Miscible Binary Blends Containing the Polyhydroxy Ether of Bisphenol-A and Various Aliphatic Polyesters

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Synopsis

Blends of the polyhydroxy ether of bisphenol-A, Phenoxy, with the polyesters poly(1,4-butylene adipate), poly(ethylene adipate), poly(2,2-dimethyl-1,3-propylene succinate), poly(2,2-dimethyl-1, 3-propylene adipate), poly(1,4-cyclohexane-dimethanol succinate), and poly(ε-caprolactone), are found to exhibit the single, composition-dependent glass transition temperatures characteristic of miscible systems. Phenoxy blends containing poly(ethylene succinate), poly(hexamethylene succinate), or poly(pivalolactone) were found to be immiscible. Blend interaction parameters, obtained from analysis of the melting-point depressions observed for miscible blends containing crystallizable polyester components, are found to vary with polyester chemical structure so as to suggest an optimum density of ester groups in the polyester chain for achieving maximum interaction with Phenoxy. Too many or too few ester groups lead to immiscible polyester–Phenoxy blends.

INTRODUCTION

It has been well established that miscible blends of polymeric materials result when exothermic physical interactions, such as hydrogen bonding, occur between unlike blend components.[1-12] As a first approximation, one might expect that the secondary hydroxyl moiety present in the polyhydroxyether of bisphenol-A, known as Phenoxy, would interact through formation of a hydrogen bond with a variety of proton acceptors to yield miscible blends. Heats of mixing and spectral shift data for low-molecular-weight binary mixtures suggest that carbonyl moieties are good proton acceptors[13,14] as are certain aromatic compounds.[15,8] Consequently, one might expect that both aromatic and aliphatic polyesters would likely form miscible mixtures with Phenoxy.

Several polyesters have recently been reported to be miscible with Phenoxy,[16-19] and these are summarized in Table I. As indicated in Table I, most of the polyesters investigated have been of the aromatic type. The fact that poly(ε-caprolactone) (PCL) is also found to be miscible with Phenoxy suggests, however, that the intermolecular interactions between the carbonyl on an aliphatic polyester and the hydroxyl of the Phenoxy can be sufficient to achieve miscible systems. One would further expect that a variety of aliphatic polyesters are likely to be miscible with Phenoxy but that structural shielding effects,[7,20] the stereo configuration of the polymer,[21] and competing endothermic interactions,[7,22,23] among other possibilities, may interfere with the miscibility process as have been observed in other systems. The purpose of this paper is to begin to explore the range of aliphatic polyester structural units which are miscible with Phenoxy and to provide further insight into the mechanisms responsible for miscible blend formation.

MATERIALS AND PROCEDURES

The PCL and Phenoxy used in this study were obtained from Union Carbide Corporation, Bound Brook, NJ, through the courtesy of Dr. L. M. Robeson. Other materials were obtained from a specialty chemical house. All of the polymers used in this study are shown in Table II along with characterizing in-

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TABLE I
Summary of Previous Polyester–Phenoxy Blend Studies

Polymer	Structure	Comment	Ref.
Poly(ε-caprolactone)		miscible	1
Poly(ethylene terephthalate)		miscible immiscible	2 4
Poly(butylene terephthalate)		miscible	2,3,4
Poly(hexamethylene terphthalate)		miscible	4
Poly(1,4 cyclohexane-dimethanol iso/ terephthalate (Kodar)		miscible	4
Poly(1,2 propylene terephthalate)		immiscible	4
Poly(1,3 propylene terephthalate)		immiscible	4

formation, identifying nomenclature, and source. Polymer molecular weights are provided, where known. Intrinsic viscosities are also reported for the purpose of roughly estimating the molecular weights of those specialty polymers whose Mark–Houwink parameters are unavailable. All of the densities shown in Table II are amorphous liquid densities obtained by extrapolating experimentally determined melt thermal expansion data to 25°C.

Blends are prepared by dissolving the polymer components in tetrahydrofuran (THF) or in dimethylformamide (DMF). Blends containing the lower melting polyesters—PCL, PBA, PEA, and PDPA—were solution cast from THF at room temperature with the solvent initially removed by a gentle stream of air passed over the solution. This was followed by a final drying of the film in vacuo at 100°C for 24 h to remove residual solvent. Blends containing the higher melting polyesters—PCDS and PDPS—were cast near the melting temperature to prevent phase segregation by crystallization during the solvent removal process. For these systems the higher boiling DMF was used as a solvent, initial drying was carried out in a convection oven, and final drying was accomplished using the vacuum drying protocol above.

