

Phase Behaviors of Polymer Blend(PEO–PPO) Electrolyte/ LiCF₃SO₃ Systems in Lithium Battery

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ABSTRACT: Polymer blend (poly(ethylene oxide) (PEO)–poly(propylene oxide) (PPO)) systems with two different mole ratios, complexed with LiCF₃SO₃ salt, have been characterized at various temperatures and compositions using a thermo-optical analysis (TOA) technique. We also developed a new melting point depression theory based on the modified perturbed hard sphere chain model to interpret phase behavior of polymer blend electrolyte systems. The obtained results show that the eutectic points move toward

higher T_m and lower weight fraction of salt with decreasing PEO mole ratio and also indicate that the mole ratio of PEO–PPO for each polymer blend plays an important role in determining the eutectic point of the polymer blend system. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 98: 2314–2319, 2005

Key words: polyelectrolytes; melting point; molecular dynamics; modeling

INTRODUCTION

Solid polymer electrolytes have received considerable attention owing to their wide range of applications such as solid-state batteries, electrochromic devices, and chemical sensors. Since the concept of a solid polymer electrolyte was first proposed by Wright and colleagues^{1,2}, global interest has especially been focused on polymer electrolyte batteries because of their high energy density, safety, and flexibility in fabrication.

Poly(ethylene oxide) (PEO) has been favored as a solvating medium due to its ability to effectively coordinate with salt cations and form homogeneous solutions. But PEO tends to crystallize below 60°C, whereas fast ion transport is a characteristic of the amorphous phase. In this respect, much research has been directed to the characterization of new polymer electrolytes such as polymer blends that exhibit higher ionic conductivity at ambient temperature. Blending polymers is a quick and economic alternative for obtaining materials with optimized properties and easy control of physical properties by compositional change. Work has been done on binary PEO-based blends, where the second component is able to inhibit

crystallization of PEO.^{3,4} Acosta and Morales⁵ described the electrical characterization of polymer electrolytes based on PEO–PPO blends. Wen et al.⁶ reported on an application of blend-based polymer electrolytes with a hyperbranched polymer–PEO. Rocco et al.⁷ reported on the electrical characterizations of polymeric solid electrolyte based on a PEO–PMVE–MAC blend, complexed with LiClO₄.

Phase behavior appears to be an appropriate area of study for a better understanding of crystallinity phenomena and conductivity observed for these PEO-based electrolytes. In fact, the objective of several studies has been to determine domain existence as a function of salt concentration and temperature.⁸ For example, Prud'homme and coworkers^{9,10} reported on complete phase diagrams for PEO–NaSCN and PEO–KSCN systems. Lee and Crist¹¹ also reported on the phase behavior for PEO–NaSCN mixtures, which show eutectic points containing important physical meanings in SPE–salt systems. Fauteux^{12,13} extensively studied phase behavior of binary SPE systems such as PEO–LiX (X = CF₃SO₃[−], ClO₄[−], AsF₆[−], N(CF₃SO₂)₂[−], C(CF₃SO₃)₃[−]), and PEO–NaI.

However, it is hard to find a theoretical consideration that describes the phase behavior for a polymer blend–salt system with various compositions.

In this study, we develop a suitable thermodynamic model based on the modified perturbed hard sphere chain (PHSC) theory^{14–20} and melting point depression theory²¹ to describe phase behaviors of the given systems. We then compare the proposed model with the experimental data for various mole ratios of poly-

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mer blend systems obtained by the thermo-optical analysis (TOA) technique.

EXPERIMENTAL

Sample preparation

Poly(ethylene oxide) ($M_n = 10,000$) and poly(propylene oxide) ($M_n = 2000, 3500$) were obtained from Aldrich Chemical and used without further purification. LiCF_3SO_3 (99.995%) and acetonitrile (99.9%) also supplied by Aldrich Chemical were used as received.

