# First-Order Disordered-to-Lamellar Phase Transition in Lithium Salt-Doped Block Copolymers

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ABSTRACT: We study the microphase separation of block copolymer electrolytes containing lithium salts. Taking poly(ethylene oxide)-b-polystyrene (PEO-b-PS) as an example, we show that in the presence of lithium salts the disordered-to-lamellar phase transition becomes first-order even at the level of mean-field theory, with a moderate range of temperature in which both the disordered and lamellar phases coexist, and different salt concentration in the coexisting phases. The coexistence arises from the different partitioning of the salt ions between the disordered phase and the lamellar phase, driven primarily by the solvation energy of anions. A striking consequence of the coexistence is that heating a lamellar phase into the coexistence region leads to increased order in the remaining lamellar phase.
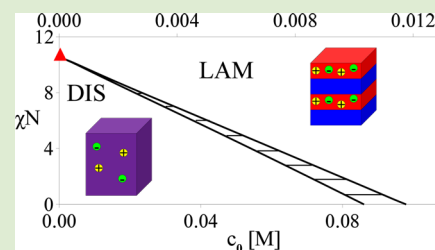
Salt-doped block copolymers consisting of ion-dissolving and inert blocks constitute a new class of material that combines ionic conductivity with mechanical robustness. In the energy arena, this hybrid functionality is being exploited for rechargeable lithium battery applications.[1−3]

At the level of mean-field theory as first developed by Leibler,[4] the transition from the disordered state to the lamellar phase of salt-free AB block copolymers is second order. For symmetric diblock copolymers, the transition occurs at $\chi N = 10.495$, where N is the number of segments in the polymer chain and χ is the Flory−Huggins interaction parameter. The second-order nature of the transition remains unaltered (at the level of mean-field theory) when one or both blocks are charged.[5] However, Fredrickson and Helfand showed that composition fluctuation makes this transition first-order,[6] with an order parameter at the transition that varies with the degree of polymerization as $N^{-1/6}$, thus approaching a second-order transition in the limit of infinite chain length. In this work, we show that salt doping makes the disordered-to-lamellar transition first order even at the level of mean-field theory, and the discontinuity in the transition persists at infinite chain length.

Experimentally, the transition from disordered to lamellar phases in poly(ethylene oxide)-b-polystyrene (PEO-b-PS) containing lithium bis(trifluoromethylsulfonimide) (LiTFSI) salt has recently been studied by small-angle X-ray scattering (SAXS) and ionic conductivity measurements.[7,8] Near the transition, the scattering intensity exhibits a superposition of both sharp and broad peaks that persists in a temperature range. While the origin of this superposition has yet to be clarified by theory, analysis of both the SAXS and conductivity data by Teran et al.[8] supports the scenario of coexistence between the disordered phase and the lamellar phase in a finite range of temperature, as anticipated in ref 7. The abrupt increase in the conductivity across the transition[8] is also consistent with a first-order phase change. While one might argue that a first-order transition could be explained by the Fredrickson and Helfand fluctuation mechanism,[6] the transition in that theory occurs at a specific transition temperature for a given block composition, whereas the suggested phase coexistence in the block copolymer electrolytes extends over a relatively wide temperature range (110−118 °C). Therefore, fluctuation is unlikely to be the primary mechanism for this coexistence.

We have recently developed a theory for understanding the effects of salt doping on the miscibility between the constituent diblocks and the domain spacing of the ordered phases[9,10] in block copolymers such as PEO-b-PS. A key ingredient in our theory is the preferential solvation of the anion by the more polar component (e.g., PEO); the anions effectively play the role of a selective solvent, making the two blocks less miscible. We expect this preference to lead to different partitioning of the salt ions between the disordered phase and the lamellar phase, which can then give rise to a first-order transition. However, in contrast to a neutral selective solvent, the partitioning of the salt ions between the two phases depends on the electrostatic potential arising from the Coulomb interactions. In the absence of the preferential solvation energy, refs 5, 9, and 10 showed that electrostatic interactions alone would make the two blocks more miscible. Our theory treats the coupled effects of the preferential solvation energy and electrostatic interactions. We now use this theory to examine the full behavior of the disordered-to-lamellar phase transition.

