

Mechanisms Underlying Ion Transport in Lamellar Block Copolymer Membranes

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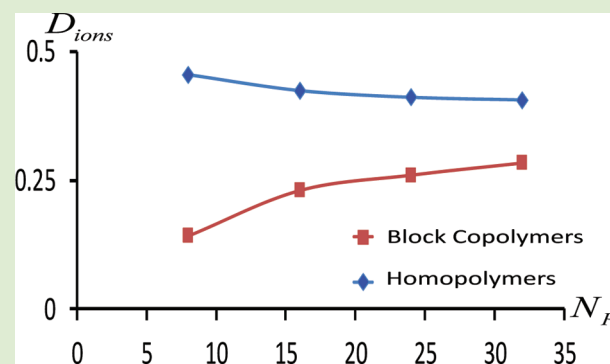
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S Supporting Information

ABSTRACT: Recent experiments have reported intriguing trends for the molecular weight (MW) dependence of the conductivity of block copolymer lamellae that contrast with the behavior of homopolymer matrices. By using coarse-grained simulations of the sorption and transport of penetrant cations, we probe the possible mechanisms underlying such behavior. Our results indicate that the MW dependence of conductivity of homopolymeric and block copolymeric matrices arise from different mechanisms. On the one hand, the solvation energies of cations, and, in turn, the charge carrier concentrations, themselves, exhibit a MW dependence in block copolymer matrices. Such trends are shown to arise from variations in the thickness of the conducting phase relative to that of the interfacial zones. Moreover, distinct mechanisms are shown to be responsible for the diffusivities of ions in homopolymer and block copolymer matrices. In the former, diffusivity effects associated with the free ends of the polymers play an important role. In contrast, in block copolymer lamellae, the interfacial zone between the blocks presents a zone of hindered diffusivity for ions and manifests as a molecular weight dependence of the ionic diffusivity. Together, the preceding mechanisms are shown to provide a plausible explanation for the experimentally observed trends for the conductivity of block copolymer matrices.



Recently, there has emerged an active interest in exploiting the nanostructured phases of block copolymers as membranes for Li ion batteries, proton conducting fuel cells, alcohol separation devices, and so on.^{1–8} The underlying idea is to use one or more of the blocks as a means to endow mechanical strength to the membrane, while using the other component as a phase that facilitates transport of ions and permeants. However, in many such applications, it has been found that self-assembled morphologies possess transport properties that are significantly different from their homopolymeric counterparts.^{4,5,8} While the mechanisms that underlie the transport properties of homogeneous polymer membranes are reasonably well established, the influence of inhomogeneous morphologies upon ion and penetrant transport is still not well understood.

The work reported in this communication is specifically motivated by some recent experimental results reported in the context of conductivity of lithium ions in the poly(ethylene oxide) (PEO) block of the lamellar phase of poly(styrene-*block*-ethylene oxide) copolymer electrolytes.^{4,9} Explicitly, it was demonstrated that the conductivity of the block copolymer electrolytes *increases* with increasing molecular weight of the polymer (and reaches a plateau when the copolymer molecular weight approached around 100 kg/mol). The latter was in contrast to the trend reported for the corresponding PEO

homopolymer electrolytes,¹⁰ where the conductivity decreases with increasing molecular weight (and reaches a plateau when the homopolymer molecular weight approaches 1 kg/mol). These results motivate the fundamental question addressed in this work, namely, “what are the mechanisms underlying the conductivity behavior of self-assembled block copolymers, and how do they differ from those in homopolymer matrices?”

In this communication, we report the results of a coarse-grained computer simulation study of the mechanisms underlying the molecular weight dependencies of the conductivities of *cations* in block copolymers and homopolymer matrices. We specifically focus on the situation of an *aligned* lamellar morphology of the block copolymer melt and study the molecular weight dependence of the conductivity in such systems. We compare and contrast the conductivities of the block copolymers with the corresponding homopolymer matrix and identify the mechanisms underlying the two situations.

