Compatibility Behavior in Thermoplastic Polymer Blends Containing Poly(t-butylstyrene-co-acrylonitrile)

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SYNOPSIS

The phase behavior of a series of binary component polymer blends of poly(ϵ-caprolactone) (PCL) and poly(t-butylstyrene-co-acrylonitrile) (TBSAN) containing varying contents of acrylonitrile (AN) was examined to determine the influence of copolymer composition and PCL content on blend miscibility or immiscibility. Thermal measurements were extensively used to determine phase behavior, i.e., a single compositionally dependent glass transition temperature implies blend miscibility. Otherwise, immiscibility is assumed to dominant blend behavior. It was determined that TBSAN and PCL form miscible blends over a broad range of AN content, i.e., spanning from below 43.2 mol % (19.8 wt %) to about 66.4 mol % (39.6 wt %), a range considerably different from that found in poly(styrene-co-acrylonitrile) copolymers. TBSAN-containing blends were found to be immiscible when the AN content is less than about 43 mol % or greater than about 67 mol %. Small-angle light-scattering and polarized light microscopy was used to probe the substantial morphological changes in the miscible blends. Little change was observed in the immiscible blends. These results clarify the phase separation observed in these blend systems. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

The precise control of the behavior of polymer blends has been the subject of intense investigation. Extensive experimentation has shown that blends of random copolymers can often form miscible blends with other polymers even though the corresponding homopolymers are completely immiscible. This phenomenon occurs in the absence of specific interactions. It has been proposed that miscibility is due to the repulsion between two different monomer units composing the copolymer.[1-5] In a mean-field approach, the overall Flory–Huggins interaction parameter between the monomer units can be expressed in terms of the respective segmental interaction parameters. When the interaction parameter between the segments that make up the copolymer is positive and larger than the values between the copolymer and homopolymer segments, miscibility occurs. As a result, miscibility should occur in a specific range of copolymer composition.

A salient example of this behavior occurs with homopolymer–copolymer blends containing poly(ϵ-caprolactone) (PCL) and poly(styrene-co-acrylonitrile) (SAN). These latter copolymers are effective in this regard, due undoubtedly to the high polarity of the acrylonitrile (AN) units in comparison to the low polarity of the styrene units. As a result, SAN copolymers are known to be miscible with a relatively large number of homopolymers, including poly(ϵ-caprolactone),[6-9] poly(methyl methacrylate),[10-12] poly(ethyl methacrylate),[13] aliphatic polyesters,[14] polycarbonate,[15] and poly(vinyl chloride).[16] Miscibility occurs, however, when the AN content falls within a specific range. For example, SAN copolymers containing 8–28 wt % AN is miscible with PCL.

The purpose of this work was to report on a comprehensive study involving a series of blends containing PCL with t-butylstyrene–acrylonitrile copolymers (TBSAN). These copolymers contain a broad range of AN content. The blends were prepared via a solution–precipitation technique and examined for their glass transition temperature be-

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havior. It is of interest to examine the influence of the increased aliphatic content (due to the TBSAN copolymers) on the phase behavior of these blends. These results are compared with the well-known SAN–PCL blends. A miscibility window is found in the t-butylstyrene (TBS)-containing blends due largely to the strong repulsion between the TBS and AN units. In addition, these materials are the springboard to forming other miscible blend compositions, including graft copolymers where the grafts are composed of copolymers in which repulsive interactions dominate interfacial properties with the dispersed and/or continuous phase.

EXPERIMENTAL

The TBSAN copolymers with varying AN contents were prepared via a free-radical bulk copolymerization of freshly distilled TBS monomer with a specific concentration of AN monomer. The synthesis procedure is similar to that used by Chiu and Smith in the preparation of SAN copolymers.[7] Table I summarizes the preparation conditions, copolymer composition, molecular weight, conversion, and glass transition temperature (T_g) of the copolymers synthesized for this study. It should be noted that the (T_g) of the TBS homopolymer prepared under essentially identical conditions is 148°C. Low copoly-

mer conversions were selected to avoid compositional heterogeneity.

