

# Compatibility of Poly( $\epsilon$ -Caprolactone) (PCL) and Poly(styrene-Co-Acrylonitrile) (SAN) Blends.

## II. The Influence of the AN Content in SAN Copolymer upon Blend Compatibility

SHAO-CHENG CHIU\* and T. G. SMITH,<sup>†</sup> *Department of Chemical Engineering, University of Maryland, College Park, Maryland 20742*

### Synopsis

The compatibility of polymer blends of poly( $\epsilon$ -caprolactone) (PCL) and poly(styrene-co-acrylonitrile) (SAN) containing various acrylonitrile (AN) contents was studied to evaluate the influences of copolymer composition and PCL concentration upon blend compatibility. Blend compatibility was characterized by the occurrence of a single glass transition intermediate between the transitions of the respective pure components. The glass transitions were determined by differential scanning calorimetry (DSC) and dynamic mechanical measurement (Rheovibron). It was found that SAN and PCL form compatible blends when the AN content of SAN ranges from 8% to 28% by weight. These blends are compatible in all proportions except for SAN 28 (AN wt % = 28) and PCL blends containing 70 or 85 wt % PCL. Blends of PCL and SAN were found to be incompatible when the AN content in SAN is greater than 30 wt % or less than 6 wt %. Lower critical solution temperature (LCST) behavior, which can be attributed to phase separation, was found to occur when these blends were heated to elevated temperatures. The cloud point, or phase separation, was found to vary with AN content in SAN and the concentration of SAN in the blend.

### SUMMARY

The results of this work indicate that the compatibility of SAN/PCL blends is greatly affected by the AN content in SAN. It was found that SAN and PCL are compatible if the AN content in SAN ranges from 8 to 28 wt %. These blends are compatible in all proportions except SAN 28/PCL blends with 70 or 85 wt % PCL. Evidences of compatibility include the presence of a single compositionally dependent glass transition, as determined by dynamic mechanical analysis and differential scanning calorimetry, intermediate between the transitions of the respective components in blends. SAN was found to be incompatible with PCL, if the AN content in SAN is less than 6 wt % or greater than 30 wt %. These blends were found to be opaque at all temperatures and exhibit two glass transition temperatures corresponding to the two separate phases.

It is believed that the main factor governing compatibility in the SAN/PCL blend is the magnitude of the specific interaction between component molecules. Varying the AN content in SAN varies this interaction and affects the blend

\* Present address: Union Carbide Corporation, Parma Technical Center, P.O. Box 6116, Cleveland, Ohio 44101.

<sup>†</sup> To whom correspondence should be addressed.

compatibility. The observation of phase separation at elevated temperatures, in which LCST behavior was observed, supports this.

## INTRODUCTION

In recent years, an exothermic enthalpy of mixing which is the consequence of specific interactions between polymer pairs in a blend has been regarded as a criteria for polymer blend compatibility.<sup>1</sup> The motivation for this work is the belief that, through the study of blends of a homopolymer with a random copolymer in which copolymer composition and consequently interactions between polymer pairs are varied, the principles governing blend compatibility can be better understood.

Random copolymers are often a constituent component of compatible blends.<sup>1-3</sup> It is often found that blend compatibility exists only when the composition of the copolymer constituent is within a specific range. Examples which have been cited are (PVC)/poly(butadiene-co-acrylonitrile) (NBR) blends<sup>4</sup>; PVC/poly(ethylene-co-vinyl acetate) (EVA) blends<sup>5</sup>; poly(2,6-dimethyl-1,4-phenylene oxide (PPO)/poly(styrene-co-parachlorostyrene)<sup>6</sup>; PPO/poly(para-chlorostyrene-co-orthochlorostyrene) blends<sup>7</sup>; polymethyl methacrylate (PMMA)/SAN blends<sup>8</sup>; and methyl-substituted polysulfone/SAN blends.<sup>9</sup> With the exception of PPO, which is compatible with polystyrene (PS), the homopolymers from which copolymers are made are not compatible with the first homopolymer in the blend. For example, neither poly(para-chlorostyrene) nor poly(ortho-chlorostyrene) are compatible with PPO; yet certain of their copolymers are, i.e., copolymers containing 23-64 mol % para-chlorostyrene are compatible with PPO. This phenomena most probably arises from the contribution of specific and dispersive interactions between polymer pairs to the overall enthalpy of mixing.<sup>10</sup>

It has been reported that PCL is compatible with SAN when the AN content in SAN is between 24, 25, and 28 wt %.<sup>11-14</sup> It is of interest to investigate the effect of AN content in SAN upon blend compatibility when SAN is blended with PCL. Studies have been made of blend transition behavior as well as the dependence of compatibility upon blend thermal history for PCL/SAN 24 (AN wt % = 24) blends.<sup>15</sup> The present paper reports the effects of AN content in SAN on the compatibility of PCL/SAN blends. The transition behavior of blends were studied by both dynamic mechanical and thermal analysis methods. The appearance of blends cast from solutions into films and lower critical solution temperature (LCST) measurements were both used in this study to gain insight into the range of compatibility of the blends.

## EXPERIMENTAL

**Materials.** The PCL used in this work is designated as PCL-700 by the Union Carbide Corporation and has a reported molecular weight of  $M_n = 15,500$  and  $M_w = 40,400$ .<sup>16</sup>

The SAN copolymers with various AN contents were prepared at 60°C by bulk radical copolymerization of freshly distilled styrene monomer with a particular composition of acrylonitrile monomer.<sup>17</sup> Table I summarizes the composition, molecular weight, and preparation conditions for SAN copolymers used in this study.

TABLE I  
Reaction Conditions, Compositions, and Molecular Weights of SAN's

Sample	Feed $f_{AN_0}$	Calculated <sup>a</sup>		Experimental		Composition <sup>b</sup>		Molecular weight <sup>c</sup>				
		$F_{AN_0}$	$x_{\text{limited}}$ (mol %)	Conversion (mol %)	Reaction time (h)	AN % (mol %)	AN % (wt %)	$M_n \times 10^{-3}$	Uncorrected $M_w \times 10^{-3}$	Corrected $M_n \times 10^{-3}$	Corrected $M_w \times 10^{-3}$	$M_w/M_n$
SAN 6	0.05	10.44	10	5.06	2.50	10.31	5.53	212	359	201	341	1.69
SAN 8	0.075	14.46	9	4.36	2.00	15.34	8.45	219	387	203	358	1.76
SAN 11	0.10	17.92	9	5.67	2.50	19.17	10.78	228	409	209	371	1.78
SAN 14	0.15	23.56	11	5.40	2.00	24.67	14.30	259	446	228	392	1.72
SAN 17	0.20	27.98	14	8.37	2.50	28.40	16.81	272	471	233	405	1.74
SAN 21	0.30	34.47	30	6.83	2.00	34.20	20.94	271	479	225	398	1.77
SAN 24	0.3846	38.46	100	13.89	3.00	38.59	24.25	303	550	246	446	1.81
SAN 28	0.50	42.62	30	9.70	2.00	42.77	27.58	304	518	240	409	1.70
SAN 30	0.60	45.56	19	6.91	1.50	44.81	29.62	284	513	222	400	1.80
SAN 33	0.70	48.28	14	6.30	1.25	49.45	33.26	324	545	245	413	1.69
SAN 36	0.80	51.33	9	3.96	0.83	52.85	36.35	362	584	268	433	1.62

<sup>a</sup> Calculation was based on  $r(\text{ST}) = 0.4$  and  $r(\text{AN}) = 0.04$ ;  $f_{AN_0}$  = mole fraction of AN in feed;  $F_{AN_0}$  = mole fraction of AN in initial copolymer;  $x_{\text{limited}}$  = conversion selected to avoid compositional heterogeneity.

