# Thermodynamics of Salt-Doped Block Copolymers

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ABSTRACT: We provide a perspective on the thermodynamics of salt-doped block copolymer electrolytes consisting of ion-conducting and inert blocks, taking poly(ethylene oxide)-*b*-polystyrene and lithium salts as an example. We focus on the origin for enhanced immiscibility between the constituent blocks upon addition of lithium salts and discuss issues from selected experiments and from our recent self-consistent field study.
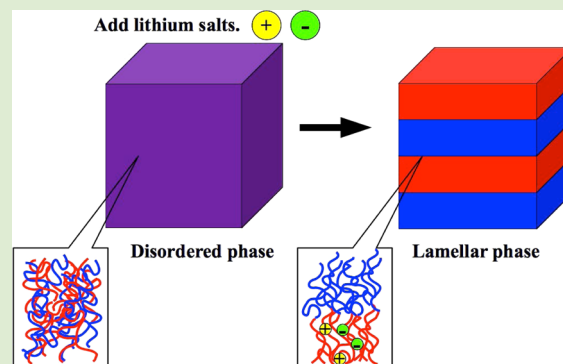
There is considerable current interest in polymers containing salt ions,[1,2] such as lithium ion (Li^{+}) doped block copolymers, as new energy materials. A promising system for rechargeable battery applications consists of block copolymers with an ion-dissolving block,[2,3] typically poly(ethylene oxide) (PEO), and a nonconducting block such as polystyrene (PS),[1,3] as it combines the ionic mobility of the Li^{+} ions with the mechanical stability of the diblock copolymer microstructure. Electrochemical stabilities and mechanical robustness can be tuned by designing the system, for example, through the selection of the anion types, molecular weight of the two blocks, and the chemical structure and the architecture of the block copolymers.

The primary interest for Li-ion battery applications is the ionic conductivity; however, conductivity is intimately related to the thermodynamics of the lithium salt-block copolymer mixture and the distribution of ions in the block copolymer domains.[4,5] These latter two aspects are the focus of this perspective.

Experimentally, the addition of lithium salts such as lithium bis(trifluoromethylsulfonyl)imide (LiTFSI) and lithium trifluoromethanesulfonate (LiCF$_3$SO$_3$) has been shown to have drastic effects on the order−order and order−disorder transitions in block copolymers. Ruzette et al.[6] first reported large increases (by 10−100 °C) in the order−disorder transition temperature in a LiCF$_3$SO$_3$ doped block copolymer [poly(methyl methacrylate)-*b*-poly(oligo oxyethylene methacrylate)] compared to the salt-free system, upon addition of a small amount of salt ([Li^{+}]/[EO] < 0.05). Furthermore, the observed phase diagrams of the salt-doped block copolymers are topologically quite different from that of the salt-free system.[7,8] These effects have been analyzed to imply an increase in the effective Flory parameter χ_{eff} from its intrinsic value χ for the segmental interaction between the different blocks. This change in the effective Flory parameter χ_{eff} has been quantitatively evaluated by the increase in the domain spacing D of the lamellar and cylindrical structures using the dependence of D on χ in salt-free systems ($D \sim \chi^\nu$, with $\nu = 1/6$ for the strong segregation regime),[9,10] and the shift in the spinodal temperature of the disordered phase or order−disorder transition temperature.[8,11,12]

From a theoretical point of view, lithium salt-doped block copolymers constitute a new class of material as ion-containing polymers.[13,14] Since the binding energy between Li^{+} and oxygen is very large, the Li^{+} ions are strongly bound to the EO groups, making PEO with its bound Li^{+} ions effectively a polyelectrolyte, but with annealed charge distribution due to the ability of the Li^{+} ions to redistribute on the backbone of the PEO. Previous theories for diblock copolymers with a charged block and a neutral block predict enhanced miscibility between the blocks compared to the uncharged system,[15−17] contrary to experimental observations. Moreover, the effective χ_{eff} shows a systematic dependence on the radius of the counterions (anions).[8−10]

