Phase Behavior of Binary Mixtures of Oligomeric Styrene/Allyl Alcohol Copolymers and Aliphatic Polyesters

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Synopsis

The phase behavior of binary mixtures of copolymers containing varying amounts of styrene and allyl alcohol (SAA) with a wide range of aliphatic polyesters has been examined. All of the copolymers and most of the polyesters had low molecular weights in the oligomeric range; hence, entropy effects were a significant factor in the observed phase behavior. The polyesters employed had CH_2/COO ratios over the entire range from 2 to 12. The SAA copolymers were completely miscible with polyesters in the middle of this range based on the observation of a single composition-dependent glass transition for these mixtures. Upper critical solution temperature behavior was observed for blends of SAA copolymers with polyesters having ratios of CH_2/COO immediately on either side of this optimum region of polyester structure. Complete immiscibility was noted for blends with polyesters having CH_2/COO ratios at either extremity of the range examined. Interaction parameters were deduced from either melting point depression data or the cloud point observations and correlated with the structure of the components.

INTRODUCTION

Binary blends of certain oligomeric styrene/allyl alcohol copolymers (SAAs) were reported in a previous paper[1] to be miscible with poly(ε-caprolactone). This paper reports on an extension of this investigation to include a wider range of aliphatic polyesters. The objective was to understand how the phase behavior of these blends changes when the density of hydroxyl and ester groups, known to be responsible for miscibility in other blend systems, varies in one or both of the components. For this purpose, a homologous series of polyesters with different carbonyl contents as well as the previously used family of SAAs with different contents of allyl alcohol were chosen for study.

The present paper includes observations of complete miscibility, complete immiscibility, and phase separation caused by an upper critical solution temperature (UCST). Quantitative values of interaction parameters have been estimated from cloud point information for systems showing UCST behavior and from melting point depression for completely miscible systems. The relationship between polymer structure and the interaction parameters so obtained aids understanding of the diverse phase behavior exhibited by these mixtures.

MATERIALS AND EXPERIMENTAL PROCEDURES

Three of the poly(styrene-co-allyl alcohol) copolymers used here are commercial materials, and all are described in Table I. Their allyl alcohol contents are expressed in terms of wt % of hydroxyl (OH) groups, and they

TABLE I
Properties of Styrene/Allyl Alcohol Copolymers

Designation used here	Commercial designation	Source	% OH by weight	$\overline{M}_w$	Density, (g/cm³)	T_g (°C)	$\overline{V}$ (cm³/ mol)
SAA-7	RJ101	Monsanto	7.7	1700	1.09	45	1560
SAA-5	RJ100	Monsanto	5.7	2340	1.06	60	2200
SAA-2	Filtrez	FRP Co.	2.5	1420	1.05	41	1350
SAA-1	RF9266	Monsanto	1.3	2100	1.05	44	2000
SAA-0	Polystyrene	Pressure Chemical Co.	0	2000	1.02	40	2000

are redesignated for convenience as SAA-7, SAA-5, SAA-2, and SAA-1 with the number indicating the nominal level of their OH content. For comparison purposes, an oligomeric polystyrene, SAA-0, was also included in this study since it represents the limit of 0% OH. The oligomeric polyesters, except those which are available commercially (Table II), were synthesized in small quantities in this laboratory by standard polyesterification procedures.[2-4] Various characterization data are shown in Table II.

Due to their low softening temperatures, molecular weights, and melt viscosities, blends of these polymers were conveniently prepared by direct melt mixing in a small glass vial at temperatures about 50°C above the melting points of the polyesters or about 70°C above the glass transitions of the SAAs. Three to five minutes of vigorous stirring at these temperatures ensured thorough mixing.

Glass transition temperatures and melting points were measured using a Perkin-Elmer DSC-2 Differential Scanning Calorimeter at a heating rate of 20°C/min and 10°C/min, respectively. The 20°C/min heating rate was found to be the best scanning rate for good sensitivity and resolution. Sensitivity is necessary to identify the glass transitions of multiphase blends, espcially that of a minor component. For measurement of the glass transition, the samples were quenched in the DSC at the most rapid rate possible prior to heating in order to minimize crystallization of the polyester. This maximizes the magnitude of the heat capacity change at T_g and minimizes alteration in the composition of the amorphous phase caused by depletion of polyester to form crystals which would alter the temperatures of the glass transition.[5] Continuous cyclic heating and cooling was used to measure the melting point.

Cloud points caused by UCST behavior were observed by directly heating samples on a hot plate. The temperature at the cloud point, measured by a thermocouple placed in the vial, represents the closest judgement of the onset from a cloudy blend to a transparent one at a heating rate of approximately 10°C/min.