Model and Methodology Details: There have been a number of prior theoretical works that have addressed issues related to the conductivity of lithium ions in *homopolymer* PEO matrices. These researches have used techniques ranging from

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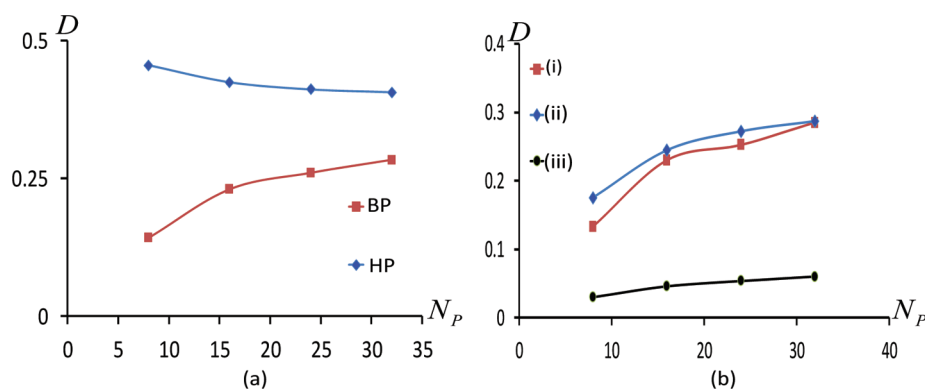


Figure 1. (a) A comparison of the MW dependence of the diffusivity D of ions in a block copolymer lamellae (BP) and a homopolymer matrix (HP). D is expressed in the units of lattice spacing²/time scale of ionic motion. N_p denotes the number of segments in the polymers. The parametric conditions correspond to $\omega_A = 1.0$ and $\omega_B = 0.01$; (b) A comparison of MW dependency of the diffusivity of ions in block copolymer lamellae for different conditions of relative time scales of the matrix to the ion motions: (i) $\omega_B = 0.0$, $\omega_A = 1.0$; (ii) $\omega_A = 1.0$, $\omega_B = 1.0$; (iii) $\omega_A = 0.05$, $\omega_B = 0.05$ (all time scales are expressed in units of the fundamental time scale for the motion of ions). In the plots, the lines are meant to be a guide to the eye.

simulations at both atomistic and coarse-grained level to analytical models describing the transport of ions in polymer matrices.^{11–16} Based on these studies it is now understood that the lithium cations are strongly coordinated to the PEO segments and that the motion of the cations and the resulting ionic conductivities are both strongly coupled to the segmental dynamics of the polymer chains. More recently, other studies have examined the general issue of ion solvation in block copolymer electrolytes¹⁷ and have demonstrated that, while electrostatic interactions play a role in influencing ion distributions and solvation in block copolymer matrices, much of the thermodynamical aspects controlling the ion distributions in electrolytes can be mapped onto the physics of a strongly selective solvent in block copolymer phases.

Inspired by the above findings, in this work we employed a simple coarse-grained simulation approach to study the transport of cations in polymeric matrices. Our method adapts the bond fluctuation lattice Monte Carlo method (BFM) of Carmesin and Kremer^{18,23} to simulate homopolymer and block-copolymer melts. The use of such a coarse-grained model is justified by noting that the physics of ion motion is strongly coupled to the segmental dynamics of polymer chains,^{11–15} a length scale that is adequately captured in BFM simulations. We considered both homopolymeric and symmetric block copolymeric (denoted as AB copolymer, with A and B denoting, respectively, the conducting and nonconducting phases) matrices and probed the conductivities of the system for four different molecular weights corresponding to $N_p = 8, 16, 24,$ and 32 segments in lattice units. For the block copolymer case, the results reported below are for a fixed degree of segregation between the units of the block copolymer and corresponds to a Flory–Huggins parameter of $\chi = 4.0$. The simulation cell sizes were chosen to be commensurate with the period of the block copolymer lamella.