To evaluate the influence of the polymer mole ratio, we used PPO ($M_n = 3500, 2000$) and PEO ($M_n = 10,000$). We prepared polymer blend systems with two different mole ratios of PEO-PPO = 3 : 1 (system I) and 5 : 1 (system II).

To prepare the polymer blend films, known amounts of poly(ethylene oxide) ($M_n = 10,000$) and poly(propylene oxide) ($M_n = 3500, 2000$) were dissolved in acetonitrile and LiCF_3SO_3 was dissolved in a minimum amount of DMF. The acetonitrile solution was then mixed with the DMF solution, stirred for 24 h at room temperature, and cast on a pre-cleaned microscope slide. Films were air-dried for several hours and then transferred to a vacuum oven. They are desolvated under vacuum at 60°C for 48 h. All samples were used when crystallization was completed.

Thermo-optical analysis

Melting point measurements of the given systems were carried out using a TOA technique, consisting of a heating-cooling stage, a photodiode (Mettler FP80), and a microprocessor (Mettler FP90). The scan rate was $2.0^\circ\text{C}/\text{min}$. An IBM PC was used for data acquisition.

Figure 1 shows the determination of two different melting points using the TOA technique for the given system. The model system is system I (PEO-PPO mole ratio = 3 : 1) with a weight fraction of $\text{LiCF}_3\text{SO}_3 \approx 0.3$. The melting point I is approximately the same for all poly(ethylene oxide)-poly(propylene oxide)/salt mixtures. Melting point II is attributed to the transition from intracrystalline amorphous polymer and crystalline complex to intercrystalline amorphous polymer.

MODEL DESCRIPTION

Two theoretical aspects are taken into account: one is a modified PHSC theory and the other is Flory's melting point depression of polymers.

For polymer systems, PHSC theory has been proved to be a practically and widely used powerful model. We employ a modified PHSC model to describe phase

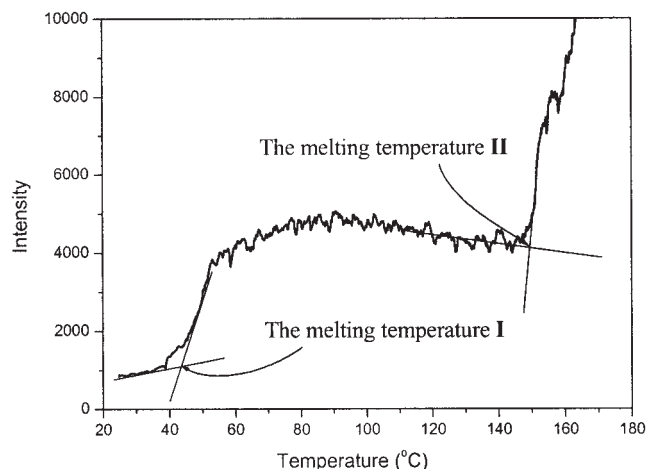


Figure 1 A typical TOA result for determining the melting point temperature of a polymer blend-salt system. The model system is system I with a weight fraction of $\text{LiCF}_3\text{SO}_3 \approx 0.3$. The scan rate was $2.0^\circ\text{C}/\text{min}$.

behaviors of polymer blend-salt systems and compare results with experimental melting point data for each system.

The melting point depression theory proposed by Flory well describes the effect of impurities such as salts on melting point when the concentration of each is low.

Modified PHSC theory

Equation of state

The equation of state for hard spheres and hard sphere chains generally consists of two contributions,

$$Z = Z_{\text{ref}} + Z_{\text{pert}} \quad (1)$$

where the first term represent the reference equation of state for hard sphere chains, while the last term is the van der Waals perturbation to take into account attractive forces.