BACKGROUND

A convenient simplification of the thermodynamics for mixtures of high molecular weight polymers is to ignore the contribution of combinatorial entropy of mixing. In this limit, complete miscibility in blends is possible

only when the heat of mixing is exothermic. Except in unusual circumstances, UCST behavior is not expected, and lower critical solution temperature (LCST) behavior has become the expected, owing to the exaggerated importance of excess entropy considerations when the combinatorial entropy change is effectively zero. However, all of the polyesters, except for PCL and PHS, used here have rather low molecular weights and may be regarded as essentially oligomeric. Consequently, contributions from the combinatorial entropy of mixing is expected to be a significant factor in the phase behavior of their mixtures. The purpose of this section is to review some thermodynamic relations used later to estimate interaction parameters for certain SAA/polyester mixtures.

The Flory–Huggins theory[6] provides a convenient formalism for treating blend thermodynamics in the present case since it does include the best-known estimate of the combinatorial entropy, although it fails to include "free volume" notions incorporated into more modern theories.[7] Our interest is to extract information about interaction parameters which are introduced, in effect, using a simple van Laar expression for the heat of mixing, i.e.,

$$\Delta H_m = VB\phi_1\phi_2 \tag{1}$$

even in the more modern theories. Here, V is the total volume of the mixture, ϕ_i is the volume fraction of component i, and B is an interaction energy density.

Several interaction parameters are in common usage, which may be easily interrelated by the following:

$$\frac{B}{RT} = \frac{\chi_1}{\tilde{V}_1} = \frac{\chi_{12}}{V_1} = \tilde{\chi}_{12} \tag{2}$$

where $\tilde{V}_1$ is the molar volume of species 1 and V_1 is a characteristic volume for species 1 such as the molar volume of its repeat unit. We prefer to use the dimensional interaction energy density B because of the clarity of its meaning. Each of these interaction parameters may include entropy contributions in addition to heat of mixing effects when deduced from experimental observations which require use of the Flory–Huggins theory in their analysis because of the failure of this theory to account properly for all entropic effects.

For mixtures having a positive interaction parameter and when the components are of finite molecular weight, complete miscibility in all proportions is expected for high enough temperatures. However, liquid–liquid phase separation is predicted when the mixture is cooled sufficiently, i.e., UCST behavior. The critical solution point, where first and second derivatives of the component chemical potentials with respect to composition vanish, may be deduced from appropriate manipulation of the Flory–Huggins equation. This occurs for a critical value of the interaction parameter most often expressed in the following form[6]:

$$(\chi_1)_c = \frac{(1 + \sqrt{r})^2}{2r} \tag{3}$$

TABLE II
Properties of Polyesters Used in This Study

Polyester	Repeat unit	CH_2/COO	Abbreviation	Density (g/cm^3)	$[\eta]$ (dL/g)	MW	T_m (°C)	T_g (°C)	Source
Poly(ethylene succinate)	$-(CH_2)_2-O-C(=O)-(CH_2)_2-C(=O)-O-$	2	PES	1.32	0.111[a]	—	100	-22	SPP#150[6]
Poly(propylene succinate)	$-(CH_2)_3-O-C(=O)-(CH_2)_2-C(=O)-O-$	2.5	PPS	1.29	0.163[a]	—	40	-38	SPP#592
Poly(ethylene adipate)	$-(CH_2)_2-O-C(=O)-(CH_2)_4-C(=O)-O-$	3	PEA	1.21	0.11[c]	—	53	-50	SPP#147
Poly(trimethylene glutarate)	$-(CH_2)_3-O-C(=O)-(CH_2)_3-C(=O)-O-$	3	PTG	1.25	0.104[a]	—	39	-70	SPP#591
Poly(propylene adipate)	$-(CH_2)_3-O-C(=O)-(CH_2)_4-C(=O)-O-$	3.5	PPA	1.28	0.097[a]	—	37	-69	SPP#594
Poly(butylene adipate)	$-(CH_2)_4-O-C(=O)-(CH_2)_4-C(=O)-O-$	4	PBA	1.13	0.157[c]	—	53	-70	SPP#149
Poly-(ϵ-caprolactone)	$-(CH_2)_5-O-C(=O)-$	5	PCL	1.095	0.67[d]	$M_n = 15{,}500$ $M_w = 40{,}500$ $M_v = 46{,}700$	63	-71	Union Carbide (PCL-700)

