

UC Berkeley

UC Berkeley Previously Published Works

Title

Effect of Composition on the Phase Behavior of Ion-Containing Block Copolymers Studied by a Minimal Lattice Model

Permalink

<https://escholarship.org/uc/item/1783p7b1>

Journal

Macromolecules, 47(7)

ISSN

0024-9297

Authors

Knychała, P
Banaszak, M
Balsara, NP

Publication Date

2014-04-08

DOI

10.1021/ma402454j

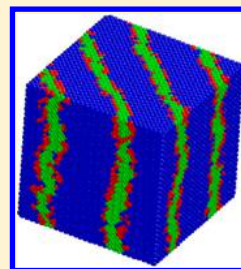
Peer reviewed

Effect of Composition on the Phase Behavior of Ion-Containing Block Copolymers Studied by a Minimal Lattice Model

P. Knychala,^{†,‡} M. Banaszak,^{*,†} and N. P. Balsara^{§,||}[†]Faculty of Physics, A. Mickiewicz University, ul. Umultowska 85, 61-614 Poznan, Poland[‡]The President Stanislaw Wojciechowski Higher Vocational State School in Kalisz, ul. Nowy Swiat 4, Kalisz, Poland[§]Materials Sciences Division and Environmental Energy Technologies Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720, United States^{||}Department of Chemical and Biomolecular Engineering, University of California, Berkeley, California 94720, United States

S Supporting Information

ABSTRACT: We performed Monte Carlo simulations using a minimal lattice model with short-range interactions modeled using Flory–Huggins interactions parameters, χ , to investigate morphology of ion-containing A–B diblock copolymers. A fraction of the segments in the A block, p , were ionic (labeled S) while the B block segments were nonionic (p was held fixed at 0.588). The dielectric constants of the polymers is assumed to be low, and thus charge dissociation effects are negligible. The magnitude of the χ between ion and nonionic species, determined in previous experiments on poly(styrenesulfonate)-*b*-poly(methyl butylene), PSS–PMB, is an order of magnitude larger than that between the nonionic segments. Simulations indicate that complex morphologies such as gyroid and perforated lamellae are obtained in symmetric block copolymers wherein the volume fraction of the B block, ϕ_B , is about 0.5, while simple unperforated lamellae are obtained in asymmetric block copolymers wherein ϕ_B is about 0.25. This result is very different from the well-established phase behavior of nonionic block copolymers but consistent with experimental results of Wang et al. [*Macromolecules* **2010**, *43*, 5306]. We also make a number of additional predictions, still awaiting an experimental verification, such as the emergence of the hexagonal phase in the weak segregation limit, and a remarkable insensitivity of the product $p^2\chi N$ (N is the total number of segments in a copolymer chain) at the order–disorder transition to ϕ_B .



■ INTRODUCTION

There is a continuing interest in ion-containing block copolymers due to their use in clean-energy-related applications such as fuel cells and batteries.^{1–4} As is the case with conventional block copolymers that do not contain ions, these systems exhibit microphase separation. However, one (or more) of the microphases has the capacity to transport ions. It is obvious that conductivity of ion-containing block copolymers depends crucially on the morphology of ion-containing microphase.

In many systems of interest, the ions are connected to polymers with low dielectric constants such as polystyrene. In such systems, ions exist in the form of ion pairs and long-range Coulombic interactions are absent. It is intuitively obvious that the interactions between ionic and nonionic segments are highly repulsive. If one uses the language used to describe interactions between polymers, one would conclude that these systems are characterized by an extremely high Flory–Huggins interaction parameter (χ). To our knowledge, all of the experimental data on the thermodynamics of ion-containing block copolymers (e.g., refs 2, 5, and 6) have used χ parameters to quantify thermodynamic interactions between ionic and nonionic segments. The use of χ to describe the interactions between ionic and nonionic segments is, in some cases,

justified, as shown in ref 7, where simulations that explicitly account for ionic interactions in copolymers are reported.

As early as 1993, Semenov and co-workers developed the superstrong segregation limit to describe the thermodynamics of block copolymers comprising ionic and nonionic blocks.^{8,9} Self-assembly in conventional nonionic block copolymer chains is governed by the competition between the energy associated with chain stretching and the interfacial energy. However, it was argued by Semenov et al. that in the limit of large χN (N is the number of segments per block copolymer chain) one obtains the superstrong segregation limit (sSSL) wherein only the interfacial energy dictates the morphology. It was postulated that sSSL can be achieved in chains with ionic and nonionic segments. The morphology of block copolymer melts and micellar solutions in the sSSL are essentially dictated by the tendency to form flat interfaces. In other words, lamellar morphologies are predicted in block copolymers with highly asymmetric composition; cylindrical and spherical morphologies are predicted by standard block copolymer theories in this regime.^{10,11} Lodge and co-workers¹² demonstrated that the behavior characteristic to sSSL was obtained in solutions

Received: November 30, 2013

Revised: February 18, 2014

Published: March 25, 2014

containing fluorinated and non-fluorinated segments due to the large χ parameter between them: disk-like micelles were observed (rather than the usually observed spherical micelles). Recent theories on phase behavior of ion-containing block copolymers account for the effect of charge dissociation on thermodynamics.^{1,13–19} The relevance of these theories to systems such as charged polystyrenesulfonate where ion-pairing dominates is, however, unclear.