<sup>b</sup> Composition was determined by the Kjeldahl method.

<sup>c</sup> Molecular weight distribution was determined by GPC. The GPC column was calibrated with polystyrene standards. The copolymer molecular weight was corrected for different copolymer composition, i.e.,  $M_{\text{SAN}} = M_{\text{PS(STD)}} \times \{(1 - F_{\text{AN}}) + [(53.06/104.14) \times F_{\text{AN}}]\}$ .

It is important when a copolymer is used as the constituent component in blends that the preparation of copolymer be carefully controlled to obtain a material without compositional drift during polymerization. A relation developed by Meyer and Lowry,<sup>18</sup> which relates conversion and instantaneous monomer concentration, was used to determine the instantaneous copolymer composition at any conversion. For each copolymer a limiting conversion was selected to ensure that the instantaneous copolymer composition and the initial copolymer composition differ by no more than 1 mol %. These are listed in Table I. All of the copolymerizations performed in this study were terminated at a conversion less than the selected limiting conversion. Therefore, there is little possibility of significant compositional heterogeneity in the prepared SAN copolymers.

The composition of SAN copolymer was determined by the conventional Kjeldahl method of nitrogen analysis.<sup>19</sup> The composition of each copolymer prepared from various feed mixtures agrees well with theoretical values based on the reported reactivity ratios for the styrene-acrylonitrile copolymerization, i.e., for styrene  $r = 0.4$  and for acrylonitrile  $r = 0.04$ .<sup>20</sup>

The molecular weights and molecular weight distribution of SAN were determined by using a Waters Associates GPC, ALC/GPC Model 244. The GPC system was calibrated using standard NBS polystyrene samples. Measured molecular weights of SAN samples were corrected to account for the AN content in the copolymers by the method used by Schultz and Beach<sup>6</sup> with the assumption that molecules having equal contour lengths elute at equal volume.

Two homopolymers, polystyrene, Styron from Dow Chemical Co., and polyacrylonitrile (PAN) from Aldrich Chemical Co. were also used in this study.

**Blend Preparation.** Blends were prepared by a solution blending method<sup>15</sup> and were identified according to their composition. For instance, SAN 28—70%/PCL—30% represents the blend containing 70 wt percent SAN 28 and 30 wt % PCL, where SAN 28 is poly(styrene-co-acrylonitrile) containing 28 wt % AN.

**Measurements.** Dynamic mechanical measurements (Rheovibron), thermal analysis (DSC), and cloud point measurements were conducted using methods described in Ref. 15.

## RESULTS AND DISCUSSION

**Appearance of Cast Film.** Cast films of blends were prepared by a solution blending method using dichloroethane as the solvent. After solvent removal the films could be classified into four categories: type A, transparent; type B, translucent to opaque at room temperature but clear above  $T_m$  of PCL; type C, opaque at all temperatures; and type D, opaque and broken. Samples shown in Figure 1 illustrates the appearance of films in each of the four categories. The dependence of film appearance upon blend composition and AN content in the SAN copolymer is shown in Figure 2.

Type A film was obtained for PCL/SAN blends containing 75 wt % or more SAN, where SAN has AN contents ranging from 8 to 28 wt %. In general, the transparency of a film is an indication of blend compatibility. However, this cannot be considered as conclusive evidence of compatibility because of the possibility of identical refractive indices of separate phases. The refractive index

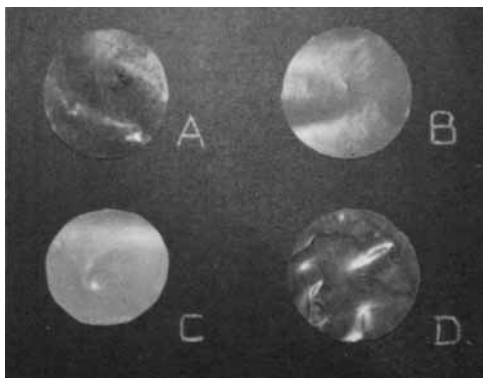


Fig. 1. Film appearance of cast sample for SAN/PCL blends: (A) SAN 24—90%/PCL—10%; (B) SAN 24—30%/PCL—70%; (C) SAN 30—70%/PCL—30%; (D) SAN 6—70%/PCL—30%.

of PCL is 1.480.<sup>11</sup> The refractive index of SAN copolymer can be estimated from its component composition and the refractive indices of the corresponding homopolymers<sup>21</sup>:

$$RI(SA) = RI(PS) \times wt\% (PS) + RI(PAN) \times wt\% (AN)$$

The refractive index of PS is 1.591 while that of PAN is 1.519. The refractive index of SAN copolymer should lie between these two limiting values. Bohn<sup>21</sup> has indicated that, for transparency to occur, the critical difference between refractive indices of separate phases can be no greater than 0.01. Therefore, the transparency of type A films cannot be a consequence of nearly identical refractive indices of separate phases.

Type B films were obtained for PCL/SAN blends containing 30 wt % or more PCL when SAN has AN contents ranging from 8 to 28 wt %, except for SAN 28—30%/PCL—70% and SAN 28—15%/PCL—85%. Type B films were observed to vary from translucent to opaque, depending on the amount of PCL in the blend. The appearance of these films was similar to that of solvent cast pure PCL, which is semicrystalline. When heated above the  $T_m$  of PCL, type B film became clear. Upon being annealed at 25°C, the film became opaque due to the

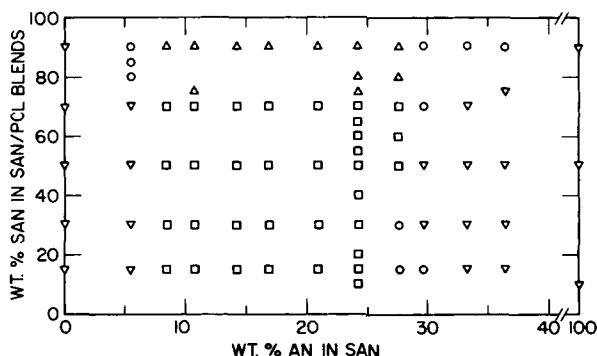


Fig. 2. Dependence of film appearance upon blend composition and SAN copolymer composition: ( $\Delta$ ) type A, ( $\square$ ) type B; ( $\circ$ ) type C; ( $\nabla$ ) type D.

