Miscibility and Phase Behavior in Blends of Poly(hydroxyether of bisphenol A) with Poly(ethylene oxide-co-propylene oxide)

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SYNOPSIS

The miscibility of poly(hydroxyether of bisphenol A) (phenoxy) with a series of poly(ethylene oxide-co-propylene oxide) (EPO) has been studied. It was found that the critical copolymer composition for achieving miscibility with phenoxy around 60°C is about 22 mol % ethylene oxide (EO). Some blends undergo phase separation at elevated temperatures, but there is no maximum in the miscibility window. The mean-field approach has been used to describe this homopolymer/copolymer system. From the miscibility maps and the melting-point depression of the crystallizable component in the blends, the binary interaction energy densities, B_{ij}, have been calculated for all three pairs. The miscibility of phenoxy with EPO is considered to be caused mainly by the intermolecular hydrogen-bonding interactions between the hydroxyl groups of phenoxy and the ether oxygens of the EO units in the copolymers, while the intramolecular repulsion between EO and propylene oxide units in the copolymers contributes relatively little to the miscibility. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Miscibility in polymer blends has been extensively studied during the past decades.[1-4] Because of the very small entropic contribution in high molecular weight polymer blend systems, polymers are normally not miscible unless they are very similar chemically or there is a specific interaction between them. Specific intermolecular interactions such as hydrogen bonding are usually considered to be the driving force for miscibility, and they are responsible for the exothermic heat of mixing that is the thermodynamic basis of miscibility in polymer blends.

Recently, it has been demonstrated that systems consisting of a homopolymer and a copolymer or two different copolymers can be miscible for a certain range of copolymer compositions even though the mixtures of their corresponding homopolymers are immiscible.[5-21] Miscibility of copolymers has

been proposed to be caused by the repulsion between the two different monomer units comprising the copolymer. In a mean-field approach,[5-7] the overall interaction energy density, B_{blend}, between the two polymers can be simply expressed in terms of the binary interaction energy densities, B_{ij}, ten Brinke et al.[6] extended this formulation to blends composed of two different copolymers. Paul and Barlow[7] and Shiomi et al.[8,9] applied it to blends of two random copolymers having a common monomer.

In binary mixtures of a homopolymer A with a random copolymer $C_y D_{1-y}$, where y represents the mole fraction of C units in the copolymer, the blend interaction energy density B_{blend} is given by following expression:[5-7]

$$B_{\text{blend}} = yB_{AC} + (1 - y)B_{AD}$$
$$- y(1 - y)B_{CD} = f(y). \quad (1)$$

For infinite molecular weight polymers phase separation occurs when $f(y) = 0 = B_{\text{crit}}$.

Application of eq. (1) to the understanding of the

phase behavior of copolymer mixtures has met with great success. This paper presents the results of our study on the miscibility of a homopolymer A, poly(hydroxyether of bisphenol A) (phenoxy), and a random copolymer of ethylene oxide (EO), C, and propylene oxide (PO), D. This pair was chosen for several reasons. First, poly(ethylene oxide) (PEO) is miscible with phenoxy over the entire composition range at accessible temperatures.[22-24] As a semi-crystalline/compatible blend system, the binary interaction parameter B_{AC} can be[25,26] and has been[24] determined simply from the melting-point depression of PEO in the blend. Second, both B_{AD} and B_{CD} values should be positive since neither phenoxy[22] nor PEO[27] is miscible with poly(propylene oxide) (PPO). Third, poly(ethylene oxide-co-propylene oxide) (EPO) with high EO content is crystallizable, hence the overall interaction energy density, B_{blend}, for the blends of phenoxy with these EPO copolymers can be evaluated from the melting-point depression of EO sequences in the blend as well. This through eq. (1) allows us to obtain values of B_{AD} and B_{CD}, which, together with the value of B_{AC}, can be used to further interpret our results. Fourth, miscibility of phenoxy with PEO has been revealed by Coleman and Moskala[23] to be due to hydrogen-bonding interactions between them. Miscibility of phenoxy with EPO copolymers can be considered to be caused by hydrogen-bonding interactions between pendant hydroxyl groups of phenoxy and EO units that were introduced into PPO, as well as by the repulsion between the EO and PO units in the copolymer. The contributions to miscibility enhancement from these two aspects are discussed.