In previous work,^{20,21} we developed a minimal lattice model for predicting the morphology of diblock copolymers. This is the spirit of the sSSL theory^{8,9} which does not account for Coulombic interactions, but the results of our model differ significantly from sSSL predictions. Since ion pairs can, to a first approximation, be considered as highly polar neutral species, the ion-containing block is made up of two kinds of segments: charged segments that we label S and uncharged segments that we label A. The fraction of ionic segments in this block is labeled p . The nonionic block is made up of one kind of segments that we label B. We limit our attention to polymers with low dielectric constants such as polystyrene and polymethylbutylene wherein charges are tightly bound in the form of ion pairs. The χ parameters between ionic and nonionic monomers were estimated in ref 2 using measurements of domain sizes (block copolymers with large N), neutron scattering profiles obtained from disordered samples (block copolymers with small N), and the random copolymer theory. All of these measurements suggest that those χ parameters between ionic and nonionic segments range from 5 to 10 at 25 °C. Similar estimates were obtained by others.^{5,6} In our model, the χ parameter between ionic and nonionic segments is assumed to be an order of magnitude larger than that between two nonionic segments.

Our previous papers on this subject, where we showed results of Monte Carlo simulations of our minimal lattice model, were restricted to symmetric copolymers with $\phi_B = 0.5$; ϕ_B is the volume fraction of the nonionic block. These copolymers exhibit a wide range of microphase-separated morphologies including gyroid (G), double diamond (DD), perforated lamellae (PL), and hexagonally packed cylinder (HEX), in addition to the expected lamellar phase (L); L represents simple nonperforated lamellae. The observed morphology depended on p , number of segments per chain, N , and χ . In spite of the many limitations of our model, all of the results described above are consistent with experimental observations on poly(styrenesulfonate)-*b*-polymethylbutylene (PSS–PMB) copolymers with $\phi_B \approx 0.5$.² It should be noted that the behavior described above is very different from the well-established behavior of nonionic block copolymers^{10,22,23} or the predictions of the sSSL theory of Semenov^{8,9} wherein the phase behavior is dominated by the L phase in symmetric copolymers with $\phi_B \approx 0.5$, regardless of N . In Table 1, we present experimentally observed morphologies of two sets of PSS–PMB copolymers with $\phi_B \approx 0.55$ and $\phi_B \approx 0.75$ and a fixed sulfonation level of the PSS block of $42 \pm 3\%$; the data are taken from refs 1 and 2. The number of PSS and PMB segments, N_{PSS} and N_{PMB} , were calculated from the known monomer volumes of polystyrene and PMB chains, 0.179 and 0.147 nm³, and assuming the reference volume of the segment $v = 0.1 \text{ nm}^3$.^{24,25} These results are plotted in Figure 1 where the morphology obtained from each sample is shown on a plot of N_{PSS} versus ϕ_B . Horizontal lines on this plot indicate the change in morphology obtained when the composition of PSS–PMB block copolymers is changed by lengthening the PMB block. In

Table 1. Molecular Characteristics and Morphology of PSS–PMB Copolymers^a

sample	ϕ_{PMB}	SL	$M_{\text{PSS}} - M_{\text{PMB}}$ (kg/mol)	$N_{\text{PSS}} - N_{\text{PMB}}$	morphology
P1(44)	0.55	0.44	1.4–1.4	24–29	G
P3(44)	0.56	0.44	2.5–2.6	43–54	PL
P4(44)	0.56	0.45	3.5–3.7	60–78	PL
P5(40)	0.54	0.40	4.8–4.6	82–96	PL
P9(39)	0.54	0.39	9.1–8.7	156–182	HEX
A1	0.75	0.42	1.6–4.0	27–84	L
A2	0.76	0.41	3.2–8.1	55–170	L
A3	0.73	0.40	5.9–13.4	101–281	L

^aSamples PX(Y-Z) taken from ref 2 (Park et al.) and samples AX taken from ref 1 (Wang et al.), ϕ_B is the volume fraction of the nonionic PMB-rich phase, SL is the sulfonation level (mole fraction of sulfonic acid groups in the PSS block), M_{PSS} and M_{PMB} are the molecular weights of the polystyrene precursor of the PSS–PMB block copolymer and the PMB blocks, N_i is the number of repeat units in the i block, G = gyroid, PL = hexagonally perforated lamellae, HEX = hexagonally packed cylinders, L = lamellae. Morphology of the samples do not depend on temperature in the 25–110 °C range.

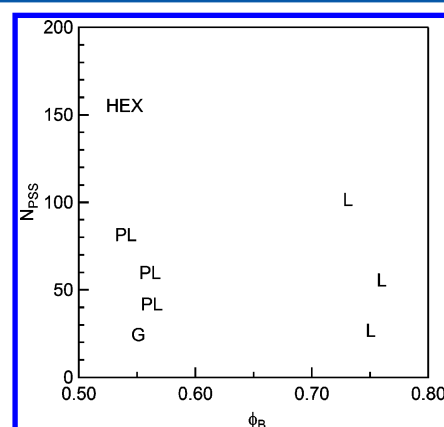


Figure 1. Experimentally determined morphology of PSS–PMB samples listed in Table 1 given as a function of the number of monomers in the PSS block ($v_{\text{ref}} = 0.1 \text{ nm}^3$) versus the volume fraction of the nonionic PMB block, ϕ_B . G = gyroid, PL = hexagonally perforated lamellae, HEX = hexagonally packed cylinders, and L = lamellae.

conventional uncharged block copolymers, increasing ϕ_B from 0.55 to 0.75 results in a change in morphology from lamellae to hexagonally packed cylinders of the minor component.²⁶ In contrast, increasing ϕ_B from 0.55 to 0.75 in PSS–PMB block copolymers results in a change in morphology from gyroid and perforated lamellae to simple unperforated lamellae. To our knowledge, none of the previous theories on diblock copolymer self-assembly, with or without charges,^{1,8–11,13–19,22,23,27} predict behavior that is similar to that described in Figure 1.