We have recently developed a theory for the thermodynamics of lithium salt-doped block copolymer melts.[13,14] A key ingredient in our theory is the solvation energy of anions (because the Li^{+} ions are strongly bound to the EO groups, we do not explicitly consider the solvation energy of the Li^{+} ion): For a free anion, we ascribe a composition dependent Born energy $V_{Born} = e^2/[8\pi a\varepsilon_0\varepsilon_r(\vec{r})]$, where a is the radius of the ion, e is the elementary charge, ε_0 is electric permeability of vacuum, and ε_r is the local dielectric constant. We assume ε_r to be given by a simple volume-fraction-weighted average, $\varepsilon_r(\vec{r}) =$

$\varepsilon_{PEO}\phi_{PEO}(\vec{r}) + \varepsilon_{PS}\phi_{PS}(\vec{r})$, where $\phi_{PEO}(\vec{r})$ and $\phi_{PS}(\vec{r})$, and ε_{PEO} and ε_{PS} are the volume fractions and the bulk dielectric constants of PEO and PS, respectively. The preferential solvation of anions in the higher-dielectric component (PEO) provides a large driving force for microphase separation between the blocks.

The local, composition-dependent Born energy together with the electrostatic interactions between the ionic species are treated within the self-consistent field framework for diblock copolymers, with a modified Poisson−Boltzmann equation accounting for the electrostatic interactions. A two-state Ising-like variable is introduced to indicate whether an EO has a bound Li^+ ion, which automatically results in an annealed distribution of Li^+ ions on the PEO backbone. In addition, ion-pair formation between EO-complexed Li^+ and anion (X^-) is allowed with an equilibrium constant. The minimal model requires two additional parameters to reflect the change in χ due to the altered monomer identity in the EO−Li^+ and EO−Li^+−X^- monomers, respectively.

With reasonable choice of parameters, our theory is able to capture the behavior in the effective χ_{eff}. In particular, to within orders of magnitude, the theory predicts the systematic dependence of χ_{eff} on the radius of the anions, in agreement with experiments. The predicted order−disorder boundary in the block composition and salt concentration is also in qualitative agreement with experiments.[13]

A useful insight from our theoretical analysis is the difference between the different definitions of the effective χ_{eff}. While ref 11 used the scattering peak in the disordered phase to define χ_{eff}, Epps and co-workers defined χ_{eff} by using the scaling of the domain spacing with χ for salt-free block copolymers.[9] Wanakule et al., on the other hand, used the shift in the order−disorder transition to define χ_{eff}.[8] Our analysis shows that χ_{eff} defined from the structure factor of the disordered phase is a more fundamental measure of the effective interaction between the blocks. In particular, our study shows that while the χ_{eff} determined from the structure factor of the disordered phase shows a strong dependence on the anion radius, the dependence is much weaker in the χ_{eff} defined from the domain spacing of the ordered phases. This may explain the finding in ref 10 that showed little difference in χ_{eff} derived from the domain spacing of the lamellar phase, between the ClO_4^- and TFSI anions with ionic radii of 0.24 and 0.38 Å, respectively.

In contrast to salt-free block copolymer melts where the order−disorder transition and order−order transition occur at a well-defined temperature (for a given block composition), the presence of salt changes the transition into a coexistence range because of the different partitioning of salts in the different phases. Even at the level of the mean-field theory,[18] the transition between the disordered phase and the lamellar phase becomes strongly first-order, with a significant miscibility gap for the salt. Thus, χ_{eff} derived from the disordered → lamellar transition will in general be different from the one derived from the lamellar → disordered transition. An interesting consequence of the different salt partition in the coexisting disordered and lamellar phase is that, upon partial melting of the lamellar phase, the spacing and degree of order of the remaining lamellar phase can increase. This prediction appears to have been borne out by a recent experiment.[19] For both theory and experiments, the study of the phase coexistence in the various order−disorder and order−order transitions will be quite worthy of pursuing.

