Window of Acrylonitrile Content for Miscibility in Blends Comprising Poly(styrene-*co*-acrylonitrile)s and Poly(benzyl methacrylate)

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ABSTRACT: For the first time, miscibility between poly(styrene-*co*-acrylonitrile) (SAN) and poly(benzyl methacrylate) (PBzMA) was proved. The miscibility window was found in SAN/PBzMA as the copolymer structure was varied systematically by altering weight percent of the acrylonitrile (AN) unit in the SAN copolymers. The lower bound of AN content in SAN for miscibility of SAN/PBzMA blend is 3.5 wt %, and the upper bound is 24.4 wt % AN in the copolymer. The trend of T_g broadening and LCST (cloud point) behavior for the SAN/PBzMA blends in that these phase-related quantities were all affected by AN content in SAN copolymers. Within the window, the copolymer/polymer mixtures formed a true miscible blend system. The effect of SAN structure (by controlling AN weight percent) on the window miscibility of SAN/PBzMA blends is interpreted and discussed in detail.

Introduction

Miscibility in blends involving copolymers of styrene and acrylonitrile (SAN's) has been an interesting subject of diversified studies. Most notably, the miscibility of SAN with poly(methyl methacrylate) (PMMA)[1−6] and with poly(ϵ-caprolactone) (PCL)[7−9] has been widely reported since 1974. Miscibility in SAN with acrylic polymers other than PMMA has not been reported until lately (1991) when Kishore et al.[10] and Mandal et al.[11] independently and simultaneously reported miscibility of poly(phenyl acrylate) with SAN's (15−35 or 11.5−32 wt % AN, respectively). In many reported miscible binary blend systems whose constituents involve at least one copolymer, it has been commonly observed that miscibility occurs in a range of copolymer compositions. This phenomenon has been attributed to the so-called "copolymer effect" by some investigators. The "copolymer effect" suggests that mutual repulsion between the constituents (copolymer units) of the copolymer prevails over other interactions and that the repulsion in the copolymer leads to miscibility in the homopolymer−copolymer pair.[12−14]

An alternative view from different perspectives may be needed for explaining the window miscibility. The two monomeric units in a copolymer are chained by covalent bonds. Thus, mutual repulsion in a copolymer, even in existence, cannot be literally taken as what would be encountered in a mixture comprised of the two monomers physically mixed. The covalent bond simply overwhelms interunit repulsion. Polymer miscibility usually resulted in a mixture whose two different chains/segments are in proximity within a domain small enough (normally several or tens of repeat units), regardless of the types of interactions. Any chain segment in a homopolymer molecule comprises the same monomer unit; however, a chain segment in a copolymer molecule may consist of some number of two different monomers in random combination (covalent bonded). In contrast with a random copolymer, the polarity of a homopolymer molecule (or any fragment segment) remains the same throughout the entire chain as long as the repeat unit is the same. By comparison, the polarity of a copolymer segment may be a statistical average of the two monomers in a random combination. A favorable intermolecular secondary force can be expected if the polarity in the copolymer is close to or matches that of the homopolymer. The range of copolymer compositions (ratios of two constituent units), within which miscibility occurs, indicates such an averaging effect of two monomers.

The objective of this study was to investigate miscibility in blends of SAN copolymers with acrylic polymers other than PMMA. Furthermore, alternative views for interpreting the window miscibility were examined and compared to the existing copolymer repulsion mechanism. To examine the window bounds, a systematic variation in SAN was introduced by changing AN content in the copolymer. The effects of AN content in SAN on blend miscibility, phase behavior, lower critical solution temperature (LCST), intermolecular interaction, and phase homogeneity/heterogeneity transition, etc., were thoroughly examined.

