

Ternary Hydrogen-Bonded Polymer Solutions

YUHONG HU, PAUL C. PAINTER, MICHAEL M. COLEMAN

Department of Materials Science and Engineering, The Pennsylvania State University, University Park, Pennsylvania 16802

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ABSTRACT: Ternary-phase diagrams have been experimentally determined at 100°C for systems containing a series of poly(*n*-alkyl methacrylates), poly(ethylene oxide) (PEO), and a solvent [4-ethyl phenol (EPh)]. A totally miscible phase diagram is experimentally determined for the poly(methyl methacrylate)/PEO/EPh system, while a closed-loop diagram is observed for the analogous system containing poly(ethyl methacrylate). The corresponding phase diagrams of analogous mixtures containing poly(*n*-propyl methacrylate) or poly(*n*-butyl methacrylate) exhibit large heterogeneous areas. Theoretically predicted phase diagrams calculated using an association model developed in our laboratory are in general accord with these observations for ternary hydrogen-bonded polymer/polymer solutions. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 70: 1265–1271, 1998

Key words: polymer solutions; hydrogen bonds; ternary systems

INTRODUCTION

The thermodynamics of ternary polymer mixtures dates back to early work on symmetric ternary polymer solutions by Scott and Tompa.^{1,2} Zeman and Patterson³ and Hsu and Prausnitz⁴ extended these studies, calculated spinodal and binodal phase diagrams for asymmetric polymer–polymer–solvent ternary systems, respectively, and concluded that only a small difference in polymer–solvent interaction parameters can greatly affect phase behavior. In other words, a small $\Delta\chi$ difference can induce a large immiscible region in the ternary-phase diagram (the so-called $\Delta\chi$ effect) and provides a credible explanation for the experimental observations of Bank et al.⁵ and Hugelin and Dondos.⁶ Su and Fried⁷ further extended this theory to the studies of ternary polymer blends.

The theoretical basis of all these studies is the classic Flory–Huggins lattice model.⁸ Strong specific interactions and free-volume effects were not taken into account, although the latter was discussed by Klotz and Cantow,⁹ who applied Flory's equation-of-state theory to ternary systems and successfully predicted the general form of lower (LCST) and upper (UCST) critical solution temperature phase boundaries. The role of strong specific interactions (hydrogen bonds) in the phase behavior of ternary polymer blends has recently been addressed in our laboratories using an association model.^{10,11} We found that in addition to the $\Delta\chi$ effect, which is a consequence of differences in the “physical” interactions between polymer pairs, an analogous ΔK effect that results from differences in the “chemical” interactions (hydrogen bonds) occurring between polymer pairs is important and often dominant. This ΔK effect is related to differences in the values of the two interassociation equilibrium constants that describe the hydrogen-bonding competition between polymer A and polymer C for polymer B. Accordingly, completely miscible (one-phase) ter-

Correspondence to: M. M. Coleman.

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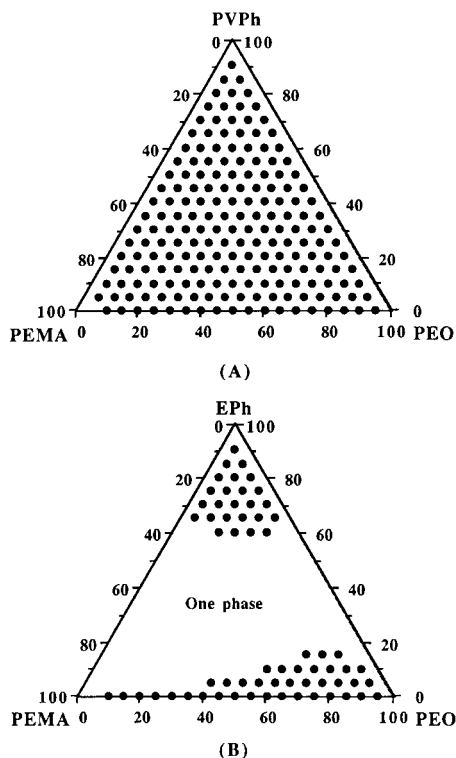


Figure 1 Theoretical ternary-phase diagrams calculated at room temperature. (Top) The ternary polymer blend system, PEMA/PVPh/PEO. (Bottom) The polymer-polymer-solvent system, PEMA/EPh/PEO.