In our simulations, the cations were modeled as a strongly selective penetrant, with the origin of selectivity ascribed to the respective Born solvation energies of the ions.¹⁷ In our work, we chose an associative interaction of $\chi = -4.0$ between the ions and the conductive phase and a strong repulsive interaction of $\chi = +4.0$ between the ions and the nonconductive phase.¹⁹ We note that our representation of ions ignores the influence of electrostatic interactions (and dielectric inhomogeneities) upon the conductivity of the ions.²⁰ Moreover, our model is also inadequate for capturing the rich features of

molecular coordination between the cations and PEO segments observed in atomistic simulations and experiments.^{16,21} On the other hand, our model is expected to be a valid approximation of the underlying physics for situations when the electrostatic screening lengths are comparable to the polymer segment sizes. An estimate of the screening length (cf., Supporting Information) for the experimental conditions indicate that such a condition is indeed fulfilled. With these considerations, we believe that our model captures the main ingredients of the ion distribution and coordination in the polymer matrices and is a useful first step to probe the physics of ion transport through inhomogeneous polymer matrices.¹⁹ We note that the qualitative trends of the results reported in the following section were found to hold equally well for other parametric values of the polymer–polymer and polymer–ion interactions. In the supplementary document we provide more details on the manner in which the simulation protocols were implemented.

Molecular weight dependence of ionic conductivity: In a material whose ionic conductivity results from the migration of unique charge carrier species, the ionic conductivity, σ , can typically be expressed as (under the assumption that the salt is monovalent and that the transference number is 0.5) $\sigma = n_s \gamma e D$, where n_s is the salt concentration, γ is the fraction of cations dissociated from the precursor salt (expressed relative to the amount of salt added), D represents the diffusivity of the (dissociated) ions, and e denotes the charge for the single charge species. The quantity $n_s \gamma$ quantifies the charge carrier concentrations in the system. For dilute concentrations of salt and charge carriers, the diffusivity of the ions D is expected to be independent of the charge carrier concentrations $n_s \gamma$. In this communication, we concern ourselves with the ion diffusivities in this dilute limit, wherein the factors influencing the ion diffusivities can be analyzed independently of the behavior of the charge carrier concentrations. Below we present the results for the polymer MW dependence of the ionic diffusivities and charge carrier concentrations.

The diffusivity of the ions were determined using a modified, kinetic Monte Carlo simulation procedure while using a *fixed* dilute concentration of the ions. In determining the latter, in our simulations we accounted for the possibility that the nonconductive polymer phase is typically closer to its glass transition temperature.^{4,5} Consequently, the time scale of segmental motions of the nonconductive segments (B) were allowed to be slower than that of the ions and that of

conductive A segments. In the results presented below, we use the following terminology to parametrize the time scale effects: The time scale for the motion of ions was chosen to be the basic unit of time. In these units, the time scale of the A segments are denoted as ω_A and that of the B units as ω_B . The length scales reported are in the units of the lattice spacing of the bond fluctuation model. Details of the kinetic Monte Carlo simulation methodology are elaborated in the supplementary section of this communication.

In Figure 1a, we display the diffusivity of the ions as a function of the molecular weight of the block copolymers for the case when $\omega_B = 0.01$ and $\omega_A = 1.0$. These simulation conditions mimic the situation when the time scale for the motion of the segments of the conductive phase is identical to that of the ions, but with the nonconductive phase being slower (by a factor of 100) than both the ions and the conducting phase. The diffusivities reported in the Figure 1a correspond to diffusivities parallel to the lamella. We did measure the diffusivities perpendicular to the lamellae, but their quantitative values were a few orders of magnitude lower than the parallel components and therefore are not displayed. Shown alongside in Figure 1a is also a comparison to the corresponding results for the homopolymer (pure conductive phase) matrix. It is seen that the diffusivities of the ions in the homopolymer matrices decreases with increasing molecular weight of the polymer. In sharp contrast, the diffusivities of the ions in block copolymers are seen to increase with increasing molecular weight of the polymer.