We consider n_c AB diblock copolymers of N segments per chain, and n_0 cations (Li⁺) and n_0 monovalent anions (X⁻) in volume V. The number of A and B segments in the block copolymer chain is N_A and N_B, respectively. The monomer

volumes for A and B and the volumes of the Li$^+$ ion and anion are, respectively, v_A, v_B, v_+, and v_-. For easy reference to the
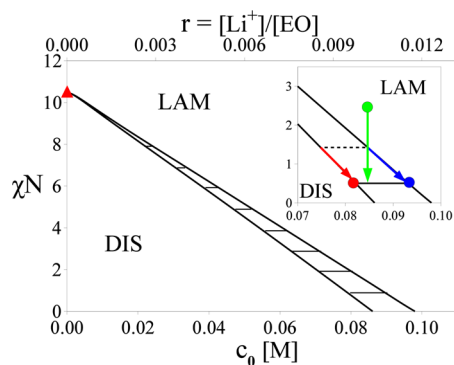

Figure 1. Phase diagram containing the lamellar phase (LAM) and disordered phase (DIS) for $\varepsilon_B = 4.0$. The shaded area indicates the phase coexistence. The red triangles correspond to the mean-field, second-order critical point of the salt-free block copolymer computed by Leibler.[4] The inset shows how the salt concentration changes along the disordered branch and the ordered branch of the phase boundaries as χN is decreased.

polymers of interest in experiments, we refer to A as the PEO block and B as the PS block. However, in the numerical calculations, we do not use the molecular parameters specific to the PEO−PS systems. Rather, we consider a generic diblock copolymer with qualitatively similar interactions with the lithium salt as the PEO−PS. In subsequent discussions, the terms PEO block and PS block are not to be taken literally but rather refer to PEO-like and PS-like blocks. To highlight the effects of salt doping, such as electrostatic interactions, the translational entropy of the anions, and most importantly the solvation energy of the anions, we consider the simple case of symmetric diblock copolymers, with equal Kuhn length b, monomer volume ($v_A = v_B \equiv v_0$), and degree of polymerization. Since the Li$^+$ ions are small, and on account of a possible electrostriction effect,[11] we ignore the volume of the Li$^+$ (i.e., $v_+ = 0$). While it is straightforward to include the volume of the anion as was done in our earlier work,[10] in order not to be encumbered by small quantitative secondary effects due to the volume of the anion, we ignore its volume as well (i.e., $v_- = 0$). In the same spirit, we do not include the shift in the χ parameter due to the altered monomer identity as a result of Li$^+$ binding to the EO monomers.[9,10] In this work, we consider only the lamellar morphology for the ordered phases—the full phase diagram that includes other ordered morphologies will be presented in the future.

Since the binding energy between Li$^+$ and oxygen is very large,[12] the Li$^+$ ions are predominantly complexed with the EO groups.[13,14] We therefore assume that all Li$^+$ ions bind to the EO groups but are free to redistribute on the backbones of the PEO chains, subject to interaction with the anions[15] and to the fixed total number of ions. As a first approximation, we ignore coordination of the Li$^+$ by multiple oxygen groups. The binding of a Li$^+$ to the s-th EO group of the i-th polymer can be conveniently represented by an Ising-like binary variable C_{is}, such that $C_{is} = 1$ if there is a Li$^+$ on the site and $C_{is} = 0$ otherwise. The anions can be bound to the Li$^+$ on the PEO, or they can be free. Our previous study showed that the fraction of ion pairs is insignificant at low salt concentrations [Li$^+$]/[EO]

< 0.1,[9] so we will ignore ion-pair formation in the rest of this paper.