The AN content within the copolymer was determined through nitrogen analysis (Kjeldahl method). The molecular weights were measured by gel permeation chromatography (tetrahydrofuran as the solvent) using monodisperse polystyrenes as standards. The reactivity ratios were determined[17,18] for this monomer combination, i.e., for TBS, r = 0.669, and for AN, r = 0.059.

Thermal analysis of the blends was performed in the Perkin-Elmer DSC-2 at a heating rate of 20°C/min. All DSC samples were weighed on a Perkin-Elmer AD-2 autobalance. Sample weight varied but typically ranged from 15 to 20 mg. Care was taken to ensure good contact between the sample pan and sample.

Each sample was first heated from room temperature to 190°C and then rapidly quenched to −50°C. The thermal behavior was recorded during a second heating with the midpoint of the heat capacity change being defined as T_g.

A photographic small-angle light-scattering (SALS) apparatus was used to determine the subtle changes that could possibly occur with blending AN amorphous copolymer, i.e., TBSAN with a semicrystalline polymer, e.g., PCL, both components of the blend system being miscible within a specific composition range. The SALS apparatus consisted of a Spectra Physics He—Ne laser (model 3000, wavelength 6328 Å), a polarizer, an analyzer, and

Table I

	Monomer								Polymer				
	Feed		Conversion		AN	AN	FAN[b]	T_g	Molecular Weight × 10⁻³				
									Uncorrected		Corrected[c]		
Sample	AN (Mol %)	f_{AN}[a]	Wt %	Mol %	(Mol %)	(Wt %)	(Mol %)	(°C)	M_n[d]	M_w[e]	M_n[d]	M_w[e]	M_w/M_n
TBSAN1	20.0	0.25	13.0	13.5	24.7	9.8	0.328	138	225	357	188	254	1.35
TBSAN2	60.1	1.55	8.8	7.2	43.2	19.8	0.761	137	238	551	169	363	2.15
TBSAN3	70.6	2.40	7.0	5.5	49.0	24.1	0.959	141	355	661	218	407	1.87
TBSAN4	90.0	9.00	4.1	2.6	57.4	30.8	1.344	135	407	926	227	518	2.28
TBSAN5	94.6	17.4	6.1	4.6	66.4	39.6	1.872	135	345	574	232	386	1.66

[a] Molar ratio of AN/TBS in feed.
[b] Molar ratio of AN/TBS in polymer.
[c] The copolymer molecular weights were corrected for different copolymer composition: $M_{corr} = M_{uncorr} \times [1 - mol \% AN + (53.06/104.14) \times mol \% AN]$.
[d] Number-average molecular weight.
[e] Weight-average molecular weight.

photographic film (Polaroid Type 57). The scattering envelop was recorded without optical density filters using 0.5 s exposures. All photographs were taken in H_v alignment. In this configuration, the incident light is polarized vertically while the scattered light is polarized horizontally. The theoretical interpretation of these patterns has been largely developed by Stein and co-workers.[19-26]