For hard sphere chains, the reference equation can be directly extended by introducing an appropriate chain connectivity term.

$$Z_{\text{ref}} = Z_{\text{hs}} + Z_{\text{chain}} \quad (2)$$

Z_{hs} is described using the well-known Carnahan-Starling expression.

$$Z_{\text{hs}} = \frac{1 + \eta + \eta^2 - \eta^3}{(1 - \eta)^3} \quad (3)$$

For Z_{chain} , two different types of bonding terms adapted for the given systems are

$$Z_1^{\text{chain}} = (1 - r)[g(d^+) - 1] \quad (4)$$

$$Z_2^{\text{chain}} = (1 - r)\rho \frac{\partial \ln g(d^+)}{\partial \rho}, \quad (5)$$

where $g(d^+)$ is the pair radial distribution function for hard sphere chains at contact and d is the effective hard sphere diameter. $\rho = (N/V)$ is the number density in the system.

Two equations were compared using the same hard-sphere reference equation by Kim and Bae.¹⁷ The results show that eq. (5) gives better results than eq. (4) to describe the computer simulation data, especially for longer chains.

PHSC theory refers the simplest type of van der Waals attractive term to the perturbation term for fluids including chain-like molecules:

$$Z_{\text{pert}} = -\frac{r^2 a \rho}{kT}. \quad (6)$$

The final equation of state expression for hard-sphere chain has the form of

$$Z = 1 + r^2 b \rho g(d^+) + (1 - r)\rho \frac{\partial \ln g}{\partial \rho} - \frac{r^2 a \rho}{kT}. \quad (7)$$

In eq. (7) three parameters with clear physical meanings are introduced: the number of effective hard spheres per molecule, r , the second virial coefficient of hard sphere, b , and the strength of the attractive forces between two nonbonded segments, a .

Both a and b are temperature-dependent parameters.

$$a(T) = \frac{2\pi}{3} \sigma^3 \varepsilon F_a(kT/\varepsilon) \quad (8)$$

$$b(T) = \frac{2\pi}{3} \sigma^3 F_b(kT/\varepsilon). \quad (9)$$

The universal functions (F_a and F_b) obtained from experimental values for methane and argon can be represented by the formulae

$$F_a(kT/\varepsilon_\alpha) = 1.8681 \exp[-0.0619(kT/\varepsilon_\alpha)] + 0.6715 \exp[-1.7317(kT/\varepsilon_\alpha)^{3/2}] \quad (10)$$

$$F_b(kT/\varepsilon_\alpha) = 0.7307 \exp[-0.1649(kT/\varepsilon_\alpha)^{1/2}] + (1 - 0.7303) \exp[-2.3973(kT/\varepsilon_\alpha)^{3/2}]. \quad (11)$$

Extension to polymer blend systems

To account for polymer blend systems, we extended the modified PHSC equation of state to mixtures,

$$\frac{P}{\rho kT} = 1 + \rho \sum_{i,j=1}^m x_i x_j r_i r_j b_{ij} g_{ij}(d_{ij}^+) - \sum_{i=1}^m x_i (r_i - 1) \rho \frac{\partial \ln g_{ii}(d_{ii}^+)}{\partial \rho} - \frac{\rho}{kT} \sum_{ij} x_i x_j r_i r_j a_{ij}, \quad (12)$$

with the segment-basis variables such as $\rho_r = N_r/V$ and $\phi_i = N_i r_i/V$, where $N_r = \sum_i^m N_i r_i$ is the total number of segments in the system of which the total volume is V ,

$$\frac{P}{\rho_r kT} = \rho_r \sum_{i,j=1}^m \phi_i \phi_j b_{ij} g_{ij}(d_{ij}^+) + \sum_i \frac{\phi_i}{r_i} - \sum_{i=1}^m \phi_i \left(1 - \frac{1}{r_i}\right) \rho_r \frac{\partial \ln g_{ii}(d_{ii}^+)}{\partial \rho} - \frac{\rho_r}{kT} \sum_{ij} \phi_i \phi_j a_{ij}, \quad (13)$$