EXPERIMENTAL

Materials and Preparation of Blends

Phenoxy and PEO with the quoted weight-average molecular weights as given in Table I were purchased from Scientific Polymer Products, Inc., Japan and Shanghai Chemicals Co., China, respectively. PPO and EPO copolymers were synthesized by ring-opening polymerization at $ca.$ 105°C in the presence of potassium hydroxide and 1,3-propanediol as an initiation system.[28] Some characteristics of the polymers are listed in Table I. Chloroform was A.R. grade and was used as received.

All the blends were prepared by solution casting from chloroform at room temperature. To remove the residual solvent, the blends were then dried in a vacuum oven at room temperature for approximately 4 weeks. The dried samples were then stored in a desiccator to avoid moisture absorption.

Cloud Point Measurements

Blend clarity as a function of temperature was studied by placing a sample of the blend between two glass slides and heating it with an apparatus similar to that used by Bernstein et al.[29] and Guo.[30] The heating rate used was about 10°C/min. The temperature at which the first faint opalescence appeared on heating was designated as the cloud point.

Differential Scanning Calorimetry

The calorimetric measurements were made on a Perkin–Elmer DSC-2C differential scanning calo-

Table I   Characteristics of Polymers Used in This Study

Sample	EO in Copolym.[a]		M_n^b	M_w^c	$[\eta]^d$		T_g^e (°C)
	(mol %)	(wt %)			(In Water)	(In Benzene)	
Phenoxy				34,000			81
PEO				10,000			−61
EPO85	84.9	81.0	8,440		23.9	22.2	−65
EPO74	73.5	67.8	5,370		17.0	16.2	−67
EPO66	65.6	59.1	7,150		17.9	17.9	−68
EPO50	50.3	43.4	4,860		15.0	15.6	−70
EPO22	22.4	18.0	3,790			11.3	−72
PPO				3,410		9.1	−71

[a] By ^{1}HNMR analysis.
[b] Determined by hydroxyl titration.
[c] As given by the suppliers.
[d] At 25°C.
[e] By DSC.

rimeter. All samples, except where indicated otherwise, were first heated to 120°C and maintained at this temperature for 3 min to melt any crystallinity as well as to remove possible moisture in it, followed by quenching to −133°C. A heating rate of 20°C/min was used in all cases. The midpoint of the transition and the minimum of the exothermic peak were taken as the glass-transition temperature, T_g, and the crystallization temperature, T_c, respectively, while the maximum of the endothermic transition was marked as the melting-point temperature, T_m.

RESULTS

All the phenoxy/PEO blends were clear at temperatures above the melting point of PEO and remained so up to temperatures above 300°C where the polymers showed remarkable depolymerization. It is evident that no phase separation was induced before the depolymerization of the polymers. This is probably caused by the high strength of hydrogen-bonding interaction between the pendant hydroxyl of
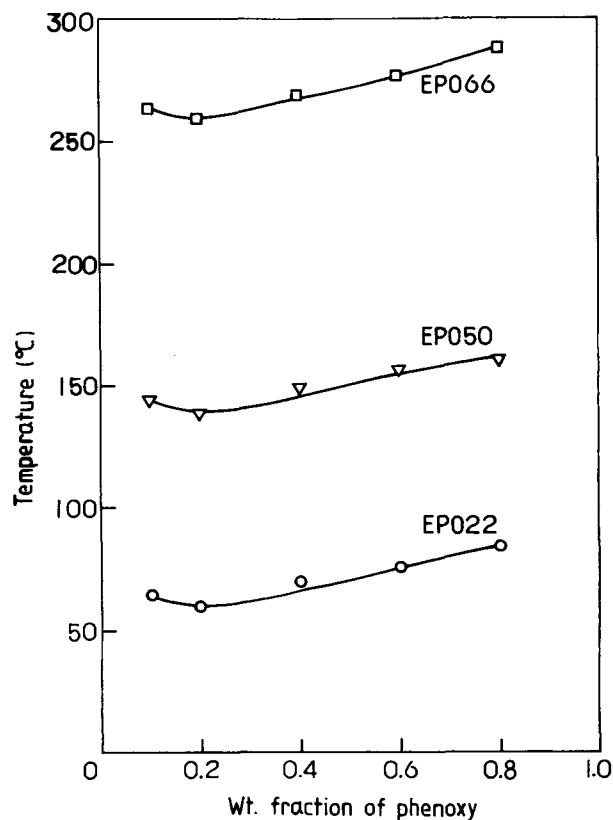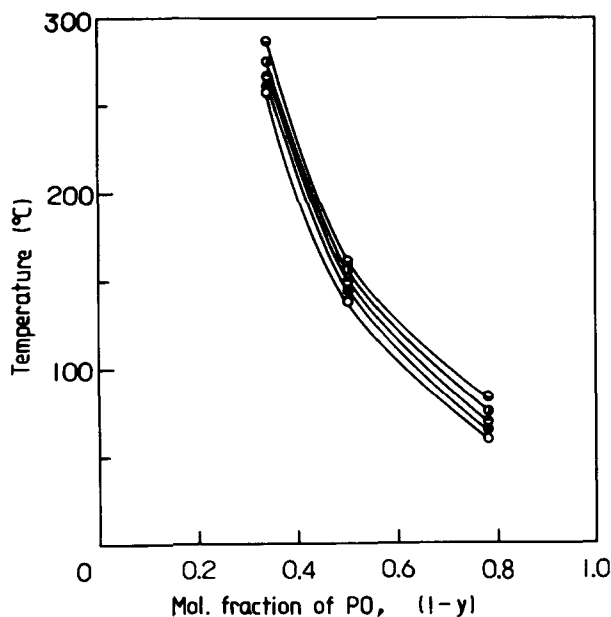
Figure 2 Miscibility maps of phenoxy blends with EPO copolymers. Weight percent phenoxy in blends: (●) 10; (○) 20; (◖) 40; (◐) 60; (◑) 80.

