

Phase Behavior of Binary Mixtures of Styrene / Acrylonitrile Copolymers and Aliphatic Polyesters

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Synopsis

The phase behavior of binary mixtures of copolymers containing varying amounts of styrene and acrylonitrile (SAN) with a large range of aliphatic polyesters was examined. Miscibility was observed over a limited range of AN contents of the SANs, for each polyester, while similarly for each SAN, miscibility was only observed over a limited range of polyester molecular structures. Thermodynamic interaction parameters for the miscible blends were obtained by analysis of the depression of the polyester melting point. A binary interaction model was used to correlate the data and six group interaction parameters were deduced by subdividing the polyester and SAN copolymer repeating units in three different ways. It is concluded that there is a strong repulsion between the segmental units within the polyesters and within the SAN copolymers, which is an important factor in the observed phase behavior.

INTRODUCTION

Recent theoretical¹⁻³ and experimental⁴⁻²² investigations have dealt with the observation that random copolymers often form miscible blends with other polymers while the corresponding homopolymers do not. For example, styrene/acrylonitrile copolymers (SANs) are miscible with poly(methyl methacrylate) (PMMA)^{17,19} and poly(ethyl methacrylate) (PEMA)^{18,19} over a certain range of AN contents, but neither polystyrene nor polyacrylonitrile is miscible with PMMA or PEMA. Another example is poly(*o*-chlorostyrene) and poly(*p*-chlorostyrene), which are both immiscible with poly(phenylene oxide) (PPO), but for a certain composition region random copolymers formed from these monomers are miscible with PPO.⁴

The observation of such "miscibility windows" is consistent with the interaction parameter of the Flory-Huggins²³ or the equation of state^{24,25} theories of mixtures being negative within this limited range of copolymer compositions and positive for compositions on either side. Recent binary interaction models¹⁻³ suggest that such behavior may be simply the result of repulsive interactions between the units from which the copolymer is formed. This reasoning can be easily extended to blends containing only homopolymers by considering the intramolecular interactions between different segments in the monomeric repeating units.³ These models are then able to explain, at least qualitatively, numerous other observations about blend miscibility.^{1,15}

It has been known for some time that a styrene/acrylonitrile copolymer containing about 25% acrylonitrile (SAN 25) is miscible with poly(ϵ -caprolac-

TABLE I
Properties of Styrene/Acrylonitrile Copolymers

Abbreviation	AN Content (weight %)	Density (g/cm ³)	T_g (°C)	Molecular weight information	Source/ (designation)
SAN 5	5.5	1.0507 ^a	107 ^a	$\bar{M}_w \sim 270,000$	Dow Chemical Company
SAN 13	13	1.0652 ^b	109 ^a	$\bar{M}_n = 56,300$ $\bar{M}_w = 149,000$ $\bar{M}_z = 293,000$	Borg-Warner (Resin 21082 - 73)
SAN 16	16.2	1.0636 ^b	108 ^a	(GPC) $\bar{M}_w = 197,800$	Dow Chemical Company
SAN 20	20.5	1.0684	109 ^a	(GPC) $\bar{M}_w = 193,800$	Dow Chemical Company
SAN 25	25	1.0775 ^b	109 ^a	—	Dow Chemical Company (Tyril 860)
SAN 32	32.3	1.0840	107 ^a	$\bar{M}_n = 50,700$ $\bar{M}_w = 75,400$	Monsanto Co.
SAN 40	40	—	108	—	Dow Chemical Company (EX2020)
SAN 70	69.7	—	108 ^a	$[\eta] = 0.80^f$	Monsanto Co.

^aThis study.

^bRef. 19.

tone), PCL (26-29). Recently, Chiu and Smith³⁰ established that miscibility with PCL exists for other SAN copolymers over a certain range of acrylonitrile contents.

The purpose of this work is twofold. First, we extend the work of Chiu and Smith to other polyesters having both higher and lower CH₂/COO ratios to establish the miscibility limits in terms of both SAN and polyester molecular structure. Since the aliphatic polyesters are crystalline polymers, an estimate of the interaction parameter B , is possible for each polymer pair through melting-point depression analysis. Second, we deduce the binary interaction parameters for each pair of segmental units in these polymers through a regression analysis as done earlier³ in an attempt to rationalize the observed phase behavior in terms of these more fundamental quantities.

MATERIALS AND PROCEDURES

The properties and abbreviations for the styrene/acrylonitrile copolymers and for the aliphatic polyesters used in this study are given in Tables I and II. The numbers included in the abbreviation for these materials indicate the approximate weight percent of acrylonitrile in SAN copolymers and the ratio between the hydrocarbon and carbonyl units in the aliphatic polyesters. The blends were prepared by solvent casting from methylene chloride solutions containing between 2 and 5% total polymer by weight. After an approximate period of evaporation at room temperature the blends were placed in a vacuum oven for three days at 80°C to complete the removal of the solvent.

