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Chimney-Shaped Phase Diagram in a Polymer Blend Electrolyte

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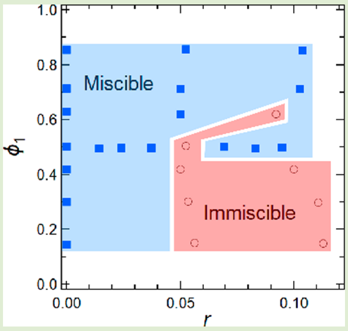
ABSTRACT: The phase behavior of polymer blend electrolytes comprising poly(ethylene oxide) (PEO)/poly(methyl methacrylate) (PMMA)/lithium bis(trifluoromethanesulfonyl)-imide (LiTFSI) was determined using a combination of light and small angle neutron scattering (SANS) experiments. The results at a fixed temperature (110 °C) are presented on a PEO concentration versus salt (LiTFSI) concentration plot. The blends are miscible at all PEO concentrations in the absence of salt. With added salt, a region of immiscibility is obtained in PEO-lean polymer blend electrolytes; blends rich in PEO remain miscible at most salt concentrations. A narrow region of immiscibility juts into the miscible region, giving the phase diagram a chimney-like appearance. The data are qualitatively consistent with a simple extension of Flory−Huggins theory with a composition-dependent Flory−Huggins interaction parameter, χ, that was determined independently from SANS data from homogeneous blend electrolytes. Phase diagrams like the one we obtained were anticipated by self-consistent field theory calculations that account for correlations between ions. The relationship between these theories and measured χ remains to be established.



The effect of added salt on the phase behavior of polymers is a subject of continuing interest.[1−4] These materials may provide an avenue for enabling the next generation of rechargeable lithium batteries. In particular, mechanically robust electrolytes have the potential to enable electrodes such as lithium metal and silicon, which can lead to batteries with increased energy density.[5] In mixtures of one homopolymer and salt, there is an inverse relationship between ion transport rates and mechanical robustness;[6] strategies to improve ion transport rates generally result in a decrease in the shear (or tensile) modulus of the electrolytes. Microphase-separated block copolymer electrolytes with an ionically conductive microphase and a rigid nonconducting microphase provide one avenue for decoupling electrical and mechanical properties of polymer electrolytes.[7,8] Rational design of such systems requires an understanding of the effect of added salt on the thermodynamic interactions between chemically distinct polymers.[2−4] Polymer blend electrolytes, wherein salt is added to a mixture of two polymers, are the simplest platform for determining this effect. While numerous theoretical papers have been written on this subject,[9−15] there are relatively few experimental data sets[1,16−18] that can be used to test the predictions of the theories.

In neat polymer blends without added salt, phase diagrams are generally presented on plots of temperature versus blend composition.[19−22] In polymer blend electrolytes, the salt concentration is the new variable that affects phase diagrams in addition to temperature. Diagrams wherein the boundary between miscible and immiscible blends (at fixed temperature) is presented on plots of salt concentration versus blend composition provide one avenue for testing theoretical predictions. It may seem surprising that there are only two such experimental phase diagrams in the current literature. In pioneering work, Xie and Lodge studied the phase behavior of a polyolefin oligomer (squalane, SQ), poly(ethylene oxide) (PEO), and lithium bis(trifluoromethane) sulfonimide (LiTFSI).[1] In the absence of salt, the interactions between SQ and PEO are characterized by a positive Flory−Huggins interaction parameter, which may be interpreted as "repulsive" interactions between the polymers. As is often the case in such systems, the two homopolymers are miscible only in the low molecular weight limit (less than 1 kg/mol for the SQ/PEO case). The phase boundary reported in ref 1, when plotted with salt concentration as the *x*-axis and the volume fraction of PEO as the *y*-axis, is shaped like a dome. In the absence of a PEO, SQ/LiTFSI mixtures are immiscible. The addition of PEO leads to a miscible system, and the boundary between miscible and immiscible depends on salt concentration; the magnitude of the immiscibility window increases with increasing salt concentration. This phase behavior was shown to be quantitatively consistent with the Born-solvation-theory-based predictions of Wang[23] which accounts for the "self-energy" of the ions. The ions have a propensity to partition into the PEO-