Name	Structure		Abbrev.			M_w = 16,500			Source
Poly(hexamethylene sebacate)	$-(CH_2)_6-O-\overset{\overset{O}{\|\|}}{C}-(CH_2)_8-\overset{\overset{O}{\|\|}}{C}-O-$	7	PHS	1.03	0.51[c]	68.9	-70[e]	SPP#124	
Poly(2,2-dimethyl-1,3-propylene succinate)	$-CH_2-\overset{\overset{CH_3}{\|}}{\underset{\underset{CH_3}{\|}}{C}}-CH_2-O-\overset{\overset{O}{\|\|}}{C}-(CH_2)_2-\overset{\overset{O}{\|\|}}{C}-O-$	(3.5)	PDPS	1.17	0.080[c]	—	-18	SPP#148	
Poly(2,2-dimethyl-1,3-propylene adipate)	$-CH_2-\overset{\overset{CH_3}{\|}}{\underset{\underset{CH_3}{\|}}{C}}-CH_2-O-\overset{\overset{O}{\|\|}}{C}-(CH_2)_4-\overset{\overset{O}{\|\|}}{C}-O-$	(4.5)	PDPA	1.123	0.084[c]	—	-53	Hooker Chemical Co.	
Poly(1,4-cyclohexane dimethyl succinate)	$-CH_2-\langle S\rangle-CH_2-O-\overset{\overset{O}{\|\|}}{C}-(CH_2)_2-\overset{\overset{O}{\|\|}}{C}-O-$	(5)	PCDS	1.16	0.342[c]	—	-3	SPP#007	
Poly(butylene sebacate)	$-(CH_2)_4-O-\overset{\overset{O}{\|\|}}{C}-(CH_2)_8-\overset{\overset{O}{\|\|}}{C}-O-$	6	PBS	1.136	0.166[a]	62.6	-70[e]	Synthesized	
Poly(butylene dodeca-methylene dicarboxylate)	$-(CH_2)_4-O-\overset{\overset{O}{\|\|}}{C}-(CH_2)_{12}-\overset{\overset{O}{\|\|}}{C}-O-$	8	PBDO	1.085	0.15[a]	76	-73[e]	Synthesized	

(continued)

TABLE II (*Continued from the previous page.*)

Polyester	Repeat unit	CH_2/COO	Abbreviation	Density (g/cm^3)	$[\eta]$ (dL/g)	MW	T_m $(°C)$	T_g $(°C)$	Source
Poly(decamethylene sebacate)	$-(CH_2)_{10}-O-\overset{O}{\underset{\|\|}{C}}-(CH_2)_8-\overset{O}{\underset{\|\|}{C}}-O-$	9	PDS	1.15[e]	0.28[a]	—	75	-75[e]	Synthesized
Poly(decamethylene decamethylene dicarboxylate)	$-(CH_2)_{10}-O-\overset{O}{\underset{\|\|}{C}}-(CH_2)_{10}-\overset{O}{\underset{\|\|}{C}}-O-$	10	PDEDE	1.1[e]	0.28[a]	—	82.5	-77[e]	Synthesized
Poly(dodecamethylene decamethylene dicarboxylate)	$-(CH_2)_{10}-O-\overset{O}{\underset{\|\|}{C}}-(CH_2)_{12}-\overset{O}{\underset{\|\|}{C}}-O-$	11	PDODE	1.1[e]	0.30[a]	—	84.4	-78[e]	Synthesized
Poly(dodecamethylene dodecamethylene dicarboxylate)	$-(CH_2)_{12}-O-\overset{O}{\underset{\|\|}{C}}-(CH_2)_{12}-\overset{O}{\underset{\|\|}{C}}-O-$	12	PDODO	1.1[e]	0.29[a]	—	89.2	-78[e]	Synthesized

[a] Measured in chloroform at 25°C.
[b] SPP = Scientific Polymer Products.
[c] Measured in benzene at 25°C.
[d] Measured in benzene at 30°C.
[e] Estimated by group contribution method given in D. W. Van Krevelen, *Properties of Polymers*, Elsevier, New York, 1976.

where $r = \tilde{V}_2/\tilde{V}_1$. This condition occurs at the following point on the phase diagram:

$$(\phi_2)_c = \frac{1}{1 + \sqrt{r}} \tag{4}$$

$$T_c = \frac{2B\tilde{V}_2}{R(1 + \sqrt{r})^2} \tag{5}$$

where the interaction parameter at this condition is expressed by our preferred term B. These results strictly apply for monodisperse components. In this simple case, the critical point is at the maximum temperature observed on the cloud point or binodal curve. Unusual molecular weight distributions may alter this location somewhat, but this has been neglected here owing to the approximate nature of the ensuing analysis.

By eliminating r between eq. (4) and (5), a more convenient expression for estimating the interaction parameter from experimentally observed coordinates, i.e., T_c and $(\phi_i)_c$, of the critical point can be obtained:

$$B = \frac{RT_c}{2\tilde{V}_1(\phi_1)_c^2} = \frac{RT_c}{2\tilde{V}_2(\phi_2)_c^2} \tag{6}$$

The two forms of this result offer a useful choice in cases where either $\tilde{V}_1$ or $\tilde{V}_2$ is known more accurately than the other. In the present work, the molecular weights of the SAAs are more accurately known than the values for the polyesters.