Glass transition temperatures and melting points were measured using a Perkin-Elmer DSC-2 Differential Scanning Calorimeter. To measure the glass transitions, a heating rate of 20°C/min was used, and the temperature of the

TABLE II
Properties of Aliphatic Polyesters

Abbreviation	Polymer	Structure	Density	Molecular weight information	T_g (°C)	T_m (°C)	ΔH_{2u} (cal/g)	Source
PES 2	Poly(ethylene succinate)	$-(CH_2)_2-O-C(=O)-(CH_2)_2-C(=O)-$	1.32 ^a	1500 ^a	-15 ^b	98 ^b	—	Scientific Polymer Products
PEA 3	Poly(ethylene adipate)	$-(CH_2)_2-O-C(=O)-(CH_2)_4-C(=O)-$	1.21 ^a	$\bar{M}_v = 1,500^a$	-47 ^b	47.9 ^b	29.2 ^g	Scientific Polymer Products
PBA 4	Poly(1,4-butylene adipate)	$-(CH_2)_4-O-C(=O)-(CH_2)_4-C(=O)-$	1.019 ^j	—	-68 ^b	54.8 ^b	30.5 ^a	Aldrich Chemical Company, Inc.
PCL 5	Poly(ϵ -caprolactone)	$-(CH_2)_5-C(=O)-$	1.095 ^a	$\bar{M}_n = 15,500^d$ $\bar{M}_v = 40,500$ $\bar{M}_w = 46,700$	-68 ^b	57.3 ^b	34.6 ^b	Union Carbide PCL 700
PBS 6	Poly(butylene sebacate)	$-(CH_2)_4-O-C(=O)-(CH_2)_8-C(=O)-$	1.136 ^c	$\bar{M}_v = 2,500^c$	-62 ^b	62.9 ^b	37.0 ^d	(i)
PHS 7	Poly(hexamethylene sebacate)	$-(CH_2)_6-O-C(=O)-(CH_2)_8-C(=O)-$	1.03 ^a	$\bar{M}_w = 16,500^a$	-60 ^f	66.4 ^b	38.5 ^d	Scientific Polymer Products
PHD 8	Poly(hexamethylene decamethylene dicarboxylate)	$-(CH_2)_6-O-C(=O)-(CH_2)_{10}-C(=O)-$	1.08 ^d	$\bar{M}_n = 3,200^e$	—	57.9 ^b	39.2 ^d	The C. P. Hall Company

^aRef. 36.
^bDetermined experimentally in this study.
^cExperimental value from this laboratory.
^dEstimated value.
^eThe C. P. Hall Company.
^fRef. 37.
^gRef. 35.
^hRef. 32.
ⁱSynthesized by E. M. Woo.
^jAldrich Chemical Co., Inc.

onset of the transition was recorded in a second heat after quenching at 320°C/min from about 150°C. The melting points were obtained from the second heat during cyclic heating and cooling at 10°C/min.

Visual observations of blend clarity just above the polyester melting point were made following a procedure described previously.³¹ None of the blends were examined at higher temperatures.

GLASS TRANSITION BEHAVIOR

The most widely used criterion for miscibility between two polymers is the existence of a single glass transition temperature (T_g) occurring intermediate to those for the pure polymers which varies in a regular way with composition.³² Clarity of blend films has also been used as an additional means to reinforce glass transition results.³²

In this study, the glass transition was studied over the whole composition range for the systems shown in Figures 1 through 3. These results clearly show that blends containing SAN 25 are miscible with PEA 3 and PBA 4 (Fig. 1) but immiscible with PBS 6. However, PBA 4 is obviously miscible with SAN 16 (Fig. 2); whereas, SAN 5 phase separates in blends with PCL. A slightly different procedure was used to study all the other blends, including those containing PCL which were examined for comparison purposes. A single blend was tested for each system. Typically, the blend composition used was 70% SAN and 30% polyester, so that effects due to polyester crystallinity could be minimized. A blend was classified as immiscible if its glass transition was not appropriately depressed relative to that for the pure SAN. A blend was classified as miscible when a single glass transition appeared at or slightly below the T_g calculated from simple additivity of the T_g s for the pure polymers. In some cases, the blend glass transition showed only a slight depression relative to that of SAN, and these were classified as partially miscible.