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rich phase which is the high dielectric constant polymer, and this induces phase separation. In other words, the addition of salt leads to an increase in the effective Flory−Huggins interaction parameter between the polymers. The same qualitative phase behavior is expected based on measurements of the effective Flory−Huggins interaction parameter based on small angle neutron scattering experiments in polystyrene/PEO/LiTFSI mixtures.[18] The phase diagram for mixtures of two polymers and salt, where one of the components is PEO and the other polymer has a positive Flory−Huggins interaction parameter with PEO in the absence of salt, is shown qualitatively in Figure 1. It may be considered as the classical phase diagram of polymer blend electrolytes.

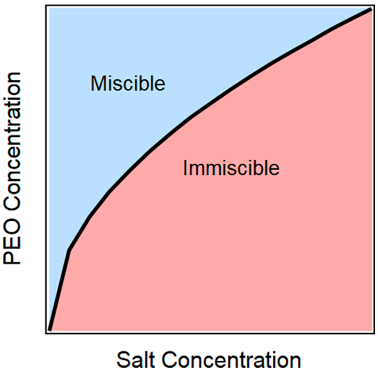

Figure 1. Classical phase diagram of a polymer blend electrolyte, a mixture of two polymers and lithium salt, mapped on a PEO concentration vs salt concentration plot. This diagram is anticipated in the case that the two polymers exhibit repulsive interactions and salt partitions selectively into the PEO-rich phase.

In addition to self-energy, the locations of ions are correlated due to Coulombic interactions that are mediated by two polymers with different dielectric constants. A theory that accounts for this was first presented by de la Cruz and co-workers.[14,24,25] In this case, phase boundaries that take on the shape of chimneys and closed loops appear when the polymer blend is characterized by a negative Flory−Huggins interaction parameter; i.e., the polymer blend is miscible in the absence of salt. The purpose of this paper is to present experimental evidence for the phase behavior of polymer blend electrolytes comprised of poly(methyl methacrylate) (PMMA), PEO, and LiTFSI. Unlike binary SQ/PEO and PS/PEO blends, which are only miscible when the molecular weights of the polymers are in the vicinity of 1.5 kg/mol,[26] PEO/PMMA blends are miscible at all molecular weights and compositions studied thus far.[27−31] The experimental phase diagram of PEO/PMMA/LiTFSI blends at a fixed temperature is presented on a PEO concentration versus salt concentration plot. In a previous study, we have reported on the phase behavior of these blends over a limited composition window based on small angle neutron scattering.[32] We augment that study with additional compositions, wherein the phase behavior was determined by light scattering. We present the first direct evidence of a chimney-shaped phase boundary in polymer blend electrolytes. Experimental data are compared with predictions based on a model presented in ref 32. In this study, we utilized PMMA with number-averaged molar mass, M_n, of 47.3 kg mol^{-1} in all blends. The other polymeric component was a combination of hPEO and dPEO polymers with M_n values ranging from 8 kg mol^{-1} to 8.5 kg mol^{-1}. We chose these molar masses to match those used in our previous PEO-PMMA/LiTFSI block copolymer study.[33] dPEO was used in blends characterized by SANS in ref 32 to obtain neutron scattering contrast. In ref 32, we presented the data on a number of blends and classified them into "miscible" and "immiscible" categories. We ran light scattering experiments on a subset of these blends to ensure that our classification based on this optics-based approach was robust. Blends characterized solely via light scattering contained only hPEO (to conserve expensive dPEO), while those characterized by both SANS and light scattering contained combinations of dPEO and hPEO. Both polymers and LiTFSI salt were dried thoroughly in an argon glovebox. Blends of PEO, PMMA, and LiTFSI were made by solution blending followed by drying. All of the steps were conducted in an argon glovebox (see ref 32 for details).