The free energy of our system is constructed within the self-consistent field theory by using standard field theoretical techniques.[16] First, we introduce the coarse-grained density field of the various components by a set of identity transformations. We then sum over the ion and chain degrees of freedom—this includes summing over the binding variable C_{is} and integrating the coordinates of the anions and the polymers. The full details of the derivation are presented in ref 10. The resulting variational Helmholtz-free energy functional in units of kT for the lithium salt-doped block copolymer is

$$
\begin{aligned}
F = &\int d\vec{r} \rho_0 \eta \left[\sum_\alpha \phi_\alpha - 1 \right] - n_c - n_c \ln \left[\frac{\xi_c V Q_c(\omega_p, \omega_+)}{n_c} \right] \\
&- n_0 - n_0 \ln \left[\frac{\xi_- V Q_-(\omega_-)}{n_0} \right] + \int d\vec{r} \left[-\frac{\varepsilon_r}{8\pi l_0} \left| \nabla \psi \right|^2 \right. \\
&\left. + \psi(c_+ - c_-) \right] - \sum_{p=A,B} \int d\vec{r} \rho_0 \omega_p \phi_p - \sum_{\gamma=+,-} \int d\vec{r} \omega_\gamma c_\gamma \\
&+ \int d\vec{r} (V_{Born} c_- + \chi \phi_A \phi_B)
\end{aligned}
\tag{1}
$$

Here, $c_\gamma(\vec{r})$ is the density field of the ion; $\phi_p(\vec{r})$ is the local volume fraction of the p block; $\omega_\alpha(\vec{r})$ is a conjugate field of the species α; $\eta(\vec{r})$ is the incompressibility field; and $\psi(\vec{r})$ is the electrostatic potential. We have introduced a reference density, $\rho_0 = 1/v_0$, to make η dimensionless. ξ_c and ξ_- are the internal partition functions of the polymers and the free anions. Q_c and Q_- are the configuration partition functions of a single Gaussian-chain block copolymer and an anion. V_{Born} is the solvation energy of the anion. χ is the intrinsic Flory−Huggins parameter for the salt-free polymer.

The terms associated with ψ arise from the Coulomb interaction between the ions. In general, the dielectric constant ε_r depends on the composition in some complicated manner. In this paper, we assume a simple volume-fraction-weighted average, $\varepsilon_r(\vec{r}) = \varepsilon_A \phi_A(\vec{r}) + \varepsilon_B \phi_B(\vec{r})$, where ε_A and ε_B are the dielectric constants of the block A and the block B, respectively. We have also introduced the vacuum Bjerrum length, $l_0 = e^2/(4\pi\varepsilon_0)$, where e is the elementary charge and ε_0 is the electric permeability of vacuum.

The solvation free energy V_{Born} plays a crucial role in our theory. Unfortunately, no simple theory exists for the solvation of small ions in polymeric liquid mixtures. Therefore, we make the simplest approximation by taking the solvation energy to be the Born energy of an ion in a dielectric medium with local dielectric constant $\varepsilon_r(\vec{r})$, $V_{Born}(\vec{r}) = e^2/[8\pi a \varepsilon_0 \varepsilon_r(\vec{r})] = l_0/[2a\varepsilon_r(\vec{r})]$, where a is the Born radius of the anion.

The self-consistent mean-field equations are obtained by the variation condition, $\delta F/\delta \Omega = 0$, where Ω is a generic notation for any of the field variables in eq 1.[10] The spatially uniform solution of the self-consistent mean-field equations provides the free energy of the disordered phase. For the lamellar phase, the equations are solved on grids spanning one period of the lamellae $[0,D]$, with 200 grid points. The free energy is then minimized with respect to the lamellar period D. For easy reference, we employ the same set of parameters as in ref 10: $N = 200$, $\varepsilon_A = 7.5$, $N_A/N = 0.5$, $v_0 = 0.1$ [nm^3], $l_0 = 43.6$ [nm], $b = 0.56$ [nm], and $a = 0.38$ [nm].

The free energy given by eq 1 applies to a closed system having a fixed number of polymer chains and salt concen-

trations. For the purpose of determining the phase coexistence, it is more convenient to introduce the thermodynamic potential $W = F - \mu c_s V$, which is the free energy corresponding to a semiclosed system where the ions are open to a reservoir with the chemical potential μ and c_s is the overall salt concentration in the system. We then minimize W with respect to c_s for the disordered and lamellar phases, respectively. By varying μ, we obtain the free energy density $w \equiv W/V$ as a function of μ for each phase. Phase coexistence is located by equality of w for the disordered and lamellar phases at the same value of μ, i.e., by the crossing of the w vs μ curves of the two phases.

