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Miscibility and Phase Behavior in Polymer Blends of Poly(styrene-*co*-acrylonitrile) with Poly(α-methylstyrene-*co*-acrylonitrile)

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ABSTRACT: The miscibility of poly(α-methylstyrene-*co*-acrylonitrile) having an acrylonitrile (AN) content of 32 wt % (MSAN-32) with poly(styrene-*co*-acrylonitrile)s (SANs) was studied by differential scanning calorimeter. To decide the phase diagrams, very long isothermal annealing (sometimes above 200 h) was required. It was found that MSAN-32 is miscible with SAN having AN contents between 28 and 40 wt % at 130 °C. The miscibility range is in good agreement with that predicted using a non-hydrogen-bonding solubility parameter approach. Three segmental interaction parameters were calculated from the boundaries separating domains of miscibility and immiscibility. Lower critical solution temperature (LCST) type phase diagrams were found for miscible blends above 130 °C. This is the first observation of the presence of LCST behavior for MSAN/SAN blends. It was emphasized that the excessively long times are required to reach equilibrium for these blends.

Introduction

Improved heat resistance, toughness, and chemical resistance have been demanded on ABS polymers to widen its applications. These improvements can often be performed by blending other polymers. Poly(styrene-*co*-acrylonitrile) (SAN) is a matrix phase of ABS polymers. To improve heat resistance of ABS polymers, several approaches have been taken. One approach is to prepare copolymers of α-methylstyrene and acrylonitrile, and the other is to prepare blends of SAN with other polymer(s).[1−4] In any case, miscibility and phase behavior of SAN blends are important factors.

There are systems in which blends consisting of a homopolymer and a copolymer or two different copolymers are miscible for a certain range of copolymer composition even though combinations of the corresponding homopolymers are immiscible. The origin of miscibility in such systems has been proposed to be the so-called “repulsion effect” between the covalently bonded comonomer units of the copolymers.[5−7]

In a previous paper,[1] we investigated the miscibility of SAN with poly[styrene-*co*-(*N*-phenylmaleimide)] (SMI) and poly(styrene-*co*-maleic anhydride) (SMA) and found that SANs are miscible with SMIs and SMAs within a specific range of copolymer composition. From the binary interaction model for copolymer mixture, segmental interaction parameters between the different monomer units were estimated to be positive for all pairs. SMI and SMA have been commercialized as a component of heat resistance ABS. Another copolymer to get improved heat resistance ABS is poly(α-methylstyrene-*co*-acrylonitrile) (MSAN). MSAN is more popular than SMI and SMA as a component of heat resistance ABS.

Recently, Cowie et al.[2] examined the miscibility of SAN and MSAN by differential scanning calorimeter (DSC). Ikawa et al.[3] studied the miscibility by nuclear magnetic resonance. Paul et al.[4] also studied the DSC miscibility maps for various blends of SAN and MSAN and calculated segmental interaction energy densities or parameters. But, they did not report the phase diagram of these blends. Especially, Paul et al.[4] concluded that these blends did not exhibit lower or upper critical solution temperature phase behavior.

Slow phase separation due to low mobility is exactly the system that components may easily be trapped into a nonequilibrium but apparent homogeneous state from solvent casting other than freeze-drying. Indeed, the recent literature describes several examples of quite slow phase separation of blends.[8−10] Diffusion is very slow at temperature just above T_g, so that the temperature range where phase separation proceeds at a reasonable rate is even narrower.

In this paper, we investigated the miscibility and phase behavior of MSAN, whose AN content is 32 wt %, with SANs having AN contents between 23 and 45 wt %. The miscibility and phase behavior were studied from T_g behavior of the blends in DSC. The interaction parameters for MSAN-32/SAN systems were calculated utilizing the Flory−Huggins theory.