Figure 1 Phase diagrams of phenoxy blends with EPO copolymers.

phenoxy and the PEO ether oxygen, as revealed by Coleman and Moskala.[23] Our present result is in agreement with observations of other authors.[22-24]

Phenoxy/PPO blends were inhomogeneous and brittle despite the fact that PPO did not crystallize. Their films did not become transparent on heating to any temperature. This observation, combined with the existence of two T_g's as shown below, confirmed the conclusion by Robeson et al.[22] that phenoxy is immiscible with PPO.

All examined phenoxy/copolymer blends were transparent at room temperature. When the EO content of the copolymer was 74 mol % or higher, no phase separation was observed up to temperatures above 300°C for the phenoxy/copolymers blends. For copolymers containing 66 mol % or less EO units, phase separation of their blends with phenoxy was induced at elevated temperatures. The cloud-point curves for the phenoxy blends with EPO66, EPO50, and EPO22 are given in Figure 1. It should be pointed out that the cloud points for the phenoxy/EPO66 blends are merely approximate since considerable thermal decomposition of EPO66 could have occurred before phase separation during heating. Nevertheless, it can be seen from Figure 1 that the cloud temperatures increase with an increase in EO content of the copolymer.

An alternative representation of the phase diagrams depicted in Figure 1 is a plot of cloud-point
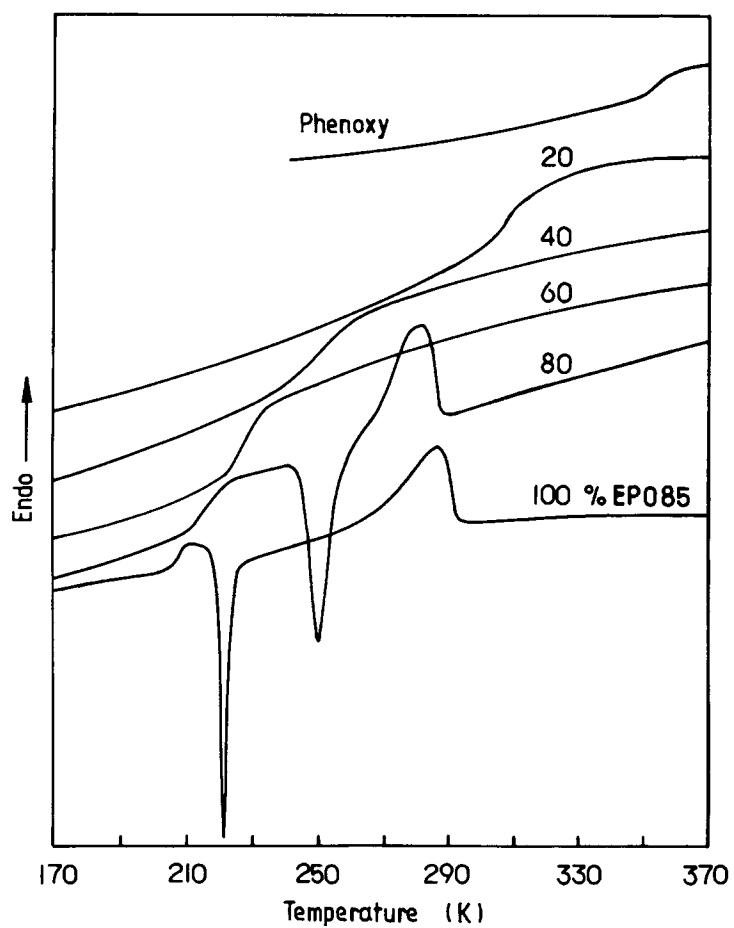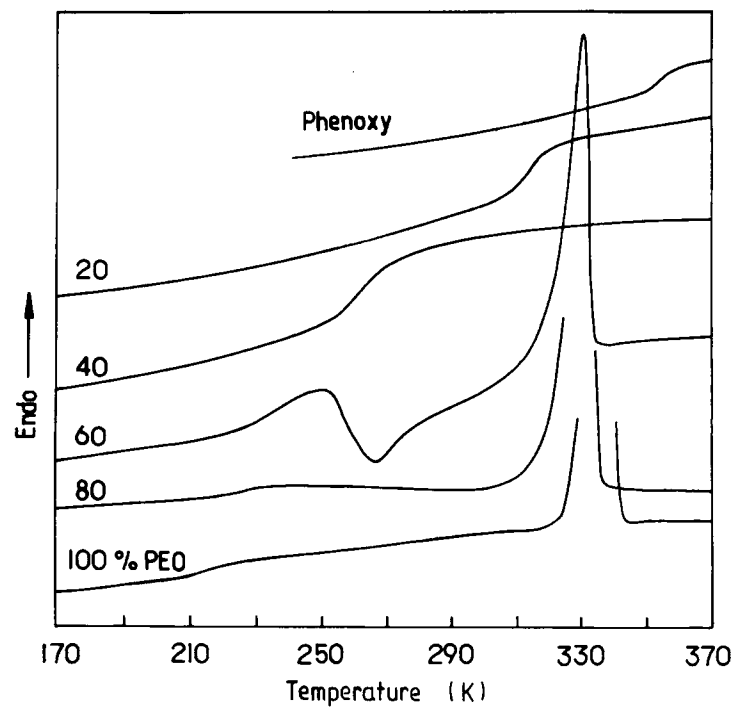
Figure 3 DSC thermograms of phenoxy blends with (A) PEO, (B) EPO85, and (C) EPO74.
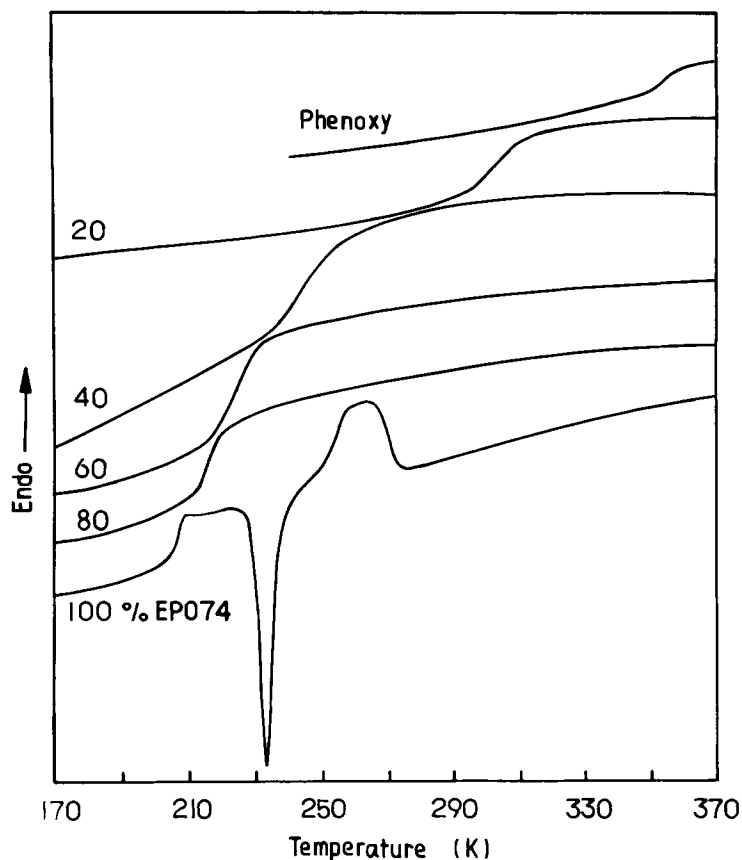
Figure 3   (*continued from the previous page*)

temperature as a function of copolymer composition at different blend ratios, which is shown in Figure 2. Miscibility occurs to the left of these curves. It is noted that there is no maximum in the displayed miscibility map.