In Figure 1 we show the calculated phase diagram of the lamellar and disordered phases. The shaded region represents phase coexistence. At a given temperature (corresponding to a given value of χ), the coexisting salt concentrations in the disordered phase and in the lamellar phase are given, respectively, by the values on the left and right boundaries. At a given overall salt concentration within the coexistence boundaries, the lever rule determines the amounts of the coexisting salt concentrations in the disordered and lamellar phases. Clearly, the coexisting salt concentration in the lamellar phase is larger than that in the disordered phase, reflecting the preference of the salt ions for the lamellar phase. It is also obvious that at a given overall salt concentration the order-disorder transition (ODT) spans *a range* of temperatures bracketed by the upper and lower boundaries of the coexistence region. As the overall salt concentration decreases, the two lines converge to Leibler's critical value 10.495[4] for the second-order phase transition of the salt-free symmetric block copolymer. (The slopes of these two lines also converge because of the critical point nature of this limit.)

From Figure 1, we note that addition of salt considerably stabilizes the lamellar phase, resulting in a significant increase in the ODT temperature. For example, using the temperature dependence in the Flory-Huggins parameter for PEO and PS, $\chi = -7.05 \times 10^{-3} + 21.3/T$[17] with $N = 200$, at an overall salt concentration, $c_0 = 0.02$ [M], the lamellar phase remains stable until 163 °C, and complete melting of the lamellar phase occurs at 173 °C. In contrast, the mean-field critical temperature of the salt-free PEO-b-PS system (85 °C) is much lower. For easy reference, we list some selective corresponding values between χN and T in Table 1.

Table 1. χN for Different Temperatures with $N = 200$[a]

T [°C]	80	100	150	200	250	300
χN	10.65	10.01	8.66	7.60	6.73	6.02

[a]$\chi = -7.05 \times 10^{-3} + 21.3/T$.[17]

The Fredrickson-Helfand theory predicts that concentration fluctuation should lead to stabilization of the disordered phase.[6,18] Thus, if coexistence in the salt-doped block copolymers was due to composition fluctuation, then the ODT temperature should *decrease* relative to the mean-field value. On the other hand, a recent theoretical study of salt-free block copolymers by Qin and Morse[18] showed that quantitatively the mean-field theory can be quite accurate or even more accurate than the fluctuation theory when χN is small. It is thus reasonable to conclude that the strongly first-order transition and coexistence behavior in the salt-doped copolymers are primarily driven by effects of the salt ions rather than by concentration fluctuation.

To investigate the effects of the solvation energy of the ions, we have also examined the case with $\varepsilon_B = 2.6$, which is the lower bound of the experimentally measured dielectric constant of PS. With the decrease of the dielectric constant of the B-block from $\varepsilon_B = 4.0$ to $\varepsilon_B = 2.6$, there is an increased preference by the anions for the higher-dielectric A-block. As a result, the salt effects on the transition temperatures are now stronger. At a given χN (given salt concentration c_0), the concentration gap (temperature range) becomes wider than that for $\varepsilon_B = 4.0$. For example, at $c_0 = 0.025$ [M], the width of the coexistence region in χN is $\Delta \chi N = 0.3$ for $\varepsilon_B = 4.0$ and $\Delta \chi N = 1.8$ for $\varepsilon_B = 2.6$, respectively. Also, there is more significant curvature in the coexistence curves for $\varepsilon_B = 2.6$ than for $\varepsilon_B = 4.0$.

Unlike salt-free diblock copolymers where the phase behavior is governed by the combination χN, for the salt-doped system, both χ and N affect the phase behavior individually. For example, if we take a shorter chain length $N = 100$, the width of the coexistence region widens at $\chi N = 2$, and the salt concentration at the disordered and lamellar phase boundaries are 0.144 [M] and 0.170 [M], respectively, compared to 0.070 [M] and 0.079 [M] for $N = 200$.

