEO block moves faster in the distributed phase. It is worth noting that hPEO is only 10 monomer beads making it more sensitive to placement near the interface than dPEO, which is 60 monomer beads. In other words, many dPEO monomer beads remain far from the dPS interface even when dPEO is the inner block (Sample B). The microphase separated structure clearly has an affect on the dynamics of hPEO near the interface, and interfacial curvature may also affect PEO dynamics. However, interfacial curvature is similar in both samples and thus, any effect of curvature on dynamics cannot be discerned from this study.

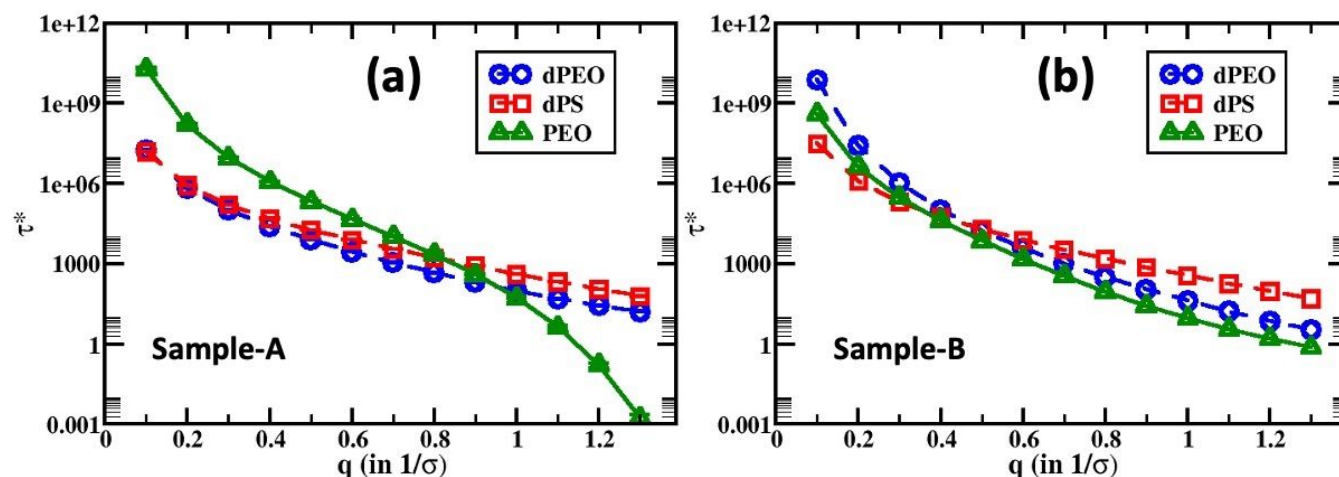


Figure 4. Relaxation times of individual blocks from MD simulation obtained from KWW fitting of the simulation data. In the simulation, both the β and A values of KWW equation (Equation 1) are fitting parameters. The relaxation time is in reduced units. In the simulation, the time step is on the order of 0.01 femtosecond. Hence,

the $10^{12} \tau^*$ in this plot is equivalent to $\sim 10^{-5}$ s in real units, i.e., 10^4 ns, similar to the order of the relaxation time observed in experiments. The β -values varies with q as shown in Figure S8.

In conclusion, we have studied structure-property relationships in the BCP containing an interfacial region that substantially changes the structural and dynamical properties using NSE, SANS and MD simulations. This was enabled by characterizing the chain dynamics of PEO in a pair of selectively deuterated block copolymers comprising *d*PS and *d*PEO using *h*PEO as a contrast segment for NSE and SANS measurements as well as MD simulations. The results showed that dynamics near the PEO chain-end are similar to homopolymer PEO at all length scales. Interesting, the interfacial PEO dynamics are also similar at ~ 5 PEO monomer length scale. However, at longer length scales, 5 monomers and above, interfacial PEO near the *d*PS slows down substantially due to confined motion of the lamellar PEO phase. The results agree with studies of confined PEO dynamics and with PEO blended with a higher T_g polymer. Thus, regarding the ongoing question of the relative importance of confinement versus tethering, this study indicates that the presence of the interface is more important to dynamics than is tethering, although tethering is essential for forming the structures observed with SANS and MD simulations. This fundamental study revealing confined chain dynamics in BCP interfaces differing from chain-end dynamics may help design materials for coatings and membranes for polymer electrolyte batteries, in which transport and mechanical properties are important as they may help or hinder dynamical boost needed for ionic transport. Since covalent bonds and tethering, e.g. BCPs and polymer-grafted nanoparticles, are an effective approach to incorporating nanostructure into materials, it is useful to know that interfacial confinement and tethering have a negligible impact on segmental dynamics and such nanostructure will only impact properties that are dictated by long-range motion (greater than 5 segments). This study of structure with SANS corroborating the NSE dynamic results with qualitative agreement from molecular dynamics simulations explaining the fundamental physics may help direct future materials design principles based on interfacial structure-property relationships in BCPs, by describing the impact that glassy interfaces have on the length-scale dependence of dynamics of a confined rubbery phase.

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