It is perhaps worth noting that several other experimental groups have studied the morphology of charged block copolymers, and many of the results are strikingly different from those obtained in conventional nonionic block copolymers.^{27–33} For example, Goswami et al. report on the formation of hexagonally packed cylinders in a block copolymer with $\phi_B = 0.75$.^{27,33} The surprising result is that the majority component, the nonionic block, was contained within the cylinders, while the ionic block was contained in the matrix. Simulations that accounted for electrostatic interactions were consistent with the observed morphology.²⁷ Such simulations

can, in principle, provide a more accurate description of the interactions between ionic and nonionic monomers. To our knowledge, however, a comprehensive phase diagram that covers a broad range of relevant variable using this model has not yet been published. It is likely that this is a reflection of the computationally intensive nature of simulations that account for long-range Coulombic interactions.

In this paper we focus on the effect of ϕ_B on the morphology of ion-containing diblock copolymers using our previously developed minimal lattice model.^{20,21} Our objective is to see if this model provides a rational basis for the observations in Figure 1.

SIMULATION METHODOLOGY

The PSS–PMB copolymer was modeled by a linear chain consisting of N segments of type A, S, and B, corresponding to styrene (S), sulfonated styrene (SS), and methylbutylene (MB), respectively. The sulfonated block was thus modeled using the A and S segments while the PMB block is modeled using B segments. The length of sulfonated block, $N_{AS} = N_A + N_S$, was constant and equal to 17, where N_A and N_S are the number of A and S segments. The sulfonation level, $p = N_S/N_{AS}$, was thus held fixed at 0.588. The length of non-sulfonated block, N_B , was changed from 5 to 47. We performed simulations for 12 different chain sequences, with the volume fraction of the B block, ϕ_B , varying from 0.23 to 0.73; $\phi_B = N_B/N$. The molecular structures of the diblock copolymers studied here are given in Table 2.

Table 2. Sequence Distributions of Simulated Copolymers

sample	N	ϕ_B	sequence
S23	22	0.23	SSSAAAASSSSAAASSS-05B
S29	24	0.29	SSSAAAASSSSAAASSS-07B
S35	26	0.35	SSSAAAASSSSAAASSS-09B
S39	28	0.39	SSSAAAASSSSAAASSS-11B
S43	30	0.43	SSSAAAASSSSAAASSS-13B
S50	34	0.50	SSSAAAASSSSAAASSS-17B
S55	38	0.55	SSSAAAASSSSAAASSS-21B
S60	42	0.60	SSSAAAASSSSAAASSS-25B
S65	48	0.65	SSSAAAASSSSAAASSS-31B
S70	56	0.70	SSSAAAASSSSAAASSS-39B
S72	60	0.72	SSSAAAASSSSAAASSS-43B
S73	64	0.73	SSSAAAASSSSAAASSS-47B
S65b	96	0.65	SSSSSSAAAAAASSSSSSSSAAAAAASSSSSS-62B
S65c	96	0.65	SSSAAAASSSSAAASSSSSSAAAAAASSSSAAASSS-62B

The following intermonomer interactions parameters, ϵ_{ij} , are applied in our simulations: $\epsilon_{AB} = 0.042\epsilon$, $\epsilon_{BS} = 0.792\epsilon$, $\epsilon_{AS} = \epsilon$, $\epsilon_{AA} = \epsilon_{BB} = \epsilon_{SS} = 0$, which lead to the following definitions of χ parameters: $\chi_{ij} = z\epsilon_{ij}/kT$ (where $i, j = A, B$, and S and z is the effective number of nearest nonbonded neighbors); $\chi_{AS} = 1.26\chi$, $\chi_{BS} = \chi$ (χ_{BS} is used to measure the relative magnitude of other χ 's), and $\chi_{AB} = 0.053\chi$. These values of ϵ are identical to those used in our earlier simulations^{20,21} and were calculated based on χ parameters obtained from experiments.² We define reduced temperature, T^* , as $T^* = kT/\epsilon$ and $\chi = z/T^*$. The PSS blocks in the experimental studies^{1,2} were obtained by random sulfonation. Indirect evidence suggests that sulfonation occurs in blocks due to dramatic differences in the solubility of PS and PSS segments. The segment sequences used in the simulations are highly simplified models of the experimental system.

The cooperative motion algorithm (CMA)^{34–36} for a face-centered cubic (FCC) lattice with the usual periodic boundary conditions was used in this paper. The number of nearest nonbonded neighbors in the simulations was $z_{\text{sim}} = 10$. Using arguments given in ref 21, this implies that the number of nearest nonbonded neighbors appropriate for the calculation of χ_{ij} , $z = 7.5$, i.e., $T^* = 7.5/\chi$. The bond length $b = \sqrt{2}a$, where a is the FCC lattice constant, and is also used as a length unit. The bonds are not allowed to be broken or stretched.