RESULTS AND DISCUSSION

The DSC data of samples of PCL, TBSANI, and their respective blends are shown in Figure 1. Pure PCL exhibits a distinct melting point at about 60°C and the pure TBSAN1 shows a T_g at 138°C. The corresponding blends spanning the complete composition range also show that the T_g of the copolymers remain essentially invariant with changes in
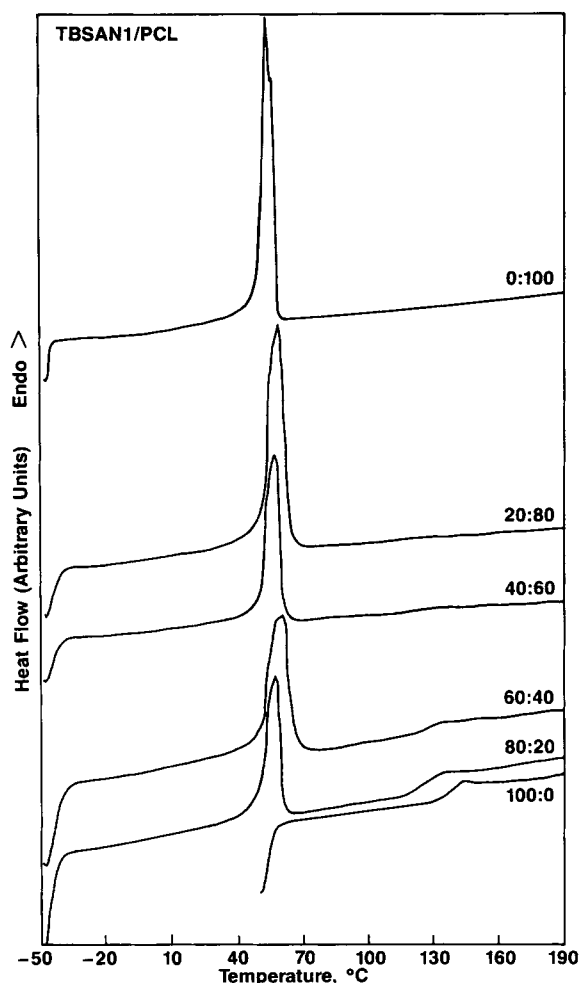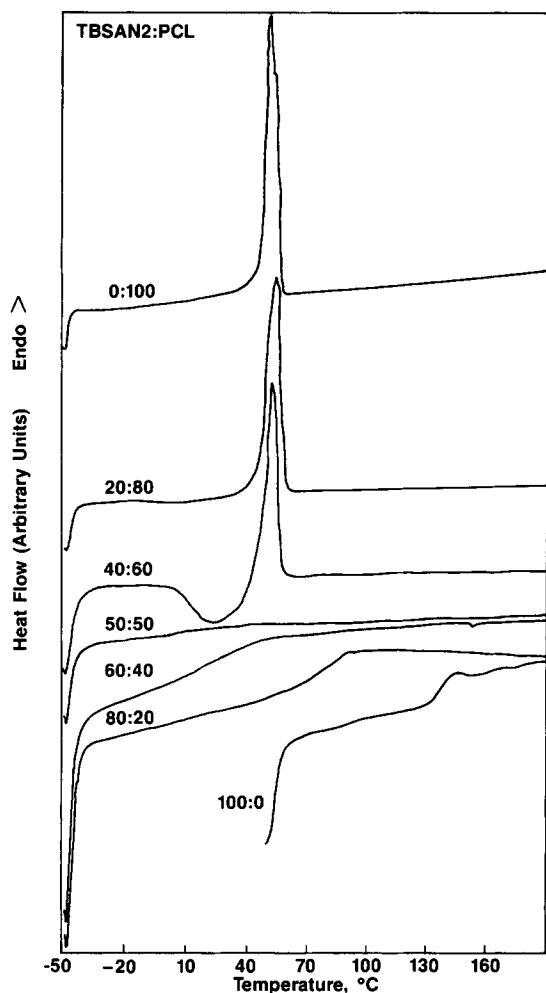

Figure 1 DSC thermograms for TBSAN1/PCL blends covering the entire composition range. AN content is 24.7 mol % (9.8 wt %).

the PCL concentration. In addition, the melting temperature of the PCL component is invariant with TBSAN concentration. These results confirm that this blend series is immiscible over the entire composition range. It is noteworthy that Chiu and Smith[7] found that immiscibility occurs in SAN–PCL blends at a specific AN content. This, as we will see, is a general trend. It is found, however, that with the changes in the aliphatic nature of the copolymer the miscibility window occurs at markedly higher AN contents. As of the present time, it is not known if this is related to the increase in the T_g of the TBSAN copolymer as compared to SAN at comparable AN content, i.e., $\Delta T_g = 22$°C.