Because Phenoxy has pendant hydroxyl groups, crosslinking of Phenoxy blends with polyesters is possible via ester interchange reactions.[17] Crosslinking was observed only in blends with PCDS which were exposed to 160°C for 24 h. PCDS containing blends dried initially at 130°C for 1 h followed by vacuum drying for as long as 96 h at 100°C showed no signs of gelation nor did blends with other polyesters prepared in the manner described above.

Transition temperatures and heats of fusion were determined with the use of an R. L. Stone Differential Thermal Analyzer (DTA) and a Perkin-Elmer DSC-2 Differential Scanning Calorimeter (DSC). All blends were cycled from 30°C above the higher pure component transition to at least 20°C below the glass transition temperature T_g of the polyester prior to measurement. All transitions were measured using a heating rate of 10°C/min, after cycling the system between the temperature limits reported above, at least once to provide a uniform thermal history, unless otherwise noted. Samples in the DTA were cooled at 50°C/min while those in the DSC were cooled at 320°C/min.

GLASS TRANSITION BEHAVIOR

The appearance in the blend of a single, composition dependent T_g is used as the criterion for blend miscibility.[1–4] Each T_g reported below and in the corresponding figures is an average of several determinations. Melting transition temperatures for the crystallizable polyesters are also shown in Figures 1–4. These melting results are discussed in the subsequent section.

Poly(1,4-butylene Adipate) (PBA)

Figure 1 shows the composition dependence of T_g for PBA blends with Phenoxy as measured by DTA. The observed T_g's for PBA[24] and Phenoxy[16] agree well with the values reported in the literature. The existence of a single T_g in the blend which varies smoothly with blend composition indicates that PBA/Phenoxy blends are miscible.

The variation of PBA melting point with blend composition is also shown in

TABLE II
Properties of Polymers Used in This Study

Polymer	Structure	Abbreviation	Amorphous density at 25°C (g/cc)	Intrinsic viscosity [dL/g]	Molecular wt	Source
Polyhydroxyether of bisphenol-A	[structure: $-O-CH_2-CH(OH)-CH_2-O-$ bisphenol-A with CH_3 groups]	Phenoxy	1.20	0.29[a]	$\overline{M}_n = 23{,}000$[e] $\overline{M}_w = 80{,}000$[e]	Union Carbide PKHH
Poly(1,4-butylene adipate)	$-(CH_2)_4-O-C(=O)-(CH_2)_4-C(=O)-O-$	PBA	1.13	0.157[b]	—	SPP,[h] Cat #149
Poly(ethylene adipate)	$-(CH_2)_2-O-C(=O)-(CH_2)_4-C(=O)-O-$	PEA	1.21	0.110[b]	—	SPP, Cat #147
Poly(2,2-dimethyl-1,3-propylene succinate)	$-CH_2-C(CH_3)_2-CH_2-O-C(=O)-(CH_2)_2-C(=O)-O-$	PDPS	1.17	0.080[b]	—	SPP, Cat #148
Poly(2,2-dimethyl-1,3-propylene adipate)	$-CH_2-C(CH_3)_2-CH_2-O-C(=O)-(CH_2)_4-C(=O)-O-$	PDPA	—	0.084[b]	—	Hooker Chem. Rucoflex Polyester S-1016-55

Poly(1,4-cyclohexane-dimethanol succinate)	PCDS	1.16	0.342[b]	—	SPP, Cat #007
Poly(hexamethylene sebacate)	PHS	1.03	0.510[b]	$\overline{M}_w = 16500$[f]	SPP, Cat #124
Poly(ethylene succinate)	PES	1.32	0.111[c]	—	SPP, Cat #150
Poly(ε-caprolactone)	PCL	1.095	0.67[d]	$\overline{M}_n = 15500$[e] $\overline{M}_w = 40500$[e] $\overline{M}_v = 46700$[g]	Union Carbide, PCL 700
Poly(pivalolactone)	PPL	—	—	—	Polysciences Cat #6535

[a] In 2-butanone at 25°C.
[b] In benzene at 25°C.
[c] In chloroform at 25°C.
[d] In benzene at 30°C.
[e] From Ref. 3.
[f] From Ref. 42.
[g] From Ref. 41.
[h] SPP = Scientific Polymer Products.
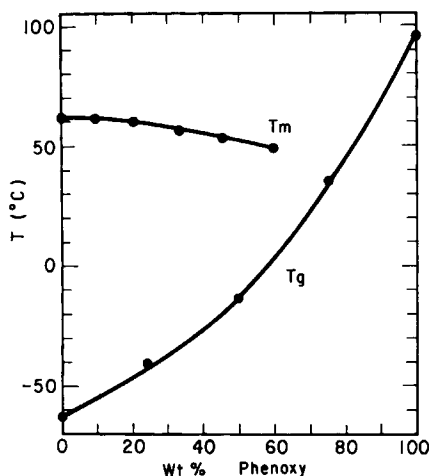
Fig. 1. Transitions for Phenoxy—PBA blends.

