Compatibility of Poly(ε-Caprolactone) (PCL) and Poly(styrene-Co-Acrylonitrile) (SAN) Blends. I. Blends Containing SAN with 24 Wt% Acrylonitrile

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Synopsis

Polymer blends of poly(ε-caprolactone) (PCL) and poly(styrene-co-acrylonitrile) (SAN), containing 24 wt % acrylonitrile (AN), were prepared, and their transition behavior was examined by thermal analysis and dynamic mechanical testing. The blends were judged to be compatible on the basis of the presence of a single, compositionally dependent glass transition. The results of thermal treatment upon blend glass transition behavior and the dependence of thermal history upon the crystallization of semicrystalline PCL were also studied. The crystallization of PCL from SAN/PCL blends was found to be retarded by the presence of SAN, and crystalline PCL was found to exist only in blends containing a high PCL concentration. Blends which do not contain crystalline PCL were transparent, and their glass transition behavior can be correlated by the Gordon–Taylor equation. Phase separation, which was characterized by lower critical solution temperature (LCST) behavior, was found to occur when blends were heated to elevated temperatures.

SUMMARY

Polymer blends of PCL and SAN, which contains 24 wt % AN, show a single glass transition by both DSC and dynamic mechanical measurements over the entire blend composition range. This is evidence that the amorphous phase in these blends is a single phase containing a mixture of both polymers. The glass transition of blends was found to be dependent on the thermal treatment of the samples, i.e., on the extent of crystallization of PCL from the compatible blend. Crystallization of PCL in a blend extracts material from the amorphous regions and hence changes the composition in the amorphous phase. For samples free of PCL crystals, the glass transition temperatures were able to be correlated as a function of composition by the Gordon–Taylor equation.

Crystallization of PCL is retarded and the T_m of PCL is depressed by the addition of SAN in the blend. The onset temperature of a PCL crystallization exotherm on a DSC thermogram, T_c, for the reheating scan after quenching from the molten state, increases with increasing SAN concentration in the blends. These results provide further evidence to confirm compatiblity for this blend.

A liquid–liquid-type phase separation at high temperature because of the existence of a LCST was also observed for this compatible system. The cloud point curve was found to be skewed toward high PCL concentrations due to differences in the molecular weight of blend components. A preliminary phase

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diagram for this polymer blend was also constructed by combining results from various measurements.

INTRODUCTION

As the result of interest and research in the area of polymer blends, a number of compatible blends have been discovered in the past decade. The basis for blend compatibility has been summarized in several reviews.[1-3] In recent years specific interaction between the constituent polymer chains has been regarded as the main factor required to achieve blend compatibility and the promotion of such interaction has been suggested as an effective means of enhancing blend compatibility. In order to have a better understanding of specific interactions as well as blend compatibility, the study of polymer blends containing a random copolymer as one of the constituent components is of interest. When copolymer composition varies, the degree of specific interaction between polymer chains should vary, and, consequently, blend compatibility should be affected. Based on this reasoning, the authors studied blends of poly(ε-caprolactone) (PCL) and poly(sytrene-co-acrylonitrile) (SAN) containing various percentages of acrylonitrile (AN) to investigate the dependence of blend compatibility upon copolymer composition.

Blends of PCL with other polymers, particularly with PVC have been the subject of several investigations.[4-8] The study of PCL/SAN blends has received relatively little attention, with only studies using SAN's with 24, 25, and 28 wt % AN reported.[9-12] In addition the transition behavior for blends with high concentrations of PCL has not been reported.

This paper deals with an investigation of the compatibility of PCL/SAN blends when the SAN component contains 24 wt % AN; the azeotropic composition when SAN is prepared by radical copolymerization at 60°C. The influence of PCL concentration and thermal treatment upon blend transition behavior is considered in this work. This work serves as the basis for a further study where the influence of varying the AN content in SAN upon blend compatibility is considered.[13]

EXPERIMENTAL

Materials. The PCL (PCL-700) used in this work has a number average molecular weight of M_n = 15,500 and a weight average molecular weight of M_w = 40,400.[5] In this study PCL was used as received from Union Carbide Corp.

SAN was prepared by the bulk radical copolymerization of freshly distilled styrene monomer and acrylonitrile monomer at the azeotropic composition and 60°C. The AN content in SAN was determined by nitrogen analysis as 24.25% by weight. The molecular weight of SAN was determined to have values of M_n = 246,000 and M_w = 446,000 relative to polystyrene as the GPC calibration standard. Details of the SAN copolymerization and characterization are available.[13]

Blend Preparation. One gram of polymer of a particular blend composition was dissolved in 30 mL of dichloroethane. The solution was transferred into an evaporation dish and solvent allowed to slowly evaporate at 25°C for 2 days.

The films produced were transferred to a vacuum oven for further drying at 45°C for 3 days. The films were then covered with Mylar film and pressed into sheets between two aluminum plates in a Carver laboratory press for 5 min at 130°C. Films were slowly cooled while in the press to room temperature at a cooling rate of approximately 1.5°C/min. The films were then annealed at 45°C for 3 days followed by annealing at 25°C for 1 week before being subjected to glass transition measurements. Samples prepared by this method containing 35 wt % or more PCL were found to be opaque due to the presence of a PCL crystalline phase, while samples containing 30 wt % or less PCL were transparent.