where $g_{ij}(d_{ij}^+)$ is the pair radial distribution function of hard sphere mixtures, which takes the form of the Boulik–Mansoori–Carnahan–Starling equation,

$$g_{ij}(\eta, \xi_{ij}) = \frac{1}{1 - \eta} + \frac{3}{2} \frac{\xi_{ij}}{(1 - \eta)^2} + \frac{1}{2} \frac{\xi_{ij}^2}{(1 - \eta)^3}, \quad (14)$$

where η is the packing fraction:

$$\eta = \frac{\rho_r}{4} \sum_i \phi_i b_i \quad (15)$$

$$\xi_{ij} = \left(\frac{b_i b_j}{b_{ij}}\right)^{1/3} \frac{\rho_r}{4} \sum_i \phi_i b_i^{2/3}. \quad (16)$$

To describe the coexistence curve of the binary system, we use the following combining rules to obtain binary parameters σ_{ij} and ε_{ij} :

$$\sigma_{ij} = \frac{(\sigma_i + \sigma_j)}{2} \quad (17)$$

$$\varepsilon_{ij} = \sqrt{\varepsilon_i \varepsilon_j}. \quad (18)$$

Thermodynamic functions

Helmholtz energy for mixtures is obtained from the general thermodynamic relationship

$$\frac{A}{N_r kT} = \frac{A^0}{N_r kT} + \int_0^{\rho_r} \left(\frac{P}{\rho_r kT} - \frac{N}{N_r} \right) \frac{d\rho_r}{\rho_r} + \sum_i^m \frac{\phi_i}{r_i} \ln \left(\frac{\phi_i}{r_i} \rho_r kT \right). \quad (19)$$

Substitution of eq. (13) into eq. (19) yields

$$\begin{aligned} \frac{A_H}{NkT} &= \sum_{i=1}^m \frac{\phi_i}{r_i} \frac{A_i^0}{NkT} + \rho_r \sum_{ij=1}^m \phi_i \phi_j b_{ij} W_{ij} - \sum_{i=1}^m \phi \\ &\times \left(1 - \frac{1}{r_i} \right) \int_0^{\rho_r} \frac{\partial \ln g_{ii}(d_{ii}^+)}{\partial \rho_r} d\rho_r - \frac{\rho_r}{kT} \sum_{ij=1}^m \phi_i \phi_j a_{ij} \\ &+ \sum_{i=1}^m \frac{\phi_i}{r_i} \ln \left(\frac{\phi_i}{r_i} \rho_r kT \right). \quad (20) \end{aligned}$$

The correlating equations are as follows:

$$\begin{aligned} W_{ij} &= \frac{1}{\rho_r} \int_0^{\rho_r} g_{ij} d\rho_r \\ &= \frac{I_1}{\eta} + \frac{3}{2} \frac{\xi_{ij}}{\eta^2} I_2 + \frac{1}{2} \frac{\xi_{ij}^2}{\eta^3} I_3 \quad (21) \end{aligned}$$

$$Q_{ij} = \int_0^{\rho_r} \frac{\partial \ln g_{ii}(d_{ii}^+)}{\partial \rho_r} \frac{d\rho_r}{\rho_r} = \ln g_{ii}(d_{ii}^+) \quad (22)$$

with

$$I_n = -I_{n-1} + \frac{1}{n-1} \frac{\eta^{n-1}}{(1-\eta)^{n-1}}, I_1 = -\ln(1-\eta). \quad (23)$$

Chemical potential

The definition of chemical potential is

$$\mu_i = \left(\frac{\partial A_H}{\partial N_i} \right)_{T, \rho, N_{j \neq i}}. \quad (24)$$