A pertinent question is whether the diffusivity trends seen for the ions in block copolymers arise from the lower diffusivity of the nonconducting phase. To illustrate more clearly the role of ω_A and ω_B upon the above trends, in Figure 1b, we display the ion diffusivities for parametric conditions such that (i) $\omega_B = 0.0$, $\omega_A = 1.0$, which corresponds to a frozen nonconductive phase; (ii) $\omega_B = 1.0$, $\omega_A = 1.0$, which corresponds to a case when the time scales for the nonconductive and the conductive phases are identical to each other and to that of the ions; (iii) $\omega_B = 0.05$, $\omega_A = 0.05$, which corresponds to a case when the time scales for the nonconductive and the conductive phases are identical to each other, but slower than that of the ions. From the results displayed, we observe that the diffusivity of the conductive phase has a significant effect (compare results of Figure 1a and of cases of (i), (ii) of Figure 1b with the results for the case (iii) of Figure 1b) upon the ionic diffusivities in block copolymer matrices. In contrast, the diffusivity of the nonconductive phase is seen to have a much smaller influence upon the overall ionic diffusivities. More interestingly, we observe that the MW dependence of the ionic diffusivities exhibit the same qualitative trend for all the different situations portrayed. These results suggest that the diffusivity disparity of the nonconductive phase is not a main contributor to the MW trends seen in ionic conductivity and that, quite generally, the ionic diffusivities in block copolymer matrices increases with increasing MW of the block copolymer. We defer a discussion of the mechanisms underlying these trends until after we present our results for the charge carrier concentrations of the ions.

Due to the neglect of electrostatic interactions in our model, simulation of dissociation of the salt and the direct calibration of the charge carrier concentrations is not possible in our framework. As an alternative, within our coarse-grained model, we view the ion dissociation as an equilibrium reaction of the form: $C-X \rightleftharpoons C^+ + X^-$, where $C-X$ stands for the salt, C^+

stands for the positively charged (lithium) ions, and X^- stands for the anion.²² Based on this perspective, the amount of dissociated ions, that is, the charge carrier concentrations, can be deduced to be proportional to $e^{-\Delta G}$, where ΔG denotes the free energy change accompanying the above reaction. Furthermore, we have $\Delta G = G_{C^+} + G_{X^-} - G_{C-X}$, where G_α represents the solvation free energy of species α . Equivalently, the preceding considerations suggest that the solvation free energies of the ions are expected to be correlated inversely to the dissociation of salt and the charge carrier concentrations.

In this section, we present simulation results which quantify the change in solvation free energies of the cations as a function of the MW of the polymeric matrix. As noted in the introduction, we assume that the solvation free energies G_α primarily arises from the Born solvation energy of a charged species dissolved in a polar medium. As a consequence, the terms G_{C^+} and G_{X^-} are expected to exhibit the same qualitative dependence upon the polymer MWs.^{17,22} Moreover, since $C-X$ is uncharged, G_{C-X} is expected to exhibit only weak or no polymer MW dependence. Whence, knowledge of G_{C^+} suffices to predict the variations in the charge carrier concentrations arising from changes in the MW of the polymer matrix.

The polymer MW dependence of the quantity G_{C^+} is directly accessible in our framework through the use of grand canonical simulations effected at a fixed fugacity coefficient of the ions. Explicitly,²² the slope of the linear relationship (at dilute ion concentrations) between the equilibrium ion concentrations and the fugacity coefficient of the ions is identically equal to $e^{-G_{C^+}}$. In Figure 2, we present the results for the polymer