Measurements. Dynamic mechanical properties were determined using a Rheovibron Dynamic Mechanical Spectrometer, Model RHEO-200, made by Toyo Baldwin Co., Ltd. The measurements were conducted in a tensile mode at a constant frequency of 110 Hz over a wide temperature range. Measurements were taken at 2–4° intervals and the heating rate was adjusted to about 1.5°C/min. Measurements were begun at −150°C and continuing until the sample became too soft to be tested. The T_g is specified in this study as the temperature at which the loss modulus E'' is a maximum. In some cases, generally for pure SAN or blends containing high SAN concentrations, the magnitude of the mechanical damping peak exceeded the maximum range of the Rheovibron tan δ meter (1.73 at 60 db). These tan δ values are represented qualitatively by dotted lines on figures in the Results section. For all measurements, E'' reached a maximum before the tan δ value exceeded the instrument range, and T_g could be determined for each of the blends.

A Perkin-Elmer Differential Scanning Calorimeter, Model DSC-2, equipped with a Scanning Auto Zero Accessory (SAZ), was used in this study to investigate the influence of thermal history upon blend compatibility and component crystallinity. Glass transition measurements were made by first cooling samples to the starting temperature, 150 K, and then examining them in the heating mode at a rate of 20°C/min up to 400 K. This upper temperature allows samples to have similar thermal histories for subsequent measurements. The samples were then quenched to 150 K at 320°C/min and reheated at 20°C/min to 400 K for the second scan. The T_g was considered to occur at a position located at one half of the discontinuity. For crystallinity and T_m measurements, the annealed samples were first cooled to 250 K and examined during heating at 20°C/min to 360 K (first scan). The samples were cooled at the rate of 20°C/min to 250 K and immediately reheated at 20°C/min to 360 K (second scan). The T_m was taken as the temperature corresponding to the endothermic peak location. The degree of PCL crystallinity was calculated as the ratio of measured heat of fusion per gram of PCL in the sample to the heat of fusion per gram of 100% crystalline PCL, 32.4 cal/g.[14] Pure Indium was used in instrument calibration and in converting the PCL fusion endothemic peak area to energy units.

The cloud point of a film sample was measured by using the method developed by Paul and co-workers.[15] The temperature at which the first appearance of opalescence occurred upon heating at 5°C/min was designated as the cloud point. For some samples, the cloud point temperature is so high that it approaches the decomposition temperature of one of the components. In order to minimize decomposition, samples were transferred to the hot plate device which was maintained at a high temperature. The cloud point was specified as the temperature at which opalescence was first observed.
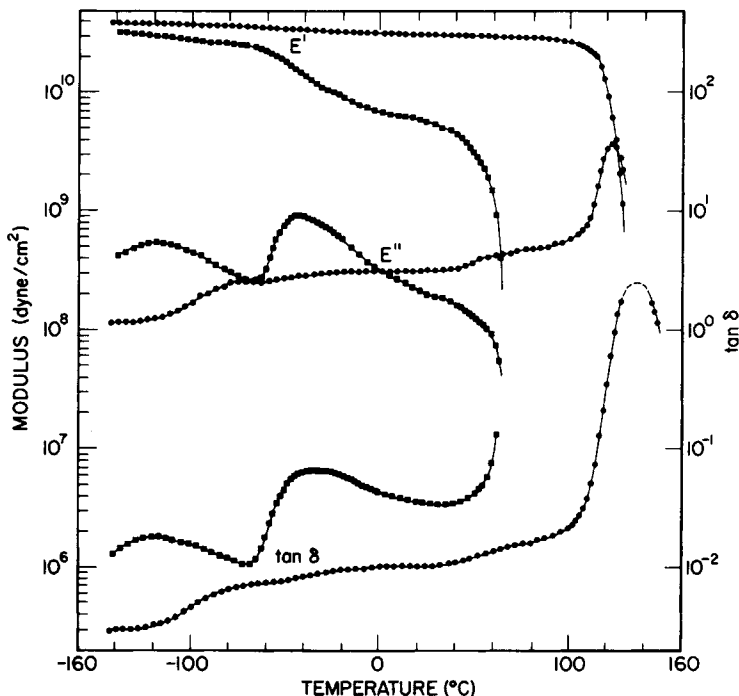
Fig. 1. Dynamic mechanical behavior of SAN (●) and PCL (■) at 110 Hz.

RESULTS AND DISCUSSION

Pure Components

The temperature dependence of the dynamic properties of pure PCL and SAN are presented in Figure 1. For pure PCL the maximum located at $-120°$C and $-116°$C on the E'' and tan δ curves, respectively, arises from a secondary or β-relaxation. This relaxation has been attributed to the motion of five-membered methylene groups.[16,17] The glass or α-transition of PCL occurs at $-44°$C and $-34°$C on the E'' and tan δ curves, respectively. In the temperature range of this transition, the storage modulus E' decreases appreciably, although the decrease is not as marked as that for completely amorphous material. At about $60°$C, tan δ increases rapidly, while E' and E'' decrease markedly corresponding to the melting of the PCL crystalline phase.