It is widely recognized that the equilibrium melting point of a crystallizable component, say species 2, will be depressed by dilution with another polymer miscible with it. In the limit of very high molecular weights, the equilibrium melting point depression is well approximated by the following result developed from the Flory–Huggins model[8]:

$$T_{m2}^0 - T_{m2} = -T_{m2}^0\left(\frac{V_{2u}}{\Delta H_{2u}}\right)B\phi_1^2 \tag{7}$$

where $\Delta H_{2u}/V_{2u}$ is the heat of fusion per unit volume of completely crystalline component 2. This result completely ignores any contributions to melting point depression from the combinatorial entropy of mixing, and the more complete expression including this effect is[1]

$$\left(\frac{1}{T_{m2}} - \frac{1}{T_{m2}^0}\right)\frac{\Delta H_{2u}}{RV_{2u}} + \frac{\ln \phi_2}{\tilde{V}_2} + \phi_1\left(\frac{1}{\tilde{V}_2} - \frac{1}{\tilde{V}_1}\right) = \frac{-B}{RT_{m2}} \tag{8}$$

where in both equations T_{m2}^0 is the melting point of pure 2 and T_{m2} is the melting point of this component, when blended, in the limit where crystal lamella are quite thick. Clearly, eq. (8) must be used when both components are oligomeric.[1,8]

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RESULTS

For the various SAA–polyester blends examined here, three distinct categories of phase behavior were observed. In the first, complete miscibility, as judged by observation of a single composition-dependent glass transition, was found, and these systems were completely transparent in the melt state at all temperatures. Haziness or opacity existed below the melting point of the polyester in those cases where this component formed a separate crystalline phase. However, in these cases there was a coexisting homogeneous amorphous phase comprised of a mixture of both components as evidenced by the glass transition behavior. Such systems are termed *miscible* for present purposes.

In the second category, the blend melts were cloudy at low temperatures, but they became clear on heating at a temperature designated as the cloud

TABLE III
Miscibility and UCST Behavior of Polyester/SAA Blends

Polyester	$CH_2/$ COO	SAA-7	SAA-5	SAA-2	SAA-1	SAA-0
PES	2	X[a]	X	X	X	X
PPS	2.5	130°C[b] (0.50)	X	X	X	X
PTG	3	55°C (0.5)	80°C (0.3)	X	X	nt[c]
PEA	3	80°C (0.51)	90°C (0.52)	X	X	X
PPA	3.5	55°C (0.5)	55°C (0.5)	90°C (0.5)	X	X
PBA	4	Miscible	Miscible	Miscible	X	X
PCL[d]	5	Miscible	Miscible	Miscible	Miscible	X
PBS	6	80°C (0.4)	Miscible	Miscible	Miscible	X
PHS	7	120°C (0.45)	90°C (0.45)	Miscible	Miscible	X
PBDO	8	110°C (0.5)	nt	nt	nt	X
PDS	9	X	120°C (0.4)	Miscible	Miscible	X
PDEDE	10	X	150°C (0.5)	100°C (0.5)	90°C (0.5)	100°C (0.5)
PDEDO	11	nt	nt	150°C (0.5)	200°C (0.5)	X
PDODO	12	X	X	X	X	X
Nonlinear polyesters						
PDPS	(3.5)	120°C (0.4)	X	X	X	X
PDPA	(4.5)	70°C (0.4)	40°C (0.25)	Miscible	180°C (0.3)	X
PCDS	(5.0)	Miscible	Miscible	Miscible	Miscible	X

[a] X = total immiscibility.
[b] Coordinates of maximum point on cloud point curve. Number in parentheses is the volume fraction of SAA at this point.
[c] nt = not tested.
[d] Data from Ref. 1.

point. Thus, these systems have a UCST within the observable temperature range. Based on the foregoing discussion, their miscibility at elevated temperatures is a result of a sufficiently large combinatorial entropy of mixing stemming from their low molecular weights rather than a negative interaction parameter required for miscibility in the limit of high molecular weights for both components.

The final category includes blends which were cloudy in the melt state and could not be made clear upon heating up to temperatures where decomposition of the components occurred. Such systems have been termed *completely immiscible* for present purposes.

It should be pointed out that, in principle, upper critical solution temperatures may exist for all these blends. In the first category, those called miscible, the possible T_c may simply lie below the T_g of the blend; hence, for kinetic reasons phase separation on cooling cannot be observed. In the third category, those called immiscible, the possible T_c may lie above the decomposition temperature of the components; hence, for chemical stability reasons formation of a single phase mixture cannot be observed.