Chiu and Smith[7] found that miscible SAN/PCL blends (AN content 16.8 wt %) exhibited a high-temperature relaxation (i.e., T_g) that was compositionally dependent, decreasing with increasing PCL concentration. Blends containing 30 wt % or less PCL did not have a PCL crystalline phase. However, for blends containing 50 wt % or more PCL, the single compositionally dependent T_g is slightly broadened due to the presence of a PCL crystalline phase. A similar phenomenon occurs with the TBSAN–PCL blends (Fig. 2). In this instance, however, the influence of the PCL crystallites are found at about 50 wt % PCL. It is concluded that the crystallization of PCL is markedly inhibited due to association of the TBSAN with PCL chains in the compatible amorphous phase. This behavior is probably being controlled to a large extent by the variation of T_g with composition, i.e., as the TBSAN concentration in the blend is increased, the blend T_g increases and the rate of crystallization is strongly inhibited. A similar conclusion was reached in a recent extensive melting behavior study.[9] Even though at higher PCL concentrations crystallization is inhibited, it is not completely eliminated. As anticipated, the PCL crystallites restrict the chain mobility in the amorphous phase further, shifting the T_g to higher temperatures. However, the superposition of the T_g and the PCL melting point contributes to the inability in accurately determining the T_g of the miscible amorphous phase.

It should be further noted that one should expect the TBSAN copolymer to be in a thermodynamically favorable environment in the amorphous phase of these semicrystalline blends. As a result of the copolymer's inability to diffuse away from the crystalline growth front (i.e., PCL crystallites), marked changes in morphology should result. This behavior can be summarized in terms of the parameter δ, which is defined as the ratio of the diffusion coefficient (D) of the noncrystallizing component in the crystallizing matrix and the linear growth rate (G)

Figure 2   DSC thermograms for TBSAN2/PCL blends spanning the entire composition range. AN content is 43.2 mol % (19.8 wt %).

of the crystals.[27] δ has the dimensions of length, therefore, representing the distance the rejected component can move during the time that crystallization is occurring. For example, if δ is comparable with interlamellar distances, then the rejected component may occupy space between the crystalline lamellae. At larger D (or smaller G), the rejected component may reside in larger domains within the spherulite structure itself. Marked changes in spherulite structure will result. Figure 3 shows typical results of a miscible blend system spanning a broad range of PCL concentration. It is readily apparent that a spherulitic morphology is the distinguishing characteristic of pure PCL. With increasing TBSAN content, the spherulites rapidly disintegrated into incomplete spherulites and/or a more or less random arrangement of lamellae. At TBSAN levels approaching and slightly exceeding 50 wt %, crystalline lamellae are not observable. These results

essentially parallel the previously described thermal measurements except that the films used in the optical studies were slowly cooled to room temperature. Qualitatively, these results appear to indicate that δ is at least comparable with interlamellar distances.

SALS[19-26] was used to more quantitatively probe the morphology of these miscible blends (Fig. 4). These measurements were taken on the identical samples used in the previous optical study. Figure 4 shows a series of H_v patterns obtained from blends of increasing TBSAN2 content. A spherulitic-type four-leaf clover pattern with its corresponding intensity maximum at the azimuthal angle of 45° was obtained for the pure PCL component. A very small amount of TBSAN was found to change the scattering pattern to one best described as originating from incomplete spherulites having a rodlike texture. Very similar patterns are noted in the early stages in the crystallization of polymers. Because of the reciprocity relationship between the size of the scattering pattern, it is quite clear that the "spherulitic precursors" are substantially reduced in size with increasing TBSAN copolymer content. At concentrations above about 50 wt % TBSAN, the SALS pattern can be best described in terms of theories[26] that reflect random orientation correlations as arising from crystals randomly dispersed in an amorphous matrix. It is noteworthy that spherulitic morphologies are observed over the entire composition range in the immiscible blend systems.

Figures 5 and 6 show the DSC thermograms of a series of TBSAN-PCL blends in which the level of AN in the copolymer has been systematically increased. Again, we observe a single compositionally dependent T_g up to a 50 : 50 wt ratio, and as seen previously, the appearance of the PCL melting transition inhibits further examination of the T_g transition. As in the previous blends, the crystalline phase begins to appear at PCL concentrations greater than 50 wt %.