Figure 1. Melting points were measured by DSC for samples which were iso-thermally crystallized at 25°C for at least 24 h prior to measurement. The melting temperature of PBA either in the pure state or in the blend is observed to increase slightly with annealing times up to 24 h. Beyond 24 h the melting point T_m stabilizes, indicating no further crystalline refinement.

Poly(ethylene Adipate) (PEA)

Figure 2 demonstrates a single composition-dependent glass transition for blends of PEA with Phenoxy, which serves to demonstrate the miscibility of this polymer binary. The observed T_g for PEA is in good agreement with the −50°C value reported in the literature.[25]

As a result of the slow rates of crystallization of PEA, no crystallinity is de-tected during measurement of blend T_g when the cyclic protocol described above is employed. The melting points reported in Figure 2 were measured by DSC
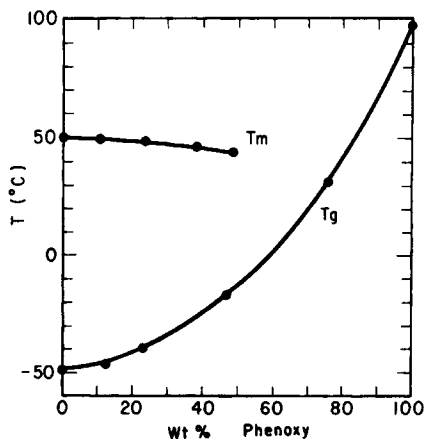

Fig. 2. Transitions for Phenoxy—PEA blends.

on samples crystallized for two months at 25°C.   Subsequent measurements for samples crystallized at 25°C for 96 h show comparable melting points.

Poly(2,2-dimethyl-1,3-Propylene Succinate) (PDPS)

The T_g-composition curve measured by DTA and shown in Figure 3 indicates that this polymer pair forms a miscible system.   The observed T_g for pure PDPS, −18°C, agrees well with that reported by Garfield et al.[26]

PDPS crystallizes very slowly even in the pure state.   The melting points shown in Figure 3 were measured by DTA on samples crystallized at room temperature for 6 months.

Blends of PDPS with Phenoxy exhibit lower critical solution temperature, LCST, behavior above 115°C.   This phenomena is discussed later in this paper.
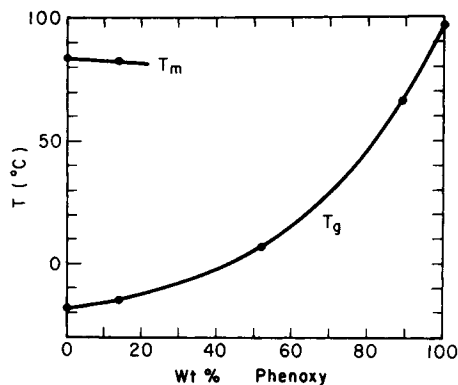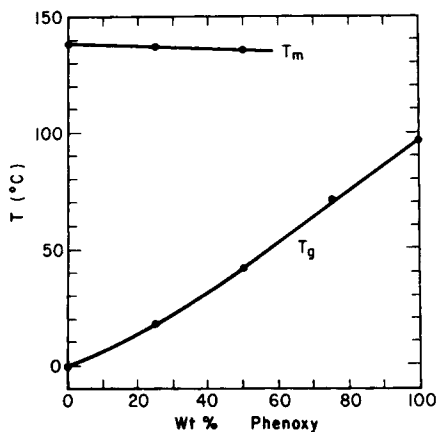

Fig. 3. Transitions for Phenoxy—PDPS blends.

Fig. 4. Transitions for Phenoxy—PCDS blends.

