

Correlation between ionic mobility and microstructure in block copolymers. A coarse-grained modeling study

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In this supplementary information document, we provide details related to force-field parameterization, simplifications, and supporting results.

I) Electrostatic Screening:

Electrostatic interactions are not explicitly considered in our model due to the fact that even for low ion concentration, the dielectric constant of PEO is $5-16^1$ which ensures a Debye screening length (λ_D) that is approximately 0.23 nm for typical PEO system at 300 K and 0.01 [Li]/[PEO]. The Kuhn length of PEO is 0.8 nm^2 , which is the length scale of the system (i.e., polymer bead size $\sim \sigma_{AA} = \sigma_{BB}$). By considering a screened Coulomb interaction potential, such as the Yukawa Potential (eq. S1), we find that the interaction is effectively screened at a separation distance of 2.5σ as shown in Figure S1 along with the Lennard Jones (LJ) potential that was used in this study, where A is a fitting energy parameter.

$$U(r_{ij}) = A \frac{e^{-\lambda_d r_{ij}}}{r_{ij}} + U^{WCA}(r_{ij}) \quad (\text{S1})$$

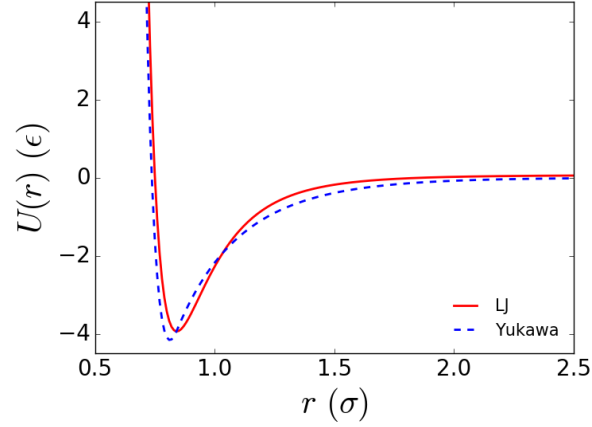


Figure S1. Different interparticle pair potentials ($U(r)$) as a function of separation distance (r) for ion-polymer interaction.

II) Interaction Potential Parameters:

On the premise that electrostatic interactions are effectively screened for typical polyelectrolyte systems upon coarse-graining (as discussed in a previous section), the polymer-ion interaction was assumed to be describable by a LJ interaction potential and calibrated in a Lamellae (L) morphology (i.e., symmetric volume fractions of the constitutive blocks) due to the ease of characterizing the ions (C) distributions in the polymer and the readily available data in the literature³. C ions were effectively trapped in the conductive domain (A) and excluded from the non-conductive domain (B) (as in real systems³) for $\epsilon_{AC} = 4.0 \epsilon$ as shown in Figure S2.

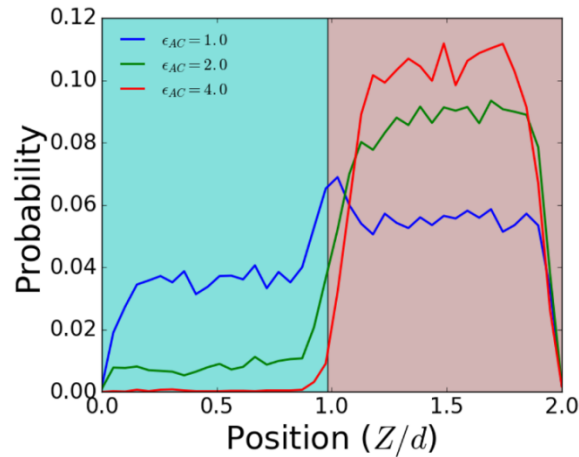


Figure S2. Effect of interaction strength between A and C (ϵ_{AC}) on the distribution of C in the direction perpendicular to the Lamellae interface (Z) in a DBP system with $N = 40$, where each layer has a thickness $\approx d$. The pink area represents the A domain and cyan area represents the B domain.

III) Ion Diffusion Mechanism:

Given the degree of coarse graining in the model employed (i.e., 3 PEO monomers per LJ bead given that a PEO monomer is $\approx 0.28 \text{ nm}^4$), short-time dynamics associated with atomistic details of intrachain diffusion and C coordination are not captured explicitly in our simulations. However, the long-time diffusive process associated with interchain hopping⁵ is captured, which in our systems is attained at a very short time as shown in the dependence of ions displacement (Δx) in the direction of applied external force (F) on time (t), indicative of a dominant interchain diffusion mechanism in Figure S3.