In contrast to the previously described TBSAN-containing blends that are miscible with PCL in essentially all proportions, TBSAN5 (66.4 mol % AN content)-PCL was found to be miscible, containing up to approximately 50 wt % of each component. Immiscibility is the norm at higher TBSAN5 levels. The thermal data for this blend system are summarized in Figure 7. These results essentially parallel SAN-PCL blends[7] in which the copolymer contains 42.8 mol % (27.6 wt %) AN contents. In addition, these results show that the miscible-immiscibility transition for the TBSAN-containing blends has been shifted to higher AN contents (as compared to SAN-containing blends) and higher temperatures due to the higher T_g of the TBSAN component. Also,
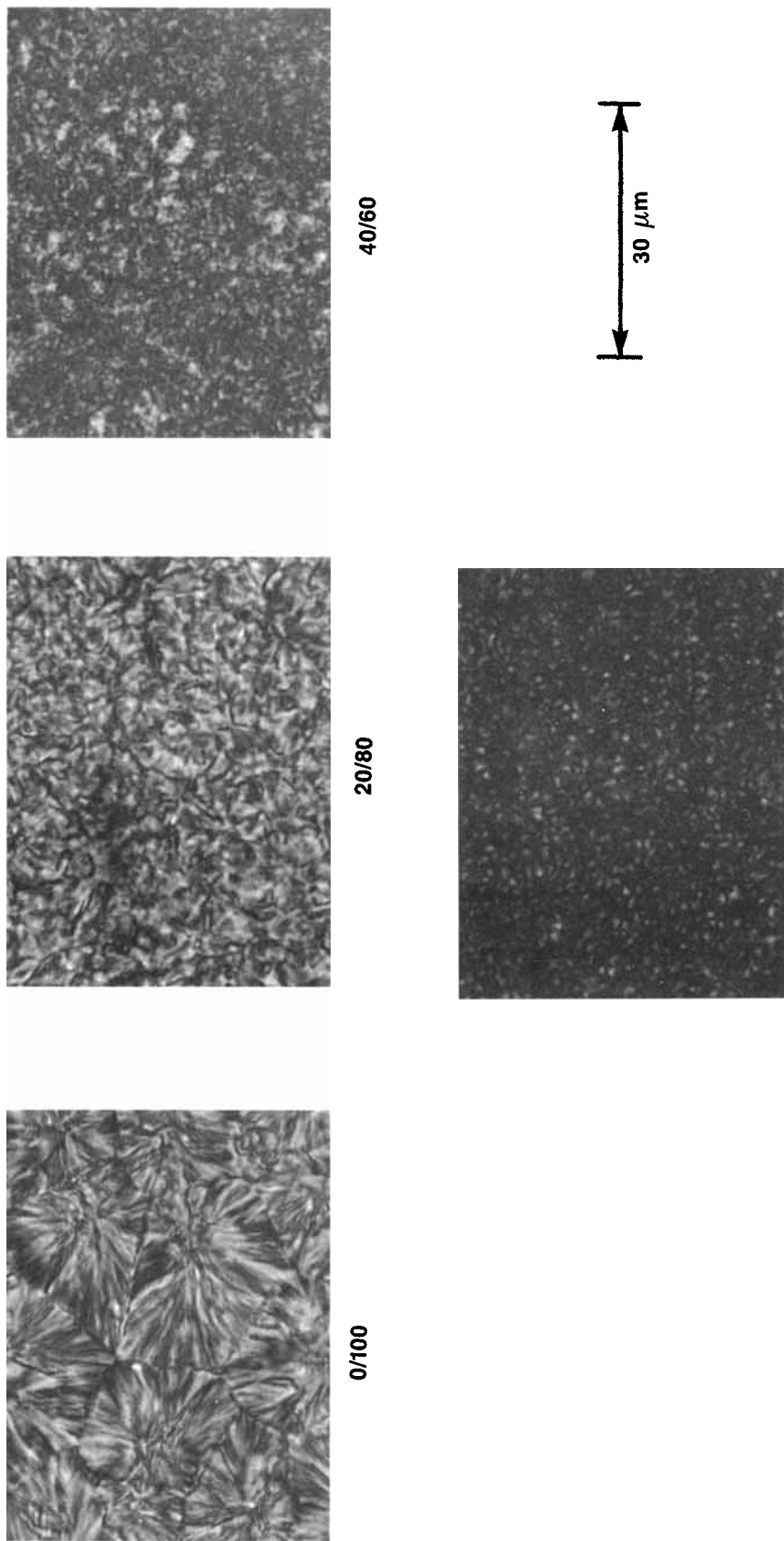
Figure 3 Typical polarized light photomicrographs of miscible random copolymer (TBSAN2)-homopolymer (PCL) blends. The 60/40 blend (not shown) lacked any discernible morphological entities. The first number relates to the TBSAN content.
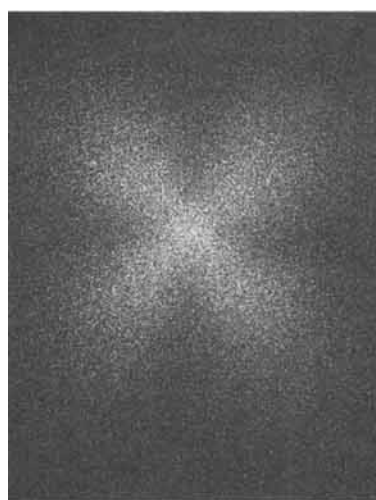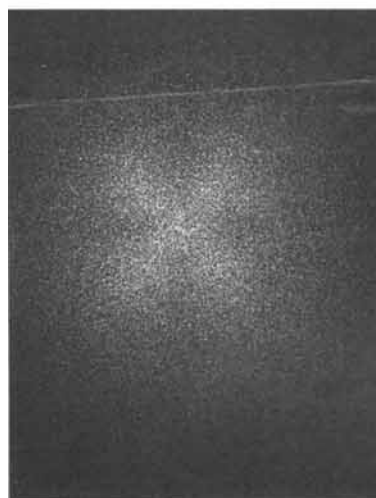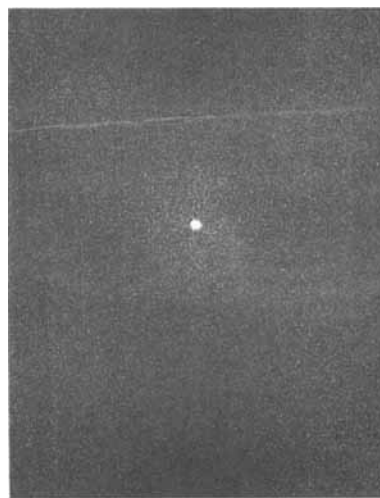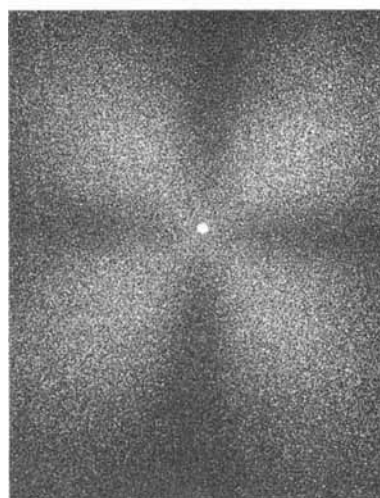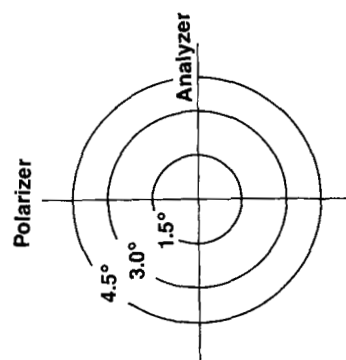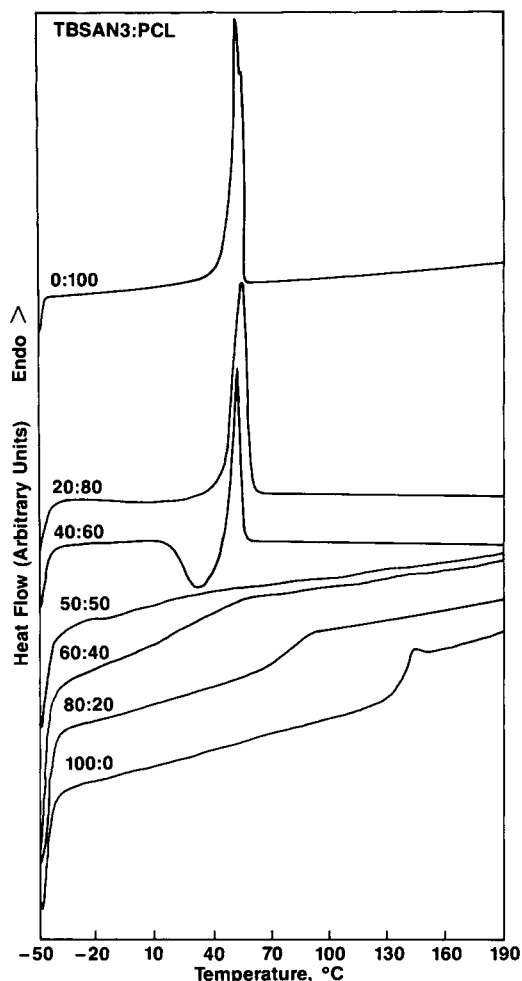
Figure 4 Typical H_v small-angle light-scattering patterns obtained from the miscible random copolymer (TBSAN2)–homopolymer (PCL) blends of various composition.