TABLE II  
Results of  $T_g$  Measurements by Rheovibron for SAN/PCL Blends<sup>a</sup>

Wt % SAN in blends	Blends					
	SAN 8/PCL	SAN 11/PCL	SAN 17/PCL	SAN 24/PCL	SAN 28/PCL	SAN 30/PCL
100	116	116	120	122	124	—
90	92	92	96	98	98	—
80	—	—	—	76	78	—
70	46	50	52	54	58	-44, 112
60 <sup>b</sup>	—	—	—	30	28	—
60	—	—	—	52	—	—
50 <sup>b</sup>	—	—	—	-4	—	—
50	—	50	48	50	54	—
30	—	38	38	44	-40, —	—
15	—	0	-4	0	-40, —	—
0	-44	-44	-44	-44	-44	-44

<sup>a</sup> Temperature in °C. Rheovibron frequency = 110 Hz. All the samples were annealed for an extended time unless otherwise noted.  $T_g$  determined as peak location on the  $E''$  curve.

<sup>b</sup> Quenched sample without PCL crystallinity.

formation of PCL crystallites. Annealing time required for the reappearance of opaqueness increased with increasing SAN concentration in the blends. Cast film containing 70 wt % SAN were slightly translucent, indicating the presence of a small quantity of crystalline PCL.

Type C films are shown to occur in Figure 2 at the boundaries of the type A or type B films. Type C film was observed to be continuous but opaque. When film heated above the  $T_m$  of PCL remained opaque, it was taken as an indication of component incompatibility. Upon moving further away from the region of type A and B films, broken films of type D were obtained. These films were opaque and contained "island"-like structures of one phase embedded in a matrix

TABLE III  
Results of  $T_g$  by DSC for SAN/PCL Blends<sup>a</sup>

Blends	Wt % SAN in blends								
	100	90	80	70	60	50	30	15	0
PS/PCL	376	210, 373	—	210, 372	—	—	—	—	208
SAN 6/PCL	379	211, 360	—	210, 362	—	—	—	—	208
SAN 8/PCL	380	348	—	299	—	255	226	220	208
SAN 11/PCL	381	350	—	302	—	256	225	221	208
SAN 14/PCL	381.5	351	—	302	—	—	—	—	208
SAN 17/PCL	382	351	—	302	—	258	227	220	208
SAN 21/PCL	383.5	353	—	303	—	—	—	—	208
SAN 24/PCL	384	352	326	302	279	260	228	218	208
SAN 28/PCL <sup>b</sup>	385	355	329	305	284	256	209, —	209, —	208
SAN 30/PCL	387	209, 382	—	209, 382	—	—	209, 382	209, 381	208
SAN 33/PCL	387	210, 379	—	208, 379	—	—	—	—	208
SAN 36/PCL	386	210, 383	—	—	—	—	—	—	208

<sup>a</sup> Temperature in K. All the samples were scanned at 20 K/min from 150 K to 400 K after being quenched at 320 K/min from 400 K to 150 K, unless otherwise noted.

<sup>b</sup> SAN 28/PCL sample with 50% or more SAN was scanned at 20 K/min upon heating after being quenched at 320 K/min to 150 K from a temperature above  $T_g$  of blend and  $T_m$  of PCL but below its cloud point.

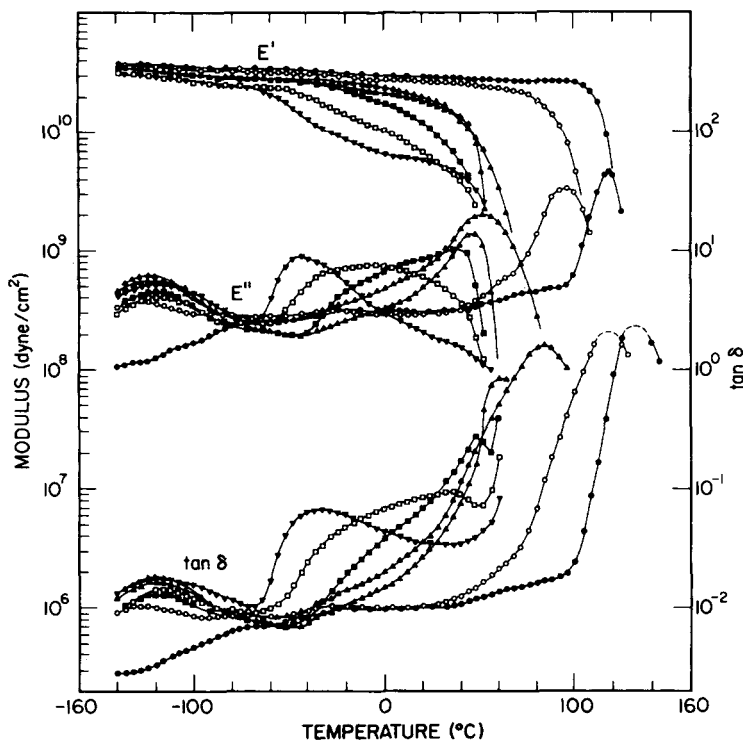


Fig. 3. Dynamic mechanical behavior of SAN 17/PCL blends at 110 Hz; % SAN 17: (●) 100; (○) 90; (▲) 70; (△) 50; (■) 30; (□) 15; (▼) 0.

of the second phase. It was also noted that adhesion between the phases was poor. Opaqueness and poor mechanical properties indicate component incompatibility in type D films.

Because PAN is not soluble in dichloroethane and is very difficult to melt process, PAN/PCL blends were prepared using dimethyl formamide (DMF) as the solvent. Since PCL is soluble in DMF only at an elevated temperature, the two polymers were dissolving at 65°C. Film obtained upon casting the mixture was observed to be of type D.

**Rheovibron, DSC, and Cloud Point Measurements.** The glass transition temperatures of various SAN/PCL blends determined from Rheovibron and DSC measurements are summarized in Table II and Table III, respectively. In a previous paper,<sup>15</sup> the transition behaviors of the compatible SAN 24/PCL blends have been discussed in detail. Those observations help to characterize the compatibility of the various SAN/PCL blends reported in the present paper.