Table 1. Compositions of Blends Studied, Light Scattering Results, and Conclusions Regarding Miscibility[a]

Sample number	ϕ_1	r	P_t [%]	P_s [%]	Miscibility	Characterization method
1	0.16	0.22	0.21	7.93	Immiscible	LS
2	0.30	0	71.4	1.26	Miscible	LS + SANS
3	0.30	0.053	0.051	1.08	Immiscible	LS + SANS
4	0.30	0.11	0.74	2.49	Immiscible	LS + SANS
5	0.30	0.14	0.037	2.23	Immiscible	LS
6	0.31	0.20	0.33	12.8	Immiscible	LS
7	0.42	0	64.9	2.63	Miscible	LS
8	0.42	0.048	0.050	2.19	Immiscible	LS
9	0.42	0.098	0.016	1.09	Immiscible	LS
10	0.50	0	19.6	19.0	Miscible	LS + SANS
11	0.50	0.053	0.072	2.26	Immiscible	LS + SANS
12	0.63	0	71.4	0.68	Miscible	LS
13	0.62	0.049	20.9	9.05	Miscible	LS
14	0.62	0.092	0.085	1.58	Immiscible	LS
15	0.71	0	71.2	1.90	Miscible	LS + SANS
16	0.71	0.050	32.5	15.8	Miscible	LS + SANS
17	0.71	0.10	41.0	5.92	Miscible	LS + SANS

[a] In Table 1, P_t is the percent of power transmitted through the sample, and P_s is the percent of power scattered by the sample in the forward direction.

The compositions of the blends studied by light scattering are listed in Table 1. The entire set of samples used to determine phase behavior is given in Table S2 of the SI.

Blend compositions are defined by two parameters, ϕ_1, the volume fraction of PEO (defined as component 1) on a salt-free basis, and r, the molar ratio of LiTFSI to ether oxygens in PEO. For simplicity, we use ϕ_1 to represent the PEO volume fraction (including both hPEO and dPEO in the case of blends studied by SANS and light scattering). The volume fractions of hPEO and dPEO in each blend are given in Table S2 of the SI. We calculate ϕ_1 as

$$\phi_1 = \frac{\frac{w_1}{\rho_1}}{\frac{w_1}{\rho_1} + \frac{w_2}{\rho_2}} \tag{1}$$

and

$$\phi_2 = 1 - \phi_1 \tag{2}$$

where w_i and ρ_i are the mass and density, respectively, of component i in the blend. All of our analysis is at 110 °C where ρ_1 = 1.16 g cm^{-3} (dPEO) and ρ_2 = 1.16 g cm^{-3} (PMMA).[34] For blends comprising mixtures of hPEO and dPEO, appropriate corrections were made to account for deuteration (ρ_1 = 1.06 g cm^{-3} for hPEO). The total polymer volume fraction of our blend electrolyte is given by

$$\phi_{\text{pol}} = \frac{\frac{w_1}{\rho_1} + \frac{w_2}{\rho_2}}{\frac{w_1}{\rho_1} + \frac{w_2}{\rho_2} + \frac{w_{\text{salt}}}{\rho_{\text{salt}}}} \tag{3}$$

where w_{salt} is the mass of LiTFSI in our blend and ρ_{salt} = 2.023 g cm^{-3}.

We define salt concentration, r, as

$$r = \frac{[\text{Li}]}{[\text{EO}]} = \frac{\frac{w_{\text{salt}}}{M_{\text{LiTFSI}}}}{\frac{w_1}{M_{\text{EO}}}} \tag{4}$$

where M_{LiTFSI} = 287.09 g/mol and M_{EO} = 44.05 g/mol. For blends comprising mixtures of hPEO and dPEO, appropriate corrections were made to account for deuteration (M_{dEO} = 48.08 g/mol).