Poly(1,4-cyclohexanedimethanol Succinate) (PCDS)

Blends of PCDS with Phenoxy are also miscible as demonstrated by the single T_g behavior, Figure 4. Like PDPS, PCDS crystallizes very slowly. The melting points reported in Figure 4 are those for samples crystallized for 6 months prior to measurement with the DTA. The values for T_m and T_g of pure PCDS agree with those found by Cruz.[27]

Poly(2,2-dimethyl-1,3-Propylene Adipate) (PDPA)

As shown in Figure 5, blends of PDPA and Phenoxy are miscible by the single T_g criterion. Further evidence of their miscibility is provided by their LCST behavior at temperatures above 170°C, as is discussed in a later section. Of all the polyesters used in this study, PDPA crystallized the most slowly. No crystallinity was observed even after annealing for 1 month at room temperature.

Poly(ε-caprolactone) (PCL)

Figure 6 shows that T_g vs. composition curve for blends of PCL with Phenoxy. The T_g values are in good agreement with those of Brode and Koleske,[16] who first reported the miscibility of this polymer pair. The melting points shown
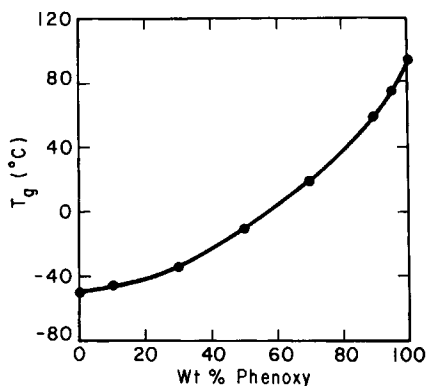

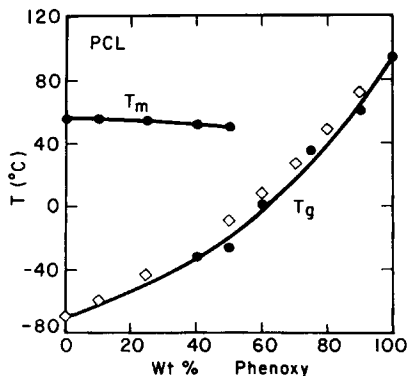Fig. 5. Transitions for Phenoxy—PDPA blends.

Fig. 6. Transitions for Phenoxy—PCL blends. (●) Present work; (◊) Brode and Koleske.[16]

in Figure 6 were determined from samples crystallized at 27°C for 30 min.   All transition measurements were performed with the DSC.

Poly(ethylene Succinate) (PES)

PES does not appear to be miscible with Phenoxy when cast from DMF at 120°C.   At this temperature, which is above the melting point of PES, milky white films result which contain large domains of Phenoxy.   No measurements were made on this system because of the large degree of heterogeneity obtained in the films.

Poly(hexamethylene Sebacate) (PHS)

Films cast from DMF at 80°C were milky white above the melting point of the polyester and gave every appearance of being composed of multiple phases. Again, film quality was so poor that measurements could not be consistently made.   The system was judged to be immiscible on the basis of its multiphase melt.

Poly(pivalolactone) PPL

Blends of PPL and Phenoxy, cast from orthodichlorobenzene were opaque at room temperature and remained cloudy to temperatures as high as 310°C where they began to decompose.   The T_g of Phenoxy, 97°C, is too close to the 100°C value observed for PPL[28] to permit assessing the state of blend miscibility by examination of its glass transition behavior.

The PPL melting temperature was also found to remain at 234°C regardless of the PPL concentration in the blend.   As indicated in Figures 1–4, the melting point of the crystallizable component in a miscible blend is usually observed to decrease as the concentration of that component in the blend decreases as a result of exothermic interactions on mixing which reduce its chemical potential.[10,29]

In addition, Figure 7 shows that the heat of fusion per total sample mass, as measured by DSC, is a linear function of the amount of PPL in the blend, and
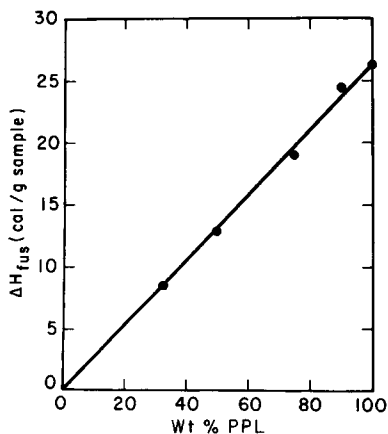