For pure SAN the transition occurring above $100°$C is the glass or α-transition. The T_g occurs at $122°$C on the E'' curve. The β-relaxation which occurs between $40°$C, and the T_g has been widely observed for polystyrene and its copolymers.[18,19] A broad γ-relaxation occurs in the low temperature region of about $-100°$C. The origin of this relaxation is thought to be due to structural irregularities or impurities in the material.[20,21]

Because of the semicrystalline nature of PCL, values of T_g and T_m determined from the DSC thermogram for pure PCL may be influenced considerably by the thermal history of the sample. For annealed PCL samples, the T_g and T_m appear at 211 K and 339 K, respectively, and the degree of crystallinity was found
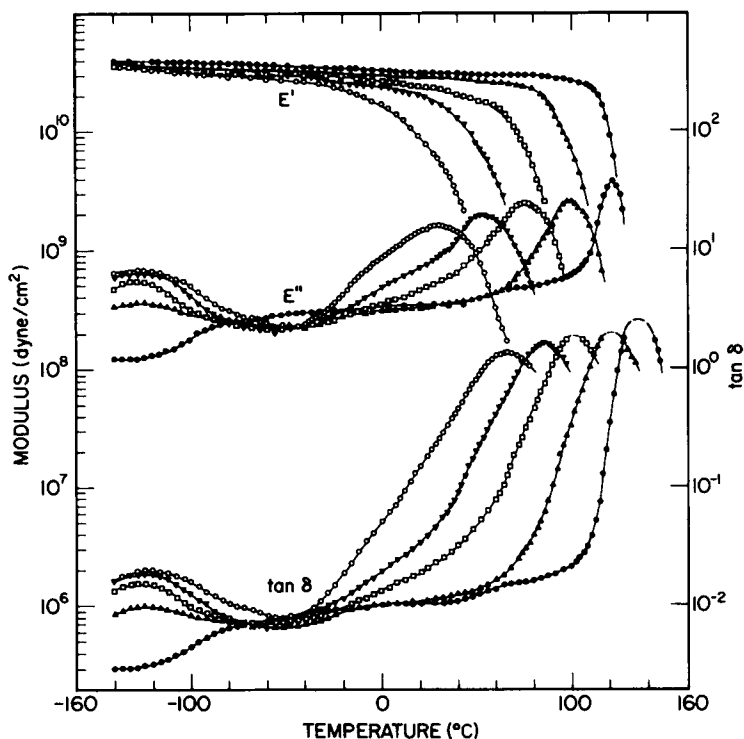
Fig. 2. Dynamic mechanical behavior of SAN/PCL blends at 110 Hz.   % SAN: (●) 100; (△) 90; (□) 80; (▽) 70; (○) 60.

to be 67.1%.   The thermogram for quenched PCL reveals that T_g and T_m occur at 208 K and 329 K, respectively.   The T_g for pure SAN was determined to be 384 K by DSC.

PCL/SAN Blends

Dynamic Mechanical Behavior.   The dynamic mechanical properties of annealed samples containing 70, 80, and 90 wt % SAN and an unannealed sample containing 60 wt % SAN are shown in Figure 2.   Annealed samples containing 30 wt % or less PCL were transparent while annealed samples containing 40 wt % PCL were opaque due to the presence of crystallinity.   Samples containing 40 wt % PCL became transparent after being heated above the T_m of PCL, and retained their clarity after being quenched to room temperature.   They did not exhibit noticeable opalescence even after being maintained at 25°C for 24 h. This indicates that the process of PCL crystallization in a 40 wt % PCL blend is slow at room temperature and is greatly hindered by the presence of the second compatible component.   This observation agrees with observations reported for PVC/PCL systems containing the same PCL concentration.[7]