Experimental Section

Materials. The characteristics of copolymers used in this study are listed in Table 1. The copolymers were synthesized by radical polymerization. The AN contents of the copolymers were determined by elemental analysis for nitrogen. The number after SAN denotes the weight percentage of AN in the copolymer.

Preparation of Blends. Various blends were prepared by solution casting from butanone. A desired weight ratio of MSAN/SAN blends was dissolved in butanone at 5 wt % of total polymer. The solutions were poured into flat-bottomed Petri dishes. Evaporation of solvent initially was carried out slowly at room temperature. After the solvent had been evaporated at room temperature, the cast film was dried in a vacuum oven for several days, and careful stepwise heating from 70 to 130 °C prevented bubbling. Finally, subsequent annealing at 130 °C for 100 h was designed to ensure perfect removal of solvent. The well-annealed specimen was cooled rapidly at room temperature. Blends of MSAN-32 with SANs were transparent at room temperature. It is difficult to learn much about the phase behavior of their blends by visual

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Table 1. Sample Codes and Molecular Characteristics of Samples

sample	AN wt % (vol %)	$M_w/10^4$	M_w/M_n
MSAN-32	31.2 (30.4)	6.3	2.1
SAN-23	23.2 (22.2)	12.2	2.1
SAN-26	25.3 (24.3)	9.5	2.8
SAN-30	28.6 (27.5)	7.8	2.3
SAN-33	31.9 (30.7)	6.2	2.2
SAN-37	36.4 (35.1)	8.5	1.9
SAN-40	39.1 (37.9)	6.3	2.0
SAN-45	43.7 (42.4)	7.0	1.9

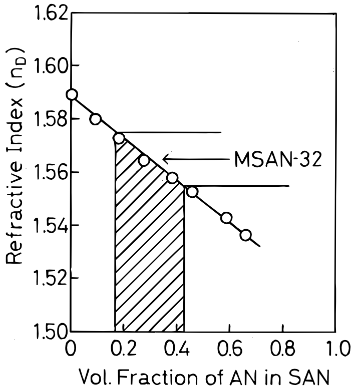

Figure 1. Refractive indices of SAN plotted against volume fraction of AN in SAN. Refractive index of MSAN-32 is indicated by an arrow.

observation, because the two components are estimated to have very similar refractive indices, as seen in Figure 1.

Measurements of Glass Transition Temperature. The glass transition temperature (T_g) of various samples was measured with a Perkin-Elmer DSC-7 differential scanning calorimeter using a heating rate of 10 K/min. A sample weight of 7−15 mg was used on the measurements. T_g was taken as the temperature corresponding to half of the heat capacity change; that is, T_g is defined as the midpoint of the glass transition. The error of T_g determination is ± 0.5 °C. Glass transitions were normally taken from a second scan to ensure reproducible thermograms. The maximum temperature in the first scan was kept below the annealing temperature of the sample. Annealing of various blends was carried out at a desired temperature for about 100 h. After annealing, the sample was cooled rapidly at room temperature, and another DSC scan was made to assess the change in LCST behavior caused by the annealing.

A typical measurement consisted of heating at 10 K/min to annealing temperature T_a, keeping at that temperature for 5 min, and cooling at 80 K/min to 328 K, and this cycle was repeated several times in succession. A fresh sample gave a thermogram with minor irregularities in the first run, but if it was held at a temperature 10−20 K higher than the T_g for 5 min or longer, all subsequent runs were completely reproducible within the instrumental noise level.

Measurements of Phase Separation Point. The miscible blends at 130 °C were examined for the existence of lower critical solution temperature (LCST) behavior. Because of the similarity of the refractive indices of MSAN and SAN, we cannot use the visual indication method of LCST behavior. An alternative way to test LCST behavior is to heat the blends to a temperature above the suspected cloud point, quench them, and examine their T_g behavior. The appearance of a single T_g of a blend after annealing is no LCST. When the temperature is above the cloud point, two T_g's are found in the DSC thermogram.