**SAN 17/PCL Blends.** The dynamic mechanical properties of annealed samples of PCL, SAN 17, and their blends are shown in Figure 3. Pure PCL exhibits a  $\beta$ -relaxation at -120°C, and an  $\alpha$ -transition at -44°C as shown on the  $E''$  curve. It melts at about 60°C. The  $E''$  curves show that pure SAN 17 has an  $\alpha$ -relaxation at 120°C and broad  $\beta$  and  $\gamma$  secondary relaxations. Each SAN 17/PCL blend has a low temperature secondary relaxation in the region of -120°C, which is contributed mainly by the  $\beta$ -relaxation of the PCL component. Each blend also exhibits a high temperature relaxation, which is the glass

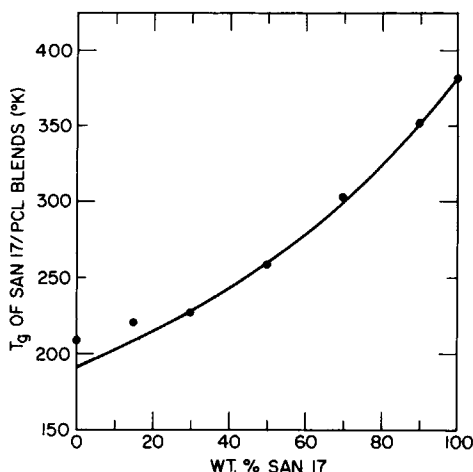


Fig. 4. Dependence of the  $T_g$  of SAN 17/PCL blend upon blend composition. The solid curve represents the Gordon-Taylor equation, using  $K = 0.576$ ,  $T_g(\text{SAN 17}) = 382 \text{ K}$  and  $T_g(\text{PCL, 100\% amorphous}) = 190 \text{ K}$ .

transition. Blends containing 30 wt % or less PCL do not have a PCL crystalline phase and the compositionally dependent  $T_g$  decreases with increasing PCL concentration. For samples containing 50 wt % or more PCL, the single glass transition, which exists at a temperature intermediate between those of the respective pure components, is somewhat broadened or skewed due to the presence of crystalline PCL.<sup>15</sup> The crystallization of PCL reduces the quantity of PCL associated with the SAN in the compatible amorphous phase. The presence of PCL crystallites also further shifts the glass transition temperature of the compatible amorphous phase to a higher temperature. The overlapping of the PCL crystal melting point and the broad glass transition also contribute to the complexity in the dynamic mechanical behavior observed in these samples.

The single glass transition reported by DSC analysis for the SAN 17/PCL blends demonstrate their compatibility. Figure 4 shows how the glass transition temperatures of these samples, as determined in the reheating step after quenching from 400 K, decreased monotonically with increasing concentration. The glass transition temperatures can be correlated with the Gordon-Taylor equation.<sup>22</sup> Using  $T_g(\text{SAN 17}) = 382 \text{ K}$ ,  $T_g(\text{PCL, 100\% amorphous}) = 190 \text{ K}$  and  $K = 0.576$ , where the last two values were obtained by studying SAN 24/PCL blends.<sup>15</sup> The presence of PCL crystallites formed during the rapid crystallization of PCL from blends containing high PCL concentrations is again responsible for the observed discrepancy between the measured  $T_g$  for the 85 wt % PCL blend and that predicted by the Gordon-Taylor equation.

Each of the SAN 17/PCL blends were transparent above the  $T_m$  of PCL which is an indication of blend compatibility and the absence of PCL crystallites. The thermal instability of these polymers at high temperatures, made the cloud points for these samples difficult to determined before the polymer decomposed.

**SAN 8/PCL, SAN 11/PCL, SAN 14/PCL, and SAN 21/PCL Blends.** The dynamic mechanical properties of SAN 8/PCL and SAN 11/PCL are similar to those of SAN 24/PCL and SAN 17/PCL blends. Each blend displays a simple compositionally dependent glass transition, which is evidence of compatibility.



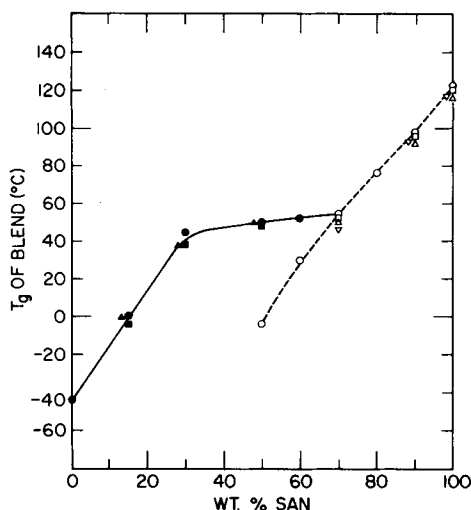


Fig. 5.  $T_g$  of SAN/PCL blend vs. blend composition: (O) SAN 24/PCL; ( $\square$ ) SAN 17/PCL; ( $\Delta$ ) SAN 11/PCL; ( $\nabla$ ) SAN 8/PCL, where open symbols are for samples without PCL crystallinity and filled symbols for samples with PCL crystallinity. Rheovibron at 110 Hz.

The composition and thermal history dependence of the glass transition temperatures for SAN 8/PCL, SAN 11/PCL, and SAN 17/PCL blends, as shown in Figure 5, are similar to those for SAN 24/PCL blends.

The DSC analysis also provides further evidence of compatibility for these blends and their  $T_g$ -composition relation can be correlated by the Gordon-Taylor equation, as shown in Figure 6.

Additional evidence of compatibility is shown by the existence of phase separation, LCST behavior at high temperatures for SAN 8/PCL and SAN 11/PCL blends. Their cloud point curves are shown in Figure 7. It should be noted that

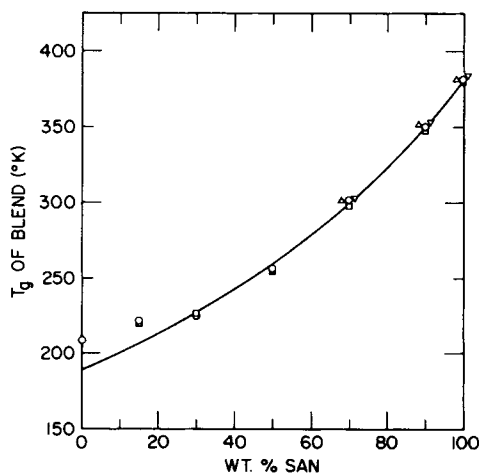


Fig. 6. Dependence of the  $T_g$  of SAN/PCL blend upon blend composition: ( $\nabla$ ) SAN 21/PCL; ( $\Delta$ ) SAN 14/PCL; (O) SAN 11/PCL; ( $\square$ ) SAN 8/PCL. The solid curve represents the Gordon-Taylor equation, using  $K = 0.576$ ,  $T_g(\text{SAN 11}) = 384$  K and  $T_g(\text{PCL, 100\% amorphous}) = 190$  K.