nary polymer phase diagrams are rare and most ternary blend systems exhibit large areas of immiscibility.¹¹

More interesting phase behavior (i.e., a greater region of miscibility) is expected in hydrogen-bonded polymer-polymer-solvent systems primarily because of the increased contribution from combinatorial entropy. This is illustrated in Figure 1, where the predicted ternary phase diagram at 25°C for the polymer blend system¹¹ poly(ethyl methacrylate) (PEMA)/poly(4-vinyl phenol) (PVPh)/poly(ethylene oxide) (PEO) is compared to that of the analogous polymer-polymer-solvent system PEMA/4-ethyl phenol (EPh)/PEO. Only those compositions that are essentially binary mixtures of PVPh with PEMA or PEO are predicted to be single phase in the former, while there is a large area of single-phase mixtures predicted for the latter. Details of the parameters used in these calculations will be presented later in the text. The object of the work described here was to establish a theoretical basis for predicting the phase behavior of ternary polymer-polymer solutions involving strong intermolecular interactions (hydrogen bonds) and compare the predictions to experimental observations.

EXPERIMENTAL

Four ternary hydrogen-bonded polymer-polymer-solvent systems were examined in this study. EPh, purchased from Aldrich (Milwaukee, WI), was employed as the common low molecular weight solvent. EPh is a strongly self-associating (hydrogen-bonded) crystalline solid at room temperature, with a melting point of 44°C and boiling point of 219°C. PEO, having a reported molecular weight (MW) of 20,000, a crystalline melting point (T_m) of $\approx 65^\circ\text{C}$, and a glass transition temperature (T_g) of -67°C , was purchased from Fluka (Milwaukee, WI) and was a common polymer used in the ternary mixtures. The remaining polymer was one of the series of atactic poly(*n*-alkyl methacrylate)s (PAMA): poly(methyl methacrylate) (PMMA), poly(ethyl methacrylate) (PEMA), poly(*n*-propyl methacrylate) (PPMA), or poly(*n*-butyl methacrylate) (PBMA). PMMA (MW = 25,000; $T_g = 105^\circ\text{C}$) and PPMA (MW = 125,000; $T_g = 35^\circ\text{C}$) were purchased from Polysciences, Inc. (Warrington, PA), while PEMA (MW = 126,000; $T_g = 71^\circ\text{C}$) and PBMA (MW = 73,600; $T_g = 27^\circ\text{C}$) were purchased from Aldrich.

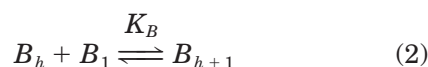
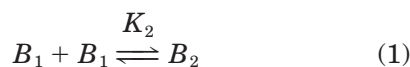
A series of dilute PAMA/PEO/EPh ternary polymer solutions in sealed vials were prepared by directly mixing appropriate amounts of PAMA and PEO in the EPh solvent. Experimental observations of turbidity were performed after a period of approximately 24 h (to ensure equilibrium conditions) at temperatures significantly above the melting point of PEO ($\approx 70^\circ\text{C}$). For those PAMA-PEO-EPh solutions rich in polymer (i.e., $>30\%$ by weight), it was necessary to alter the experimental methodology. Known quantities of PAMA and PEO were initially dissolved in excess EPh in a tarred sealed vial and stirred for 24 h to ensure complete mixing. A measured quantity of the EPh solvent was then removed under reduced pressure to yield EPh lean ternary mixtures of known composition. Turbidity observations were then performed at specific temperatures after an appropriate "annealing" period to achieve equilibrium conditions.

RESULTS AND DISCUSSION

In this study, we considered ternary systems in which the common solvent (EPh), denoted *B*, strongly self-associates through the formation of intermolecular hydroxyl-hydroxyl hydrogen-