Results and Discussion

Glass Transition Temperature. The appearance of a single, composition dependence glass transition temperature of a blend is a generally accepted criterion for blend miscibility. Figure 2 shows the DSC curves for various MSAN/SAN (=50/50 in weight) blends annealed at 130 °C for 100 h. The MSAN-32/SAN-30, SAN-33, SAN-37, and SAN-40 show only one glass transition. The MSAN-32/SAN-23, SAN-26, and SAN-45 show two glass transitions. The results show that MSAN-32 is miscible with SAN-30, -33, -37, and -40 but not with the other SAN samples of higher or lower AN content at 130 °C. A sample that has undergone phase separation will contain in it some regions richer in MSAN and other regions poorer in MSAN than the original mixing composition. As a consequence, its DSC curve will show T_g's higher or lower than T_g expected of the component polymers. We designated T_g(MSAN) for MSAN-32-rich phases and T_g(SAN) for SAN-rich phases. The T_g−composition curves for the various blends are shown in Figure 3a−g. The two T_g values for the immiscible blends (MSAN-32/SAN-23 and MSAN-32/SAN-45) are close to those of MSAN-32 (T_g = 123 °C) and the respective SAN sample. T_g's stay relatively constant as shown in Figure 3a,g. On the other hand, the immiscible blend (MSAN-32/SAN-26) T_g(SAN) is raised and T_g(MSAN) lowered with increasing in MSAN content. This behavior indicates that MSAN-32/SAN-26 blends are just at the threshold of miscibility and immiscibility.

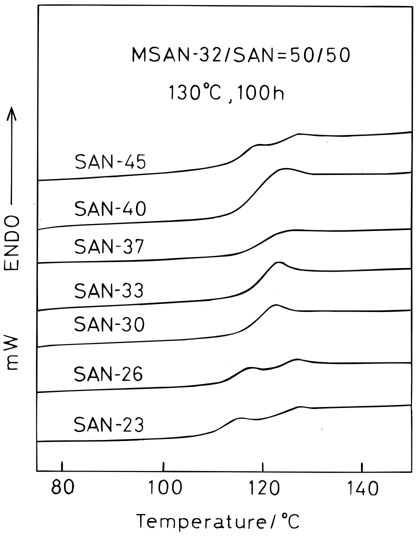

Figure 2. DSC thermograms of blends of MSAN-32 and SAN with various AN contents.

Blends of MSAN with SAN containing 28.6−39.1 wt % AN showed one composition-dependent T_g, indicating completely miscibility between MSAN and these SAN samples. The glass transition region is noticeably broader when the two components are present in comparable amounts. This phenomenon, which occurs with many other miscible blends, was noticed also by other workers and is probably due to the existence of concentration fluctuation in the miscible blends. It is concluded that MSAN-32 is miscible with SAN having AN contents between 28 and 40 wt % at 130 °C.

Phase Behavior. Miscible polymer blends tend to phase separation at elevated temperatures. This lower critical solution temperature (LCST) behavior is typical for miscible polymer blends. The phase diagrams of the MSAN-32/SAN blends were constructed from the phase separation temperatures obtained from the DSC method described in the Experimental Section. Figure 4a−c shows the DSC traces for the MSAN-32/SAN-30 = 50/50 samples annealed at 145, 150, and 160 °C for various