Parallel tempering (replica exchange) Monte Carlo (PT) simulations were used to equilibrate our systems.^{37–39} Our approach is identical to that used in our previous study.²¹ The FCC lattice is generated from a simple cubic lattice by removing every second site (i.e., sites that satisfy the condition that the sum of integer coordinates of the site, $x + y + z$, is an odd integer are removed). The box size is chosen to fit the chain, and the lattice sites are completely filled with chain segments; there are no vacancies. The initial box size used in our simulations is $N \times N \times N$ for shorter chains ($N \leq 42$) and $N/2 \times N/2 \times N/2$ for longer chains ($N > 42$). For example, the box $34 \times 34 \times 34$ was used for chain length $N = 34$, and it contains $n_a = 34^3/2 = 19\,652$ sites occupied by $n_c = 578$ polymer chains, and for $N = 64$ we apply the box $32 \times 32 \times 32$ with $n_c = 256$ chains. The effect of box size and shape on our results was studied in selected cases. For example, for $N = 34$ we carried out additional studies in a $68 \times 68 \times 68$ box, and for $N = 64$ we used both $64 \times 64 \times 64$ and $64 \times 34 \times 34$ boxes in addition to the standard $32 \times 32 \times 32$ box. The morphologies obtained in the simulations were not dependent on the box sizes.

The ensemble-averaged energy per lattice site, E^*/n_a , heat capacity at constant volume, C_v , and structure factor, $S(k)$, for each temperature, T^* , are calculated. The structure factor, $S(k)$, is defined by the equation

$$S(\vec{k}) = \frac{1}{n_a} \langle (\sum_{m=1}^{n_a} \cos(\vec{k} \cdot \vec{r}_m))^2 + (\sum_{m=1}^{n_a} \sin(\vec{k} \cdot \vec{r}_m))^2 \rangle_{\text{thermal average}}$$

where n_a denotes the number of segments of type α and $\vec{r}_m$ denotes the position of m th segment of type α ; in this paper we focus on $\alpha = B$. The visual observation of the morphology from simulations and analysis of $S(k)$ peaks using well-known results for the dependence of the peak locations were used to identify morphology of nanostructures. The peaks in the dependence of C_v on T^* were used to determine the order–disorder (ODT) and order–order (OOT) transition temperatures.

RESULTS AND DISCUSSION

Typical simulation results are shown in Figure 2. In Figures 2a,b we show snapshots of sample S70 ($\phi_B = 0.70$) at $T^* = 1.59$ and $T^* = 2.47$. In the case of conventional block copolymers, the HEX phase is obtained at this composition at temperatures well below the order–disorder transition temperature.²⁶ In contrast, a lamellar phase is obtained at both temperatures in our minimal model. It is evident that the A monomers are segregated to the “interface” between the S and B segments at $T^* = 1.59$. The driving force for this segregation is obvious: the strong incompatibility between S segments with the two nonionic segments. At $T^* = 2.47$, clusters of S segments are located throughout the A-rich domains. The difference in the morphologies at $T^* = 1.59$ and $T^* = 2.47$ is quantified in Figures 2c,d where averaged concentration profiles of A, S, and B segments of sample S70 are plotted as a function of distance

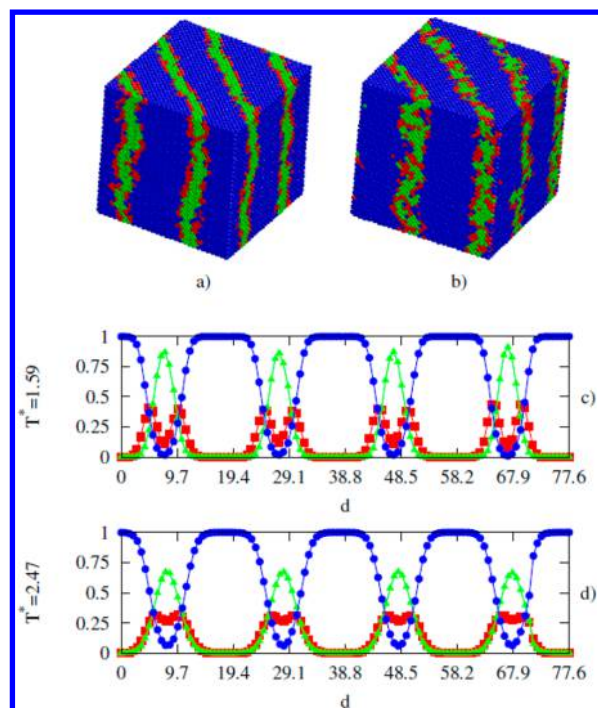


Figure 2. Simulation snapshots of the S70 sample at $T^* = 1.59$ (a) and $T^* = 2.47$ (b). Monomer concentration profiles of the same sample at $T^* = 1.59$ (c) and $T^* = 2.47$ (d). The profiles for A, B, and S segments are shown in red, blue, and green, respectively.

along the vector normal to the layers. (The concentrations were averaged in along the plane normal to the z-axis using many snapshots of the type shown in Figures 2a,b.) At $T^* = 1.59$, the peaks in the A-segment profiles are located near the inflection points in the S- and B-segment profiles (Figure 2c). In contrast, at $T^* = 2.47$, the A-segment concentration is nearly uniform in the S-rich domain. The lamellar phase formed in these systems is shown in the movie S70_T*_2_47 included in the Supporting Information.