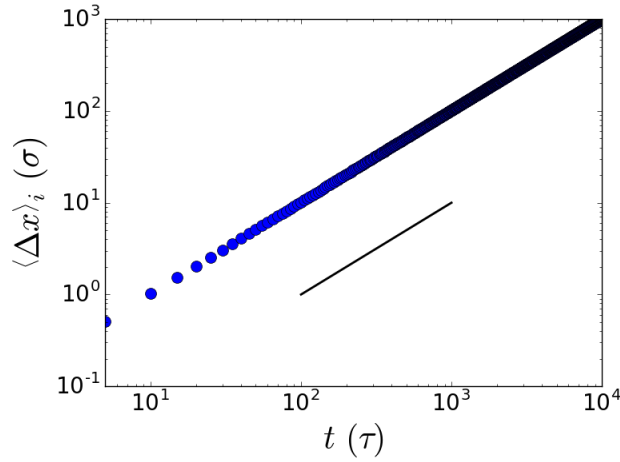


Figure S3. Ensemble average ions displacement ($\langle \Delta x \rangle_i$) in the direction of applied F for $N = 76$ at $T = 2.63 \epsilon/k_b$. The solid line represents the linear scaling.

IV) Number of Species in Each Simulation:

Refer to Table 2 of the main text for details about the volume fractions of the blocks.

Table S1. Size and composition of simulated systems

N	Structure	A Block	A Beads	B Beads	C Beads
10	Lamellae	Any	2,560	2,560	37
14			5,004	5,004	74
24			14,688	14,688	216
40			5,004	5,004	74
64			12,706	12,706	188
76			17,842	17,842	264
14	Cylinder	Minor (Major)	8,160 (29,920)	29,920 (8,160)	140 (448)
24			1,920	5,760	28
40			2,300 (6,900)	6900 (2,300)	33 (101)
60			3,720 (11,160)	11,160 (3,720)	55 (164)
18	Gyroid	Minor (Major)	7,998 (15,996)	15,996 (7,998)	117 (240)

V) Tortuosity Measurement:i. Geometric Analysis for Hexagonal Cylinders

The tortuosity of the Hexagonal Cylinder morphology when the majority component is conductive and force is applied perpendicular to the cylinders ($HC_{\perp}$) depends on the diameter of the cylinder ($2r$) and box length (L) (i.e., domain size), which can be related to the chain length (N). Using eq. S4, the tortuosity was calculated by finding

the average length of the paths travelled by an ion going across the box length, where r^* and σ_{BC}^* are the cylinder radius and the effective interaction diameter between B and C reduced by the box length (L). An effective cylinder diameter was used which includes the interaction cut-off diameter in the BC interaction potential ($2^{1/6}\sigma_{BC}$). The diameter was estimated by taking the projection of all the beads within a cylinder to the two directions normal to the cylinder axis, and calculating the width of the bead distribution in the two directions.

$$\lambda = \lambda_{cylinder} p_{cylinder} + \lambda_{free\ space} (1 - p_{cylinder}) \quad (S4a)$$

$$\lambda = \left(\frac{\pi(r^* + 2^{1/6}\sigma_{BC}^*)}{2} - (r^* + 2^{1/6}\sigma_{BC}^*) + 1 \right) \times 2(r^* + 2^{1/6}\sigma_{BC}^*) + 1 - 2(r^* + 2^{1/6}\sigma_{BC}^*) \quad (S4b)$$

ii. Brownian Dynamics for Gyroid Morphology

Since identifying λ for Gyroid when the majority component is conductive (*G Maj.*) from the geometry of the structure is rather complicated, an alternative definition of tortuosity is used based on the particle mobility in the tortuous structure of interest relative to that in free-space (i.e., Lamellae)⁹.