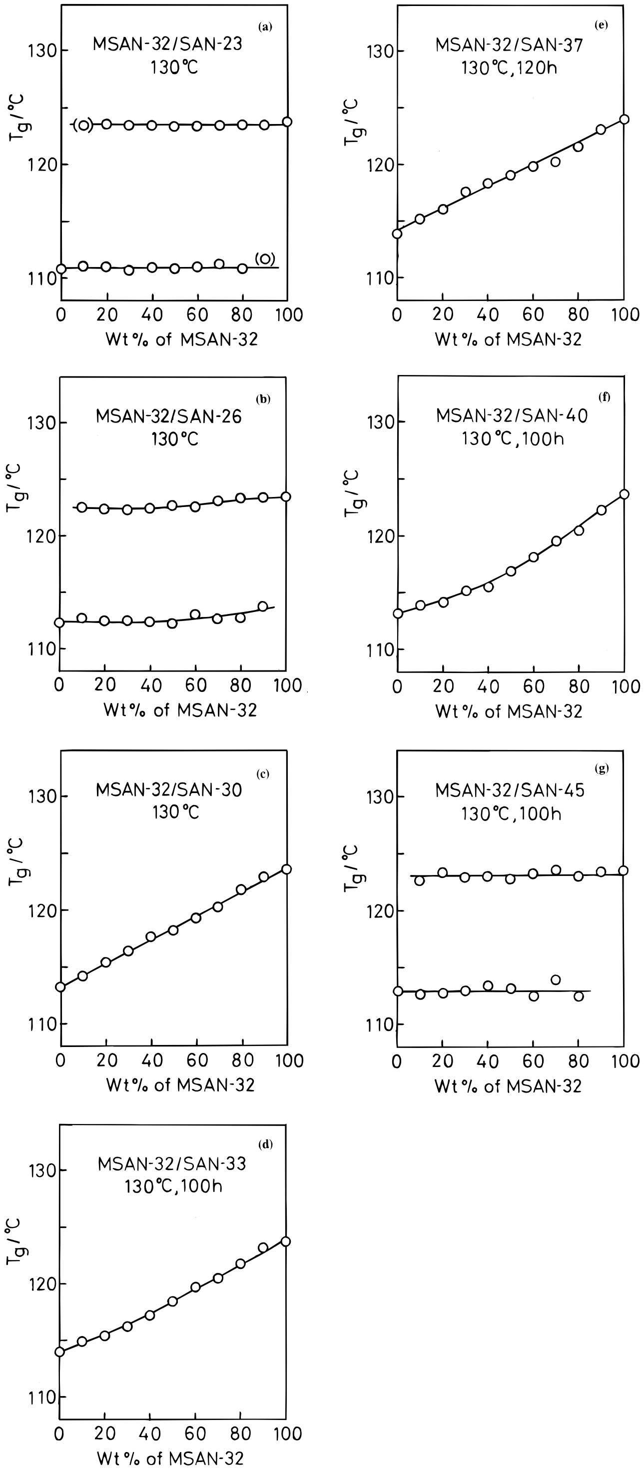

Figure 3. Composition-dependent glass transition temperature T_g for the MSAN-32/SAN blends.

hours. We can observe that the phase separation took place at longer annealing time and the phase separation time became shorter at higher temperature. Figure 5a−d shows the T_g versus composition curves for the MSAN-32/SAN-30 blends annealed at various temperatures for 100 h. The T_g varies almost linearly with MSAN-32 content for samples annealed below 140 °C, and two T_g's are found for samples annealed at 145 and 150 °C. The lower T_g value is about 4 °C higher than that of SAN (T_g = 112 °C), indicating the presence of MSAN-32 in the SAN-rich phase, but the upper T_g value is close to that of MSAN-32. These results show that