Experimental Section

Materials and Sample Preparation. Poly(benzyl methacrylate) (PBzMA) was purchased from a specialty polymer supplier, Scientific Polymers Product, Inc. (SP^2, USA), and it has $M_w = 54\,000$ g/mol, PI = 2.27 (GPC), and T_g of 57.2 °C. Poly(styrene-*co*-acrylonitrile)'s (SAN's) of a wide range of acrylonitrile (AN) contents were used in this study. This study required SAN's containing a wide range of AN contents; thus, a series of SAN samples of various AN contents were prepared in the laboratory by free-radical bulk copolymerization of styrene and acrylonitrile at 60 °C using 10^{-3} M AIBN as an initiator. For comparison, SAN samples of two different AN contents (25 and 32 wt %) were obtained from Scientific Polymer Products. Poly(styrene-*co*-acrylonitrile)'s (SAN's) with a range of acrylonitrile (AN) contents (3.5−30 wt %) were synthesized in this study. Their synthesis is briefly described in the following.

The synthesis of SAN copolymers started with purification of monomer reagents and chemicals. Monomeric styrene (Acros Organics) was washed three times with 5% NaOH aqueous solution and then with plenty of distilled water to remove the residual NaOH, dried over $CaCl_2$, and distilled under reduced

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Table 1. List of Synthesized SAN-*x* Copolymers and Characterization

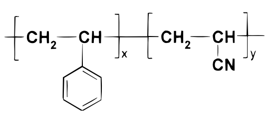
SAN-*x*	AN (wt %)	AN (mol %)	T_g (°C)	$M_w \times 10^5$	PI	sources
SAN3	3.5	6.6	106.0	2.14[a]	1.85	synthesized
SAN5	5.7	10.6	106.4	2.26	1.74	synthesized
SAN7	7.5	13.7	106.6	2.45	1.64	synthesized
SAN8	8.6	15.6	107.0	2.56	1.58	synthesized
SAN9	9.4	16.9	107.7	2.79	1.74	synthesized
SAN17	17.8	29.8	109.5	2.69	1.65	synthesized
SAN21	21.3	34.7	110.9	2.86	1.62	synthesized
SAN25	24.4[b] (25[c])	38.8	105.0	1.64	2.32	SP^2, USA
SAN27	27.8	43.0	113.1	3.43	1.61	synthesized
SAN30	30.6	46.4	114.3	3.51	1.58	synthesized

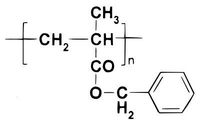
[a] M_w (g/mol) of all SAN-*x* was characterized using gel permeation chromatography. [b] Measured by elemental analysis (EA) in this lab. [c] Supplier's data (SP^2, Inc., USA)

pressure by following the standard methods. Similarly, the acrylonitrile monomer (Acros Organics) was purified by washing two times with 5% NaOH solution, twice again with 5% H_2SO_4 solution, then three times with 5% $NaHCO_3$ solution, and finally with distilled water. Subsequently, the purified monomers were dried over $CaCl_2$ and distilled under atmospheric pressure. Azobis(isobutyronitrile) (AIBN) was purified by recrystallization from methanol.

Copolymer Synthesis and Characterization. The conversion in any batches was allowed to proceed to no more than 10% to avoid compositional heterogeneity in the SAN. The copolymers were purified by dissolving in $CHCl_3$ and followed by precipitation into methanol. The procedure was repeated three times and finally dried at 140−150 °C in a vacuum oven for 3 days. The synthesized SAN's are labeled as "SAN-*x*" where *x* indicates the weight percent (to the closest integer) of AN in the SAN copolymers.

After polymerization, the exact composition (AN content) of the SAN copolymers were determined from nitrogen analysis by using an elemental analyzer (EA, Heraeus CHN-O-Rapid). The weight-average molecular weight and the polydispersity index (PI) of the synthesized SAN-*x* polymers were determined by using gel permeation chromatograph (GPC, Waters Associates) in a THF solution of the polymers. The GPC was calibrated using standard polystyrene samples. The characterization data of the polymers are given in Table 1. The structures of the SAN-*x* and PBzMA are the following:


Poly(styrene-co-acrylonitrile)


Poly(benzyl methacrylate)