We have shown that for Lamellae, Hexagonal Cylinder, and Gyroid Minority phases, the ionic mobility is dependent upon the extent of interfacial mixing (β) and the tortuosity of the domain (λ). In order to estimate λ for the Gyroid phase when the majority component is conductive (*G Maj.*), the particles were used to probe the tortuosity of the structure by removing the conductive polymer domain, freezing the non-conductive domain, and applying a stochastic thermostat to induce Brownian-like dynamics to decorrelate the trajectories of the ions, particularly important to probe tortuous paths. By doing so, we minimize the effect of interface roughness (already captured by β in the ionic mobility) on the probe particle, and remove any density inhomogeneity in the conductive domain. The Langevin thermostat was used with a damping parameter of $0.1\ \tau$ and a temperature of $2.6\ \epsilon/k_b$ applied to the particles only. An external force $F = 1\ \epsilon/\sigma$ was applied to bias the motion of the probe particles in the direction of interest to estimate the tortuosity from the distance traveled. The λ obtained from this calculation is comparable, but consistently higher, to the geometric values⁹ (see Figure S4) for Lamellae, Hexagonal Cylinder,

and Gyroid when the minority component is conductive. For each morphology, the structure corresponding to the longest chain length was used to probe the tortuosity with this method to minimize spurious effects (i.e., confinement and roughness of the interface).

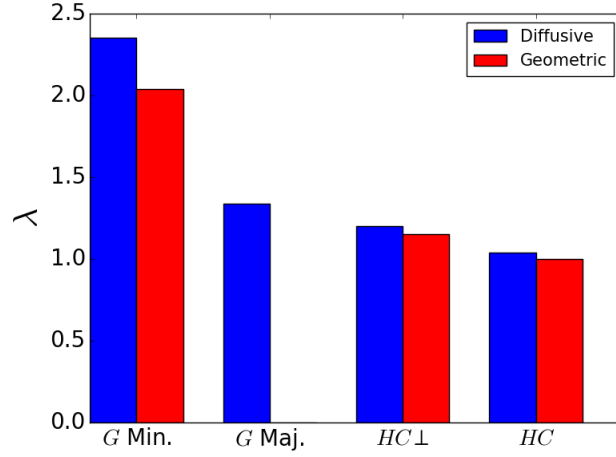


Figure S4. Comparison of the diffusive and geometric tortuosity factor (λ) for different morphologies.

VI) Linear Response Regime Verification:

To ensure that under the external force, the ionic mobility is extracted from the linear response regime, a range of force magnitudes (F) in the vicinity of the one used in the study were tested. As shown in Figure S5, the ensemble average drift velocity ($\langle v \rangle_i$) in the direction of applied F is linearly related to F .

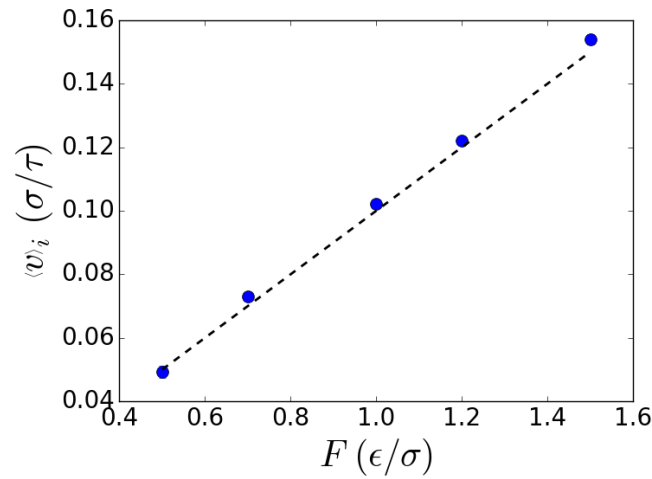


Figure S5. Effect of F on $\langle v \rangle_i$ for $N = 14$ at $T = 2.63 \epsilon/k_b$.

VII) Effect of Global Density on Ionic Mobility:

Figure S6 shows the effect of global density (ρ) on ionic mobility (μ) for two sizes of C ($\sigma_{cc} = 0.25 \sigma$ and 0.5σ) for comparison.