Fig. 7. Heat of fusion vs. composition for Phenoxy—PPL blends.
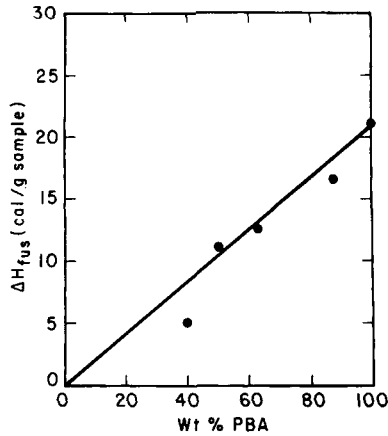
Fig. 8. Heat of fusion vs. composition of Phenoxy—PBA blends.

from Figure 7 the observed heat of fusion for PPL, 26 cal/g, is consistent with that reported for pure PPL.[28] This means that PPL crystallizes to the same extent in the blend as it does in the pure state. This observation is consistent with what would be expected for an immiscible system containing the crystallizable component as a separate phase; however, it does not constitute proof of immiscibility because miscible systems containing crystallizable components can behave in an identical manner provided the crystallization conditions are appropriate,[23,30] as illustrated by Figure 9.

These observations, that the melt is opaque, that no PPL melting point depression is observed, and, to a lesser extent, that crystallization from the blend is consistent with that expected for an immiscible system, lead to the conclusion that blends of PPL and Phenoxy are immiscible.

CRYSTALLIZATION AND MELTING BEHAVIOR

If the temperature of a miscible blend containing a crystallizable component is below the melting point of that component but above the T_g of the blend, the crystallizable component will theoretically crystallize from the blend.[30] The
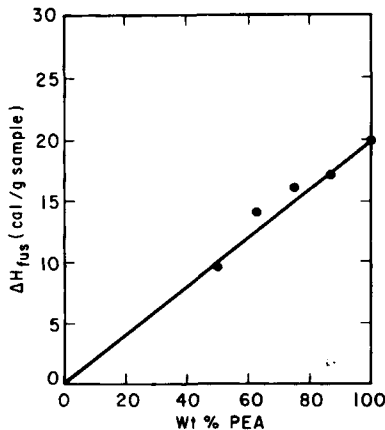

Fig. 9. Heat of fusion vs. composition for Phenoxy—PEA blends.

rate at which it does so, and consequently the observed degree of crystallization at any given time, will depend on the crystallization conditions employed, the blend composition as this affects blend T_g, and on the innate tendency to crystallize of the crystallizable component. As mentioned in the previous section, the crystallization rates of pure PDPS, PCDS, and PDPA were very slow even in the pure state with the result that very little reliable information regarding melting points of these components in Phenoxy blends and extents of crystallization from the blends were obtained. The remaining polyesters found to be miscible with Phenoxy, PBA, PEA, and PCL, crystallized from blends at sufficient rates, using the crystallization protocols described previously, to permit these studies.

Figures 8, 9, and 10 show the heats of fusion per unit mass of total sample obtained by heating blends, which were crystallized using the protocols mentioned previously, in the DSC. It is apparent from Figures 8 and 9 that PBA and PEA crystallize from the blends to about the same extents as they do in the pure state. These figures further suggest that chemical reactions between the blend components have not occurred to an appreciable extent, since the result of such reactions[17] should be a significant reduction in the degree of crystallinity of the polyester. Figure 10 indicates that the extent of crystallization of PCL from blends with Phenoxy is somewhat less than that obtained in the pure state at identical conditions of crystallization. While this behavior could be the result of chemical reactions with the Phenoxy, recent information concerning the crystallization of PCL from miscible blends with various amorphous copolymers of styrene with allyl alcohol (SAA)[23] suggests otherwise. In these systems, the SAA T_g's are 40–60°C less than that for Phenoxy, and the PCL is observed to crystallize from the blends to exactly the same extent as it does from the pure state when crystallization conditions identical to those used in the present study are employed. This occurs despite the fact that allyl alcohol contains a primary hydroxyl group which should be more chemically reactive then the secondary hydroxyl group present in the Phenoxy repeat structure. These additional considerations suggest that the reduced extent of crystallization of PCL from Phenoxy blends is merely the result of its inherently lower crystallization rate caused by the increase in blend T_g with Phenoxy addition.
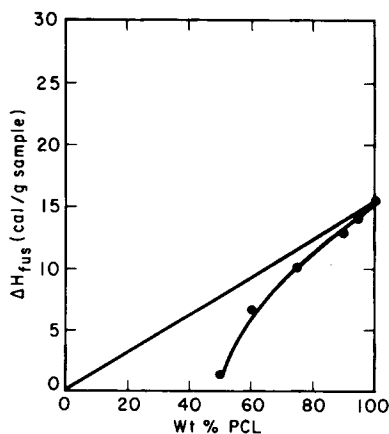

Fig. 10. Heat of fusion vs. composition for Phenoxy—PCL blends.