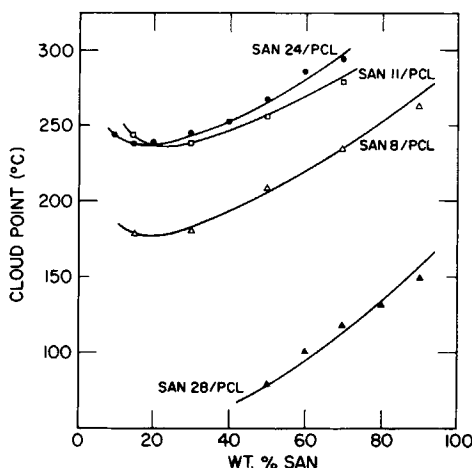


Fig. 7. Cloud point curves for SAN/PCL blends.

SAN 8/PCL blends have lower phase separation temperatures than SAN 11/PCL blends at the same blend concentration.

**SAN 28/PCL Blends.** In contrast to the previously discussed SAN copolymers which are compatible with PCL in all proportions, SAN 28 was found to be compatible with PCL in blends containing up to 50 wt % PCL and incompatible with PCL in blends containing 70 or 85 wt % PCL.

The cloud points of SAN 28/PCL blends shown in Figure 7 are located in a temperature range much lower than those for blends containing SAN 24, SAN 11, and SAN 8. Blends of SAN 28 containing 30 wt % or less PCL were transparent at all temperatures below the cloud point. Annealed samples with 40 wt % or 50 wt % PCL which were opaque at room temperature due to the presence of crystalline PCL became transparent above  $T_m$  of PCL and became opaque above the cloud point. Blends with 70 wt % or 85 wt % PCL were opaque at room temperature and remained opaque above the  $T_m$  of PCL. This opacity can be attributed to either the presence of PCL crystallites below the  $T_m$  or the phase separation above the cloud point. By extrapolating the cloud point data from the higher SAN concentration region to the lower SAN concentration region it can be seen that the cloud point for blends with 70 or 85 wt % PCL, if it exists, is apparently below the  $T_m$  of PCL. The observation of a cloud point lower than the  $T_m$  of the crystallizable component has been reported by Bernstein and co-workers<sup>23</sup> for PVF<sub>2</sub>/PEA [poly(vinylidene fluoride)/poly(ethyl acrylate)] blends.

The cloud point curve for SAN 28/PCL blends observed in this study is lower in temperature than that reported by McMaster.<sup>13</sup> This difference is believed to arise from different molecular weights for the SAN samples used. The SAN used in McMaster's study, which contained 28 wt % AN, has a molecular weight of  $M_n = 88,600$  and  $M_w = 223,200$ , while the SAN 28 sample used in this work has a molecular weight of  $M_n = 240,000$  and  $M_w = 409,000$ . As the molecular weight of either component in a blend increases, the mutual solubility of the two polymers decreases, and, consequently, the cloud point curve shifts to lower temperatures.<sup>24</sup>

The dynamic mechanical properties of SAN 28, PCL, and their amorphous

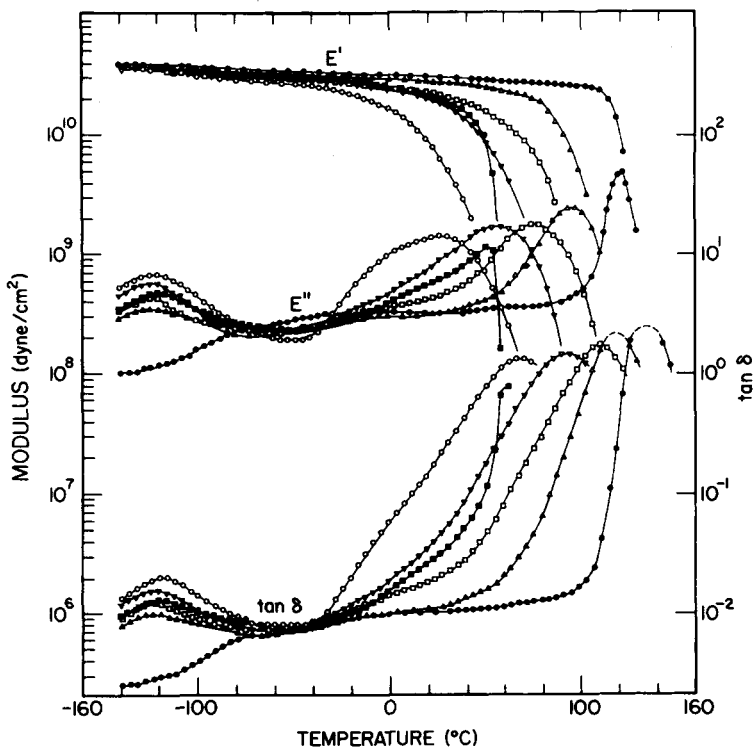


Fig. 8. Dynamic mechanical behavior of SAN 28/PCL blends at 110 Hz; % SAN 28: (●) 100; (Δ) 90; (□) 80; (▽) 70; (○) 60; (■) 50.

blends containing 60–90 wt % SAN are shown in Figure 8. The 60 wt % SAN sample was first quenched to room temperature from a temperature above the  $T_m$  of PCL but below its cloud point. A low temperature secondary relaxation appears for each blend. A glass transition for either pure component is not observed, but each blend displays a single compositionally dependent glass transition. Figure 8 also shows the dynamic mechanical properties of an annealed SAN 28—50%/PCL—50% sample. This sample displays a single glass transition, which is not as symmetric as those of amorphous samples due to the presence of PCL crystallites.

The dynamic mechanical behavior of the 15 and 30 wt % SAN samples exhibit blend incompatibility, as shown in Figure 9. Both blends have a glass transition in the temperature range of the  $\alpha$ -transition of unblended PCL. This indicates the existence of an essentially pure PCL phase.