DSC studies revealed that EPO85 and EPO74 are crystallizable. DSC thermograms for phenoxy blends with PEO, EPO85, and EPO74 are shown in Figure

3. They show a single, composition-dependent T_g for all the three blend systems, indicating that phenoxy is miscible with them. It can also be seen that crystallization did not occur in the blends with high phenoxy content. However, EPO74 did not crystallize in the blends containing only 20 wt % of phenoxy. The decrease in crystallinity of PEO or EPO copolymers in the blends is due to the increase

Table II   Thermal Properties of Phenoxy/PEO Blends

Phenoxy/PEO	T_g (°C)	T_c (°C)	ΔH_c (J/g)	T_m (°C)	ΔH_f (J/g)
0/100	−61			61	125.8
10/90	−39			60	122.6
20/80	−47			58	134.5
30/70	−39	−32	−29.1	57	98.3
40/60	−34	−7	−51.9	55	73.1
50/50	−18	14	−21.4	51	22.2
60/40	−10				
80/20	39				
100/0	81				

Table III   Thermal Properties of Phenoxy/EPO85 Blends

Phenoxy/EPO	T_g (°C)	T_c (°C)	ΔH_c (J/g)	T_m (°C)	ΔH_f (J/g)
0/100	−65	−52	−51.6	12	61.9
10/90	−56	−39	−38.8	7.5	50.7
15/85	−52	−35	−30.1	7	43.1
20/80	−51	−33	−24.6	6.5	37.4
25/75	−50	−37	−22.2	6	27.0
30/70	−48	−23	−14.1	5	14.8
40/60	−45				
50/50	−32				
60/40	−21				
80/20	35				
100/0	81				

in T_g of the system. The thermal properties of phenoxy/PEO and phenoxy/EPO85 blends are listed in Tables II and III, respectively.

PPO and the EPO copolymers containing 66 mol

% or less EO units are not crystallizable. The thermograms of their blends with 60 wt % phenoxy are shown in Figure 4. A single T_g was observed for the phenoxy/EPO66 and phenoxy/EPO50 blends, hence phenoxy is miscible with EPO66 and EPO50. However, two T_g's were detected for the 60/40 phenoxy/EPO22 blend prepared in the standard way, that is, first heated for 3 min at 120°C (Fig. 4, curve F). Since the cloud-point temperatures of these blends are lower than 120°C (Fig. 1), the observed phase separation might be strictly caused by the above heat treatment. To confirm this idea, another sample of the 60/40 phenoxy/EPO22 was preheated to only 50°C and examined by DSC. Here indeed only a single T_g was observed (curve G in Fig. 4). Thus both methods consistently show that phenoxy and EPO22 are miscible at low temperatures. However, the phenoxy/PPO blends have two T_g's that cannot be affected by thermal history, indicating that phenoxy is immiscible with PPO.

The T_g data are depicted in Figure 5 as a function of copolymer composition at different blend ratios.
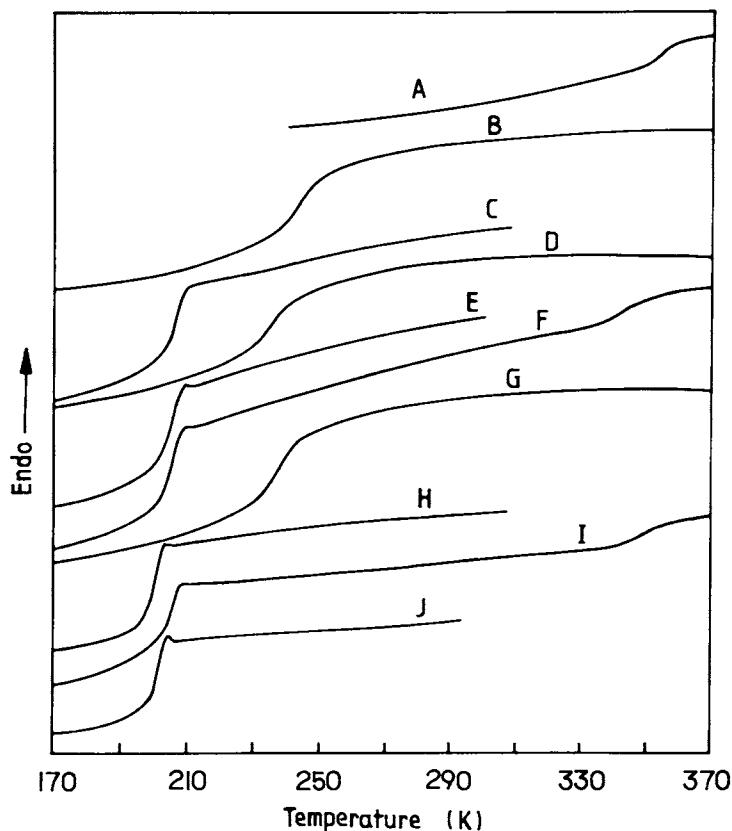