Each blend shown in Figure 2 exhibits a single α-transition.   This peak corresponding to the glass transition on the tan δ and E'' curves shifts toward lower temperatures with increasing amounts of PCL.   The existence of a single, compositionally dependent glass transition is considered to be confirmation of
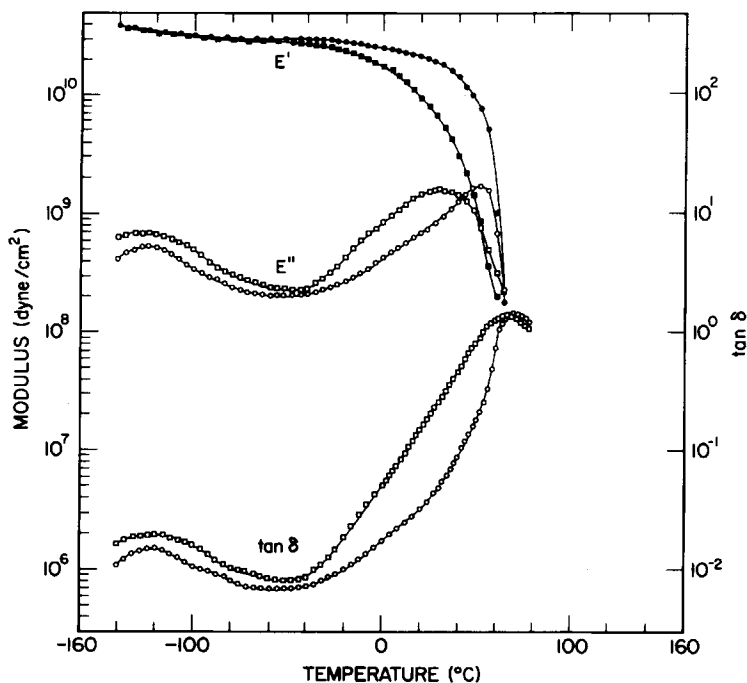
Fig. 3. Dynamic mechanical behavior of SAN-60%/PCL-40% blend at 110 Hz. (●,○) Annealed; (■,□) unannealed.

the compatibility of these SAN/PCL blends. A secondary relaxation appears at low temperatures for all of the blends, but no systematic change in the location of this relaxation is apparent as blend composition varies. Since for PCL the intensity of the γ-relaxation of SAN is much smaller than that of the β-relaxation of PCL and because these two relaxations are in close proximity, it is believed that the β-relaxation of PCL dominates the low temperature relaxation for the blends.

Figure 3 shows the temperature dependence of the dynamic mechanical properties for both annealed and unannealed samples containing 40 wt % PCL. Both samples display a single glass transition. A single α-transition is observed in the unannealed blend sample, while on α-transition affected by PCL crystallinity is observed in the annealed counterpart. Upon annealing, PCL crystallized from the compatible SAN/PCL amorphous phase to form an PCL crystalline phase. The remaining amorphous phase retained its compatibilty, although its composition was altered by the removal of some but not all of the PCL during partial crystallization. Therefore, the compatible amorphous phase in an annealed sample has a higher SAN concentration than that in an unannealed sample, and, consequently, the annealed sample has a higher T_g. Furthermore, the presence of PCL crystallites in an annealed sample shifts the T_g of the compatible amorphous phase to an even higher temperature, as it does for pure PCL. In addition to the above factors, the melting of PCL crystallites may also contribute to the observed peak. The overlapping of the α-transition and the melting transition of PCL crystallites contribute to the resultant un-
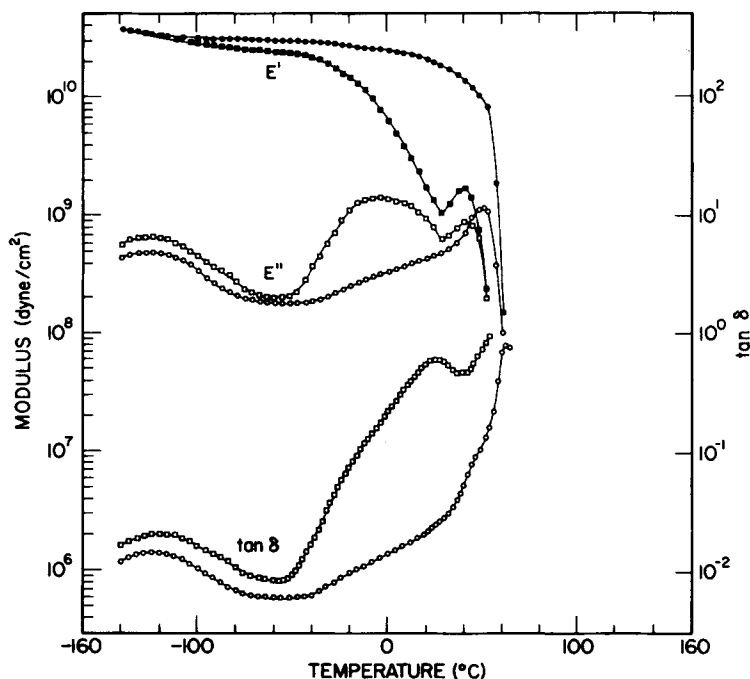
Fig. 4. Dynamic mechanical behavior of SAN-50%/PCL-50% blend at 110 Hz. (●, ○) Annealed; (■, □) quenched.

symmetrical peak. This becomes more apparent for the annealed sample containing 50 or 70 wt % PCL, as shown in later figures. At temperatures above the melting point of PCL both samples display almost identical dynamic mechanical properties which can be attributed to the destruction of PCL crystallinity and rapid molecular mixing above the T_m of PCL.