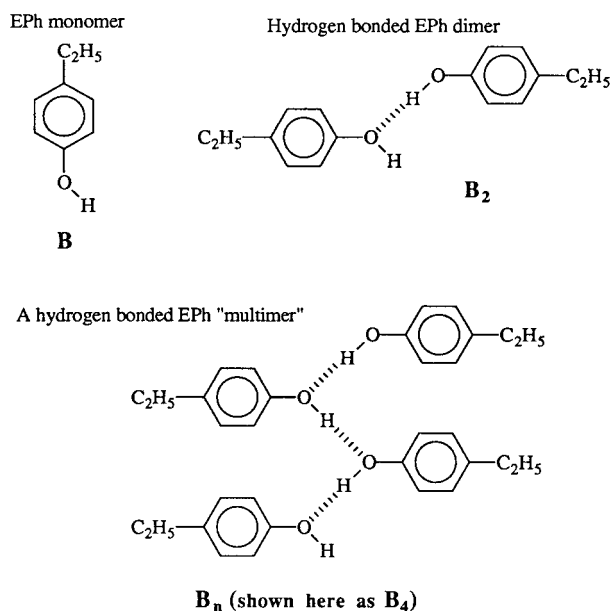
bonded dimers and chainlike multimers as illustrated schematically in Scheme 1.

The self-association of EPh can be adequately described by two equilibrium constants: K_2 , which represents the formation of dimers and K_B , the formation of multimers,¹⁰ as depicted in eqs. (1) and (2):

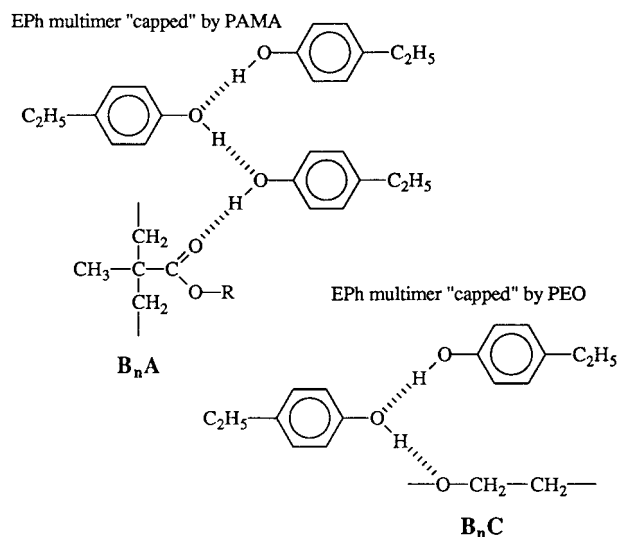


The two polymers, PAMA and PEO, do not inherently self-associate, and there are no strong intramolecular interactions (hydrogen bonds) formed between them. However, both polymers have acceptor groups that are able to form hydrogen bonds to EPh as illustrated in Scheme 2.

These hydrogen bonds can be described by the equilibrium constants, K_A and K_C , respectively:



Scheme 1



Scheme 2

The stoichiometric equations relating the equilibrium constants to the volume fractions of the species present and the derivation of an equation describing the free energy of mixing of the hydrogen-bonded blends, $\Delta G_m/RT$, was previously discussed in detail.^{10,11} Accordingly, we simply present the result for the ternary polymer-polymer-solvent system described above:

$$\begin{aligned} \frac{\Delta G_m}{RT} = & \frac{\Phi_A}{r_A N_A} \ln \Phi_A + \Phi_B \ln \Phi_B \\ & + \frac{\Phi_C}{r_C N_C} \ln \Phi_C + \Phi_A \Phi_B \chi_{AB} + \Phi_A \Phi_C \chi_{AC} \\ & + \Phi_B \Phi_C \chi_{BC} + \frac{\Delta G_H}{RT} \quad (5) \end{aligned}$$

where Φ_B , Φ_A , and Φ_C are the volume fractions of solvent B , polymer A , and polymer C in the blend, respectively, which have degrees of polymerization, N_A and N_C (naturally, for the solvent $N_B = 1$). The parameters $r_A = V_A/V_B$ and $r_C = V_C/V_B$ are the ratios of the segment molar volumes of polymer A and polymer C to solvent B , respectively. In common with the binary- and ternary-blend systems, the polymer/polymer interaction parameter, χ_{AC} is defined by the relationship

$$\chi_{AC} = \frac{V_B}{RT} (\delta_A - \delta_C)^2 \quad (6)$$

where δ_A and δ_C are the solubility parameters of polymers A and C that are calculated from group