Figure 4   DSC thermograms of phenoxy, PPO, EPO copolymers, and 60/40 wt % of phenoxy blends with PPO and EPO copolymers: (A) phenoxy; (B) phenoxy/EPO66; (C) EPO66; (D) phenoxy/EPO50; (E) EPO50; (F) phenoxy/EPO22; (G) phenoxy/EPO22, after heating to 50°C; (H) EPO22; (I) phenoxy/PPO; (J) PPO.
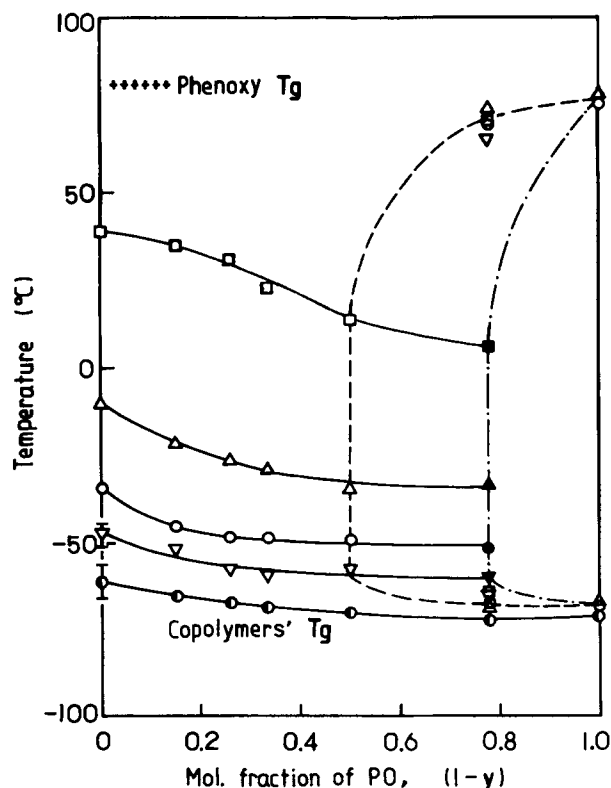
Figure 5 Dependence of the glass-transition temperature of the blend on copolymer composition. Weight percent phenoxy in blends: (∇, $\blacktriangledown$) 20; ($\bigcirc$, $\bullet$) 40; ($\triangle$, $\blacktriangle$) 60; ($\square$, $\blacksquare$) 80. The open and filled symbols refer to the T_g values obtained for the samples subject to preheating at 120°C and at 50°C, respectively.

It can be seen that the critical value of y for miscibility around 60°C is about 0.22.

DISCUSSION

Many systems have been examined where a homopolymer is miscible with a copolymer within a certain composition "window."[8,14,31-38] If y_1 and y_2, the miscibility limits of A in C_yD_{1-y}, are determined and if one of the B_{ij}'s in eq. (1) is known, the values of the remaining two B_{ij}'s can be evaluated.[31,32]

In the case that only one miscibility limit exists, it is not directly possible to obtain similar solutions to eq. (1). However, if there exists a maximum at $y = y_0$ in the miscibility window and if y_0 and one of the B_{ij}'s are determined, the remaining two B_{ij}'s can also be obtained.[20,32]

In the present case, there is only one miscibility limit and no maximum in the miscibility window as shown in Figure 2. So additional experimentally ac-

cessible information is needed to obtain similar solutions to eq. (1) under the condition that only one of the B_{ij}'s is known.

For a miscible polymer blend containing a crystallizable component, the melting-point depression of crystalline polymer by the miscible diluent is frequently used to calculate the interaction energy density B using the equation.[25,26]

$$T_m = T_m^\circ + B(V_{2U}/\Delta H_{2U})T_m^\circ\phi_1^2 \qquad (2)$$

where T_m° and T_m are the melting points of pure crystalline component and in the blend, respectively, ϕ_1 is the volume fraction of amorphous polymer in the blend, and ($\Delta H_{2U}/V_{2U}$) characterizes the heat of fusion per unit volume for 100% crystalline polymer. For phenoxy/PEO and phenoxy/EPO85 blends, the value of ($\Delta H_{2U}/V_{2U}$) for PEO was calculated from the following literature values:[39] V_{2U} = 38.9 cm^3/mol and ΔH_{2U} = 2100 cal/mol.