Analysis of the melting point depression of the crystallizable component in a miscible blend can be used to estimate the interaction parameter B between blend components[10,29] via

$$Y = \left(\frac{1}{T_{m2}} - \frac{1}{T_{m2}^0}\right)\frac{\Delta H_{2u}}{RV_{2u}} + \frac{1n\phi_2}{V_2} + \phi_1\left(\frac{1}{V_2} - \frac{1}{V_1}\right) = \frac{-B}{RT_{m2}}\phi_1^2 \qquad (1)$$

where component 2 is the crystallizable component, T_{m2}^0 its equilibrium melting temperature, $\Delta H_{2u}/V_{2u}$ its heat of fusion per unit volume of repeat unit for 100% crystalline material, V_2 its molar volume, and ϕ_2 its volume fraction in the blend. Symbols with subscript 1 refer to the corresponding quantities for the amorphous diluent, compound 1. The interaction parameter B is related to the heat of mixing per unit volume, ΔH_{mix}, through

$$\Delta H_{\text{mix}} = B\phi_1\phi_2 \qquad (2)$$

although B, in practice, is a free energy parameter related to the more familiar interaction parameter, χ_{12}, by

$$\chi_{12} = BV_{1u}/RT_{m2} \qquad (3)$$

where V_{1u} is the molar volume of the repeat unit. For miscible blends of high molecular weight materials, V_1 and V_2 are large, and those terms in eq. (1) which are inversely proportional to molar volume vanish, to give after rearrangement

$$T_m = T_m^0 + B\,(V_{2u}/\Delta H_{2u})T_m^0\,\phi_1^2 \qquad (4)$$

from which B can be directly evaluated by a plot of $(T_m^0 - T_m)$ vs. ϕ_1^2. Miscible blends of low-molecular-weight materials can be similarly analyzed, provided that the molar volumes are known, by using eq. (1) and plotting Y vs. ϕ_1^2.

Explicit in the arguments leading to eqs. (1)–(4) is the view that the melting point depression observed for the crystallizable polymer is primarily the result of thermodynamic interactions between the crystal and the miscible polymer–polymer amorphous phase with which it is in equilibrium. In actuality, Hoffman and Weeks[31] observed that the crystals in a semicrystalline pure component polymer can show melting point variations which are the result of annealing conditions and their effect on the crystalline lamella thickness. Consequently, there is also an implicit assumption in the melting point depression analysis above that the crystalline lamella formed during crystallization from the blend are
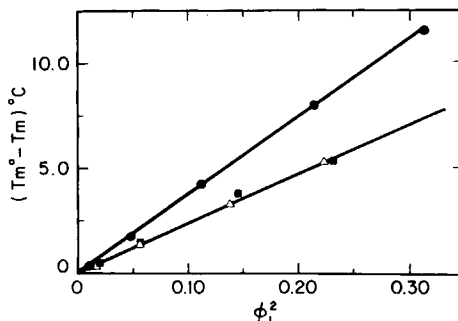

Fig. 11. Melting point depression of various polyesters in Phenoxy. (●) PBA; (△) PEA; (■) PCL.

comparable in thickness to those formed during crystallization of the pure component crystallizable polymer. Since the crystallization conditions employed are the same for the pure component as for the blends containing it, we shall assume in this study that the melting point depression observed is primarily the result of thermodynamic interactions between unlike components.

Figure 11 shows plots of $(T_m^0 - T_m)$ vs. ϕ_1^2 for PBA, PEA, and PCL containing blends which seem to follow eq. (4) insofar as a linear dependence is observed. Unfortunately, the molecular weights of the PBA and PEA used in this study are unknown; however, a rough idea of these values can be made by comparing the intrinsic viscosities of these polymers with those whose molecular weights are known (Table II). This comparison suggests that the molecular weights of PBA and PEA are probably between 2000 and 10,000. Table III shows the values of B computed from the melting point depression data of Figure 11, for PCL and for PEA and PBA using eq. (1) and these two estimates of their molecular weights together with values of $\Delta H_{2u}/V_{2u}$ obtained from the literature. As shown here, the B values obtained assuming the lower-molecular-weight estimate are roughly 10% lower than those calculated using the higher estimate of molecular weight. This is a natural consequence of the greater weighting given to the entropic contributions to melting point depression by assumptions of the lower values of molecular weight. At any rate, the B values do not change substantially with variations in polyester molecular weight in this range, and one can conclude that the primary contribution to the melting point depression is due to enthalpic interactions which lead to negative B values and, from eq. (2), exothermic heats of mixing.