The identification of phase transitions is facilitated by plots of the specific heat, C_p , versus T^* . In Figure 3a, we show such a plot for S65 where two peaks are evident: a large broad peak at $T^* = 2.1$ that we label $L_{A/S}$ and a sharper but less pronounced peak at $T^* = 2.96$ that we label ODT. The phase behavior of S65 is remarkably simple. The ordered phase is lamellar regardless of T^* with a lamellar-to-disorder transition at $T^* = 2.96$. At temperatures $T^* < 2.1$, the A-segments segregate to the S–B interface. At temperatures $T^* > 2.1$, the A-segments are located throughout the S-rich domain. The “transition” (or crossover) between the two kinds of lamellae is not sharp; the peak in the C_p versus T^* curve in Figure 3a is broad. In contrast, the transition from order-to-disorder corresponding to the less pronounced peak at $T^* = 2.96$ in Figure 3a is sharp. In Figure 3b, we show the S_{BB} structure factor in the vicinity of low temperature peak. The primary and higher-order peaks clearly indicate the presence of a lamellar phase.

The analysis described above was repeated for all of the samples listed in Table 2, and the observed phase behavior is summarized on a T^* versus ϕ_B plot in Figure 4. The plot can also be used to obtain phase behavior on a χ versus ϕ_B plot using right-hand-side y -axis in Figure 4 ($T^* = 7.5/\chi$ as discussed in ref 21). The dominant phase in the $0.25 \leq \phi_B \leq 0.55$ window is the lamellar microphase (with and without perforations). The nonionic lamellae in samples labeled L/PL

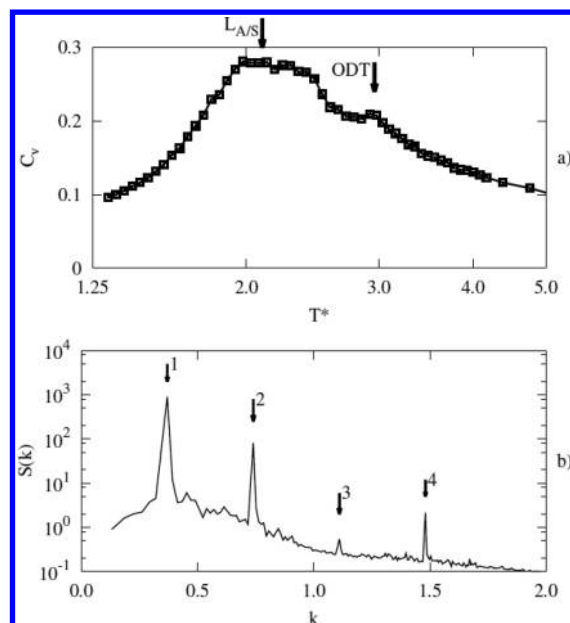


Figure 3. Simulation results for sample S65: (a) heat capacity, C_v , as a function of T^* . The arrows indicate ODT at $T^* = 2.96$ and layering of S-segments in the A-rich lamellae at $T^* = 2.1$ ($1_{A/S}$). (b) The B segment structure factor, $S(k)$, of sample S65 at $T^* = 2.09$. The arrows show peaks at 1, 2, 3, and 4 indicate L phase.

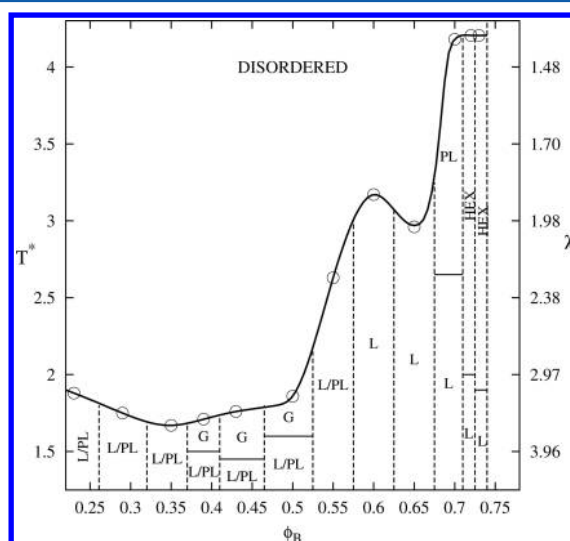


Figure 4. Phase diagram of simulated copolymers on a T^* versus volume fraction of the nonionic B block, ϕ_B . G = gyroid, PL = perforated lamellae, HEX = hexagonally packed cylinders, and L = lamellae.

in Figure 4 are occasionally perforated by columns of the ion-containing microphase, but the perforations are not organized on a lattice. The presence of perforations depends on the initial configuration of the simulation; some simulations lead to simple nonperforated lamellae (L) while others lead to occasionally perforated lamellae (PL). This is probably due to the similarities of the free energies of the perforated and nonperforated morphologies due to the fact that the dominant interaction parameters in the system χ_{AS} and χ_{BS} are similar in magnitude. For ϕ_B values between 0.39 and 0.50, a gyroid phase emerges in weakly segregated block copolymers in the vicinity of the ODT. For $\phi_B = 0.60$ and $\phi_B = 0.65$ we only