Table I Values of the Parameters Used in the Calculations

Solvent and Polymers	Segment Molar Volume (cm ³ /mol)	Degree of Polymerization	Solubility Parameter (cal ^{1/2} cm ^{-3/2})	Equilibrium Constants at 100°C (Dimensionless)
EPh	130	1	9.9	$K_2 = 2.40$ $K_B = 8.74$
PMMA	84.9	250	9.1	$K_A = 32.4$
PEMA	101.4	1000	8.9	$K_A = 32.4$
PPMA	117.9	1000	8.8	$K_A = 32.4$
PBMA	134.4	500	8.7	$K_A = 32.4$
PEO	38.1	450	9.4	$K_C = 162$

molar attraction and molar volume constants designed to specifically exclude contributions from hydrogen bonding.^{10(a)} However, in the case of the two polymer/solvent interaction parameters, χ_{AB} and χ_{BC} , where there is a large mismatch of the so-called free-volume parameters for the polymer and solvent, it has been found necessary to add a constant to eq. (6) (typically, a value close to 0.34), resulting in the following expressions¹²:

$$\chi_{AB} = 0.34 + \frac{V_B}{RT} (\delta_A - \delta_B)^2$$

$$\chi_{BC} = 0.34 + \frac{V_B}{RT} (\delta_B - \delta_C)^2 \quad (7)$$

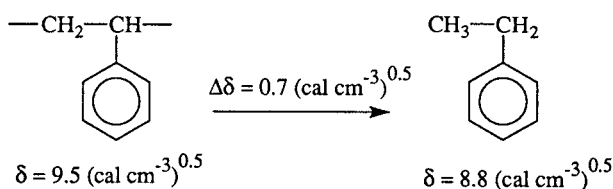
We will not dwell on the equation that describes the "chemical" contribution to the free energy of mixing emanating from the changing pattern of hydrogen bonds in the mixture [the $\Delta G_H/RT$ term in eq. (5)], nor will we repeat the equations that are used to calculate the ternary spinodal phase diagrams as these were previously discussed in detail.^{10,11} The computer program written previously to calculate the free energy of mixing and phase diagrams of binary hydrogen-bonded blends¹⁰ was modified to permit the calculation of ternary spinodal phase diagrams¹¹ with values for χ_{AB} and χ_{BC} calculated according to eq. (7).

Values of the parameters used in the calculations are listed in Table I and these require some elaboration. To ensure equilibrium conditions, a temperature of 100°C was chosen for this work, which is above the glass transition temperatures of all the mixtures and above the crystalline melting temperature of PEO. The self-association equilibrium constants for EPh at 100°C, K_2 and

K_B , were calculated from the standard values (i.e., at 25°C and a molar volume $V_B = 100$ cm³/mol) for the PVPh segment ($K_2 = 21.0$ and $K_B = 66.8$) by scaling to the EPh molar volume ($V_B = 130$ cm³/mol) and using the enthalpies of hydrogen-bond formation $h_2 = -5.6$ and $h_B = -5.2$ kcal/mol.^{10,13} The interassociation equilibrium constant that describes the interaction between EPh phenolic hydroxyl and PAMA carbonyl groups was assumed to be the same as that previously determined¹³ for the analogous hydrogen-bonded polymer/solvent system, PVPh/ethyl isobutyrate (EIB), that is, $K_A = 132$ at 25°C, which translates to a value of $K_A = 32.4$ at 100°C ($h_A = -4.1$ kcal/mol). We are less confident in the value of K_C , the interassociation equilibrium constant that describes the interaction between EPh phenolic hydroxyl and PEO oxygen groups. From the studies of Le Menestrel et al.¹⁴ on the ternary polymer blend system PVPh/PEO/poly(vinyl acetate), K_C was experimentally found to be approximately five times that of K_A at 100°C. Subsequent studies by Zhang et al.¹¹ indicated that this may have been overestimated somewhat, but in the absence of a more accurate measurement, we will assume in this work a K_C value of 162 at 100°C ($5 \times K_A$).