The temperature dependence of the dynamic mechanical properties of annealed and quenched 50 wt % PCL are shown in Figure 4. Since, at room temperature, the rate of crystallization of PCL is rapid in a blend containing 50 wt % PCL, the samples were first heated to a temperature above the T_m of PCL and then quenched in liquid nitrogen. Quenched samples were than mounted in the Rheovibron chamber which had been precooled to −60°C. Sample cloudiness, which is an indication of the presence of PCL crystals, was not observed at the end of this step. An evaluation of the results shown in Figure 4 reveals that both samples exhibit the usual low temperature secondary relaxation at −120°C with no glass transition for pure PCL. For the quenched sample, the T_g is −4°C, which is 34° lower than that of an unannealed sample containing 40 wt % PCL. The magnitude of E' also decreases in the region of the glass transition. However, as the temperature was increased above the T_g, crystallization of PCL from the blend becomes more likely. As a consequence of crystal formation, an increase in E' begins to become apparent at 28°C. Crystallization proceeded with increasing temperature until the crystalline phase melts. Melting of these samples begins to occur at a temperature lower than that for an annealed sample because of the imperfect nature of the spherulitic structure which grows from
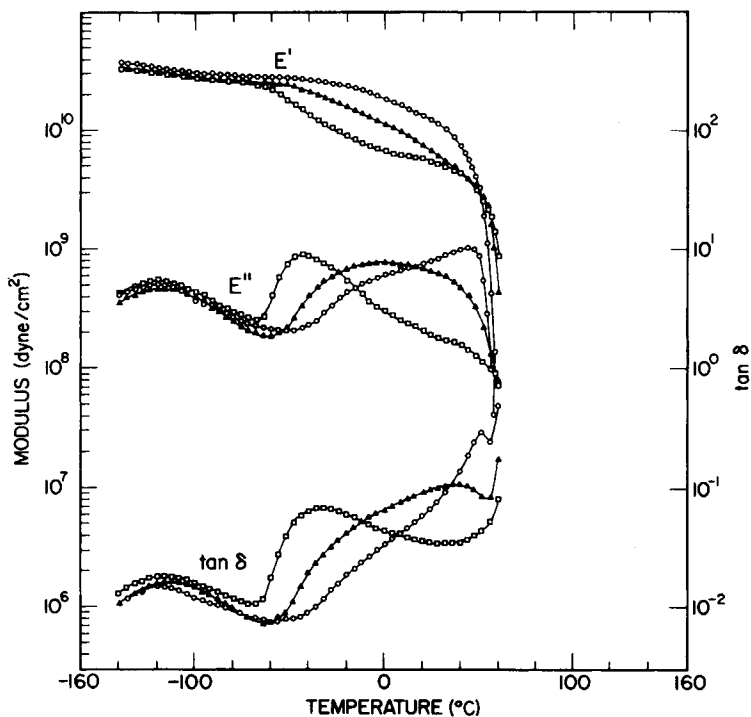
Fig. 5. Dynamic mechanical behavior of SAN/PCL blends at 110 Hz. (O) 30% SAN; (△) 15% SAN; (□) 100% PCL.

the viscous media. For the annealed sample containing 50 wt % PCL, a single glass transition for the blend was observed with indications of the presence of PCL crystallites.
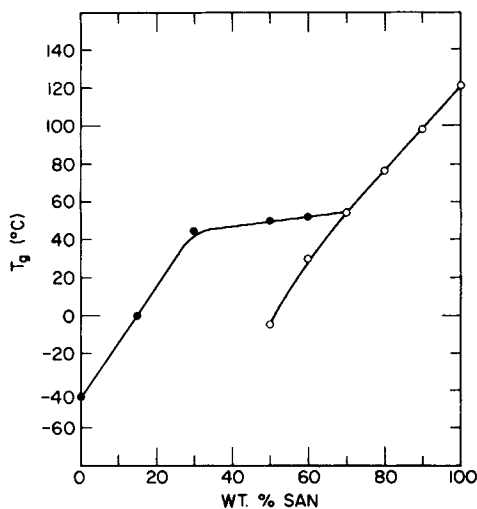

Fig. 6. Dependence of the T_g of SAN/PCL blend upon blend composition and thermal history: (O) sample without PCL crystallinity; (●) sample with PCL crystallinity. Rheovibron at 110 Hz.
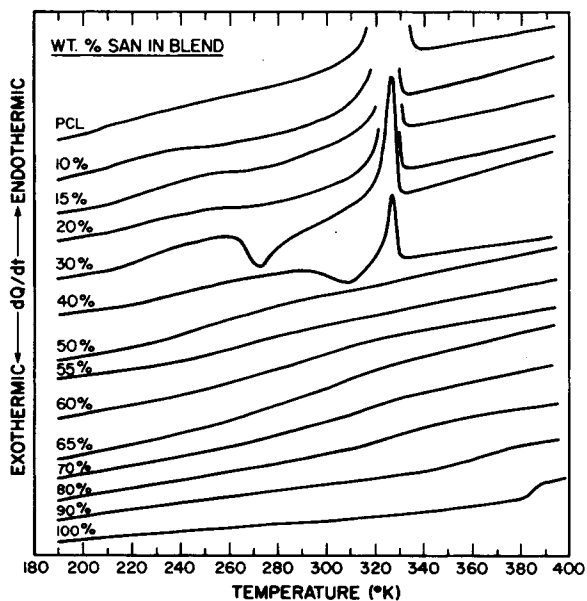
Fig. 7. DSC thermograms for SAN/PCL blends.