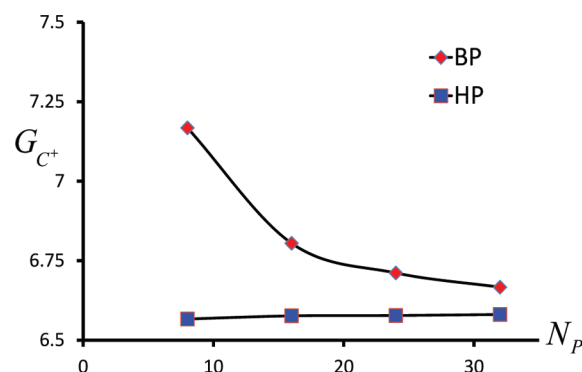


Figure 2. Solvation free energies of the cations G_{C^+} (in $k_B T$ units) as a function of the polymer molecular weight (N_p) for block copolymers (BP) and homopolymers (HP). Lines are meant to be a guide to the eye.

molecular weight dependence of the quantity G_{C^+} extracted from ion solubility results deduced using such a simulation protocol. Based on the results depicted, we observe that G_{C^+} does not exhibit any perceptible MW dependence for the case of homopolymer matrices. In contrast, we observe that G_{C^+} decreases upon increasing the MW of the block copolymers. When recast in terms of the charge carrier concentrations, the results of Figure 2 suggests that the charge carrier concentrations are expected to be independent of the polymer MW for homopolymers. In contrast, the dissociation of the salt and the concentration of the dissociated C^+ ions is expected to increase with increasing polymer MW for block copolymers. The mechanisms underlying these results are discussed in the following section.

Discussion: In this section, we propose tentative explanations for the trends seen in Figures 1 and 2. Specifically, for the case of homopolymers, the solvation free energies and hence the charge carrier concentrations were demonstrated to be practically independent of the polymer MW. However, the diffusivities of the ions were shown to decrease with increasing MW of the homopolymer. As a consequence, the overall conductivity (which is the proportional to the product of the charge carrier concentrations and the ionic diffusivities) is expected to decrease with increasing MW of the homopolymer. In contrast, for block copolymer lamellae, both the charge carrier concentrations and the ionic diffusivities increased with increasing MW of the block copolymer. Consequently, the ionic conductivities are expected to increase with increasing MW of the block copolymers.

We suggest that the behavior of ionic diffusivities in homopolymers can be rationalized as arising from the diffusivity of the free ends of the polymers.¹² For homopolymers of smaller MWs, the density of free ends is much higher, and hence, the time scale of pathways for ionic motion is also expected to be faster. With increasing MW, the density of free ends decreases, and hence, the time scale for the pathways of ions and their diffusivities also become reduced.

To corroborate the above hypothesis, in Figure 3 we display the MW dependence of the averaged time scale for the

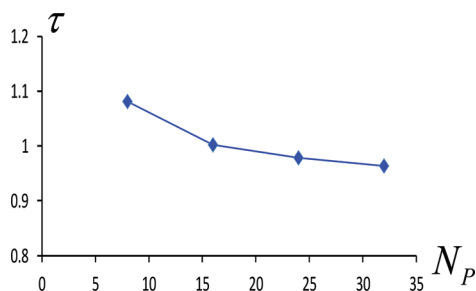


Figure 3. MW (N_p) dependence of the time scale of dynamics of holes (in units of the fundamental time scale for the motion of ions) in the homopolymer matrix. Lines are meant to be a guide to the eye.

dynamics of “holes” in a conductive homopolymer matrix. In our simulations, holes were identified as the lattice sites that were neither occupied by the polymer segments nor the ions but that, in principle, could be occupied by the polymer or ions. In other words, such sites do not overlap with adjoining polymer or ion units. Due to the motion of the polymer segments, such holes switch from being accessible to becoming inaccessible for the ion molecules. The time scale of “flickering” of the holes provides a useful quantitative measure of the time scale of the dynamics of the media in which the ions are moving. From the results displayed in Figure 3, we observe that indeed the dynamics of the holes displays a behavior consistent with the free end effects discussed above. Moreover, the trends seen in Figure 3 exhibit a striking resemblance to the results displayed in Figure 1a, thereby rationalizing our hypothesis for the MW dependence of the diffusivity of the ions in the homopolymer matrix.