The categorization of the various blends is summarized in Table III. Detailed descriptions through selected examples are given in the following subsections and discussed.

Miscible Blends

As noted in Table III, aliphatic polyesters having CH_2/COO ratios in the middle of the range examined are miscible with all or some of the four SAAs. These blends exhibited a single glass transition (see Figs. 1–5) without any evidence for liquid–liquid phase separation within the accessible temperature range. Glass transition data are not reported for blends with PDS,
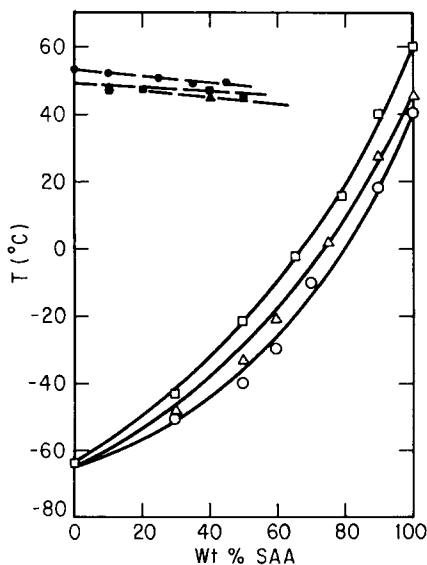

Fig. 1. Glass transitions (open points) and melting points (closed points) for blends of PBA with SAA-2 (△), (▲), SAA-5 (□, ■), and SAA-7 (○, ●).
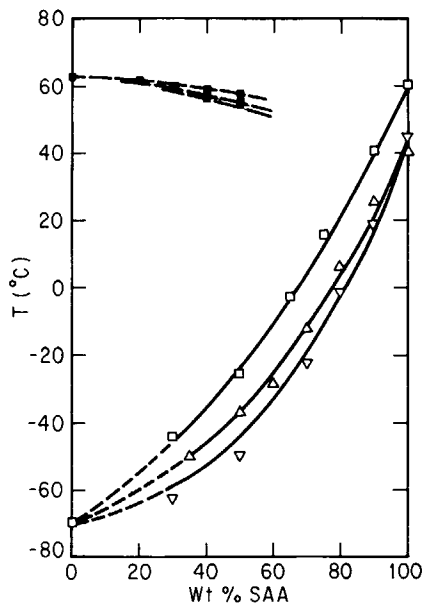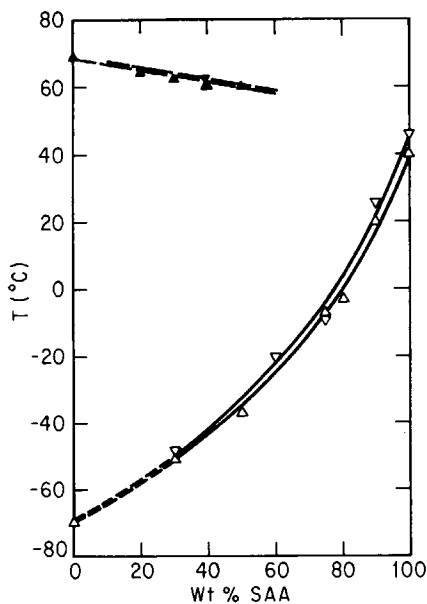
Fig. 2.   Glass transitions (open points) and melting points (closed points) for blends of PBS with SAA-1 (∇, $\blacktriangledown$), SAA-2 ($\triangle$, $\blacktriangle$), and SAA-5 ($\square$, $\blacksquare$).

but based on all other evidence, it would appear to be similarly miscible with SAA-1 and SAA-2 and is so recorded in Table III. Owing to the quenching procedure in the DSC prior to measurement of T_g, most of the specimens were free of polyester crystallinity upon heating through the glass transition except for some systems very rich in rapidly crystallizable polyesters.

Fig. 3.   Glass transitions (open points) and melting points (closed points) for blends of PHS with SAA-1 (∇, $\blacktriangledown$) and SAA-2 ($\triangle$, $\blacktriangle$).
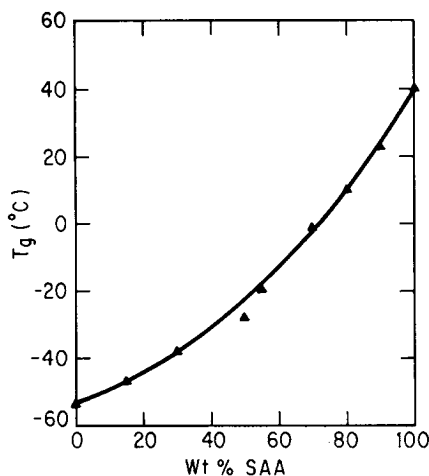
Fig. 4. Glass transitions for PDPA/SAA-2 blends.