We begin by describing the model developed in ref 32 to predict the phase behavior of polymer blend electrolytes. The free energy of mixing, ΔG_m, is given by a simple extension of the Flory−Huggins theory that accounts for the presence of salt

$$v\frac{\Delta G_m}{k_B T} = \phi_{\text{pol}}\left(\frac{\phi_1 \ln \phi_1}{N_1} + \frac{\phi_2 \ln \phi_2}{N_2} + \chi(\phi_1, \phi_s, T)\phi_1\phi_2\right) \tag{5}$$

where ΔG_m is the Gibbs free energy of mixing; k_B is the Boltzmann constant; T is the absolute temperature; N_i is the number of repeat units in chain i; ϕ_i is the volume fraction of component i; v is the reference volume (set to 0.1 nm^3); the volume fraction of added salt is ϕ_s; $\phi_{\text{pol}} = 1 - \phi_s$; and the interactions between the salt and the polymers is captured by an effective χ parameter that depends not only on temperature but also on salt concentration.[2−4] Both ϕ_1 and ϕ_2 represent the volume fractions of polymers 1 and 2, respectively, on a salt-free basis. χ for PEO/PMMA /LiTFSI blends at 110 °C is given by

$$\chi(\phi_1, r) = \left(A(r) + \frac{B(r)}{3} + \frac{C(r)}{6}\right) + \left(\frac{B(r)}{3} + \frac{C(r)}{6}\right)\phi_1 + \frac{C(r)}{6}\phi_1^2 \tag{6}$$

where A, B, and C were obtained by fitting SANS data from the blends at 3 different r values. In Figure 2, we plot these fitting parameters as a function of r. Their values at intermediate values of r are given by linear interpolation

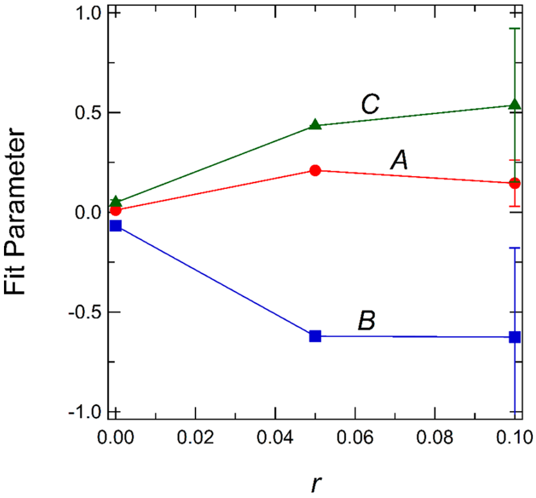

Figure 2. Fit parameters A, B, and C from ref 32 are plotted as a function of salt concentration, r. These are the parameters used in eq 6 to determine χ. The solid lines from $0 \le r < 0.05$ and $0.05 \le r < 0.10$ are used to interpolate the data: see eqs 7, 8, and 9. For the interpolation lines in the $0 \le r < 0.05$ range, $\zeta_A = 3.99$ and $\tau_A = 0.0108$; $\zeta_B = -11.1$ and $\tau_B = -0.0666$; and $\zeta_C = 7.70$ and $\tau_C = 0.0488$. For the interpolation lines in the $0.05 \le r \le 0.10$ range, $\zeta_A = -1.29$ and $\tau_A = 0.275$; $\zeta_B = -0.09$ and $\tau_B = -0.615$; and $\zeta_C = 2.06$ and $\tau_C = 0.331$. Adapted with permission from Shah, N. J.; He, L.; Gao, K. W.; Balsara, N. P. Thermodynamics and Phase Behavior of Poly(Ethylene Oxide)/Poly(Methyl Methacrylate)/Salt Blend Electrolytes Studied by Small-Angle Neutron Scattering. *Macromolecules* **2023**, *56* (7), 2889−2898. Copyright 2023 ACS Macromolecules.

$$A(r) = \zeta_A r + \tau_A \tag{7}$$

$$B(r) = \zeta_B r + \tau_B \tag{8}$$

and

$$C(r) = \zeta_C r + \tau_C \tag{9}$$

The values of ζ_i and τ_i ($i = A$, B, or C) for the two regimes, $0 \le r < 0.05$ and $0.05 \le r < 0.10$, are given in the caption of Figure 2. The phase boundary between miscible and immiscible systems is assumed to be given by the spinodal curve (details are provided in ref 32).