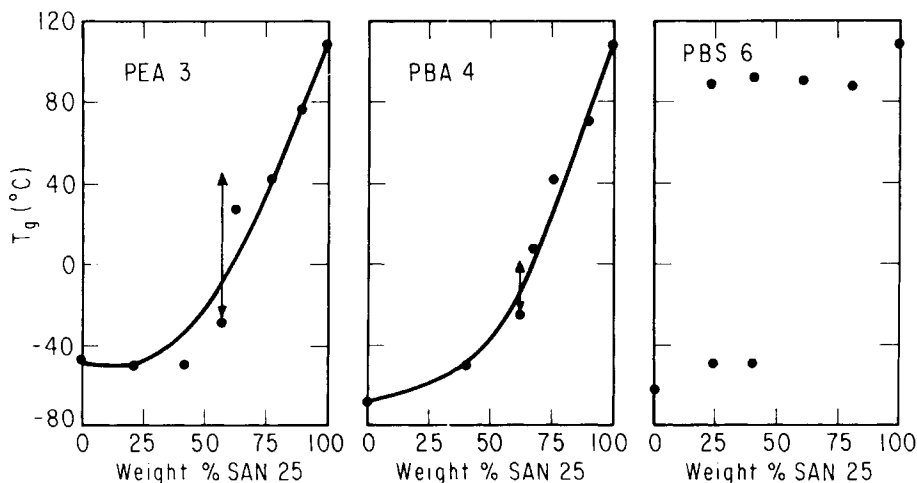


Fig. 1. Glass transition behavior for SAN 25 blends with PEA 3, PBA 4, and PBS 6.

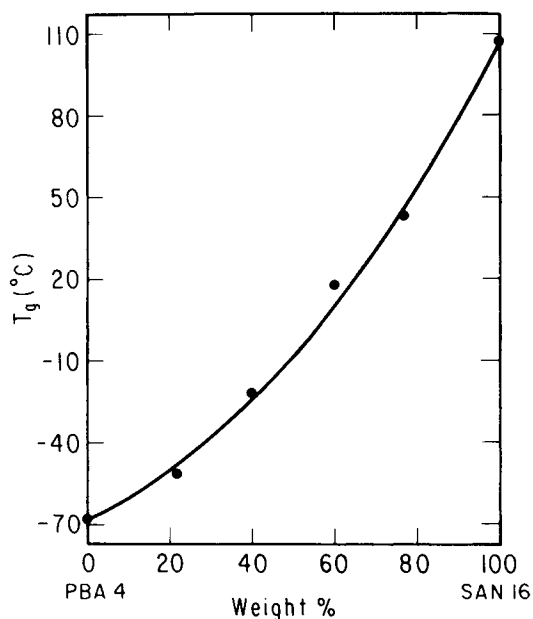


Fig. 2. Glass transition behavior for SAN 16/PBA 4 blends.

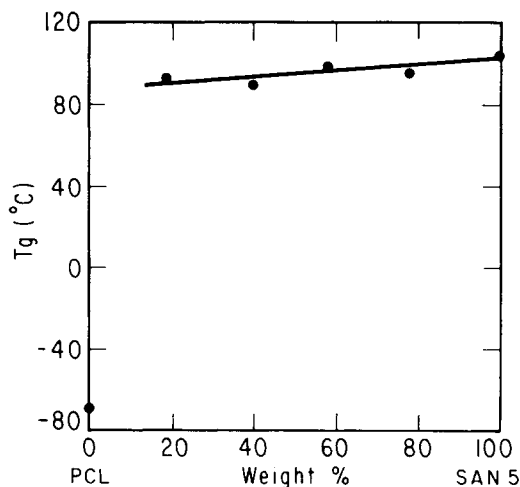


Fig. 3. Glass transition behavior for SAN 5/PCL blends.

Due to the development of polyester crystallinity, all blends were generally opaque at room temperature, but the blends initially classified as miscible became clear on heating immediately above the polyester melting point, in opposition to those classified as immiscible which remained cloudy well above that temperature.

All the blends classified as miscible or partially miscible were tested for melting-point depression using the procedure described in the experimental section, and the glass transition results were confirmed *a posteriori* through the value obtained for the interaction energy density B .

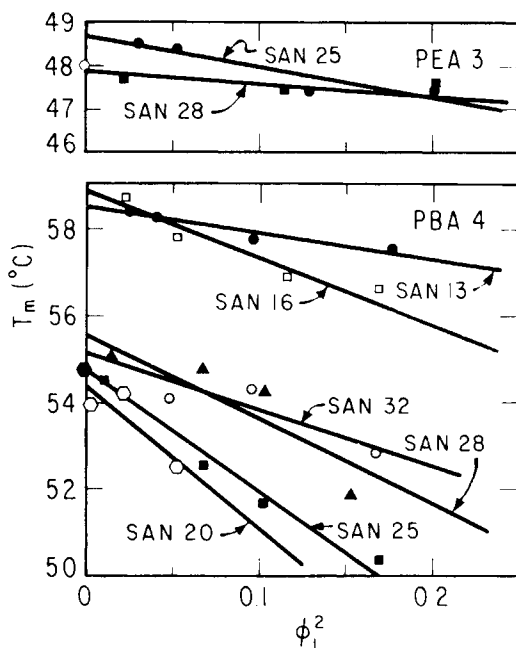


Fig. 4. Analysis of PEA 3 and PBA 4 melting-point depression in blends with various SAN copolymers.