Due to the rapid crystallization of PCL in blends with high PCL concentrations, completely amorphous samples were difficult to produce by the quenching method used in the preparation of quenched samples containing 50 wt % PCL. In this study measurements on quenched samples containing 70 wt % or more PCL were not made, even though the evaluation of a quenched sample would be of interest, since the presence of transitions in the absence of PCL crystallites is of interest. Figure 5 shows the dynamic mechanical curves for annealed samples containing 70, 85, and 100 wt % PCL. The glass transition for PCL was not detected during the study of these blends.

The compositional and thermal history dependence of the T_g, as determined by Rheovibron measurements, are shown in Figure 6. It should be noted that all the dynamic mechanical measurements of blends substantiate the absence of glass transitions for either pure PCL or pure SAN, and they demonstrate the existence of single glass transitions for blends whether or not they contain PCL crystallites. For blends not having a PCL crystalline phase, the T_g–composition behavior is clear. The presence of PCL crystallinity in blends with high PCL concentrations causes the dynamic mechanical behavior observed to be more complex. However, the glass transition temperatures of these blends, taken as the peak position on the somewhat broadened or skewed E'' curve, also exhibit their dependence upon blend composition.

DSC Analysis–T_g Measurement. All of the DSC thermograms confirm the presence of a single glass transition temperature throughout the composition range for SAN/PCL blends. For blends containing 30 wt % or less PCL, the fusion endotherm characterizing the presence of PCL crystallites was not observed. The T_g was found to occur at about the same position for both annealed and quenched samples. Annealed samples exhibited a small endothermic peak at the T_g, which is commonly observed for glassy polymers undergoing an en-

TABLE I
Results of DSC Analysis for SAN 24/PCL Blends

Blend (wt % SAN 24)	T_g measurement[a]		PCL T_m and crystallinity (X_c) measurement			
			1st scan[b]		2nd scan[c]	
	T_g (K)	T_c (K)	T_m (K)	X_c (%)	T_m (K)	X_c (%)
100	384	—	—	—	—	—
90	352	—	—	—	—	—
80	326	—	—	—	—	—
70	302	—	—	—	—	—
65	293	—	335.5	17.0	—	—
60	279	—	336.0	37.0	—	—
55	267	—	336.2	52.9	—	—
50	260	—	336.0	59.4	—	—
40	242	294	336.2	61.8	327.3	5.6
30	228	264	336.5	62.3	327.3	38.6
20	225	258	337.3	64.2	328.3	45.7
15	218	253	338.0	64.7	328.7	46.0
10	216	—	338.8	65.9	329.0	48.4
0	208	—	339.0	67.1	329.0	53.9

[a] 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.

[b] Long-term annealed samples were scanned at 20 K/min from 250 K to 360 K.

[c] Sample after the first scan was cooled at 20 K/min from 360 K to 250 K, then scanned at 20 K/min from 250 K to 360 K.

thalpy relaxation.[22,23] For blends containing 35 wt % or more PCL a fusion endotherm corresponding to the melting of PCL crystals was observed for annealed samples. As a result of the presence of crystalline PCL, the magnitude of the glass transition is greatly reduced and consequently the detection of T_g became difficult for thermograms of annealed samples.[24] For the quenched samples, the DSC scans contain conclusive evidence of compatibility, i.e., a single compositionally dependent glass transition can be seen on the thermograms, as shown in Figure 7. The T_g values obtained with the DSC are listed in Table I.

For quenched samples, crystallization of PCL from blends may occur during either the quenching step or the reheating step. As a consequence, a fusion endotherm may appear in the thermogram for blends containing 60 wt % or more PCL. A crystallization exotherm, occurring above the T_g of the blend, can also be seen for some of the blends. This exotherm is small for samples with high PCL concentrations and is almost unnoticeable for pure PCL. This behavior may be attributed to the rapid crystallization of PCL in blends having high PCL concentrations, where crystallization can occur to a great extent during the quenching step. This exotherm becomes more distinct as the amount of SAN increases the T_g of blends, as molecular mobility is retarded as the $T_m - T_g$ difference is decreased, and, in general, as increased SAN content tends to restrict the formation of PCL crystals. For blends containing 30 or 40 wt % PCL, the crystallization of PCL may not occur or it may occur only slightly during the quenching step. However, crystallization of PCL does occur to a great extent during the reheating step. The onset temperatures of the crystallization exo-
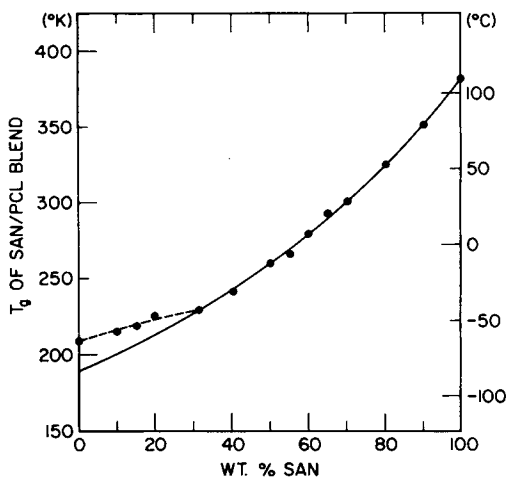
Fig. 8. Dependence of the T_g of SAN/PCL blend upon blend composition. The solid curve represents the Gordon–Taylor equation, using $K = 0.576$, T_g (SAN) = 384 K, and T_g (PCL, 100% amorphous) = 190 K.