Next, we discuss the light scattering (LS) data. While light scattering has often been used to determine blend miscibility,[35−39] its efficacy can vary based upon the relative refractive indices of the system components.[37,40] In some cases, it is sufficient to measure the intensity of the forward-scattered light,[38] while in samples exhibiting such strong multiple scatterings they are nearly opaque. It is more informative to measure the fraction of the incident beam power that is transmitted through the sample.[1,41,42] The addition of salt to a binary polymer blend system poses further complications due to the large difference between the refractive index of salt and polymers and the partitioning of salt in the phase separated systems. In Figure 3, we plot the % of transmitted power against the % of scattered power in the forward direction (between scattering angles of 1.3 and 13°). The % scattered power varied from 1 to 19%. There was no correlation between this parameter and miscibility determined by SANS. In contrast, the measured % of transmitted power values fell clearly into two groups: the blends that were determined to be immiscible by SANS exhibited % of transmitted power values less than 1%, while blends that were determined to be miscible by SANS exhibited % of transmitted power values greater than 20% (in some cases, as high as 80%). We thus used the % of transmitted power to distinguish between miscible and immiscible samples in cases where we only had access to light scattering data. All samples that fell within the dashed box in Figure 3 were labeled immiscible, while those outside the box were labeled miscible.

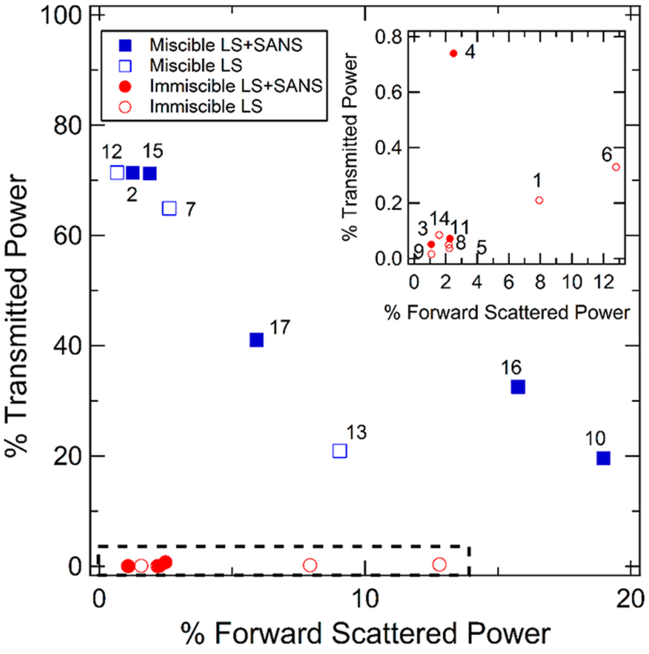

Figure 3. Plot of % transmitted power versus % forward-scattered power obtained by light scattering on PEO/PMMA/LiTFSI blends at 110 °C. Inset shows an enlargement of the dashed box at the bottom of the main plot. Data from miscible samples are indicated by squares, and data from immiscible samples are indicated by circles. Filled squares and circles represent samples characterized by both light scattering and SANS, while empty squares and circles represent samples characterized by light scattering alone. The numbers correspond to the sample numbers indicated in Table 1.

The compositions of the miscible and immiscible PEO/PMMA/LiTFSI blend electrolytes are depicted in Figure 4a on a ϕ_1 versus r plot. The phase boundary is determined by bisecting lines drawn between two adjacent data points at the miscible/immiscible boundary. The vertical line at $r = 0.045$ is a parsimonious extrapolation of the phase boundary determined at $\phi_1 = 0.5$. All salt-free PEO/PMMA blends are miscible. A region of immiscibility develops upon the addition of salt. Particularly striking is the appearance of an immiscible "chimney" in Figure 4a. This chimney is defined by two immiscible samples: $\phi_1 = 0.50$, $r = 0.053$, and $\phi_1 = 0.62$, $r = 0.092$. Several samples with compositions close to those of these two samples were miscible. In Figure 4b, we show the phase boundary for our PEO/PMMA/LiTFSI blends at 110 °C based on the model described above. The model-based boundary contains two separate immiscible regions. The lower region at $\phi_1 \leq 0.50$ is in quantitative agreement with the experimental phase diagram. The upper region, which is narrow along ϕ_1 and broad along r, is in qualitative agreement with the experimental chimney (Figure 4a). The main discrepancies between the experiments and the model are: (1) the experimentally determined upper immiscible window occurs at lower values of ϕ_1, and (2) the experimentally determined upper immiscible window is connected to the large lower immiscibility window.