The T_g–composition relations shown in Figures 1–5 are well described by the Gordon–Taylor equation

$$T_g = \frac{w_1 T_{g1} + k w_2 T_{g2}}{w_1 + k w_2} \tag{9}$$

where T_{gi} and w_i are the glass transition and weight fraction of component i, respectively. The parameter k, obtained by a least square regression analysis, showed a consistent trend with the OH content of the SAA component for PCDS, PBS, and PBA, as seen in Figure 6. The trend for PCL using data from the earlier study[1] is strikingly different and probably reflects a difference in thermal protocol between this and the earlier work. Since rapid quenching was not possible in the instrument used for PCL
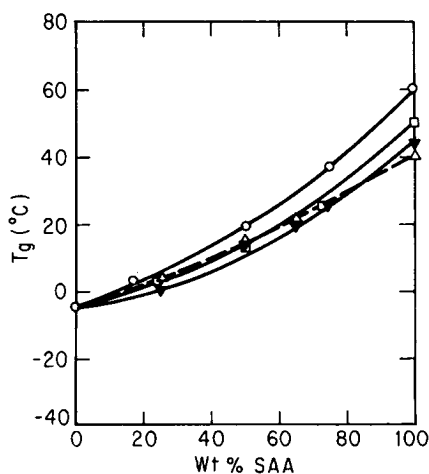
Fig. 5. Glass transitions for blends of PCDS with SAA-1 (▼), SAA-2 (△), SAA-5 (□), and SAA-7 (○).
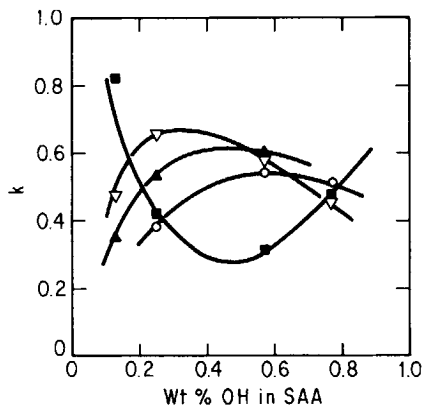
Fig. 6. Gordon–Taylor parameter k obtained by fitting T_g vs. composition data like that shown in Figures 1–5 to eq. (9) for SAA blends with PCDS ($\triangledown$), PBS ($\blacktriangle$), PBA ($\bigcirc$), and PCL ($\square$).

work, the different trend is likely a result of alteration in the amorphous composition of the blends by polyester crystallization.

Figure 7 shows the melting points of the crystallizable polyesters, except PCL, for the various miscible blends obtained using the cyclic heating/cooling procedure noted earlier. The results may be analyzed using eq. (8) to obtain an estimate of the interaction parameter B. Of course, as pointed out by others,[9,10] one also has the problem of separating out melting point effects due to changes in crystal lamella thickness. Such effects were neglected here since only an estimate of B was desired. As noted in Figure 7, in several cases there is a sizeable offset between the melting point of the pure polyester and that extrapolated from blend data to zero SAA
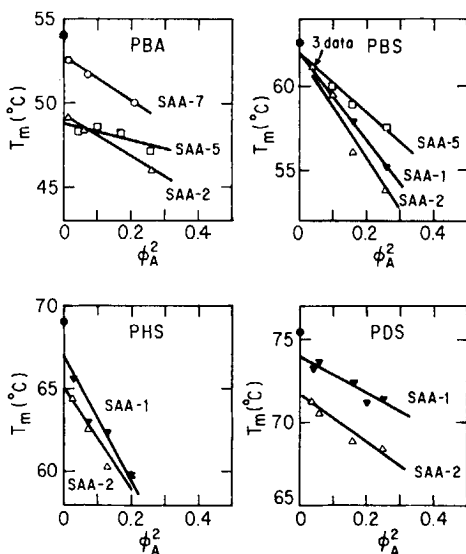

Fig. 7. Polyester melting points as a function of the volume fraction of SAA, ϕ_A, squared. This is the simple form suggested by eq. (7); however, the more complex form given by eq. (8) was used to compute B. Pure polyester melting points are given by ($\bullet$).
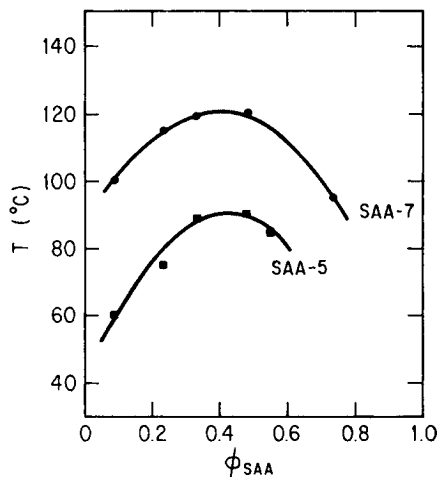
Fig. 8. Cloud point curves for PHS/SAA blends.