The DSC analysis also shows the existence of compositionally dependent glass transitions for SAN 28/PCL blends over the composition range of 50–90 wt % SAN. The  $T_g$ -composition relation is shown in Figure 10, and follows the Gordon-Taylor equation for blends containing up to 50 wt % PCL. Since cloud points for these blends occur in a relatively low temperature range, the upper limit temperatures for PCL scans were carefully selected to be below the respective cloud point for each composition to avoid phase separation. However, this temperature was sufficiently great to assure the same thermal history in the

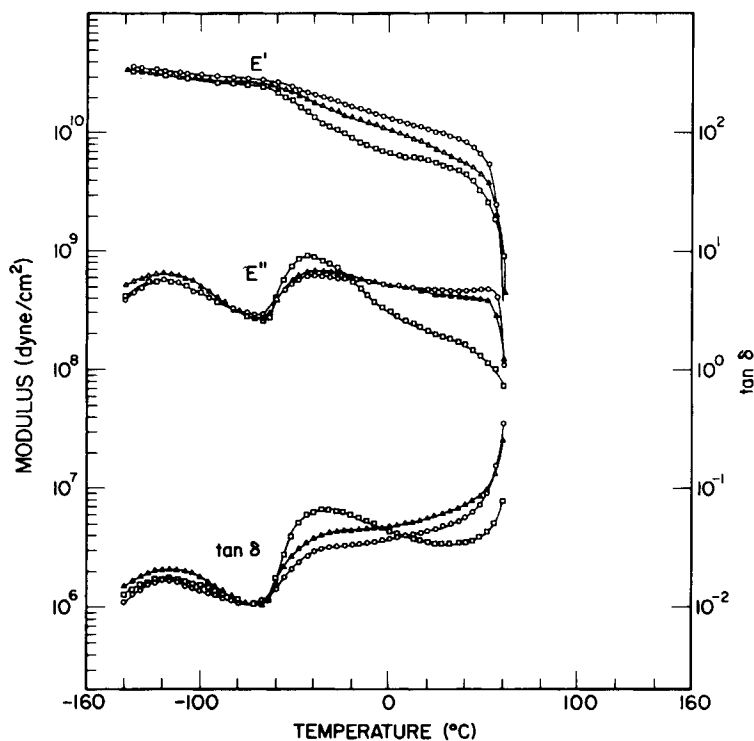


Fig. 9. Dynamic mechanical behavior of SAN 28/PCL blends at 110 Hz: (O) 30% SAN 28; ( $\Delta$ ) 15% SAN 28; ( $\square$ ) 100% PCL.

following scan after quenching to 150 K for each sample. The DSC analysis demonstrates blend incompatibility in the 15 or 30 wt % SAN sample by the existence of a  $T_g$  for the PCL phase.

It is interesting to observe the thermally induced phase separation behavior which occurred during the DSC analysis. Figure 11 shows a series of DSC thermograms for the SAN 28—70%/PCL—30% sample. Each thermogram has the same starting temperature (150 K) but varying ending temperatures; each 10 K higher than that of the preceding scan. Exactly 15 s after reaching the ending temperature, the sample was quenched to the starting temperature and kept there for 5 min to establish the low temperature isotherm. The sample was reheated at a heating rate of 20°C/min to the new ending temperature. As can be seen in Figure 11, the first three thermograms display a single glass transition, which is an evidence of compatibility, and do not display the PCL fusion endotherm. Beginning with the fourth thermogram, a PCL fusion endotherm appears. The size of this fusion endotherm increases as the sample is quenched from higher and higher temperature. As has been stated before, when the same DSC scanning cycle was applied, the PCL fusion endotherm is not observed for compatible blends containing 30 wt % PCL, but appears for blends containing high PCL concentrations. The presence of the PCL fusion endotherm on the thermograms in Figure 11 signals the appearance of pure PCL or a PCL-rich phase, which separates at elevated temperatures above the cloud point from the originally compatible blend. The first appearance of the PCL fusion endotherm in the fourth

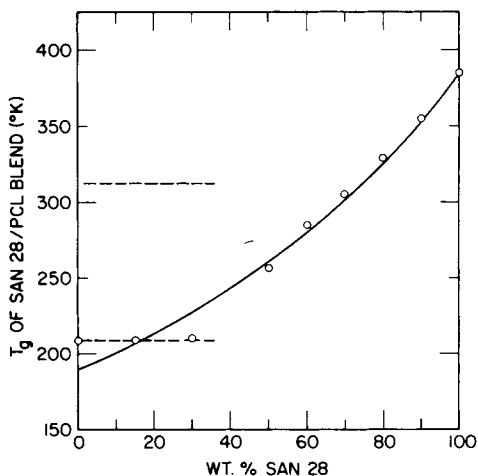


Fig. 10. Dependence of the  $T_g$  of SAN 28/PCL blend upon blend composition. The solid curve represents the Gordon-Taylor equation, using  $K = 0.576$ ,  $T_g(\text{SAN 28}) = 385 \text{ K}$  and  $T_g(\text{PCL, 100\% amorphous}) = 190 \text{ K}$ . The broken lines represent the  $T_g$ 's expected for incompatible blends with low SAN concentration in blends.

thermogram in Figure 11 implies that phase separation occurs at temperatures between 390 K and 400 K, which agrees with the visually observed cloud point value, 391 K. The quenching step used in the DSC analysis quickly solidifies the sample and thus kinetic effects are important. At low temperatures, the thermodynamically reversible process is retarded by restricting the diffusion of molecules in the glassy state. Consequently, separate phases which appeared above the cloud point remain in the sample after the quenching step. In contrast to phase separation observed during the quenching step, phase separation was suppressed by extremely slow cooling. During reheating of the SAN 28—70%/PCL—30% sample after being cooled from 450 K to 300 K at a slow cooling

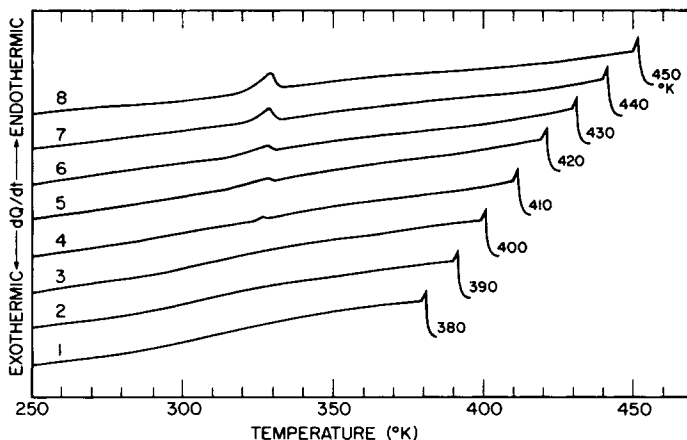


Fig. 11. DSC thermograms for SAN 28—70%/PCL—30% blend with various thermal histories. Thermograms show the phase separation at elevated temperatures.