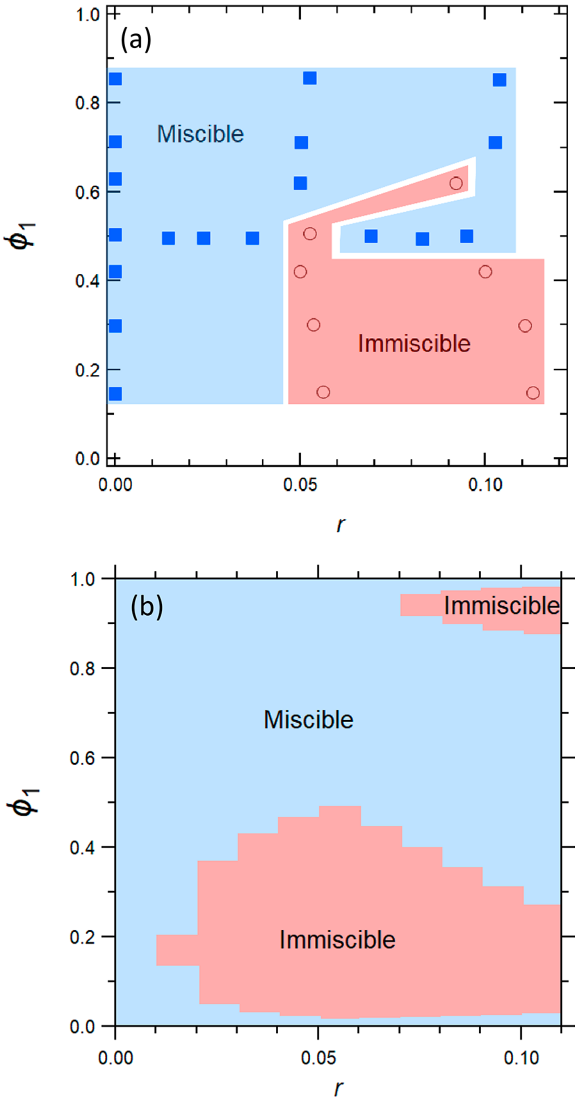

Figure 4. Phase behavior of PEO/PMMA/LiTFSI blends showing miscible and immiscible blends on a plot of salt-free volume fraction of PEO, ϕ_1, versus salt concentration, r, at 110 °C. Component 1 is PEO. (a) Experiments. Filled blue squares indicate a miscible blend, and empty circles indicate an immiscible blend. The white regions surrounding the phase diagram were not explored. (b) Model predictions.

In this study, we developed a comprehensive map of PEO/PMMA/LiTFSI phase behavior, combining data from both SANS and light scattering. The results are presented on a PEO composition (ϕ_1) versus salt concentration (r) phase diagram.

The immiscible window has a broad base at low values of ϕ_1 ($\phi_1 < 0.4$), and it narrows at higher compositions ($\phi_1 > 0.4$), resulting in a crooked chimney that is broad along the r-axis. A simple Flory–Huggins type model with χ parameters determined fitting SANS data from homogeneous systems provides a basis for predicting the complex phase behavior that we have observed. The SANS data indicate a quadratic dependence of χ on ϕ_1 with coefficients that are dependent on r. It is likely that these dependencies arise from ionic correlations,[12,13] but the connection between them and our model remains to be established. A more detailed experimental study of the dependence of the thermodynamics of PEO/PMMA/LiTFSI blends as a function of composition and chain length seems warranted.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsmacrolett.3c00285.

> Details on sample preparation, LS experimental setup and experimental conditions, a complete table of samples characterized via LS and SANS, and error analysis of phase diagrams generated via the model in this paper (PDF)

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Notes

The authors declare no competing financial interest.

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