therm, T_c, are listed in Table I, and are found to increase with increasing SAN concentration in the blend. This agrees with the general observation of an increased T_c during the reheating step after the quenching step, due to the presence of a second compatible component which has a T_g higher than the crystallizable component.[25,26]

The composition dependence of the glass transition temperatures for blends is plotted in Figure 8. The curve represents the Gordon–Taylor equation[27]

$$T_{g12} = T_{g1} + K(T_{g2} - T_{g12}) W_2/W_1$$

where W_1 and W_2 are the weight fractions in the amorphous phase, T_{g1} and T_{g2} are the glass transition temperatures of pure PCL and SAN respectively, and
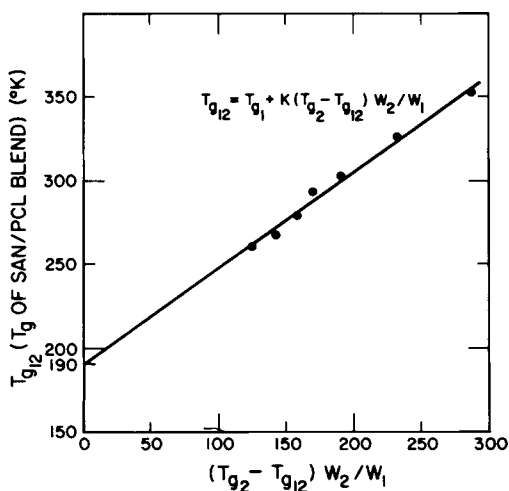

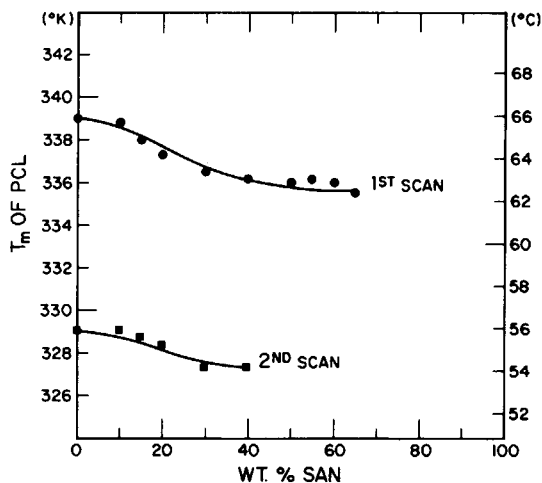Fig. 9. T_g of SAN/PCL blend plotted according to the Gordon–Taylor equation. Slope = K = 0.576.

Fig. 10. Melting point of PCL observed in SAN/PCL blends.

T_{g12} is the blend T_g. For a compatible system, the plot of T_{g12} vs. $(T_{g2} - T_{g12})$ W_2/W_1 will yield a straight line with a slope of the empirical constant K and an ordinant intercept of T_{g1}. Because of the presence of crystalline PCL in some samples, the actual value of W_2/W_1 which is directly responsible for the observed T_g may not readily be determined. A plot of T_{g12} vs. $(T_{g2} - T_{g12})$ W_2/W_1 for blends whose thermogram display no PCL fusion endotherms is shown in Figure 9. The data was fitted by a least-squares regression technique, and the slope of the straight line was found to be 0.576. The T_g of completely amorphous PCL, obtained as the ordinate intercept, is 190 K. As can be seen on Figure 8, the Gordon–Taylor equation fits the experimental data well up to 70 wt % PCL. The glass transition temperatures of blends with more than 80 wt % PCL lie above the curve because rapid PCL crystallization reduces the PCL concentration in the amorphous region. This agrees with the observation of a small crystallization exotherm but a large fusion endotherm for the thermograms of these samples, which implies that these samples were not completely amorphous at the beginning of reheating after the quenching step.