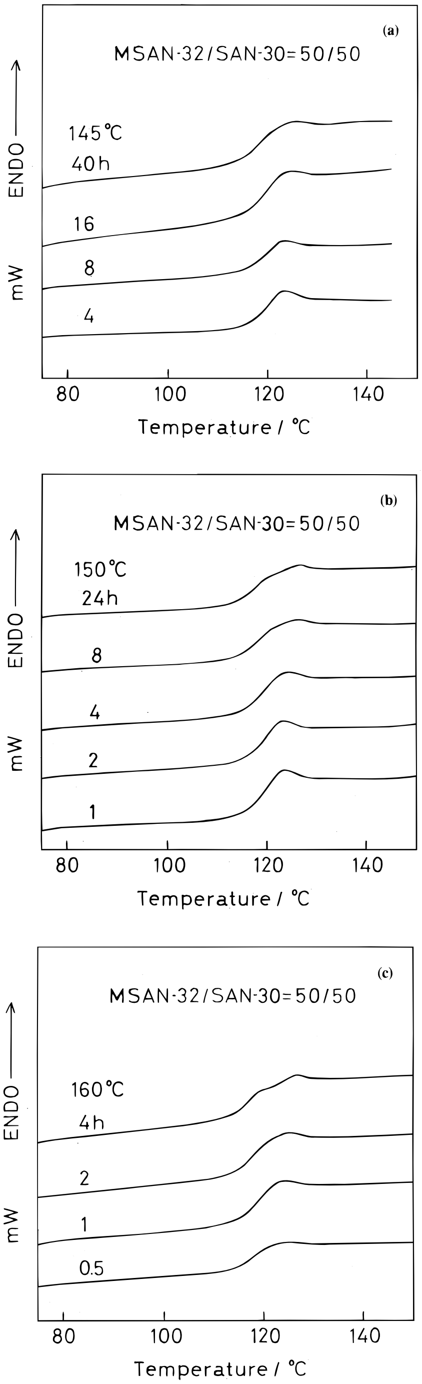

Figure 4. DSC thermograms of the MSAN-32/SAN-30 = 50/50 blends annealed at 145, 150, and 160 °C for various hours.

MSAN-32/SAN-30 blends have a phase separation temperature between 140 and 145 °C. Miscible blends of MSAN-32 with SAN-37 and SAN-40 also showed LCST behavior. The other miscible blend (MSAN-32/SAN-33) remained single phase up to 250 °C. Phase separation temperatures were not observed for the MSAN-32/SAN-33 blends. In such a case, the phase separation temperature may exist above their decomposition temperature.

The phase diagrams were constructed from the phase separation temperatures obtained from the DSC method and are shown in Figure 6a−d. Open circles denote “one phase” and closed circles “two phases”. This is the first observation of the presence of LCST behavior for MSAN/SAN blends. Paul et al. reported that MSAN/SAN

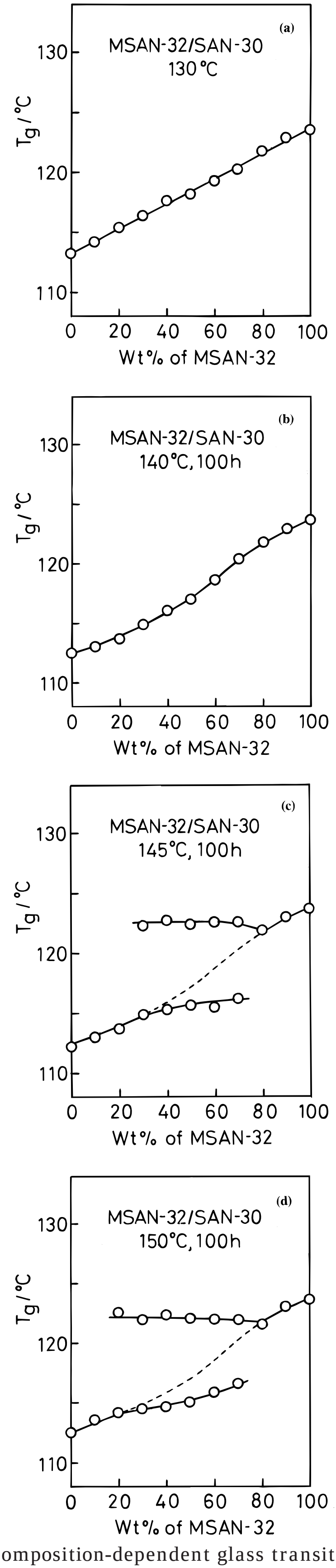

Figure 5. Composition-dependent glass transition temperature T_g for the MSAN-32/SAN-30 blends annealed at 130, 140, 145, and 150 °C for 100 h.