Figure 5   DSC curves for TBSAN3/PCL blends. AN content is 49.0 mol % (24.1 wt %).

in all cases when two distinct T_g's were observed, the films made from blends were opaque at all temperatures.

Finally, the results of this work indicate that TBSAN is miscible with PCL whenever the AN content within the copolymer is in a specific composition range. Blends containing mixtures of the homopolymer parents all show the two distinct compositionally invariant T_g's, strongly indicating that immiscibility is the norm in these particular blend systems. These results can be understood in terms of a binary interaction model[1-3] and if it is assumed that these blends closely approximate the SAN–PCL blends. The overall interaction parameter (B) for the TBSAN–PCL blends is expressed as a combination of the individual segmental interaction parameters:

$$B = B_{TBS,CL} \; \phi_{TBS} + B_{AN,CL} \; \phi_{AN}$$

$$- \; B_{TBS,AN} \; \phi_{TBS} \; \phi_{AN} \quad (1)$$

where ϕ's describe the specific monomer composition (i.e., volume fraction) of the (TBS)(AN) copolymer and P(CL) homopolymer, and $\phi_{TBS} + \phi_{CL} = 1$. For this particular blend system, $B_{TBS,CL}$ and $B_{AN,CL}$ would be positive and if

$$B_{TBS,AN} > B_{TBS,CL} + B_{AN,CL} \quad (2)$$

then B itself would be negative, resulting in blend miscibility. The thermal measurements confirm that within a specific AN content miscibility occurs and therefore the phase behavior of TBSAN–PCL blends can be explained by strong repulsions between the segmental units composing the copolymer. The highly unfavorable interactions between the AN and TBS monomer apparently cause an overall exothermic mixing situation without the need for any specific or associating-type interactions.