DSC Analysis—Melting Point and Crystallinity Measurements. The melting point of blends containing PCL depends on blend composition and thermal history, as shown in Figure 10. The results of a second thermal scan by the DSC indicates a much lower T_m than that obtained in the first thermal scan. This indicates that PCL spherulites formed during the DSC cooling (20°C/min) and heating (20°C/min) cycle are less perfect than spherulites in the annealed sample. It has been shown that the T_m of a crystallizable component in a compatible blend is depressed because of the reduction of chemical potential of that component in the amorphous phase due to the presence of diluent polymer.[28–30] This effect is believed to be one of the factors involved in the T_m depression of PCL observed here. However, other factors of morphological origin such as spherulite size and lamellar thickness are also important in the system reported here, as evidenced by the sizeable effect of thermal history on the T_m of PCL.
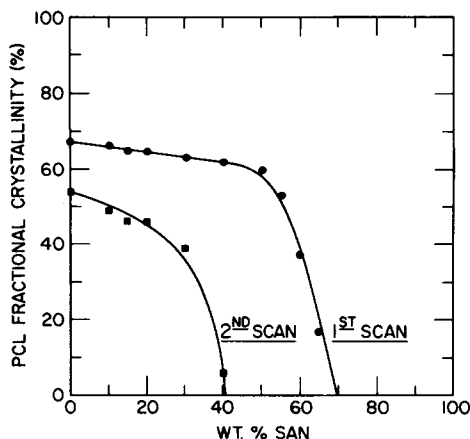
Fig. 11. Percent crystallinity of PCL in SAN/PCL blends. The value is normalized by the total weight fraction of PCL in each sample.

The dependence of crystallinity upon blend composition and thermal history is evident as shown in Figure 11. For annealed samples, PCL crystallinity decreases slightly with increasing SAN concentration until about 50 wt % SAN is added, whereupon it decreases sharply and PCL does not exist as a crystalline component for blends containing 70 wt % or more SAN. A material balance based on the classical two phase model for semicrystalline polymers was made for annealed samples containing 50–65 wt % SAN when PCL crystallinity was observed. The results indicate that the SAN concentration in the amorphous phase has a value of about 70 wt %. This result agrees with the observation of
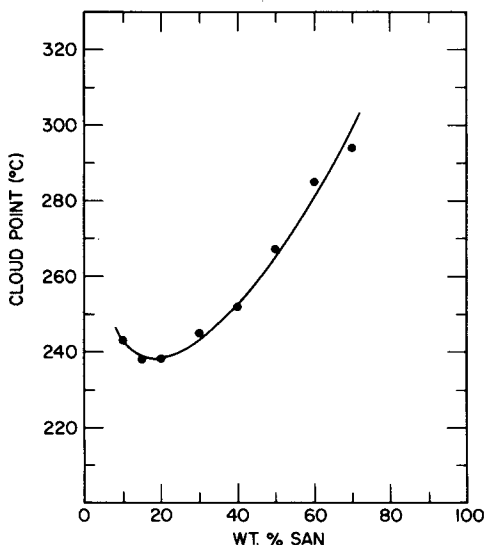

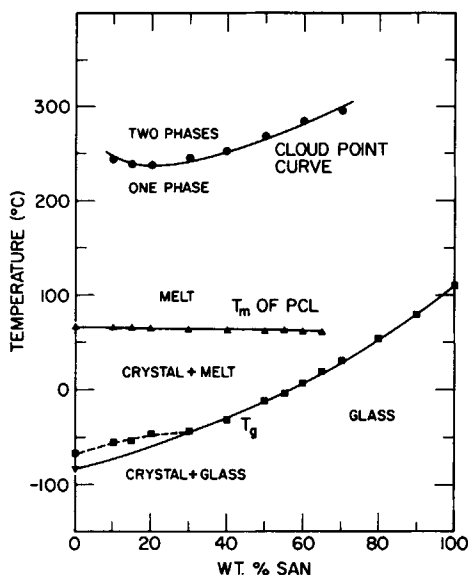Fig. 12. Cloud point curve for SAN/PCL blends.

Fig. 13. Phase diagram for SAN/PCL blends.

the absence of crystalline PCL in blends with 70 wt % or more SAN. Due to a different thermal history, material measured in the DSC in the second scan displays a much lower crystallinity than material measured in the first scan. Crystalline PCL can not be detected for the 50 wt % SAN sample in the second scan.

Cloud Point Measurements. All of the blends were transparent above the T_m of PCL because of their compatibility and lack of PCL crystallinity. Each blend was transparent upon further heating until it was heated above the cloud point where it became opaque because of liquid–liquid type phase separation, a lower critical solution temperature (LCST) behavior. The cloud point curve for the blends studied are shown in Figure 12. The skewness of the cloud point curve toward the high PCL concentration side arises from the difference in the molecular weight of the two components.[9,31] PCL has a molecular weight much lower than SAN used in this work. The existence of LCST behavior provides additional evidence of the compatibility of these blends.

Phase Diagram. The compatibility of SAN/PCL, with 24 wt % AN in SAN, has been shown by evidence obtained from dynamic mechanical behavior DSC, and cloud point measurements. Combining the data from these various measurements, the phase diagram[3,32] for this system can be constructed as shown in Figure 13. This diagram consists of the solid–liquid transition diagram (T_g and T_m vs. composition as determined by DSC) and the liquid–liquid phase diagram (cloud point vs. composition). This phase diagram should be regarded as preliminary, because samples with different thermal histories have different extents of PCL crystallinity, and, consequently, their composition will vary in the glassy and crystalline state as will their corresponding glass transition temperatures.

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