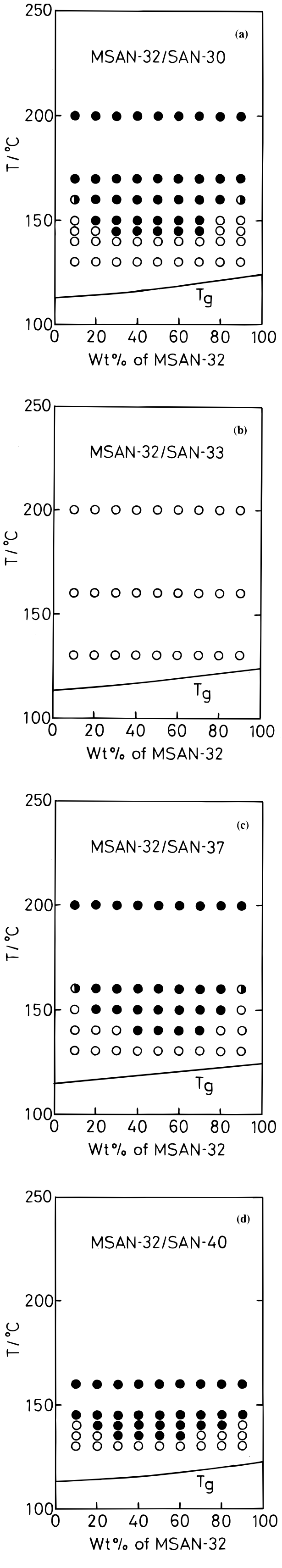

Figure 6. Phase diagram for blends of MSAN-32 and SAN with various AN contents. The open circles denote "one phase" and the closed circles "two phases".

blends did not exhibit LCST phase behavior.[4] Their samples were dried in a vacuum oven at about 150 °C for 2 days. Figure 6 shows that we cannot observe LCST behavior for MSAN-32/SAN-30, SAN-37, and SAN-40 blends, when we perform annealing or sample preparation above 150 °C.

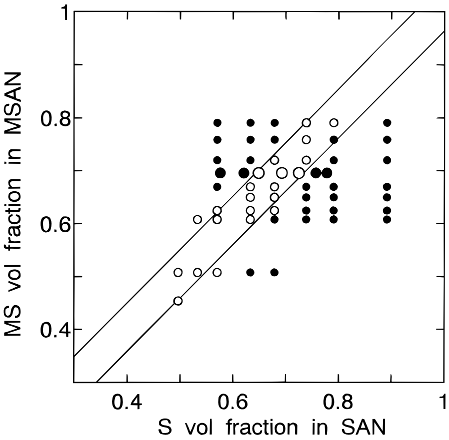

Figure 7. Miscibility map for blends of MSAN and SAN: Open and closed circles denote miscible and immiscible blends, respectively. Large circles denote our results and small circles the results by Ikawa et al.[3]

Figure 7 shows the miscibility map for 50/50 wt % blends of MSAN with SAN. Open and closed points refer to miscible and immiscible blends, respectively. Large circles denote the results of this work at 130 °C and small circles the results by Ikawa et al.[3] Our data are in good agreement with the data by Ikawa et al.