Finally, we should comment on how we arrived at the nonhydrogen-bonded solubility parameter value of 9.9 (cal cm⁻³)^{0.5} for EPh. All other solubility parameters listed in Table I were calculated from group molar volume and molar attraction constants developed in our laboratories^{10a} that exclude contributions from strong interactions. Since EPh strongly self-associates, the nonhydrogen-bonded solubility parameter cannot be directly measured or calculated. For PVPh, a rough *initial* estimate of the solubility parameter, δ_{PVPh}

$= 11.0 (\text{cal cm}^{-3})^{0.5}$, was calculated from a hypothetical segment where an ether oxygen was substituted for the hydroxyl group.¹⁰ After numerous experimental studies, the value of δ_{PVPh} was finally honed to $10.6 (\text{cal cm}^{-3})^{0.5}$ and we have used this value during the past 5 years without adjustment for (co)polymers containing the 4-vinyl phenol segment.¹⁰ Using a methodology that was described recently,¹⁵ we obtained an estimate of δ_{EPh} by considering the difference that substitution of the $-\text{CH}_2-\text{CH}-$ group by CH_3-CH_2- would make on a nonhydrogen-bonding analog and adjust the known (standard) solubility parameter of PVPh accordingly. For example, consider the calculated solubility parameters of the polystyrene segment and ethyl benzene shown below:



Substitution of the $-\text{CH}_2-\text{CH}-$ group by CH_3-CH_2- indicates that there is a difference

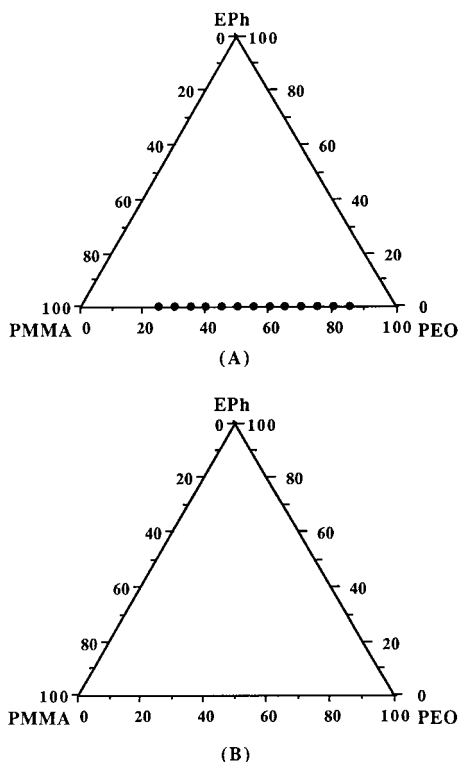


Figure 2 Ternary-phase diagrams for the PMMA/EPh/PEO system at 100°C. (Top) Theoretical prediction. (Bottom) Experimental observation.

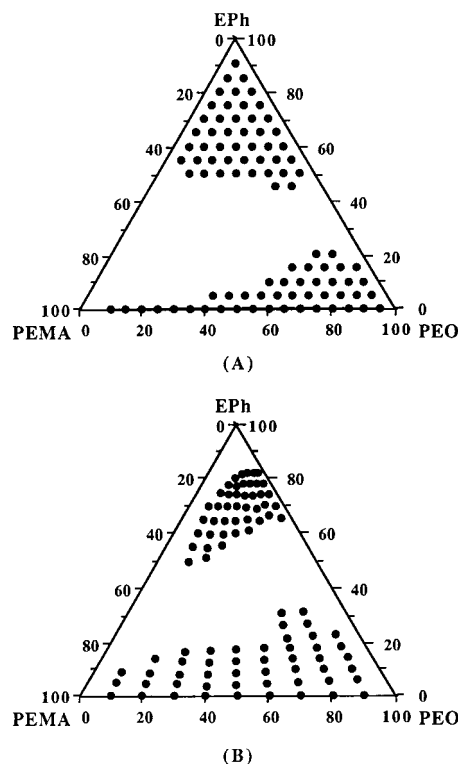


Figure 3 Ternary-phase diagrams for the PEMA/EPh/PEO system at 100°C. (Top) Theoretical prediction. (Bottom) Experimental observation.

in the solubility parameters of $\Delta\delta = -0.7 (\text{cal cm}^{-3})^{0.5}$. Thus, our initial best estimate for the nonhydrogen-bonded solubility parameter for EPh is $\delta_{\text{EPh}} = 10.6 - 0.7 = 9.9 (\text{cal cm}^{-3})^{0.5}$.