VISUAL OBSERVATIONS

All of the miscible blends with Phenoxy had transparent melts immediately above the melting point of the polyester. The melts of all blends, except those containing PDPA and PDPS, remained transparent to temperatures well above 200°C, where thermal decomposition became apparent. Melts of blends containing PDPA and of blends containing PDPS showed phase separation on heating through composition-dependent cloud point temperatures. This phase separation was reversible insofar as clear melts rapidly reformed as the melts were cooled through the cloud point.

The cloud point temperature versus composition diagrams for these two blends are shown in Figure 12, and the existence of these diagrams signals the existence

TABLE III
Estimated B Values from Melting-Point Depression Analysis

System	T_{m2}^0 (°C)	$\Delta H_{2u}/V_{2u}$ (cal/cc)	$BT_{m2}^0 V_{2u}/\Delta H_{2u}$ (°C)	B at T_{m2}^0 (cal/cc)
PBA/Phenoxy	61	34.5	−37.5[a]	−3.87[a]
			−35.0[b]	−3.6[b]
PEA/Phenoxy	49	31.0	−24.0[a]	−2.31[a]
			−21.2[b]	−2.04[b]
PCL/Phenoxy	56	35.0	−22.7	−2.41

[a] Molecular weight of polyester is assumed to be infinite.
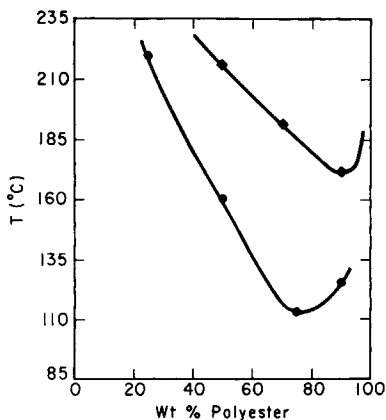[b] Molecular weight of polyester is assumed to be 2000.

Fig. 12. Cloud point temperatures vs. composition for Phenoxy—PDPS (●) and Phenoxy—PDPA (◆) blends.

of lower critical solution temperatures (LCST) for these blend systems. Basic thermodynamic theory leads one to expect LCST behavior for systems which have exothermic heats of mixing, negative volumes of mixing, and positive excess heat capacities as a result of strong solute–solvent bonds.[32–34] That these two blend systems show LCST behavior further substantiates their miscible behavior at temperatures below the cloud point and suggests that they are miscible as a result of exothermic interactions.

As exemplified in this study as well as in those of numerous other investigators,[1,2] not every miscible blend shows observable LCST behavior. One study of this phenomenon[11] shows that the cloud point temperature increases as the strength of the exothermic interaction between unlike blend components increases. On this basis, one could speculate that the interaction strengths of all the miscible polyester–Phenoxy blends, except those with PDPA or with PDPS, are sufficiently strong to move the cloud points above the blend decomposition temperatures that those blends containing PDPA or PDPS have somewhat weaker interaction strengths with resulting cloud points in the observable range. Interestingly, PDPA and PDPS, along with PPL which is immiscible with Phenoxy, are the only polyesters among these considered with branched structures. Other studies[22,27] have shown that branching may interfere with the interactions responsible for miscibility, and it therefore seems plausible that branching in these two polyesters decreases their interactions with Phenoxy to the point were LCST behavior is observable below 200°C.

DISCUSSION

This study has demonstrated that a fairly large variety of aliphatic polyesters, PBA, PEA, PDPS, PDPA, PCDS, and PCL, form miscible binary solutions with Phenoxy and that other aliphatic polyesters, PES, PHS, and PPL, individually form immiscible mixtures with this material. All of the miscible blends exhibit characteristics indicative of the presence of exothermic interactions between the binary components, and these interactions are probably responsible for the observed miscible behavior.[1–12] These interactions are probably the result of hydrogen bond formation between the hydroxyl group of Phenoxy and the car-
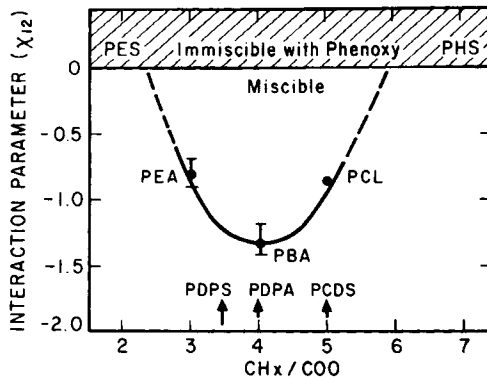
Fig. 13. Blend interaction parameter as a function of the number of aliphatic carbons per ester linkage in the polyester structure.