The differential Born energy of the anions in the PEO and PS domains has a direct consequence on the ion distribution and electrostatic potential profile. Our SCF calculation shows local charge separation at the PEO−PS interface, with positive charge on the PS side and negative charge on the PEO side.[14] This leads to a lower electrostatic potential in the PEO than in the PS domain. In contrast, for a hypothetical system where there is no Born energy difference, charge polarization at the interface changes sign and the electrostatic potential becomes higher in the PEO than in the PS domain. While these effects may be difficult to observe directly in experiments, they will affect the ion transport.

The existence of ion pairs has a significant effect on the dependence of χ_{eff} on the salt-loading $[Li^+]/[EO]$. For the disordered (homogeneous) phase, the fraction of Li^+ in ion pairs, $x \equiv [EO\text{-}Li^+\text{-}X^-]/[EO\text{-}Li^+]$, is given by

$$\frac{x}{(1-x)^2} = \left(\frac{\alpha r \overline{\varphi}_{PEO}}{\nu_{PEO}}\right)\exp(V_{Born}) \tag{1}$$

with

$$\alpha = \frac{\exp[E_b + (\chi_1 - \chi_2)\nu_{PEO}\overline{\varphi}_{PS}]}{\xi_-} \tag{2}$$

ξ_- is the internal partition function of the free anions, E_b is the binding energy between EO-Li^+ and X^-, r is the salt loading $r = [Li^+]/[EO]$, and ν_{PEO} is the volume of an EO monomer. $\overline{\varphi}_{PEO}$ and $\overline{\varphi}_{PS}$ are the average volume fractions of PEO and PS. χ_1 and χ_2 are the monomer interaction parameters that reflect the shifts in the original χ due to the altered monomer identity in the EO-Li^+ and EO-Li^+-X^- monomers, respectively. We choose the unit of energy such that $kT = 1$. The nonlinear dependence of the ion-pair fraction x on the salt loading r results in a nonlinear dependence of χ_{eff} on r.[20] Since the increase in χ_{eff} is primarily due to the Born solvation energy V_{Born} of the free (unbound) anions, the formation of ion pairs decreases the fraction of free anions and thus gives rise to a downward curvature in χ_{eff} versus r. An interesting issue is how the form for ion-pair equilibrium becomes modified in the ordered phases. Because of charge separation, we do not expect the equilibrium condition to be given in terms of local ionic concentrations. A key challenge on the issue of ion pairs is that currently there is no agreement among theory, simulation, and experiments on the degree of ion pairing in salt-doped polymer systems.[13,21−24] Further experiments and computer simulation using more accurate force fields will be necessary to clarify this issue.

Although the χ_{eff} is a simple and useful concept for characterizing the increased effective repulsion between the two blocks with added salts, the full phase diagram of a salt-doped block copolymer in general cannot be mapped to a salt-free block copolymer with an effective χ_{eff}. Besides the fact that salt is a third species and its differential solubility in the different phases will lead to finite coexistence regions, the topology of salt-doped block copolymers[7,8] can be qualitatively different from that calculated by the SCFT of the salt-free systems.[25−27] For example, adding LiTFSI and ImTFSI salts to the PEO−PS diblock copolymers induces transitions from lamellar to cylinder and lamellar to gyroid,[8] but in salt-free systems the lamellar phase will remain intact with increasing χ. Therefore, it is desirable to theoretically construct the full phase diagram for the salt-doped block copolymers.