We are now in a position to calculate ternary-phase diagrams at 100°C from the values of the parameters given in Table I and compare them to experimental observations. Figures 2–5 show such a comparison of the calculated (top) and experimental (bottom) ternary-phase diagrams for EPh/PEO mixtures with PMMA, PEMA, PPMA and PBMA, respectively. The EPh/PEO/PMMA system was found experimentally to be homogeneous (single phase) at 100°C throughout the entire range of binary and ternary compositions (Fig. 2). Results are displayed in the form of heterogeneous (multiphase) regions denoted by the small black-filled circles, while homogeneous (single-phase) regions are left blank. The calculated phase diagram for the EPh/PEO/PMMA system is in close agreement with experiment, except for intermediate binary PMMA/PEO compositions which are predicted to be two phase. Given that we have assumed that there are no favorable interac-

tions between PMMA and PEO, this anomaly is not unexpected.^{10a}

A more interesting phase diagram is seen in the EPh/PEO/PEMA system (Fig. 3). The experimental ternary-phase diagram at 100°C exhibits two independent heterogeneous areas: a "closed-loop" region (typically observed in many hydrogen-bonded systems) for compositions relatively rich in EPh and a rather extensive region for compositions rich in PEMA/PEO. While the calculated phase diagram does not perfectly match the experimental observations, the gross features are essentially correct. That we calculate two independent heterogeneous regions, including a "closed loop," that are in general agreement with experimental observations is very encouraging.

Finally, experimental and predicted phase diagrams for the EPh/PEO/PPMA and EPh/PEO/PBMA systems are shown in Figures 4 and 5, respectively. Here, the agreement between experimental observations and the predicted phase diagrams is not as good. The vast majority of the mixtures are experimentally determined to be heterogeneous, with only the essentially binary

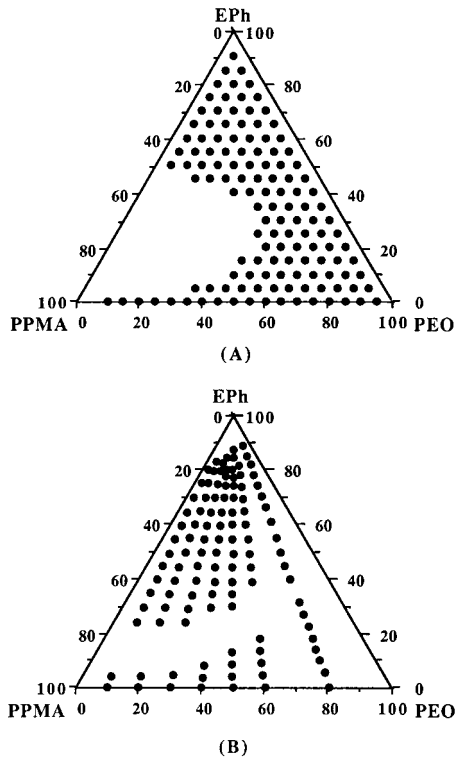


Figure 4 Ternary-phase diagrams for the PPMA/EPh/PEO system at 100°C. (Top) Theoretical prediction. (Bottom) Experimental observation.

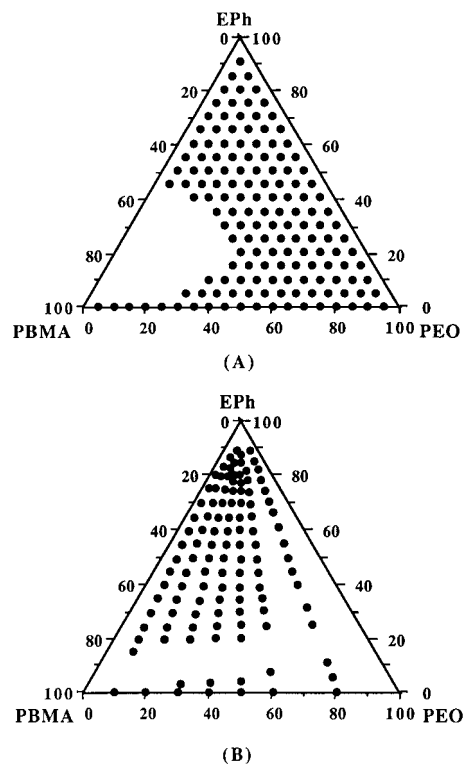


Figure 5 Ternary-phase diagrams for the PBMA/EPh/PEO system at 100°C. (Top) Theoretical prediction. (Bottom) Experimental observation.

polymer/EPh compositions and a narrow "corridor" in solvent lean compositions being single-phase mixtures. The calculated phase diagrams exhibit a segment-shaped area of a predicted single-phase material in PPMA (or PBMA)-rich compositions.

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