content. This phenomenon is partially but not completely accounted for by combinatorial entropy effects[8] included in eq. (8). The results of Morra and Stein[11] suggest that concentration dependence of the interaction parameter can lead to analogous apparent offsets. For the present case an average interaction parameter was obtained by taking the slope of plots constructed in accordance with eq. (8) using blend melting point data without forcing the line through the pure polyester point. The values of B obtained in this way were all negative and will be discussed later.

Blends Showing UCST Behavior

UCST behavior has been reported in several oligomeric blend systems,[12–14] so it is not entirely surprising that some of the present blends exhibit this phenomenon. Figures 8–10 illustrate typical cloud point curves for some of the polyester–SAA blends which showed such liquid–liquid phase behavior. The maximum in this curve is assumed to approximate the critical point and these coordinates, T_c and ϕ_{1c}, where 1 = SAA, are entered in
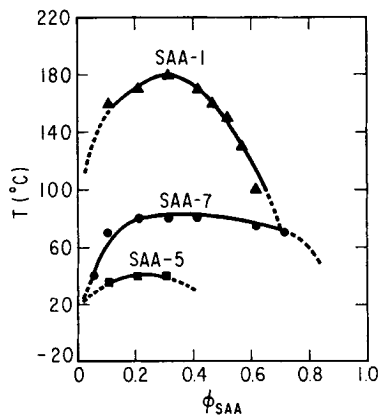

Fig. 9. Cloud point curves for blends of PDPA with SAA-1 (▲), SAA-5 (■), and SAA-7 (●).
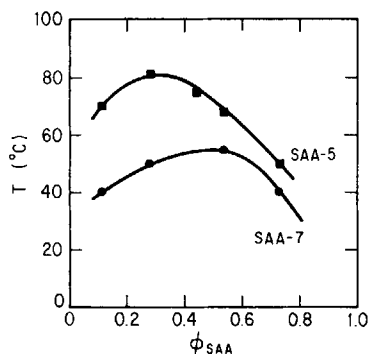
Fig. 10. Cloud point curves for PTG/SAA blends.

Table III for each system for which a cloud point curve was noted. For the linear polyesters, Table III is essentially a 2-dimensional map with the coordinates being the chemical structure of the blend components, i.e., % OH for the SAAs and the CH_2/COO ratio for the polyesters. UCST behavior occurs on either side and immediately adjacent to the group of systems found to be completely miscible. Interestingly, blends of one of the polyesters with the oligomeric polystyrene (an SAA with 0% OH) exhibited a cloud point curve, but this is not a general phenomenon. In most cases, some level of OH groups is needed to promote mixing with the polyesters.

The phase behavior at the cloud point was reversible although the kinetics varied greatly depending on the direction of temperature change and the system. On heating, a cloudy blend became clear very quickly, but when cooled again the formation of two phases, as judged by optical appearance, took much more time. This kinetic process is greatly influenced by the temperature at which the cloud point occurs. For example, PDPA/SAA-1 has T_c ~180°C while for PDPA/SAA-5 T_c ~40°C. Cooling the former produced cloudiness in a matter of minutes while it took days for the latter to do so. This is obviously related to the effect of temperature on segmental mobility which becomes exaggerated as T_g is approached.

The coordinates of the critical points given in Table III can be used to estimate the interaction parameter B using eq. (6). The values so calculated are all positive of course. These results will be discussed subsequently.

The cloud points noted here are all above the T_g vs. composition relation expected for a homogeneous mixture since equilibrium liquid–liquid phase boundaries cannot be obtained at lower temperatures. In some cases, extrapolation of the cloud point curve results in an intersection with the T_g curve. Well away from this intersection, a single T_g was noted outside the cloud point envelope whereas inside it two T_g's were seen. In the vicinity of the intersection, very broad transitions were seen in some cases. This complex behavior will not be elaborated on further here, owing to the difficulty of achieving true equilibrium results, or reproducibility, in such instances.

Immiscible Blends

Some blends failed to become clear on heating to the highest temperatures possible without decomposition of the components. These blends have been

called completely immiscible in Table III. Evidently such systems have quite large positive values of B.

DISCUSSION AND SUMMARY

Miscibility has been found to be very strongly affected by the density of the functional groups, COO in polyesters and OH in SAAs, which may be responsible for potential specific interactions. There is an optimum range of the densities of these groups for the occurrence of miscibility. Similar miscibility windows have been observed in other blend systems.[15-18] The interesting feature of the present study is that the miscibility window has been examined in 2 dimensions by variation of the CH_2/COO ratio in polyesters and of the OH content in the SAA copolymers. UCST behavior is quite common in these oligomeric blend systems, and it appears as a transition zone between complete miscibility and complete immiscibility.