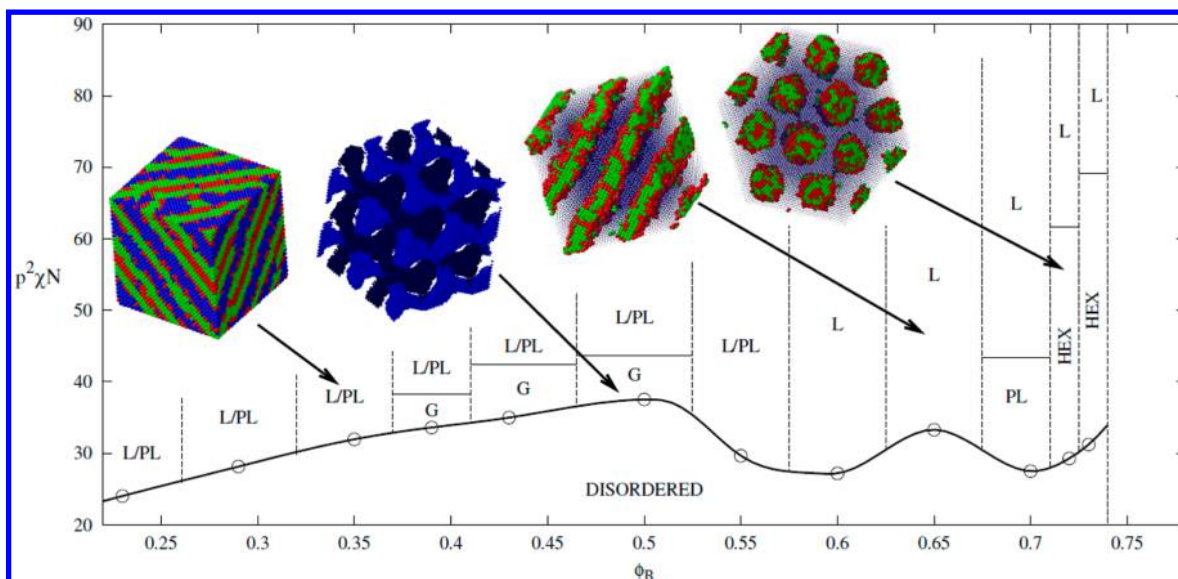


Figure 5. Phase diagram of simulated copolymers on a $p^2\chi N$ versus volume fraction of nonionic block, ϕ_B , with the snapshots of representative configurations for samples S35 ($T^* = 1.33$), S50 ($T^* = 1.79$), S65 ($T^* = 2.09$), and S72 ($T^* = 2.20$) showing PL, G, L, and HEX phases. G = gyroid, PL = perforated lamellae, L = lamellae, HEX = hexagonally packed cylinders.

observed simple unperforated lamellae and a direct transition from L to disorder. For $\phi_B = 0.70$ we obtain simple unperforated lamellae at low temperatures, perforated lamellae at intermediate temperatures (labeled PL in Figure 4), and a disordered phase at high temperatures. The label PL indicates all of the simulations resulted in disordered perforations within the nonionic lamellae. For example, all of the simulations on the $\phi_B = 0.70$ sample at T^* between 2.65 and 4.17 indicated the presence of perforations, but they did not appear to be located on a lattice, based on analysis of both position space snapshots and calculations of structure factors. The two systems with the largest ϕ_B values ($\phi_B = 0.72$ and 0.73) exhibit similar behaviors with lamellar microphases at low temperatures, HEX microphases at intermediate temperatures, and a disordered phase at high temperatures.

The qualitative consistency between the experimental results shown in Figure 1 and the phase diagram in Figure 4 is noteworthy. At the lowest value of N_{PSS} , the morphology of PSS–PMB block copolymers from gyroid to lamellae when ϕ_B is increased from 0.55 to 0.75 (Figure 1). Our simulations show exactly the qualitatively similar behavior; close to the ODT at $\chi = 3$, the gyroid phase is obtained at $\phi_B = 0.73$. At larger values of N_{PSS} , the morphology of PSS–PMB block copolymers from hexagonally perforated lamellae to simple unperforated lamellae when ϕ_B is increased from 0.55 to 0.75 (Figure 1). In conventional block copolymers increasing either χ or N results in an increase in segregation strength. In our simulations, segregation strength was varied by varying χ , while in the experiments, segregation strength was varied by varying N . (Changing N_{PSS} at fixed ϕ_B is equivalent to changing N .) In both experiments and simulations, increasing segregation strength at $\phi_B = 0.55$ results in a change of morphology from gyroid to perforated lamellae, while increasing segregation strength at $\phi_B = 0.75$ does not change the morphology. The HEX phase is obtained at $\phi_B = 0.75$ when the segregation strength is reduced, relative to that necessary to obtain for the gyroid phase (see Figure 4). One discrepancy between theory and experiment is that the perforations in the simulated PL

phase do not lie on a lattice while those in the experiment² are clearly ordered on a hexagonal lattice.

In refs 20 and 21 we have argued that the “effective” driving force for microphase separation is well-approximated by $p^2\chi N$. The phase behavior obtained in our minimal model is shown on a $p^2\chi N$ versus ϕ_B plot in Figure 5. Also shown in Figure 5 are representative snapshots of L/PL, G, L, and HEX phases. Our minimal model suggests that $p^2\chi N$ at the ODT is a weak nonmonotonic function of ϕ_B . The values of $p^2\chi N$ at the ODT at $\phi_B = 0.50$ and $\phi_B = 0.73$ are surprisingly similar (34 ± 3).