From the plot of T_m against ϕ_1^2 (Fig. 6, Line A), B_{AC}, the interaction energy density was found to be -6.2 cal/cm^3 for phenoxy/PEO blend system. This result is in good agreement with that (-6.0 cal/cm^3) reported by Iriarte et al.[24] from the equilibrium melting-point depression. It should be pointed out that our estimate may be subject to some errors, as the morphological effect on the melting-point depression of PEO has not been separated out. However, the fact that our value of B_{AC} agrees very well with that obtained by Iriarte et al. suggests that such errors should be small.

Figure 6 also gives a similar Nishi–Wang plot for phenoxy/EPO85 blends (Line B). This allows us to roughly estimate the overall interaction energy density, B_{blend}, between phenoxy and EPO85, that is, between phenoxy and EPO copolymer with y = 0.85. The B_{blend} value so obtained is -5.1 cal/cm^3. This result, combined with eq. (1), gives

$$-5.1 = 0.85 \times (-6.2) + (1 - 0.85)B_{AD}$$
$$- 0.85 \times (1 - 0.85)B_{CD}. \qquad (3)$$

As one miscibility limit has been known to be 0.22, by eq. (1) we can obtain

$$0 = 0.22 \times (-6.2) + (1 - 0.22)B_{AD}$$
$$- 0.22 \times (1 - 0.22)B_{CD}. \qquad (4)$$

Now, the remaining two interaction energy densities, B_{AD} and B_{CD} can be evaluated from eqs. (3) and (4). The values so obtained for B_{AD} and B_{CD} are 1.96 and 0.98 cal/cm^3, respectively. It is noted that the ab-
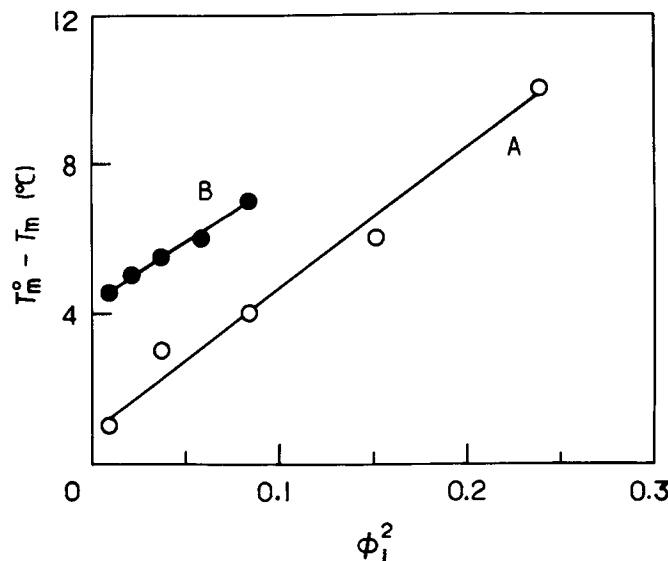
Figure 6 Melting-point depression analysis to obtain interaction parameters for (A) phenoxy/PEO and (B) phenoxy/EPO85 blends.

solute value of B_{AC} is much greater than that of B_{CD}, implying that the repulsion between the EO and PO units in the EPO copolymers contributes relatively little to the miscibility. Coleman and Moskala[23] have shown that there exist hydrogen-bonding interactions between phenoxy and PEO that are much stronger than those in pure phenoxy. Then, the miscibility between phenoxy and EPO copolymers can be considered to be caused mainly by the contribution of hydrogen-bonding interactions between the pendant hydroxyl groups of phenoxy and the EO units in EPO copolymers.