MELTING BEHAVIOR

It is well known that if one of the components in a mixture crystallizes there should be an equilibrium depression of the melting point owing to the lower chemical potential of the component in the mixed amorphous phase.²³ So, one way to quantify the interactions between polymers in blends containing one crystallizable polymer is through analysis of the melting-point depression. Based on the expression developed by Nishi and Wang³³ in terms of the Flory-Huggins theory, the interaction energy density B can be computed from the slope of the line representing the melting point versus the square of the volume fraction of the amorphous component, ϕ_1 , when both polymers have high molecular weights. This assumption was found to be legitimate for the polymer systems used in this study, as reported below. The information needed for these calculations is shown in Table I.

In general, the blends initially classified as partially miscible did not show any melting-point depression and the results were more scattered than usual. Figures 4 and 5 show T_m versus ϕ_1^2 for all the miscible systems studied here. Several comments should be made concerning these results. The straight lines were drawn in each case based on a regression analysis of the experimental data. In cases where the correlation coefficient was less than 0.900, a range of values for B was calculated instead of a single value to take into account the scatter of the data. For most polyesters, the melting was characterized by multiple peaks. In every case, the depression of the melting point was monitored by following the position of the same peak as the amount of the noncrystalline polymer was varied in the blend. This procedure was not

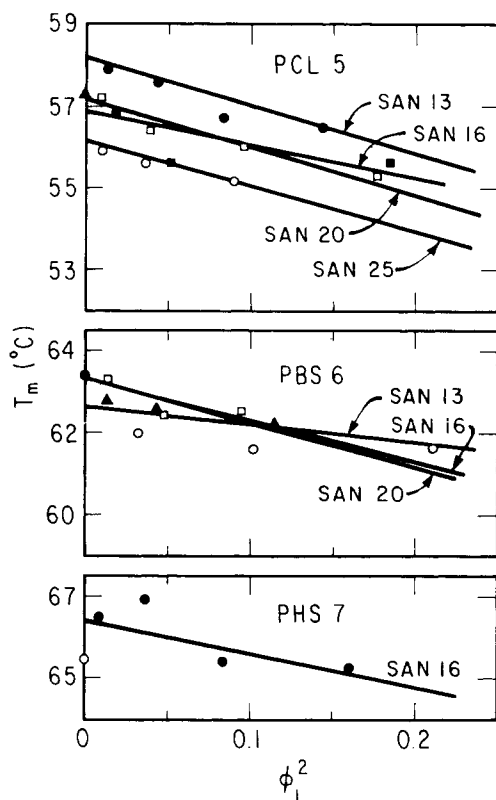


Fig. 5. Analysis of PCL 5, PBS 6, and PHS 7 melting-point depression in blends with various SAN copolymers.

possible with PBA 4 in blends with SAN 13 and SAN 16 where another peak had to be used. Hoffmann-Weeks plots are often suggested as a means to estimate an equilibrium melting point corresponding to an infinite crystal size.³⁴ We did not use this procedure because the existence of multiple peaks complicates the analysis of the data. To minimize morphological effects, the blends were subjected to the same thermal history, as described in the experimental section. Figures 5 and 6 show that the intercept of the regression lines is not always identical to the experimental melting point for the pure polymer. This deviation has been attributed to a nonzero combinatorial entropy.¹⁴ Allowing for the finite molecular weights of the polymers does not change the value of B computed by more than 8 percent in the extreme cases, so the entropic contribution to the melting-point depression has been ignored in these calculations in view of the other approximations made.

DISCUSSION

The interaction parameters, B , deduced from melting-point depression analysis are represented in Figure 6 for the various SANs as a function of the volume fraction of hydrocarbon units in the polyesters and in Figure 7 for the various polyesters as a function of the volume fraction of acrylonitrile (AN) in the SAN copolymers. Bars are presented rather than points, in some cases, to