The above results show changes in morphology as the block copolymer composition is changed by changing N_B , keeping length and the ratio of A to S segments in the ionic block fixed. This was done because the same approach was used to vary the compositions of the copolymers used in the experiments described in Figure 1. In principle, one could also change block copolymer composition by changing N_B , keeping N , the overall chain length fixed. While we have not the entire set of new simulations to examine this effect, we did examine the effect of chain length on a particular copolymer: S65. We studied the self-assembly of two copolymers that were similar to S65, but with double the chain length. We studied the following sequence distributions: SSSSSSAAAAAAAASSSSSSSS-AAAAAASSSSSS-62B (S65b) and SSSAAAASSSSAAASSSSSS-AAAASSSSAAASSS-62B (S65c). In both cases, we observe two kinds of phases: L and disordered with an ODT at $T^* = 7.4$ for S65b and $T^* = 8.0$ for S65c. The value of $p^2\chi N$ at the ODT is 26.6, which is more-or-less consistent with the phase behavior depicted in Figure 5. For completeness, we show the C_v versus T^* plot for S65b in Figure 6. The overall features on this plot are very similar to those seen in Figure 3a where we report results obtained from S65. The main difference is that the observed features are shifted to larger T^* values, consistent with the differences in N . This is consistent with the experimental observations reported in Table 1 where lamellae-to-disorder transitions were observed in samples A1, A2, and A3 that have varying N but fixed compositions that are similar to that used in these simulations. In the case of the S65c, we observed unequilibrated nanostructures in about 25% of the simulations

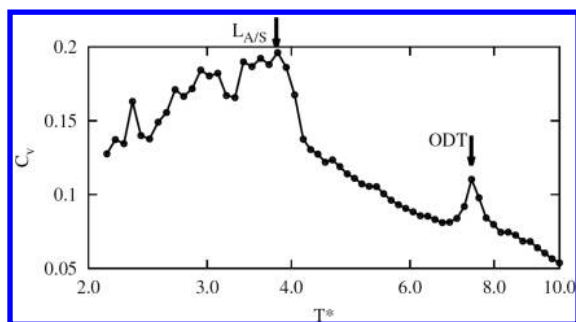


Figure 6. Heat capacity, C_p , as a function of T^* for sample S65b. The arrows indicate ODT at $T^* = 7.4$ and layering of S-segments in the A-rich lamellae at $T^* = 3.8$ ($L_{A/S}$).

in the ordered state. It is clear that these simulations are at the upper limit of the computing power available to us.

CONCLUDING REMARKS

We performed Monte Carlo simulations using a minimal lattice model with short-range interactions to investigate morphology of block copolymers wherein ionic segments are confined to one of the blocks. Results of simulations, performed on 14 different kinds of chains, point to the following conclusions:

1. We observe a qualitative agreement of the simulation data with previously published experimental data obtained from PSS–PMB copolymers presented in Figure 1.
2. Lamellar and perforated lamellar phases are stable over a wide window of compositions from $\phi_B = 0.23$ to $\phi_B = 0.73$. The formation of lamellar phases in the high $p^2\chi N$ limit is in agreement with the sSSL theory of Semenov et al.^{8,9}
3. HEX phases, expected in highly asymmetric copolymers such as those with $\phi_B = 0.73$, are only seen in the weak segregation limit.
4. The value of $p^2\chi N$ at the ODT is remarkably insensitive to ϕ_B .

Points 2–4 are predictions, as experiments aimed at addressing them have not yet been conducted. In spite of the many limitations of our minimal model, it provides a rational basis for the unexpected results shown in Figure 1. It appears that some aspects of microphase separation in low dielectric constant block copolymers with ionic segments can be modeled by considering the ionic segments to be highly incompatible with the nonionic segments and that this incompatibility can be approximated by a short-range Flory–Huggins interaction parameter.

ASSOCIATED CONTENT

Supporting Information

Movie S70_T*_2_47. This material is available free of charge via the Internet at <http://pubs.acs.org>.

AUTHOR INFORMATION

Corresponding Author

*E-mail mbanasz@amu.edu.pl (M.B.) and nbalsara@berkeley.edu (N.P.B.).

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

P.K. and M.B. gratefully acknowledge the research grant from the Polish NCN No. DEC-2012/07/N/ST4/00293 and the computational grant from the Supercomputing and Networking Center (PCSS) in Poznan, Poland. NPB's work was supported by the Electron Microscopy of Soft Matter Program supported by the Office of Basic Energy Sciences, Materials Sciences and Engineering Division, U.S. Department of Energy, under Contract DE-AC02-05CH11231. We thank Tim Lodge for educational discussions, particularly for bringing the sSSL work to our attention.