We now turn to the case of block copolymer lamellae and begin with the MW dependence of the solvation energies of the cation and its influence upon the charge carrier concentrations. We believe that such trends arise from the MW dependent enhancement of the fraction of the conducting phase relative to the interfacial zone. The conducting phase is a region that is

enthalpically favorable to the ions and promotes the dissociation of salt, whereas the interfacial zones are regions that are less favorable for the ions and the dissociation of salt. At a fixed interaction strength between A and B segments, increasing the MW of the block copolymer increases the thickness of the conducting (A) phase relative to the A–B interfacial zones. As a consequence, we expect a lower solvation energy for the C^+ ions, as confirmed by the results of Figure 2. Not surprisingly, the asymptotic value for the quantity G_{C^+} (and, hence, the charge carrier concentrations) are seen to approach the value noted for the “interfacial region-free system” corresponding to the homopolymer matrix.

To rationalize the MW dependence of the ionic diffusivities in block copolymers seen in Figure 1, we first note that the ions that are present in the conductive phase of the block copolymer lamellae are divided between the interfacial zone of the A and B segments and the interior of the conductive phase (cf., the ion distribution profiles displayed in Figure 4a,b). Our hypothesis is that the ions that are present in the interfacial zone of the block copolymer possess significantly lower diffusivity than the interior of the conductive phase. To provide support for this proposal, we demonstrate the diffusivities of ions in chemically heterogeneous media containing both conductive and nonconductive phases is lower than diffusivities of the ions in the corresponding pure phases. To this objective, we considered a polymer blend mixture of conductive (A) and nonconductive (B) polymers at different compositions, with however the interaction parameter between the A and B units set to zero. To eliminate the time scale effects, we set $\omega_A = 1.0$ and $\omega_B = 1.0$. Subsequently, we probed the diffusivities of the ions in such a blend system, while retaining the interactions between the ions and the A, B units.

Shown in Figure 4c are the results of the above-discussed blend simulations, which depict the diffusivities of the ions as a function of the composition of the blend and for different MWs of the blend components. It can be seen that the diffusivities of the ions are the highest for a system containing only the nonconductive phase (B). Indeed, in such a case, the repulsive interactions between the ions and the B polymers are expected to facilitate the fast motion of the ions through the polymer matrix. Upon adding A polymers to the B matrix, it can be seen that the diffusivity of the ions drop by a significant amount. The latter behavior can be rationalized by envisioning the A segments to act as traps for the motion of the ions and hinder their motion. When the concentration of A polymers is increased, the backbones of A segments begin to serve as connected pathways to facilitate the motion of the ions. The latter results in the observed enhancement in the diffusivity of the ions beyond a certain concentration of the A polymers.

The above result confirms that the diffusivity of ions in the zone of a mixed composition of the conductive and nonconductive phases, such as in the interfacial zone of the lamellae, to be lower than that in the bulk phase of the purely conductive polymer. Increasing the MW of the block copolymer enhances the amount of ions in the interior of the conductive phase relative to amount which is present at the AB interface. This behavior is seen in both the profiles displayed in Figure 4a,b as well as in the quantitative measure of overlap between the ions and the nonconductive phases displayed in Figure 4d. Based on such a reasoning, we propose that the enhancements in the ionic diffusivity with increasing MW of the block copolymer arises from the depletion of the fraction of ions located in the low-diffusivity interfacial zones.