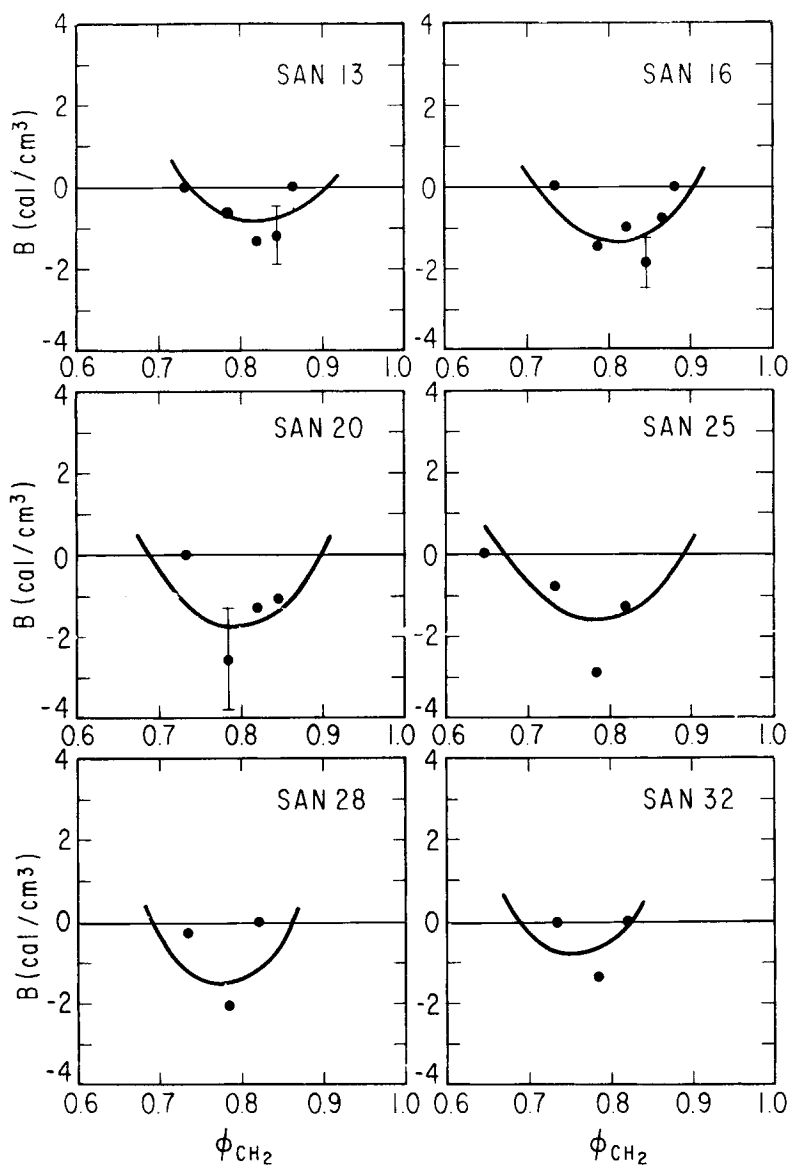


Fig. 6. Interaction parameters computed from melting-point depression for each SAN copolymer as a function of $-\text{CH}_2-$ volume fraction in the polyester structure. The solid lines were computed from Eq. (1) or (2) using the parameters in Table III.

take into account the scatter of the experimental data. It is clear from these results that miscibility is limited to a two-dimensional window of polyester and styrene/acrylonitrile copolymer molecular structures, similar to that previously observed for blends containing oligomeric styrene/allyl alcohol copolymers and aliphatic polyesters.¹⁴ The miscibility window for the PCL-containing blends is in very good agreement with the previous reported results³⁰ based on glass transition and lower critical solution temperature (LCST) behavior.

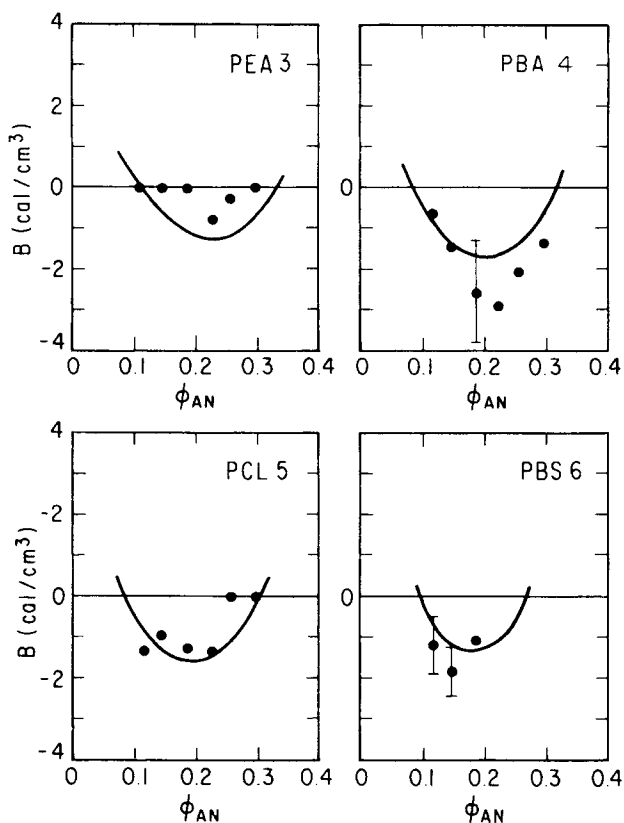


Fig. 7. Interaction parameters computed from melting-point depression for each polyester as a function of AN volume fraction in the SAN copolymer structure. The solid lines have the same meaning as in Fig. 6.