REFERENCES

- (1) Wang, X.; Yakovlev, S.; Beers, K. M.; Park, M. J.; Mullin, S. A.; Downing, K. H.; Balsara, N. P. *Macromolecules* **2010**, *43*, 5306.
- (2) Park, M. J.; Balsara, N. P. *Macromolecules* **2008**, *41*, 3678.
- (3) Hickner, M. A.; Ghassemi, H.; Kim, Y. S.; Einsla, B. R.; McGrath, J. E. *Chem. Rev.* **2004**, *104*, 4587.
- (4) Mauritz, K. A.; Moore, R. B. *Chem. Rev.* **2004**, *104*, 4535.
- (5) Tan, N. C. B.; Liu, X.; Briber, R. M.; Peiffer, D. G. *Polymer* **1995**, *36*, 1969.
- (6) Zhou, N. C.; Xu, C.; Burghardt, W. R.; Composto, R. J.; Winey, K. I. *Macromolecules* **2006**, *39*, 2373.
- (7) Banaszak, M.; Clarke, J. H. *Phys. Rev. E* **1999**, *60*, 5753.
- (8) Semenov, A. N. *Macromolecules* **1993**, *26*, 6617.
- (9) Semenov, A. N.; Nyrkova, I. A.; Khokhlov, A. R. *Macromolecules* **1995**, *28*, 7491.
- (10) Leibler, L. *Macromolecules* **1980**, *13*, 1602.
- (11) Fredrickson, G. H.; Helfand, E. J. *Chem. Phys.* **1987**, *87*, 697.
- (12) Lodge, T. P.; Hillmyer, M. A.; Zhou, Z. *Macromolecules* **2004**, *37*, 6680.
- (13) Rabin, Y.; Marko, J. F. *Macromolecules* **1991**, *24*, 2134.
- (14) Wang, Z. G. *J. Chem. Phys.* **2002**, *117*, 481.
- (15) Kumar, R.; Muthukumar, M. J. *Chem. Phys.* **2007**, *126*, 214902.
- (16) Nakamura, I.; Balsara, N. P.; Wang, Z.-G. *Phys. Rev. Lett.* **2011**, *107*, 198301.
- (17) Nakamura, I.; Wang, Z.-G. *Soft Matter* **2012**, *8*, 9356.
- (18) Sing, C. E.; Zwanikken, J. W.; de la Cruz, M. O. *Phys. Rev. Lett.* **2013**, *111*, 168303.
- (19) Sing, C. E.; Zwanikken, J. W.; de la Cruz, M. O. *ACS Macro Lett.* **2013**, *2*, 1042.
- (20) Knychala, P.; Banaszak, M.; Park, M. J.; Balsara, N. P. *Macromolecules* **2009**, *42*, 8925.
- (21) Knychala, P.; Dziecielski, M.; Banaszak, M.; Balsara, N. P. *Macromolecules* **2013**, *46*, 5724.
- (22) Lennon, E. M.; Katsov, K.; Fredrickson, G. H. *Phys. Rev. Lett.* **2008**, *101*, 138302.
- (23) Matsen, M. W.; Schick, M. *Phys. Rev. Lett.* **1994**, *72*, 2660.
- (24) Eitouni, H. B.; Rappl, T. J.; Gomez, E. D.; Balsara, N. P.; Qi, S.; Chakraborty, A. K.; Frechet, J. M. J.; Pople, J. A. *Macromolecules* **2004**, *37*, 8487.
- (25) Eitouni, H. B.; Balsara, N. P. In *Physical Properties of Polymer Handbook*; Mark, J. E., Ed.; Springer: New York, 2007; Chapter 19.
- (26) Matsen, M. W.; Bates, F. S. *Macromolecules* **1996**, *29*, 1091.
- (27) Goswami, M.; Kumar, R.; Sumpter, B. G.; Mays, J. J. *Phys. Chem. B* **2011**, *115*, 3330.
- (28) Elabd, Y. A.; Napadensky, E.; Walker, C. W.; Winey, K. I. *Macromolecules* **2006**, *39*, 399.
- (29) Baughman, T. W.; Chan, C. D.; Winey, K. I.; Wagener, K. B. *Macromolecules* **2007**, *40*, 6564.
- (30) Rubatat, L.; Li, C.; Dietsch, H.; Nykanen, A.; Ruokolainen, J.; Mezzenga, R. *Macromolecules* **2008**, *41*, 8130.
- (31) Seitz, M. E.; Chan, C. D.; Oppen, K. L.; Baughman, T. W.; Wagener, K. B.; Winey, K. I. *J. Am. Chem. Soc.* **2010**, *132*, 8165.
- (32) Hall, L. M.; Seitz, M. E.; Winey, K. I.; Oppen, K. L.; Wagener, K. B.; Stevens, M. J.; Frischknecht, A. L. *J. Am. Chem. Soc.* **2012**, *134*, 574.

- (33) Wang, X.; Goswami, M.; Kumar, R.; Sumpter, B. G.; Mays, J. *Soft Matter* **2012**, *8*, 3036.
- (34) Pakula, T. *Macromolecules* **1987**, *20*, 679.
- (35) Banaszak, M.; Wołoszczuk, S.; Pakula, T.; Jurga, S. *Phys. Rev. E* **2002**, *66*, 031804.
- (36) Pakula, T. In *Simulation Methods for Polymers*; Kotelyanskii, M., Theodorou, D. N., Eds.; Marcel Dekker: New York, 2004; Chapter 5.
- (37) Swendsen, R. H.; Wang, J. S. *Phys. Rev. Lett.* **1986**, *57*, 2607.
- (38) Earl, D. J.; Deem, M. W. *Phys. Chem. Chem. Phys.* **2005**, *7*, 3910.
- (39) Lewandowski, K.; Knychała, P.; Banaszak, M. *Comput. Methods Sci. Technol.* **2010**, *16*, 29.