We now consider the behavior of the order parameter in the lamellar phase, $\sigma(\vec{r}) \equiv (\phi_A(\vec{r}) - f_A)/f_A$, at the transition. $\sigma(\vec{r})$ is the scaled difference in the local A monomer concentration from its average value. We denote the maximum of $\sigma(\vec{r})$ (the value in the middle of the A domain) as σ. For salt-free systems, mean-field theory[4] predicts that σ increases continuously from 0 as χN is increased past the critical value (10.495 for symmetric diblocks). With the addition of salt, the appearance of the lamellar phase from the disordered phase becomes discontinuous, with a jump in the order parameter from 0 in the disordered phase to a finite value in the lamellar phase. In Figure 2, we plot the value of σ on the boundary of the lamellar
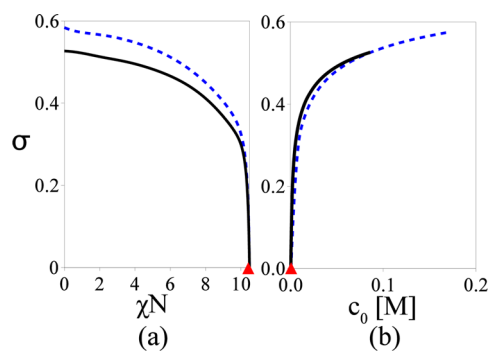

Figure 2. Value of the order parameter σ at the lamellar phase boundary (upper curve in Figure 1). The red triangles correspond to the mean-field, second-order critical point of the salt-free block copolymer computed by Leibler.[4] Black solid line and blue dashed line correspond to $N = 200$ and $N = 100$, respectively. (a) σ vs χN and (b) σ vs c_0 [M].

phase as a function of χN [Figure 2(a)] and as a function of the salt concentration c_0 [Figure 2(b)]. We emphasize that in these figures both χN and c_0 vary according to the relationship given by the upper curve in the phase diagram in Figure 1. Clearly, as χN decreases (c_0 increases), the order parameter at the transition increases. Except in the vicinity of the critical point ($c_0 = 0$, $\chi N = 10.495$), the order parameter is quite large. Thus at any moderate salt concentrations, the transition from disordered to lamellar phase is strongly first-order. There is some quantitative effect of the molecular weight on σ as shown

by the comparison between $N = 200$ (solid line) and $N = 100$ (dashed line) in Figure 2, but overall the two sets of curves behave quite similarly and converge at the critical point.

The molecular weight dependence in the order parameter of the transition in our theory differs from that in the fluctuation-induced first-order transition in the Fredrickson−Helfand theory.[6] In Figure 3, we show the asymptotic behavior of the
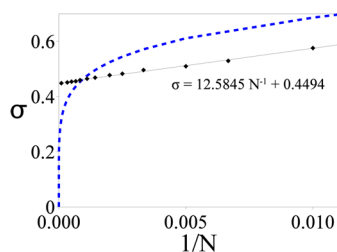

$$\sigma = 12.5845\,N^{-1} + 0.4494$$

Figure 3. Value of the order parameter σ at the lamellar phase boundary as a function of $1/N$ for $\chi N = 2$. The points and line denote our calculated results and linear regression. The blue dashed curve denotes the corresponding quantity predicted by the Fredrickson−Helfand theory,[6] which gives a molecular weight dependence of $\sigma = 1.4786/N^{1/6}$.

order parameter σ in the limit of high molecular weight, plotted as a function of $1/N$, at $\chi N = 2$ for our salt-doped system. While the order parameter discontinuity in the fluctuation theory vanishes as $N^{-1/6}$ in the limit of $1/N \to 0$, the order parameter discontinuity due to salt doping reaches a finite value $\sigma \sim 0.45$ in this limit.