Figure 8 shows a contour projection of the interaction parameter, B , as a function of the SAN copolymer composition and structure of the polyester. The numbers indicate the magnitude for the B corresponding to each contour. The blend pairs characterized by a CH_2/COO ratio and a %AN located inside the line for $B = 0$ have a negative interaction parameter and show one phase behavior; whereas, those that lie outside this boundary phase separate.

A more careful analysis of Figure 8 shows that miscibility with the aliphatic polyesters is favored for SAN copolymers having low contents in acrylonitrile (less than 32%). However, single-phase blends were never obtained when the acrylonitrile content was as low as 5.5% by weight (SAN 5) or when the CH_2/COO ratio in the polyester was equal to two (PES 2). SANs with lower contents of AN are generally more likely to be miscible with polyesters with higher CH_2/COO ratios; whereas, SANs with larger AN contents are more likely to be miscible with the polyesters having smaller CH_2/COO ratios.

We will attempt to interpret the experimental interaction parameters discussed above in terms of interactions which exist between the various structural units which make up the SANs and polyesters.³ There are a number of ways to subdivide these structures, and an obvious one is the

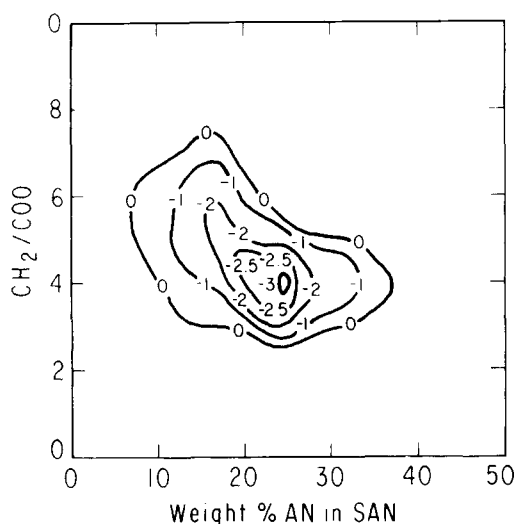
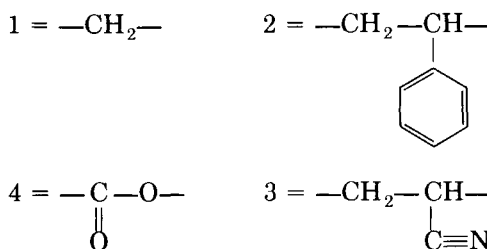


Fig. 8. A contour projection illustrating the dependence of the interaction parameter B on the composition of the SAN copolymers (weight %AN) and the structure of the polyester (CH_2/COO ratio). The numbers on the contour correspond to values of B .

following:



For this division, a simple extension of the theory developed earlier³ gives the following expression for the net interaction parameter:

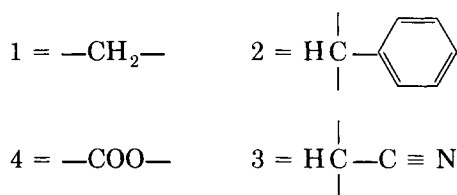
$$B = B_{13}\phi'_1\phi'_3 + B_{34}\phi'_3\phi'_4 + B_{12}\phi'_1\phi'_2 + B_{24}\phi'_2\phi'_4 - B_{23}\phi'_2\phi'_3 - B_{14}\phi'_1\phi'_4 \quad (1)$$

where: ϕ'_i and ϕ''_i are the volume fractions of unit i in the SAN and in the polyester, respectively. The volume fractions of $\text{—CH}_2\text{—}$ and —COO— units in the polyesters were evaluated using a group contribution method as described previously³⁵ and adapted to polyesters.³⁶ The volume fractions of styrene and acrylonitrile were calculated using the densities for polystyrene and polyacrylonitrile and the weight fractions of styrene and acrylonitrile in the copolymers. Equation (1) defines the overall interaction parameter B as a summation of weighted interactions between four segmental units in the blend. The terms with plus signs represent intermolecular interactions between polyester and SAN units while the terms with minus signs represent intramolecular interactions between units within the polyester and SAN, respectively.

The overall interaction parameter B , as shown in Eq. (1), is a function of the volume fraction of the structural units in the SAN and the polyester but is not a function of the relative amounts of SAN and polyester in the blend.