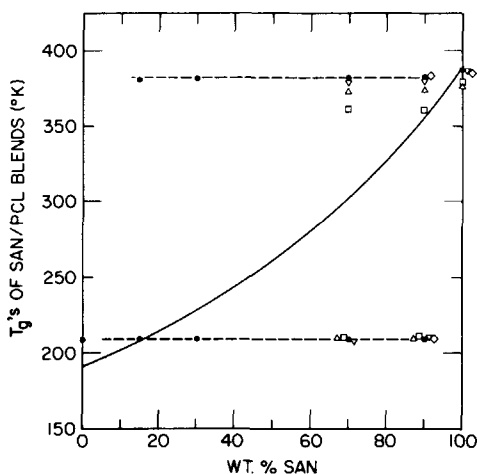


Fig. 12.  $T_g$ 's of incompatible SAN/PCL blends versus blend composition: ( $\diamond$ ) SAN 36/PCL; ( $\nabla$ ) SAN 33/PCL; ( $\bullet$ ) SAN 30/PCL; ( $\square$ ) SAN 6/PCL; ( $\Delta$ ) PS/PCL. The solid curve represents the Gordon-Taylor equation, using  $K = 0.576$ ,  $T_g(\text{SAN } 30) = 387 \text{ K}$  and  $T_g(\text{PCL, } 100\% \text{ amorphous}) = 190 \text{ K}$ . The broken lines connect the  $T_g$ 's observed for SAN 30/PCL blends.

rate of 0.31 K/min a thermogram with a single  $T_g$  and without the PCL fusion endotherm is displayed.

**Incompatible Blends.** Films made from blends of PCL with PS, SAN 6, SAN 30, SAN 33, SAN 36, and PCL were opaque at all temperatures. The DSC thermograms display not only a PCL fusion endotherm, which does not appear for compatible blends with high SAN concentrations, but also two glass transition temperatures corresponding to two amorphous regions in the separate phases. The plot of the glass transition temperatures vs. blend composition (Fig. 12) shows the typical  $T_g$  characteristics of incompatible blends.

These incompatible blends are believed to have a microstructure which is a composite of the PCL crystalline phase coexistent with two amorphous phases. Transitions corresponding to these phases can be clearly seen in the dynamic mechanical properties curves shown in Figure 13 for the SAN 30—70%/PCL—30% blend. Again the low temperature transition at  $-120^\circ\text{C}$  is attributed to a secondary relaxation. A low temperature glass transition, which is related to an essentially pure PCL phase occurs at  $-44^\circ\text{C}$  on the  $E''$  curve. A decrease in the magnitude of  $E'$  can be seen in this temperature range. The melting of the PCL crystalline phase at about  $69^\circ\text{C}$  causes a sharp drop on the  $E'$  curve. A high temperature glass transition, which is related to the SAN-rich phase occurs at  $112^\circ\text{C}$  on the  $E''$  curve. This  $T_g$  value is somewhat lower than that of unblended SAN, indicating the incorporation of some PCL in the SAN sample. Thermodynamic considerations suggest that the partial mixing of a small quantity of lower molecular weight PCL in the high molecular weight SAN phase may be possible, as evidenced from the skewness of the cloud point curves for SAN/PCL blends toward the PCL-rich region.

**Basis of Compatibility.** Based on glass transition and cloud point measurements, PCL has been found to be compatible with SAN containing AN contents ranging from 8 to 28 wt %. Due to the presence of LCST behavior at relatively low temperatures, SAN 28/PCL blends with 70 or 85 wt % PCL were

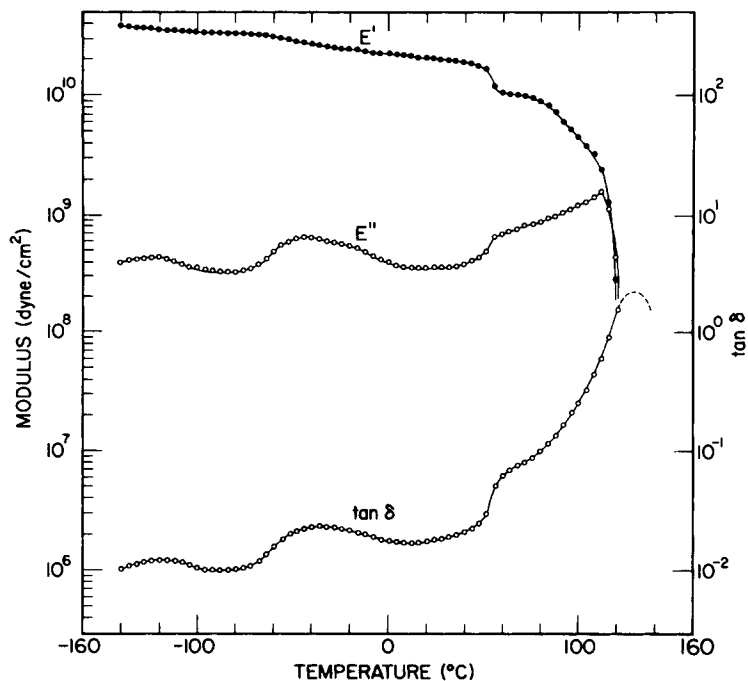


Fig. 13. Dynamic mechanical behavior of SAN 30—70%/PCL—30% blend at 110 Hz.

found to be incompatible. It has been found that PCL is incompatible with SAN when SAN consists of 6 wt % or less AN and 30 wt % or more AN. The effect of the AN content in SAN upon compatibility can be clearly noted by the presence of single or two glass transitions in blends, as shown in Figure 14 for blends with 70 wt % SAN.

The main factor required to achieve compatibility in SAN/PCL blends is believed to be the specific interaction, between component molecules. This specific

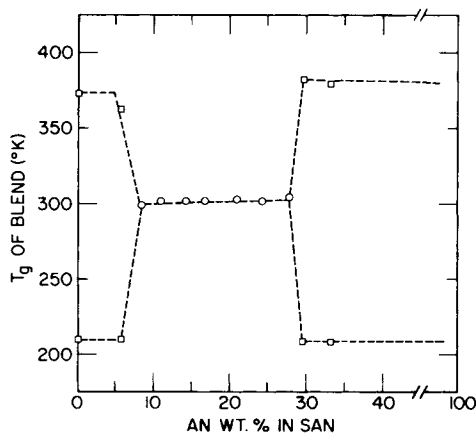


Fig. 14.  $T_g$ 's for blends containing 70% SAN as function of SAN composition.  $T_g$ 's were determined by DSC.

interaction, a proton donor-acceptor type, might exist between the oxygen atom in the carbonyl group of PCL, a proton acceptor, and the tertiary hydrogen in the acrylonitrile unit in SAN, a proton donor. This intermolecular interaction leads to an exothermic heat of mixing to allow the Gibbs free energy of mixing to become negative, thus satisfying the thermodynamic criteria for compatibility. It has been suggested by Paul and Barlow<sup>1</sup> that "without doubt, the necessary requirement for polymer pair miscibility (compatibility) is the exothermic interaction between pair segments." A similar interaction has been proposed to exist in the compatible PCL/PVC blend.<sup>16</sup>

For several compatible blends containing copolymer as a component, there generally exists a composition range for the copolymer in which it is observed to be compatible with the other polymer. There seems to need to be a delicate balance of specific and dispersive interactions between molecular segments to achieve compatibility.