Our theoretical work so far has focused on the role of the differential Born energy as a driving force for increased tendency to microphase separation. While the Born energy is certainly important and yields the right order of magnitude in the change in χ_{eff}, it is not the only effect and cannot explain, for example, the relative localization of the Li^+ ions toward the center of the PEO-rich domain in the lamellar phase as the overall molecular weight is increased at fixed block composition.[28] By combing the self-consistent field method for the polymer conformation with liquid state theory for local charge organization, Sing et al. recently showed that the high charges on the polymer backbone together with the low dielectric environment results in strong correlation effects that lead to effective attraction between the charged segments, providing a driving force for phase separation in a blend of charged and uncharged polymers.[29,30] The same physics leads to the increased tendency for microphase separation in a diblock copolymer, where it is shown that the phase boundary and morphologies of block copolymers are significantly modified by the strong charge correlation effect.[31] In particular, percolated phases that are desirable for ion transport yet are inaccessible in conventional uncharged block copolymers are shown to be stabilized by the highly asymmetric correlation effects between the two blocks.

Another effect is the cross-linking induced by the multiple coordination of the Li^+ ions with the EO groups.[21,32,33] Our preliminary work shows that cross-linking has the same qualitative effects as the Born energy and is of similar order of magnitude.[34] However, the χ_{eff} due to cross-linking in general has a nonlinear dependence on the salt concentration. Therefore, thermodynamically it will be difficult to distinguish cross-linking effects from ion-pairing effects. Quantifying the relative importance of Born energy, cross-linking, and strong local charge correlation will be an important future theoretical challenge.

Most of the studies of the effects of salt-doping and charges in block copolymers have been addressed at the mean-field level. However, fluctuations are known to have profound effects on the order−disorder transitions in uncharged block copolymers. In particular, Fredrickson and Helfand[35] showed that concentration fluctuation in salt-free block copolymers stabilizes the disordered phase and changes the mean-field critical point for the disordered-to-lamellar transition into a first order transition. The fluctuation effects in salt-free diblock copolymers have been quantified by Qin and Morse[36] in a recent computer simulation study. The combination of concentration fluctuation and charge fluctuation in salt-doped block copolymers is expected to have even richer and more complex effects. It will be highly desirable to conduct computer simulation on salt-doped block copolymers.

Although our discussion, and most experimental systems, of lithium salt-doped block copolymers have been focused on PEO-b-PS, other block copolymers are also of interest. For example, a recent study of χ_{eff} determined from the ODT temperature for poly(ε-caprolactone) (PCL)-b-PEO containing $LiClO_4$ by Huang et al. has reported nonlinear dependence of χ_{eff} with the salt loading $[Li^+]/[EO]$.[37] Because both the carbonyl group in PCL and the ether group in PEO dissolve Li^+ ions, the change in χ_{eff} is unlikely due to the solvation energy effect; cross-linking is a more likely explanation. It will be necessary to develop a theory for systems where both blocks dissolve the lithium salts.

Finally, from the theoretical viewpoint, continuum dielectric treatment of the solvation energy of ions in dielectric mixtures is clearly a gross approximation.[38−40] In ref 38, it is shown that the solvation energy of an ion is not determined by the bulk dielectric constants, but is primarily determined by the electrostatic response of the solvent molecules in close proximity to an ion, which is typically on the order of Å's. Recently it has been shown that polymer mixtures exhibit nonmonotonic behavior in the dielectric function near an ion in the range of 1 nm.[40] Thus, the bulk dielectric constants ε_{PEO} and ε_{PS} in V_{Born} must be regarded as purely phenomenological fitting parameters and how to obtain the solvation energy of ions in a polymeric liquid from a molecular description remains an outstanding challenge.

In summary, salt-doped polymers constitute an important class of energy materials with rich and complex thermodynamic behaviors. Understanding their thermodynamic behaviors is essential for a mechanistic understanding of the ion transport properties in these systems. The study of the thermodynamic behaviors in these salt-doped polymers involves a rich interplay between microscopic physics occurring at length scales a few Å's, long-range electrostatic interactions, and polymer physics.

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Notes
The authors declare no competing financial interest.

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