Based on Eq. (1), the experimental data can be represented by a surface, in a three-dimensional space, whose coordinates are B , ϕ'_3 , and ϕ''_4 . This surface defines a region of miscibility and its location in the three-dimensional space depends on the relative values for the six binary interaction parameters B_{ij} 's. The best surface representing the experimental points can be computed using a least squares method. The solid lines in Figures 6 and 7 were computed from Eq. (1) using B_{ij} values obtained in this manner and considering the scatter of the data, the fitted surface represents the experimental observations rather well. The B_{ij} obtained from the regression are listed in the first column of Table III. Since all six parameters are positive, the region $B < 0$ is only possible due to the slightly higher values obtained for B_{14} and B_{23} . These values suggest rather strong repulsions between the segmental units within the polyester and within the SAN copolymer.

The subdivision used above was somewhat arbitrary, and we can further subdivide the units of SAN without increasing the number of interaction parameters needed. To this end, we redefine the units as follows:


















The overall interaction parameter B can be expressed as shown below:

$$\begin{aligned}
 B = & B_{12}\phi'_2(\phi''_1 - \phi'_1) + B_{13}\phi'_3(\phi''_1 - \phi'_1) + B_{14}\phi''_4(\phi'_1 - \phi''_1) \\
 & - B_{23}\phi'_2\phi'_3 + B_{24}\phi'_2\phi''_4 + B_{34}\phi'_3\phi''_4
 \end{aligned} \tag{2}$$

Equation (2) was deduced as a simple extension of Eq. (1), recognizing that unit 1 exists in both the polyester and SAN. The B_{ij} parameters obtained by fitting the experimental data to the model resulting from this second subdivision are also shown in Table III. A third subdivision can also be made without increasing the number of parameters by assuming —CH— and $\text{—CH}_2\text{—}$ units interact equivalently. In this case, Eq. (2) remains valid and the B_{ij} from the regression are listed in Table III. Examination of the interaction parameters for the various subdivisions of the chemical structures reveals the following. The B_{12} interaction becomes only slightly more positive as aliphatic units are progressively stripped from the aromatic ring, and the interaction parameter between the ring and a CH_x unit is rather small compared to all others shown in Table III. On the other hand, B_{13} becomes much more positive as aliphatic units are removed from the nitrile group, and the final parameter describing the interaction between aliphatic and nitrile groups is extremely repulsive. The units for the B_{14} interaction are basically the same for all the subdivisions, and the values obtained for this parameter do not

TABLE III
 Group Interaction Parameters Obtained from Regression Analysis of the Melting-Point Depression Data Using Various Schemes of Subdividing the Polymer Structure

Designation	Subdivision 1			Subdivision 2			Subdivision 3		
	Pairs of Units	B_{ij} (cal/cc)	B_{ij} (cal/cc)	Pairs of Units	B_{ij} (cal/cc)	B_{ij} (cal/cc)	Pairs of Units	B_{ij} (cal/cc)	B_{ij} (cal/cc)
1-2	$\text{CH}_2 \leftrightarrow \text{CH}_2\text{-CH}$ 	+ 5.72	+ 8.07	$\text{CH}_2 \leftrightarrow \text{CH}$ - 	+ 8.07	+ 10.4	$\text{CH}_x \leftrightarrow$ 	+ 10.4	
1-3	$\text{CH}_2 \leftrightarrow \text{CH}_2\text{-CH}$ 	+ 97.5	+ 234	$\text{CH}_2 \leftrightarrow \text{HC}$ - 	+ 234	+ 508	$\text{CH}_x \leftrightarrow \text{-C}\equiv\text{N}$	+ 508	
1-4	$\text{CH}_2 \leftrightarrow \text{COO}$	+ 137	+ 136	$\text{CH}_2 \leftrightarrow \text{COO}$	+ 136	+ 136	$\text{CH}_x \leftrightarrow \text{COO}$	+ 136	
2-3	$\text{CH}_2\text{-CH} \leftrightarrow \text{CH}_2\text{-CH}$  	+ 122	+ 277	-CH -  $\text{HC} \leftrightarrow \text{HC}$ - 	+ 277	+ 579	 $\leftrightarrow \text{-C}\equiv\text{N}$	+ 579	
2-4	$\text{CH}_2\text{-CH} \leftrightarrow \text{COO}$ 	+ 103	+ 96.8	-CH -  $\leftrightarrow \text{COO}$	+ 96.8	+ 93.0	 $\leftrightarrow \text{COO}$	+ 93.0	
3-4	$\text{CH}_2\text{-CH} \leftrightarrow \text{COO}$ 	+ 104	+ 170	HC -  $\leftrightarrow \text{COO}$	+ 170	+ 351	$\text{-C}\equiv\text{N} \leftrightarrow \text{COO}$	+ 351	

change for the different ways of dividing the structure. The value for B_{14} is about half that found previously for analysis of other blends using this approach.^{3,15} The B_{23} interaction becomes very large as aliphatic units are simultaneously removed from the aromatic ring and the nitrile group with the final parameter for nitrile interaction with the ring being about the same as that with an aliphatic unit. The ester interaction with the ring, B_{24} , is slightly less than that with the aliphatic unit so this parameter becomes slightly smaller as the aliphatic units are stripped from the ring. On the other hand, the ester interacts more positively with the nitrile than it does with the aliphatic units, so B_{34} becomes much larger as the latter are stripped from the nitrile group.