We can describe the miscibility map according to the Flory−Huggins theory. In the first-order Flory−Huggins formulation for polymer mixtures,[14] the free energy of mixing ΔG at a temperature T for a blend of r_1-mers and r_2-mers can be written

$$\Delta G/RT = (\phi_1/r_1) \ln \phi_1 + (\phi_2/r_2) \ln \phi_2 + \chi_{\text{blend}}\phi_1\phi_2 \quad (1)$$

where R is the gas constant, ϕ_1 and ϕ_2 are the volume fractions of r_1-mer and r_2-mer in the blend, and χ_{blend} is the net segmental interaction parameter between the two polymers. For blends of two random copolymers, according to ten Brinke et al.,[6] χ_{blend} can be written as a general quadratic equation whose variables are the composition, x and y, of the two copolymers expressed in volume fraction. For MSAN/SAN blends of the copolymers containing a common monomer unit, $(\text{S}_x\text{AN}_{1-x})_{r_1}$ and $(\text{MS}_y\text{AN}_{1-y})_{r_2}$, χ_{blend} is given by

$$\chi_{\text{blend}} = \chi_{\text{S-AN}}x^2 + (\chi_{\text{S-MS}} - \chi_{\text{MS-AN}} - \chi_{\text{S-AN}})xy + \chi_{\text{MS-AN}}y^2 \quad (2)$$

where $\chi_{\text{S-AN}}$, $\chi_{\text{MS-AN}}$, and $\chi_{\text{S-MS}}$ are the segmental χ parameters between styrene and acrylonitrile, α-methylstyrene and acrylonitrile, and styrene and α-methylstyrene monomers, respectively. When χ_{blend} is smaller than $\chi_{\text{blend,crit}} = {}^1/_2(1/r_1^{1/2} + 1/r_2^{1/2})^2$, the two polymers are miscible. Even if all the segmental χ parameters are positive, the χ_{blend} can be negative in a limited range of x and y. Shiomi et al.[15] discussed the theoretical miscibility maps for blends of two random copolymers having a common monomer. We[1] investigated miscibility of blends of SAN with SMI and SMA and estimated segmental interaction parameters between the different monomer units. We found that miscibility of these blends is due to a repulsion between the different monomer units comprising the copolymer.

We adopt a solubility parameter approach to determine χ_{ij}. When there are no specific interaction between the copolymers, χ_{ij} has been expressed as[16]

$$\chi_{ij} = (V/RT)(\delta_i - \delta_j)^2 \quad (3)$$

where δ_i and δ_j are the solubility parameters of the respective components and V is a reference volume. V has been taken as the geometric mean of the molar volumes of the involved polymer repeat units, as used by Kressler et al.[17] and us.[1] From the group molar constants according to Hoy[18] and the molar volumes by density measurements, the solubility parameters at 130 °C were obtained $\delta_{\text{S}} = 18.6$, $\delta_{\text{AN}} = 24.6$, and $\delta_{\text{MS}} = 18.9$ $(\text{kJ/L})^{1/2}$. Inserting these values in eq 3, we get for the parameters $\chi_{\text{S-AN}} = 0.747$, $\chi_{\text{MS-AN}} = 0.736$, and $\chi_{\text{S-MS}} = 0.001$ at 130 °C. The straight lines in Figure 7 were calculated from eqs 1 and 2 using the χ_{ij} set and the constant value of $\chi_{\text{blend,crit}}$ (=0.002). The observed miscibility map is in good agreement with that predicted using the solubility parameter approach. It is clear that the miscibility of MSAN/SAN blends can be explained by the strong repulsion between the segmental units within the copolymers. As $\chi_{\text{S-AN}}$ and $\chi_{\text{MS-AN}}$ become small at elevating temperature, χ_{blend} can become higher than $\chi_{\text{blend,crit}}$. Phase separation on heating could be caused by free volume contributions to mixing as well as complex variations in segmental interactions with temperature.

Concluding Remarks

MSAN is miscible with SAN having AN contents between 28 and 40 wt % at 130 °C. The miscibility range is in good agreement with that predicted using a solubility parameter approach. This study reports the first observation of the presence of LCST type phase behavior for MSAN/SAN blends. Previous work could not observe LCST behavior, because the samples were prepared in a vacuum oven at higher temperature than the LCST. To decide the phase diagrams of MSAN/SAN blends, very long isothermal annealing (sometimes above 200 h) was required just above T_g.

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