As both B_{CD} and B_{AD} are positive, one can assume that both of them include the interactions as well as the free volume contributions. Therefore, the magnitude of B_{CD} and B_{AD} can also be estimated as follows: the interactional contributions, B_{CD}^{int} and B_{AD}^{int}, are calculated from the solubility parameters of PEO, PPO, and phenoxy, by using Hoy's group contribution constants,[40] to be 0.76 and 2.74 cal/cm^3, respectively. The free volume contributions, B_{CD}^{FV} and B_{AD}^{FV}, can be calculated from the Patterson and Robard approximation[41] that gives the following expression for the free volume term of binary interaction energy densities, B_{ij}^{FV}.

$$B_{ij}^{FV} = \frac{\chi_{ij}^{FV} RT}{V_i} \quad (5)$$

$$\chi_{ij}^{FV} = \frac{P_i^* V_i^*}{RT_i^*} \frac{\tilde{V}_i^{1/3}}{2(4/3 - \tilde{V}_i^{1/3})} \tau^2 \quad (6)$$

$$1 < \tilde{V}_i^{1/3} < 4/3$$

$$\tau^2 = \left(1 - \frac{T_i^*}{T_j^*} \right)^2$$

where the subscripted quantities are for pure components. In eq. (6) the reduced volumes, $\tilde{V}$, and the characteristic pressures, P^*, and temperatures, T^*, of the components are related to measurable quantities, the thermal expansion coefficient α and the thermal pressure coefficient γ. Flory's theory prescribes the following equation of state for the pure component i.[42,43]

$$\frac{\tilde{P}_i \tilde{V}_i}{\tilde{T}_i} = \frac{\tilde{V}_i^{1/3}}{\tilde{V}_i^{1/3} - 1} - \frac{1}{\tilde{V}_i \tilde{T}_i} \quad (7)$$

in which the reduced quantities are $\tilde{P}_i = P/P_i^*$, $\tilde{V}_i = V/V_i^*$ and $\tilde{T}_i = T/T_i^*$. At zero pressure the above relation becomes

$$\tilde{V}_i = \left(1 + \frac{\alpha_i T}{3(1 + \alpha_i T)} \right)^3. \quad (8)$$

T_i^* is obtained from $\tilde{V}_i$.

$$T_t^* = \frac{T\tilde{V}_t^{4/3}}{\tilde{V}_t^{1/3} - 1}. \quad (9)$$

P_i^* is obtained from the thermal pressure coefficient, γ_i.

$$P_i^* = \gamma_i T \tilde{V}_i^2. \quad (10)$$

Table IV   Parameters for PEO, PPO, and Phenoxy at 25°C

	PEO	PPO	Phenoxy
V (cm^3/mol)	38.9[a]	57.6[a]	240.4[b]
$10^4\alpha$ (K)	7.32[c]	7.8[d]	5.08[b]
γ (cal/cm^3)	0.367[c]	0.281[e]	0.409[b]
$\tilde{V}$	1.190	1.201	1.137
T^* (K)	6295	6049	8072
P^* (cal/cm^3)	155	121	158
V^* (cm^3/mol)	32.7	48.4	211.4

[a] Reference 39.
[b] Reference 44.
[c] Reference 45.
[d] Reference 46 and 47.
[e] Reference 48.

$\tilde{V}_i$, P_i^*, and T_i^* for PEO, PPO, and phenoxy have been evaluated from the experimental data of thermal expansion coefficients and thermal pressure coefficients found in the literature.[44-48] Data and calculated parameters are listed in Table IV. Using the values in Table IV, eqs. (5) and (6) give B_{CD}^{FV} = 0.02 cal/cm^3 for the PEO/PPO pair and B_{AD}^{FV} = 0.61 cal/cm^3 for the phenoxy/PPO pair.

The sum of B_{CD}^{int} and B_{CD}^{FV}, 0.78 cal/cm^3, gives B_{CD}. This result is in accordance with the above-obtained value (0.98 cal/cm^3) of the B_{CD} by the mean-field approach. On the other hand, the sum of B_{AD}^{int} and B_{AD}^{FV} gives the B_{AD} value of 3.35 cal/cm^3, which is higher than that (1.96 cal/cm^3) obtained by the mean-field approach, but we consider that it is satisfactory.

CONCLUSIONS

In summary, phenoxy has been shown to be miscible with EPO copolymers containing 22 mol % EO units or higher. The blends containing EPO85 or EPO74 did not exhibit phase separation up to temperatures where the polymers show depolymerization, behaving the same as phenoxy/PEO blends. For the blends containing EPO22, EPO50, or EPO66, phase separation occurs at elevated temperatures, but there is no maximum in the miscible window. The values of B_{CD} and B_{AD} obtained by the mean-field approach are in reasonable accordance with the results estimated from the solubility parameters and Patterson approximation. The miscibility of phenoxy with EPO copolymers can be considered to be caused mainly by the hydrogen-bonding interactions between the components, while the intramolecular repulsion between EO and PO units in the EPO copolymers contributes relatively little to the miscibility.

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