Polystyrene has been found to be incompatible with PCL. The lack of specific interaction and the dominance of dispersion interaction are responsible for the incompatibility observed. The specific interaction between SAN and PCL increases with increasing AN in SAN. However, for SAN 6/PCL such an interaction is believed to be not intensive enough to outweigh the dispersive interaction; consequently, incompatibility results. Within the compatible composition range, the proper AN content in SAN provides an adequate balance between competing interactions and leads to an exothermic heat of mixing and compatibility. The incompatibility of SAN copolymers containing 30 wt % or more AN with PCL probably arises again from dominate dispersive interactions. For SAN copolymers having high AN contents, intermolecular attractions between the AN groups on adjacent chains can be strong. Strong intermolecular interactions between SAN molecules may lead to weak intermolecular interaction between SAN and PCL molecules, consequently making the dispersive interaction between SAN and PCL dominant. Another complementary explanation can be advanced based on differences in the density of specific interactions along SAN and PCL chains. The number of proton donors per unit chain length in SAN increases with AN content in SAN, while the number of proton acceptors per unit chain length of PCL remains constant. Furthermore, phase separation observed at elevated temperature for SAN/PCL blends agrees with the fact that blends with exothermic heats of mixing usually exhibit LCST behavior.<sup>1,24</sup> The temperature locations of the cloud points observed for SAN/PCL blends are also indicative of the magnitude of interaction between blend components. From the cloud point curve in Figure 7, a trend can be noted. Those blends containing SAN with an AN content at the edge of the compatible range have cloud point curves at a lower temperature location than those containing SAN with an AN content at the middle portion of the compatible range.

It is informative to plot the cloud point values against content of AN in SAN with blend composition as a parameter, as shown in Figure 15. Since the SAN copolymers used in this study have high molecular weights with close molecular weights and distributions, the influence of molecular weight, essentially an entropic effect, upon the temperature location of the cloud point is not as significant as the enthalpic effect. The higher cloud point temperature observed for blends containing SAN with AN content in the middle portion of the compatible AN range is believed to be the consequence of strong interactions between SAN and



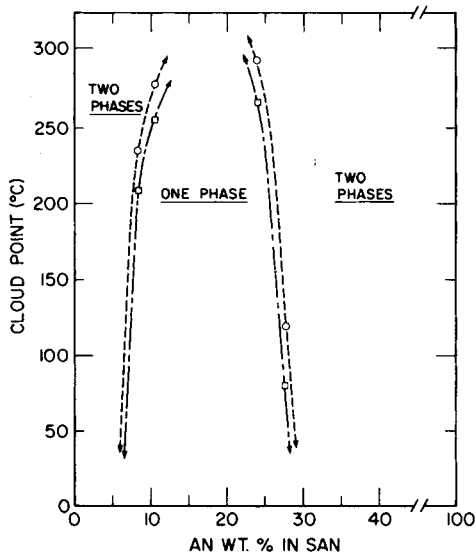


Fig. 15. Cloud points of SAN/PCL blends as function of SAN composition: (O) SAN/PCL = 70/30; (□) SAN/PCL = 50/50.

PCL. Bernstein and co-workers have demonstrated that stronger specific interaction between blend components shifts the LCST behavior to higher temperatures.<sup>23</sup> Alexandrovich and coworkers<sup>7</sup> have reported the LCST of PPO/poly(para-chlorostyrene-co-ortho-chlorostyrene) blends as a function of copolymer composition. Their results exhibit the same trends as those observed here for PCL/SAN blends.

The extrapolation of the curves in Figure 15 to SAN compositions outside the compatible AN range rapidly intersect the  $T_m$  of PCL and the temperature at which the blends were prepared from solution, illustrating that the preparation of a compatible SAN/PCL blend when SAN does not have the proper AN content becomes very difficult. This consideration may explain the sharp transition from compatibility to incompatibility observed as AN content in SAN decreases from 8 to 6 wt % or increases from 28 to 30 wt %.

### References

1. D. R. Paul and J. W. Barlow, *J. Macromol. Sci., Rev. Macromol. Chem.*, **C18**, 109 (1980).
2. O. Olabisi, L. M. Robeson, and M. T. Shaw, *Polymer-Polymer Miscibility*, Academic, New York, 1979.
3. S. Krause, in *Polymer Blends*, D. R. Paul and S. Newman, Eds., Academic, New York, 1978, Chap. 2.
4. G. A. Zakrzewski, *Polymer*, **14**, 347 (1973).
5. C. F. Hammer, *Macromolecules*, **4**, 69 (1971).
6. A. R. Schultz and B. M. Beach, *Macromolecules*, **7**, 902 (1974).
7. P. Alexandrovich, F. E. Karasz, and W. J. MacKnight, *Polymer*, **18**, 1022 (1977).
8. V. D. J. Stein, R. H. Jung, K. H. Illers, and H. Hendus, *Angew. Makromol. Chem.*, **36**, 89 (1974).
9. M. T. Shaw, *J. Appl. Polym. Sci.*, **18**, 449 (1974).
10. D. R. Paul, in *Polymer Blends*, D. R. Paul and S. Newman, Eds., Academic, New York, 1978, Chap. 1.

11. E. Clark and C. W. Childers, *J. Appl. Polym. Sci.*, **22**, 1081 (1978).
12. P. B. Rim and J. P. Runt, *Macromolecules*, **16**, 762 (1983).
13. L. P. McMaster, *Macromolecules*, **6**, 760 (1973).
14. C. G. Seefried, Jr. and J. V. Koleske, *J. Test. Eval.*, **4**, 220 (1976).
15. S. Chiu and T. G. Smith, *J. Appl. Polym. Sci.*, **29**, 1781 (1984).
16. O. Olabisi, *Macromolecules*, **8**, 316 (1975).
17. S. Chiu, PhD thesis, University of Maryland, College Park, Maryland, 1981.
18. V. E. Meyer and G. G. Lowry, *J. Polym. Sci.*, **A3**, 2843 (1965).
19. J. Cobler and G. Stobby, in *Encyclopedia of Industrial Chemical Analysis*, F. D. Snell and L. S. Ettre, Eds., Wiley-Interscience, New York, 1973, Vol. 18.
20. K. Doak, *J. Am. Chem. Soc.*, **72**, 4681 (1950).
21. L. Bohn, in *Polymer Handbook*, J. Brandrup and E. H. Immergut, Eds., Wiley-Interscience, New York, 1975, pp. III-241.
22. M. Gordon and J. S. Taylor, *J. Appl. Chem.*, **2**, 493 (1952).
23. R. E. Bernstein, C. A. Cruz, D. R. Paul, and J. W. Barlow, *Macromolecules*, **10**, 681 (1977).
24. T. K. Kwei and T. T. Wang, in *Polymer Blends*, D. R. Paul and S. Newman, Eds., Academic, New York, 1978, Chap. 4.

Received October 4, 1983

Accepted October 24, 1983