The final expression for the chemical potential can be written

$$\begin{aligned} \frac{\mu_k}{kT} &= \frac{\mu_k^0}{kT} + 2r_k \rho_r \sum_{i=1}^m \phi_i b_{ik} W_{ik} + \rho_r \sum_{i=1}^m \phi_i \phi_j b_{ij} \left(N_r \frac{\partial W_{ij}}{\partial N_k} \right) \\ &- (r_k - 1) \int_0^{\rho_r} \frac{\partial \ln g_{kk}}{\partial \rho_r} d\rho_r - \sum_i^m \phi_i \left(1 - \frac{1}{r_i} \right) \end{aligned}$$

$$\begin{aligned} &\times \left[r_k \frac{\partial}{\partial \phi_k} \int_0^{\rho_r} \frac{\partial \ln g_{ii}}{\partial \rho_r} d\rho_r \right] - \frac{2r_k \rho_r}{kT} \sum_{i=1}^m \phi_i a_{ik} \\ &+ \ln \left(\frac{\phi_k}{r_k} \rho_r kT \right) + 1, \quad (25) \end{aligned}$$

where

$$\left(N_r \frac{\partial W_{ij}}{\partial N_k} \right) = \left(\frac{\partial W_{ij}}{\partial \eta} \right) \left(N_r \frac{\partial \eta}{\partial N_k} \right) + \left(\frac{\partial W_{ij}}{\partial \xi_{ij}} \right) \left(N_r \frac{\partial \xi_{ij}}{\partial N_k} \right) \quad (26)$$

with

$$N_r \frac{\partial \eta}{\partial N_k} = \frac{\rho_r}{4} r_k b_k \quad (27)$$

$$N_r \frac{\partial \xi_{ij}}{\partial N_k} = \frac{\rho_r}{4} \left(\frac{b_i b_j}{b_{ij}} \right)^{1/3} r_k b_k^{2/3}. \quad (28)$$

Theory of the melting point depression

In a semicrystalline system, the condition of equilibrium between a crystalline polymer and the polymer unit in the solution may be described as follows,²¹

$$\mu_u^c - \mu_u^0 = \mu_u - \mu_u^0 \quad (29)$$

where μ_u^c , μ_u , and μ_u^0 are chemical potentials of crystalline polymer segment units, liquid (amorphous) polymer segment units, and chemical potential in the standard state, respectively. Now the formal difference, appearing on the left-hand side, is expected to be as follows,

$$\mu_u^c - \mu_u^0 = -\Delta H_u (1 - T/T_m^0), \quad (30)$$

where ΔH_u is the heat of fusion per segment unit, and T_m and T_m^0 are melting point temperatures of the species in a mixture and the pure phases, respectively. The right-hand side of eq. (20) can be restated as

$$\begin{aligned} \frac{1}{T_{m,k}} - \frac{1}{T_{m,k}^0} &= \frac{k_B}{\Delta H_{u,k} r_k} \left\{ 2r_k \rho_r \sum_{i=1}^m \phi_i b_{ik} W_{ik} \right. \\ &+ \rho_r \sum_{i=1}^m \phi_i \phi_j b_{ij} \left(N_r \frac{\partial W_{ij}}{\partial N_k} \right) - (r_k - 1) \int_0^{\rho_r} \frac{\partial \ln g_{kk}}{\partial \rho_r} d\rho_r \\ &- \sum_i^m \phi_i \left(1 - \frac{1}{r_i} \right) \times \left[r_k \frac{\partial}{\partial \phi_k} \int_0^{\rho_r} \frac{\partial \ln g_{ii}}{\partial \rho_r} d\rho_r \right] \\ &\left. - \frac{2r_k \rho_r}{kT} \sum_{i=1}^m \phi_i a_{ik} + \ln \left(\frac{\phi_k}{r_k} \rho_r kT \right) + 1 \right\}. \quad (31) \end{aligned}$$