The salt-induced first-order disordered-to-lamellar phase transition elucidated in this work is broadly consistent with existing experimental observations in lithium salt doped PEO-b-PS electrolytes. The simultaneous presence of sharp and broad scattering peaks in the SAXS measurements over a range of temperatures can be qualitatively explained by the finite temperature window of the transition at a fixed overall salt concentration shown by our phase diagram (Figure 1).[8] The abrupt change in the ionic conductivity through the lamellar-to-disordered transition[8] is also consistent with a first-order transition. Our work shows that adding even a small amount of lithium salts ($[Li^+]/[EO] < 0.01$) can significantly stabilize the lamellar phase, leading to large increases in the order−disorder transition temperature. This result, together with our earlier work on the shift in the spinodal of the disordered phase, explains the dramatic effects of lithium salt doping on the phase behavior of block copolymers.[9,10] Finally, we note that our phase diagram (Figure 1) and the order parameter at the transition (Figure 2) predict an intriguing phenomenon—the increase in the degree of order in the lamellae during the melting of the lamellar phase. This phenomenon arises because as a lamellar phase is heated into the coexistence region (decreasing χN in the phase diagram) the salt becomes more concentrated in the lamellar phase. The further χN decreases in the coexistence region, the higher the salt concentration in the remaining lamellar phase (see the inset in Figure 1), and hence the larger the order parameter by Figure 2. It will be interesting to confirm this prediction with future experiments.

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Notes

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REFERENCES

(1) Ruzette, A. V. G.; Soo, P. P.; Sadoway, D. R.; Mayes, A. M. *J. Electrochem. Soc.* **2001**, *148*, A537−A543.

(2) Tarascon, J. M.; Armand, M. *Nature* **2001**, *414*, 359−367.

(3) Tang, C. Y.; Hackenberg, K.; Fu, Q.; Ajayan, P. M.; Ardebili, H. *Nano Lett.* **2012**, *12*, 1152−1156.

(4) Leibler, L. *Macromolecules* **1980**, *13*, 1602−1617.

(5) Kumar, R.; Muthukumar, M. *J. Chem. Phys.* **2007**, *126*, 214902.

(6) Fredrickson, G. H.; Helfand, E. *J. Chem. Phys.* **1987**, *87*, 697−705.

(7) Wanakule, N. S.; Panday, A.; Mullin, S. A.; Gann, E.; Hexemer, A.; Balsara, N. P. *Macromolecules* **2009**, *42*, 5642−5651.

(8) Teran, A. A.; Mullin, S. A.; Hallinan, D. T.; Balsara, N. P. *ACS Macro Lett.* **2012**, *1*, 305−309.

(9) Nakamura, I.; Balsara, N. P.; Wang, Z.-G. *Phys. Rev. Lett.* **2011**, *107*, 198301.

(10) Nakamura, I.; Wang, Z.-G. *Soft Matter* **2012**, *8*, 9356−9367.

(11) Bockris, J. O.; Reddy, A. K. N. *Modern Electrochemistry 1. Ionics*; Plenum: New York, 1998.

(12) Borodin, O.; Smith, G. D.; Douglas, R. *J. Phys. Chem. B* **2003**, *107*, 6824−6837.

(13) Borodin, O.; Smith, G. D. *Macromolecules* **1998**, *31*, 8396−8406.

(14) Donoso, J. P.; Bonagamba, T. J.; Panepucci, H. C.; Oliveira, L. N.; Gorecki, W.; Berthier, C.; Armand, M. *J. Chem. Phys.* **1993**, *98*, 10026−10036.

(15) Müller-Plathe, F.; van Gunsteren, W. F. *J. Chem. Phys.* **1995**, *103*, 4745−4756.

(16) Fredrickson, G. H. *The Equilibrium Theory of Inhomogeneous Polymers*; Oxford University Press: New York, 2006.

(17) Zhu, L.; Cheng, S. Z. D.; Calhoun, B. H.; Ge, Q.; Quirk, R. P.; Thomas, E. L.; Hsiao, B. S.; Yeh, F.; Lotz, B. *Polymer* **2001**, *42*, 5829−5839.

(18) Qin, J.; Morse, D. C. *Phys. Rev. Lett.* **2012**, *108*, 238301.