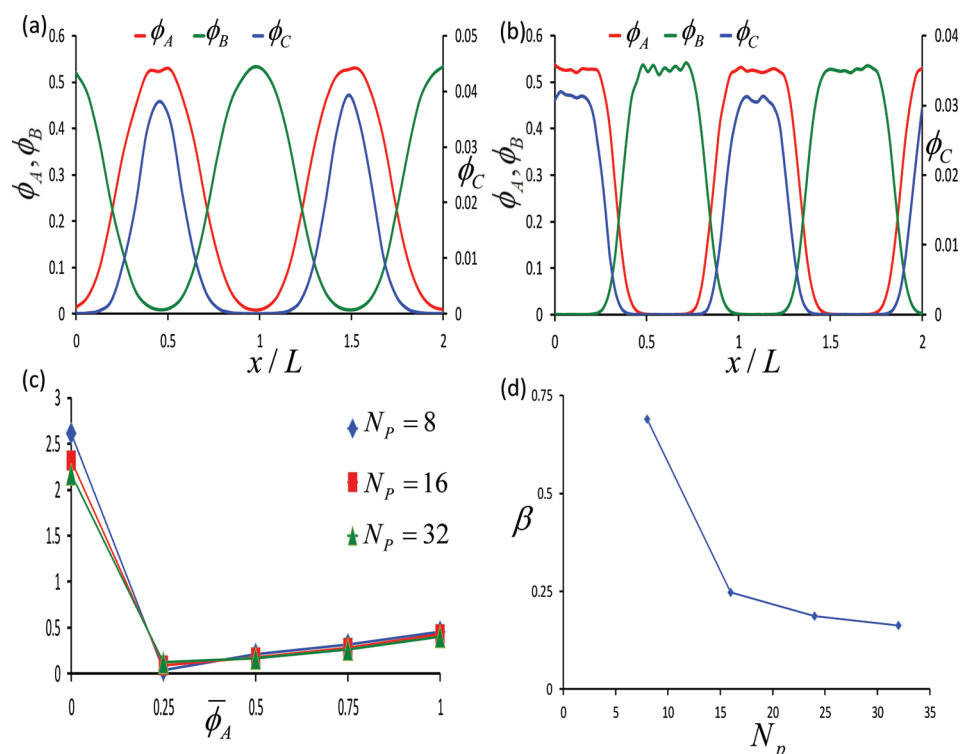


Figure 4. (a, b) Volume fraction profiles of A (ϕ_A) and B (ϕ_B) units and ions (ϕ_C) along the lamellae. L denotes the period of the lamellae. (a) $N_p = 8$; (b) $N_p = 32$. (c) Diffusivity of the ions (D , in the units of lattice spacing²/time scale of ionic motion) in a miscible blend of conductive and nonconductive polymers with MW of N_p units each. $\bar{\phi}_A$ denotes the average volume fraction of the A component in the blend. Lines are just a guide to the eye; (d) Overlap fraction (β) of the ions with the nonconductive phase (B component) displayed as a function of N_p . The overlap fraction β is defined as $\beta = (\int_0^L dx \phi_C \phi_B) / (\int_0^L dx \phi_C)$.

In summary, we presented results from a coarse-grained simulation approach to clarify the mechanistic underpinnings of the MW dependence of the ionic conductivities in block copolymer lamellae and homopolymer matrices. Our results for the ionic diffusivities mirrored the qualitative trends seen in the experiments and indicated that the MW dependencies of ionic conductivities in homopolymer matrices and block copolymer lamellae display opposite trends. We argued that different mechanisms underlie the MW dependence of ionic conductivities in homopolymer and diblock copolymer matrices. In the former, the variations in the conductivities arose primarily from the MW dependence of the diffusivity of the ions. In turn, the latter was associated with the dynamics of the free ends of the polymer chains. In contrast, in the case of diblock copolymer lamellae, the reduction in the relative thickness of the interfacial zone (with increasing MWs) was argued to be the cause of the observed behaviors in the charge carrier concentrations and the diffusivity of the ions.

To our knowledge, our study for the first time clarifies some of the important physics that needs to be taken in account in modeling and understanding transport of penetrants in structured polymeric phases. Admittedly, by neglecting electrostatic interactions, our study adopts a simplistic view of the ions and their transport in block copolymer layers. However, the fact that our simulations captured most of the qualitative trends seen in the experiments suggests that electrostatic effects may not be necessary to explain the MW dependencies. Moreover, due to the generality of our model, our work also has ramifications in the consideration of solubility and transport of neutral molecules through structured polymeric matrices.⁸

■ ASSOCIATED CONTENT

Supporting Information

Details of the simulation scheme employed. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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