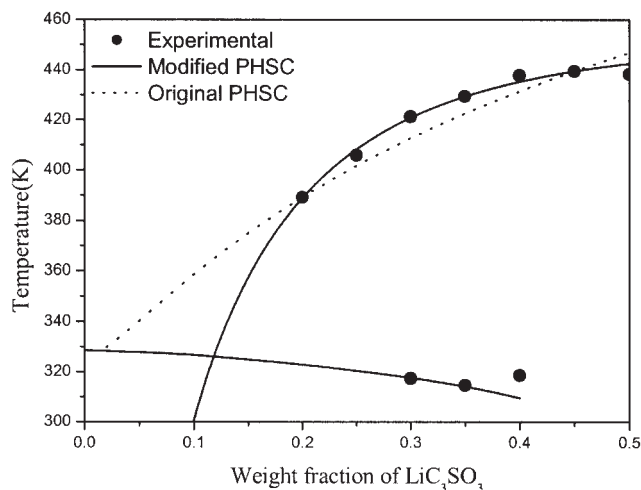


Figure 2 Phase diagram for system I. The dark circles are experimental data obtained from TOA technique at PEO-PPO mole ratio $\approx 3 : 1$. The solid and dotted lines are calculated values by the proposed model (modified PHSC theory) and that of the original one, respectively.

RESULTS AND DISCUSSION

We propose a new melting point depression model based on PHSC theory modified for the chain connectivity term of the original to describe phase diagrams of polymer blend electrolyte systems.

The proposed model needs three characteristic parameters: number of hard spheres per molecule r , a segment size σ , and nonbonded segment pair interaction energy, ε .

These parameters can be obtained from pressure-volume-temperature (PVT) data for each pure compo-

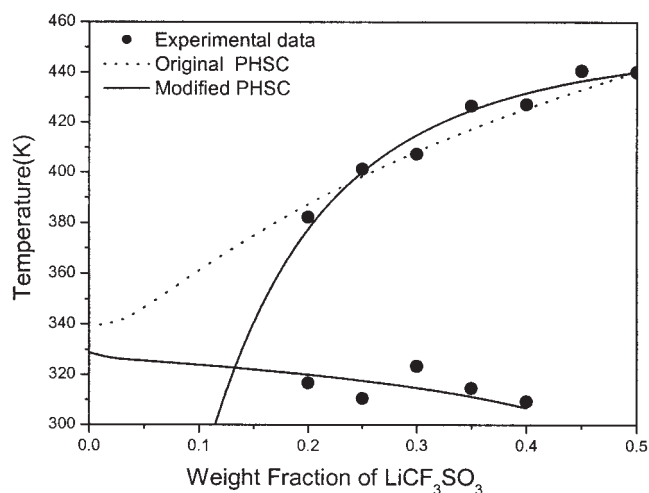


Figure 3 Phase diagram for system II. The dark circles are experimental data obtained from TOA technique at PEO-PPO mole ratio $\approx 5 : 1$. The solid and dotted lines are calculated values by the proposed model (modified PHSC theory) and the original one, respectively.

TABLE I
Melting Temperature, Heat of Fusion, and Molecular Weight for Each Sample

	T_m^0 (K)	ΔH (kJ/mol)	M_w (g/mol)
PEO	326.88	1163.750	10,000
LiCF ₃ SO ₃	499.29	10516.48	156.01

nent. However, we set r , σ , and ε for salt as adjustable model parameters without fitting the PVT data that are not available.

The characteristic parameters of PEO and PPO can be obtained from the EOS for polymers and are listed in Table II.

Figure 2 shows the phase behavior of system I ((PEO-PPO mole ratio $\approx 3 : 1$)/LiCF₃SO₃). Dark circles are experimental data obtained by the TOA technique and the solid line shows the calculated values by the proposed model. The characteristic parameters (r , σ , and ε) for salt are determined by fitting experimental data of system I.

As shown in Figure 2, the theoretical prediction not only gives good agreement with experimental data but also confirms the eutectic point at the intersection of the two liquids' curves at a weight fraction of LiCF₃SO₃ ≈ 0.117 . The eutectic point, which usually gives the highest ionic conductivity, plays an important role in determining the optimum composition of polymer and salt. Alternatively, polymer and salt can simultaneously coexist in the melted state at the eutectic point.