bonyl of the polyester[3,13,14]; however, the fact that not all polyesters are miscible with Phenoxy suggests that there may also be competing endothermic interactions between blend components which are related to the chemical structure of the polyester and which may dominate in those blends observed to be immiscible. This trend is shown in Figure 13, where the interaction parameter χ_{12}, observed from studies of melting point depression, is plotted against a measure of the proportion of ester linkages in the polyester repeat unit structure, expressed as CH_x/COO, where x may have values 0, 1, 2, or 3 depending on the substitution. Although the data are somewhat limited and there is some uncertainty in the χ_{12} values, indicated by the error bars, as a result of uncertainties in the molecular weights of PEA and PBA, the interaction parameter clearly approaches a maximum negative value indicating maximum interaction as the CH_x/COO ratio in the repeat structure is varied toward the optimum value of 4. The χ_{12} variation with structure suggests that χ_{12} will become positive for CH_x/COO ratios less than about 2.5 and for ratios greater than about 6. Both PES and PHS should have positive interactions with Phenoxy on this basis, and both materials are found to be immiscible with Phenoxy as expected from thermodynamic considerations.[1–12] While no measure of interaction is available for the miscible blends containing PDPS, PDPA, or PCDS, their CH_x/COO ratios suggest that the interactions should be negative for these mixtures. The results of this study are therefore consistent with the idea that exothermic interactions are necessary for polymer–polymer miscibility.

It should be noted that the appearance of an optimum interaction strength as a function of chemical structure variations is not unique to the polyester–Phenoxy system studied here. Similar behavior is observed in PCL blends with poly(styrene-co-allyl alcohol) copolymers as a function of copolymer alcohol content[23] and in PVC—polyester blends as a function of the CH_x/COO ratio in the polyester.[22] Miscibility limits with copolymer composition have also been reported for various blend systems[3,35–38] and the observed correlation between miscibility and exothermic interactions[7] suggests that curves similar to Figure 13 may also exist in these systems. The physical basis for this behavior is, consequently, well worth considering if progress toward predicting miscibility is to be made.

One possibility for the χ_{12} variation with polyester structure noted in Figure

13 could be that changes in polyester structure change its cohesive energy density or solubility parameter relative to that for Phenoxy and that this difference causes a positive heat of mixing contribution to partly counteract the negative heat associated with hydrogen bond formation. If this were the case, one would expect that the solubility parameter for PBA would be the same as that for Phenoxy since the net exothermic contribution is maximum for PBA/Phenoxy blends. The solubility parameter as calculated by the method of Hansen outlined in Van Krevelen[39] for Phenoxy is 10.5 $(cal/cc)^{1/2}$, whereas that for PBA is 9.4 $(cal/cc)^{1/2}$. Further, PES by this calculation has a solubility parameter of 10.5 $(cal/cc)^{1/2}$; yet it is immiscible with Phenoxy. Those polyesters found to be miscible with Phenoxy have calculated solubility parameters in the range 9.4–9.9 $(cal/cc)^{1/2}$; however, there is no detectable trend between the calculated solubility parameters and the interaction strength. For example, PCL and PBA have substantially the same solubility parameter; yet the observed χ_{12} values are quite different. PCL and PEA have solubility parameters which differ by 0.5 $(cal/cc)^{1/2}$; yet the observed χ_{12} values for blends of these materials with Phenoxy are substantially the same. About all that can be concluded is that the solubility parameter approach, at best, provides a crude estimate of possibly miscible systems and, at worst, is very misleading. Similar problems with this approach as applied to other systems have also been noted,[23,35,40] and the inaccuracy of the method may well reside with the lack of accounting for chemical structural details inherent in the group contribution methods employed to calculate solubility parameters.

A more promising approach toward understanding and perhaps predicting polymer binary miscibility might be to study the thermodynamics of mixing of low-molecular-weight analogs of the polymers of interest.[7] Work of this type is presently underway, and the results of this study will be reported in the near future.

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