The thermodynamic factors responsible for the phase behavior noted here may be summarized in an interesting way by examining more carefully the interaction parameters estimated from both melting point depression and critical point observations. These results are shown in Figure 11, where the solid points are for miscible blends determined from melting point depression and the open circles are for blends exhibiting UCST behavior calculated using information about the critical point. While the results are somewhat scattered, it is clear that there is a meaningful relationship between interaction parameters determined by the two approaches to form for each SAA a single curve vs. the CH_2/COO ratio for the homologous series of polyesters. In the middle of the CH_2/COO range the B's are negative (miscible blends) where a minimum occurs at about 5–7. On either side of this
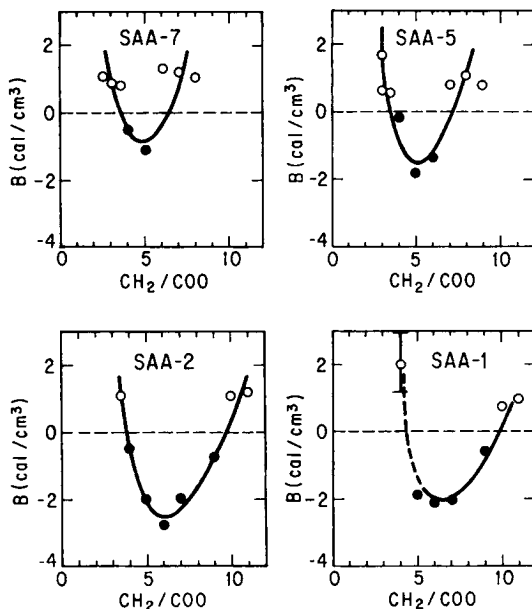

Fig. 11. Interaction parameters computed from critical point ($\bigcirc$) and melting point depression ($\bullet$) for each SAA copolymer as a function of the CH_2/COO ratio in the polyester structure.
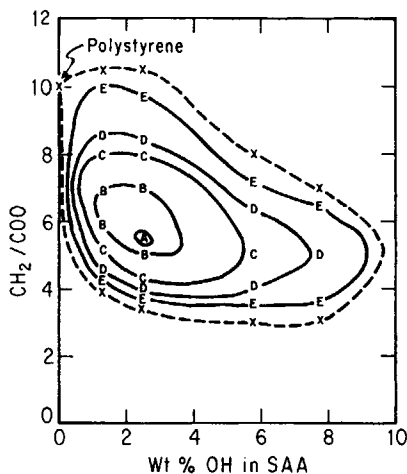
Fig. 12. A contour projection illustrating the dependence of the interaction parameter B on the composition of the SAA copolymers (% OH) and the structure of the polyesters (CH_2/COO ratio). Contours correspond to the following values of B: $X = +1$ cal/cm³, $E = 0$, $D = -1$, $C = -1.5$, $B = -2.0$, and $A = -2.5$.

range the curves increase steeply to produce positive B's for systems showing UCST behavior. At sufficiently low or high CH_2/COO ratios the values of B become so large that the cloud point curve is beyond the thermal decomposition temperatures of the component polymers; hence, single phase behavior becomes impossible to observe, i.e., immiscible blends. Figure 12 is a contour plot that allows one to get some feel for the dependence of B on both CH_2/COO and wt % OH. The shape of these contours is such that UCST behavior may be observed for polystyrene at a very limited polyester structure for the molecular weight used here. In principle, this presentation can be used to estimate the phase behavior for components with molecular weights other than the specific ones employed here. There is a finite window of structure where B is negative, and in this region miscibility should always occur regardless of how large the molecular weights are. Outside this region, B is positive, and the phase behavior will depend very much on the molecular weight of the components.

The compelling question is what factors are responsible for this relationship between the interaction parameter and the structure of the two component polymers. Obviously, one thinks of the potential for hydrogen bonding between the OH groups and the carbonyl groups in the ester linkage. However, this consideration alone does not explain a minimum or that B increases when the density of OH or carbonyls increases or decreases away from the optimum value. Two points of view may be offered as reasons for this. First, there are other intermolecular interactions to consider such as the competition for hydrogen bonding of OH with other OH groups rather than with carbonyls. Second, there are intramolecular interactions within the SAA molecules and within the polyester molecules as recently suggested,[19] which must be considered. Very likely, both of these are simultaneously at issue in these systems and give rise to the behavior observed. It would be informative to construct models which consider all of these issues for comparison with these data.

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