The dotted line obtained from the original PHSC, however, shows some deviations from the experimental data, due to the overestimation of the chain connectivity term.

In Figure 3, we compare theoretical coexistence curves with measured melting points for system II ((PEO-PPO mole ratio $\approx 5 : 1$)/LiCF₃SO₃). Dark circles are experimental data; the solid (the modified PHSC model) and dotted lines (the original PHSC model) are calculated values. As shown in Figure 3, the modified PHSC theory gives a better description of experimental data than the original one.

The results indicate that the eutectic point is shifted toward the lower salt concentration region with increasing PPO mole ratio. This is because the PPO mole

TABLE II
Characteristic Parameters for Polymers and Salt

	LiCF ₃ SO ₃	PEO	PPO
r	8.6	—	—
r/M	—	0.0441	0.0314
σ	2.7892	3.5022	4.0694
ε/k	302.23	345.75	331.25

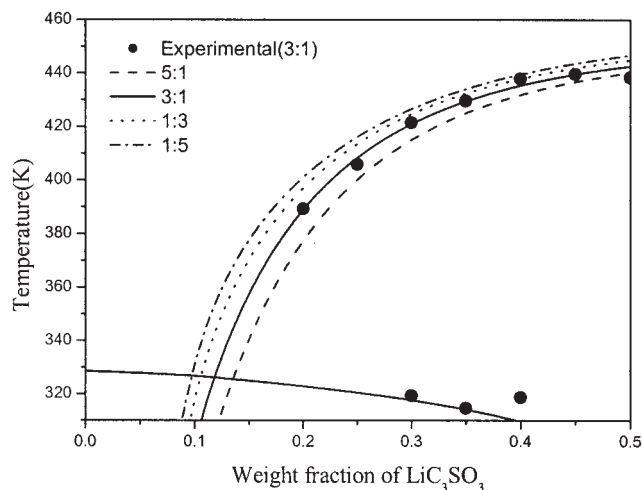


Figure 4 A hypothetical phase diagrams of polymer blend [poly(ethylene oxide)–poly(propylene oxide)]/LiCF₃SO₃ system at various PEO–PPO mole ratios.

ratio influences interaction more with salt molecules than does the PEO mole ratio.

Properties of samples used in this study are characterized in Table I. Adjustable model parameters are listed in Table II.

In Figure 4, we hypothetically calculate the eutectic points of the given polymer blend system with various mole ratios such as PEO–PPO mole ratio $\approx 1 : 5$ and $1 : 3$. The obtained results show that the eutectic points are shifted toward higher T_m and lower concentration of salt with decreasing the PEO mole ratio. The eutectic points calculated hypothetically are listed in Table III.

An interesting conclusion from the theoretical predictions shown in Figure 4 is that the mole ratio of each polymer plays a great role in determining phase behaviors of the given systems.

TABLE III
Changes of Eutectic Point with Various Mole Ratios of Polymer Blend

Eutectic point	PEO–PPO mole ratios			
	5 : 1	3 : 1	1 : 3	1 : 5
Temperature (K)	325.5	326.13	326.39	326.74
Weight fraction (salt)	0.135	0.118	0.105	0.097

CONCLUSIONS

In this work, we have established a molecular thermodynamic framework for combining the theory of melting point depression and modified PHSC model to describe phase behavior of polymer blend electrolyte–salt systems. We also extended the modified PHSC equation of state to mixtures to account for the polymer blend mixture systems.

For polymer blend(PEO–PPO)/LiCF₃SO₃ systems, the obtained results show that the eutectic points move toward higher T_m and a lower weight fraction of salt with decreasing PEO mole ratio. This indicates that the mole ratio of each polymer in the polymer blend plays an important role in determining the eutectic point of the given systems.

The proposed model gives better agreement with experimental data than the original PSC model.

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