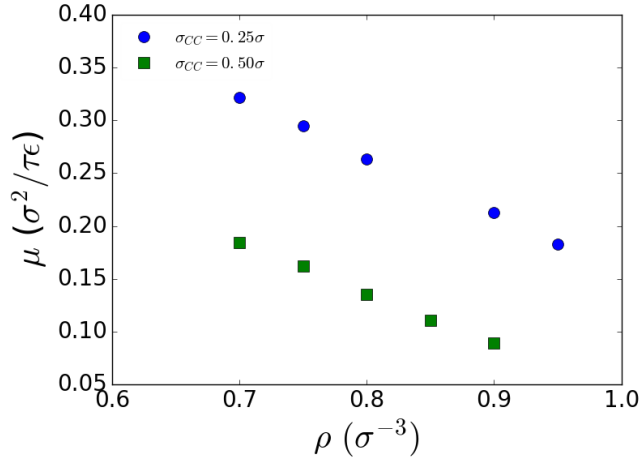


Figure S6. Effect of ρ on μ for two C sizes ($\sigma_{cc} = 0.25$ and 0.5σ) in homopolymer with $N = 40$ at $T = 2.63 \epsilon/k_b$.

VIII) Interface Thickness Calculations:

The effect of χN (estimated based on Ref. 6) on the interfacial thickness (Δ^*) of the L phase was assessed by fitting the order parameter $\psi(z)$ (eq. S2) to eq. S3, where z is the position in the direction normal to the interface (Z), $\phi_i(z)$ is the volume fraction of component i in the direction Z , and z_0 is the position at which $\phi_A(z) = \phi_B(z)$:⁷

$$\psi(z) = (\phi_A(z) - \phi_B(z)) / (\phi_A(z) + \phi_B(z)) \quad (S2)$$

$$\psi(z) = \tanh(2(z - z_0)/\Delta^*) \quad (S3)$$

Figure S7 shows a comparison of Δ^* values from the simulations and theory by Semenov⁸ (eq. 7 in main text) indicating that the former follow approximately the theoretical scaling with a slight deviation in the actual Δ^* .

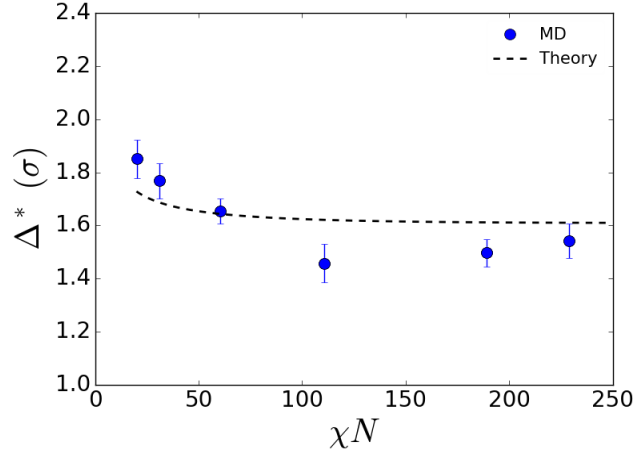


Figure S7. The dependence of Δ^* on χN from the simulations and theory at fixed $T = 2.63 \epsilon/k_b$. Error bars represent the 95% confidence interval from different configurations.

IX) Effect of Temperature on Ionic Mobility:

The effect of temperature (T) on μ for a representative homopolymer (HP) is shown in Figure S8. This curve is used to rescale μ in DBP to take into account changes in temperature: the ratio of μ in HP between the reference value of $T = 2.63 \epsilon/k_b$ and that at the DBP temperature was used in Figure 8 of the main text.

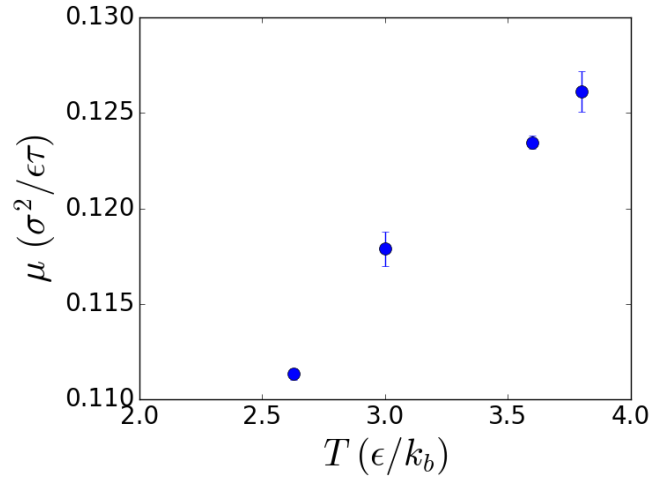


Figure S8. Effect of T on μ for homopolymer (HP) with $N = 40$.

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