CONCLUSIONS

It has been shown that miscible blends composing a semicrystalline polymer, i.e., PCL, and a random
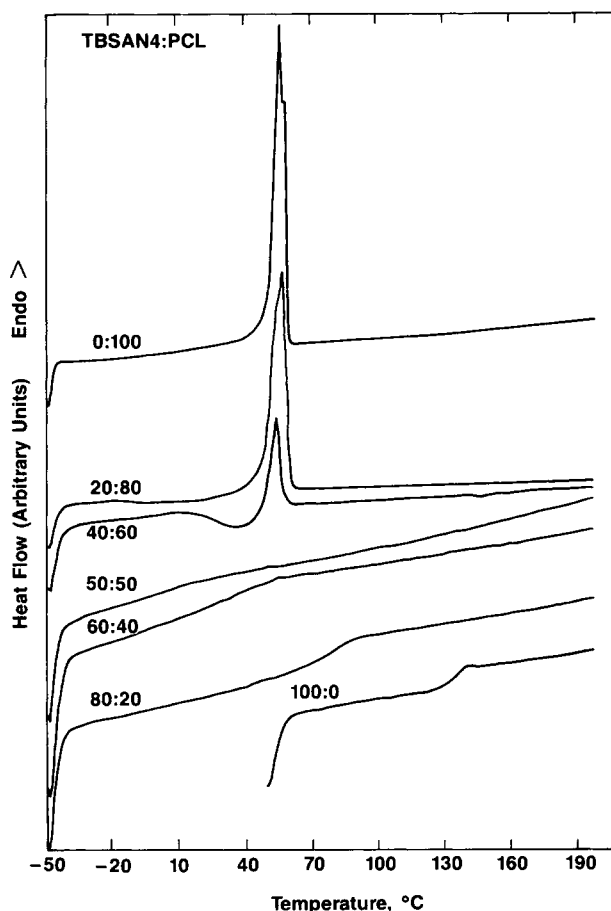
Figure 6   DSC thermograms for TBSAN4/PCL blends. AN content is 57.4 mol % (30.8 wt %).
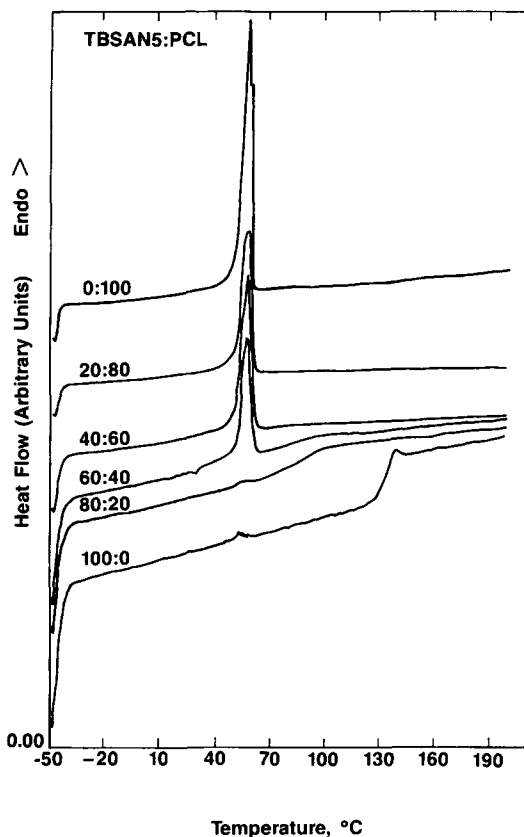
Figure 7 DSC thermograms for TBSAN4/PCL blends. AN content is 66.4 mol % (39.6 wt %).

copolymer of TBS and AN may be prepared. Extensive thermal measurements as a function of copolymer composition and composition of the blend show that a miscibility window is present whenever the AN content is between about 43 and 66 mol %. This phenomenon can be understood in terms of a binary interaction model. A salient feature of this model is the prediction that homopolymers and copolymers possessing a specific composition range can be miscible if intrasegmental repulsions within the copolymer are stronger than are the segmental interactions of these units with the homopolymer. Indeed, it appears that the interactions between TBS and AN segments are sufficiently repulsive for miscibility to occur within a specific AN content. Similar behavior is observed in styrene–AN copolymers. Furthermore, at high PCL levels, some crystallinity still remains. Although the crystallites inhibit complete characterization of the phase behavior, small-angle light-scattering and polarized light microscopy can be used to probe the morphology of these blends.

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