A closer look at the relative values for the group interaction parameters reveals that the nitrile interacts more endothermically with aliphatic units (pair 1-3) than with carbonyl units (pair 3-4) while the opposite is true for the aromatic ring which interacts more endothermically with carbonyl groups (pair 2-4) than with aliphatic units (pair 1-2). This would appear to explain why SAN copolymers with high styrene contents are more likely to be miscible with polyesters with larger CH_2/COO ratios; whereas, an increase in AN content in the copolymer narrows the miscibility window to polyesters with low CH_2/COO ratios. It is also interesting to note that the interactions involving the aromatic ring are less endothermic with $-\text{CH}_x-$ (pair 1-2) and $-\text{COO}-$ (pair 2-4) than those involving the nitrile group (pairs 1-3 and 3-4). This could explain why single-phase blends are only obtained with SAN copolymers having relatively low AN contents (less than 32%).

It would be very interesting to deduce similar group interaction parameters from heats of mixing of model compounds as this would provide a more quantitatively reliable data base. Work along these lines is in progress.

SUMMARY

Miscibility of blends containing aliphatic polyesters and styrene/acrylonitrile copolymers (SANs) has been found to be strongly affected by the CH_2/COO ratio of the polyesters and the AN content of the SANs. The phase behavior for these blends is summarized in Table IV. For each polyester, miscibility exists only for a limited range of AN contents of the SANs while, similarly, for each SAN, miscibility is only observed over a limited range of polyester molecular structures.

The interaction energy density B for the miscible blends was estimated by analysis of melting-point depression data, and it was shown that the dependence on polyester and SAN copolymer molecular structures is well approximated by a parabolic surface based on a simple binary interaction model.³ Six group interaction parameters were calculated through a regression analysis applied to that surface by subdividing the polyester and SAN copolymer repeating units in three different ways. The six binary coefficients found were all positive. This approach suggests that the observed phase behavior can be explained by strong repulsions between the segmental units within the polyesters and within the SAN copolymers. The location of the interaction energy density surface with respect to polyester and SAN copolymer molecular structures is explained based on the relative magnitudes found for the binary

TABLE IV
 Phase Behavior of Polyester/SAN Blends

Polyester/ SAN	PES 2	PEA 3	PBA 4	PCL 5	PBS 6	PHS 7	PHD 8
SAN 5	n.t. ^a	n.t.	immiscible	immiscible	immiscible	immiscible	n.t.
SAN 13	n.t.	partially miscible	miscible	miscible	miscible	partially miscible	n.t.
SAN 16	n.t.	partially miscible	miscible	miscible	miscible	miscible	partially miscible
SAN 20	immiscible	partially miscible	miscible	miscible	miscible	immiscible	n.t.
SAN 25	partially miscible	miscible	miscible	miscible	immiscible	n.t.	n.t.
SAN 28	immiscible	miscible	miscible	partially miscible	immiscible	n.t.	n.t.
SAN 32	immiscible	partially miscible	miscible	partially miscible	n.t.	n.t.	n.t.
SAN 40	immiscible	partially miscible	partially miscible	n.t.	n.t.	n.t.	n.t.
SAN 70	immiscible	n.t.	n.t.	n.t.	n.t.	n.t.	n.t.

^an.t. = not tested.

interaction parameters $B_{i,j}$ s estimated for different subdivisions of the homopolymer and copolymer repeating units.

The analysis used here contains many approximations and, consequently, the results are intended to be more an illustrative rather than definitive establishment of group interaction parameters. For example, any temperature dependence of the overall blend interaction parameters has been ignored, but this is probably not too serious since values like those shown in Figures 6–8 are applicable at the melting point of the various polyesters which all fall within $\pm 10^\circ\text{C}$ of 58°C . The model used is of the mean field type and should work best when there is random placement of the structural units within each molecule. Of course, this condition is not fully satisfied especially for the aliphatic polyesters in which the COO and the CH₂ units appear in a more or less structured manner. However, the limited information available to date on the phase behavior of blends containing these polymers seems to suggest that the relative proportions of these groups is more important than their spatial placement.^{5, 8, 10, 13–15, 36, 37}

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