Blend Preparation. The blend samples (of PBzMA and SAN's) were prepared by the solution-casting method. Polymers were blended and cast using several different solvents. The solvents, tetrahydrofuran (THF), dichloromethane (CH_2Cl_2), chloroform ($CHCl_3$), benzene (C_6H_6), and methanol, were all high-purity HPLC grade and used without further purification. In preliminary studies, several common solvents, tetrahydrofuran (THF), chloroform (CCl_3H), dichloromethane (CH_2Cl_2), and benzene, etc., were used for sample preparation (blending and film-casting). The polymers were first weighed and dissolved into the solvent with continuous stirring. Subsequently, the resulting polymer solution after complete mixing and dissolution was poured into an aluminum mold kept at a suitable temperature. Solvent in the blends was evaporated in air at different temperatures for different solvents used in blending. All the cast blend films were further dried in a vacuum oven at 120 °C for 72 h except for the SAN3/PBzMA blends, which were dried at 105−110 °C because its lower critical solution temperature (LCST) was particularly low (close to 120 °C). The LCST varied significantly for the blends of PBzMA with different SAN-*x*, and this interesting phenomenon will be discussed later in more detail.

Apparatus. The glass transition temperatures and other thermal transitions of neat polymers and their blends were measured with a differential scanning calorimeter (Perkin-Elmer DSC-7) equipped with a mechanical intracooler and a computer for data acquisition/analysis. Subambient runs starting at temperatures lower than −60 °C were performed using cooling by liquid nitrogen and helium purge. All T_g measurements were made at a scan rate of 20 °C/min, and T_g values were taken as the onset of the transition (the change of the specific heat).

Morphology (fracture surface) of blends was examined using a scanning electron microscope (SEM, model JEOL JXA-840). The blend film samples for scanning electron microscopy were solution-cast to be thick enough so that fracture surface of the thickness (cross section) could be conveniently examined. The fractured blend samples were coated with gold by vapor deposition using vacuum sputtering.

A polarized-light optical microscope (Nikon Optiphot-2, POL), equipped with heating stage (Linkam THMS-600 with TP-92 programmer), was used for determination of cloud point transition upon heating. The blends were first cast as thin films on glass slides and dried properly in a temperature-controlled oven before they were examined using the optical microscope. Measurements were performed by placing the samples on a microscope heating stage (temperature-programmed) and heated at a programmed heating rate of approximately 2 °C/min from room temperature up to initiation of phase separation. If no phase separation was observed, the heating was interrupted as it reached 300 °C, where thermal decomposition began to occur. The cloud point (phase separation temperature) was registered as the initiation temperature at which separated domains were visible in samples at 600−1000× magnification of the optical microscope.

Fourier transform infrared spectroscopy (FT-IR, Nicolet Magna-560) was used for investigating states of molecular interactions between the two blend constituents. Spectra were obtained at 2 cm^{-1} resolution, and averages of spectra were obtained from at least 64−200 scans (for enhanced signal) in the wavenumber range 400−4000 cm^{-1}. The neat polymers and their blend samples of various compositions were cast as thin films of proper thin and uniform thickness directly on KBr pellets kept at 45 °C. Subsequently, the IR measurements were performed on the cast-film samples at ambient temperature.

Results and Discussion

Glass Transition Evidence. DSC analysis was performed on the samples to reveal their glass transition behavior. For a uniform thermal history for all samples, all thermograms are the results of second runs after quenching from temperatures just above T_g. All blend samples of PBzMA and SAN copolymers (AN contents between 3.5 and 32 wt %) were cast from dichloromethane at 40 °C. All DSC thermograms for SAN2/PBzMA (eight blend compositions evenly spaced) revealed only one apparent T_g, although the T_g appeared somewhat broadened for some intermediate compositions in the SAN3/PBzMA blends. SAN5/PBzMA blends (eight compositions) were analyzed. Similarly, a single T_g was observed for the SAN4/PBzMA blends of all compositions. Exhaustive DSC characterization was performed on all SAN-*x*/PBzMA blend systems, where *x* ranged from 3.5 to 32 wt % AN in SAN. For brevity, DSC thermograms are not shown. The results indicated miscibility for SAN-*x*/PBzMA blend systems if the AN contents in SAN-*x* were within 3.5 and 24.4 wt %. Apparently, phase-separated blends of SAN-*x*/PBzMA resulted (two T_g's) if the AN content in SAN-*x* was higher than 24.8 wt % or lower than 3.5 wt %. The DSC thermograms showing single T_g and miscibility for all

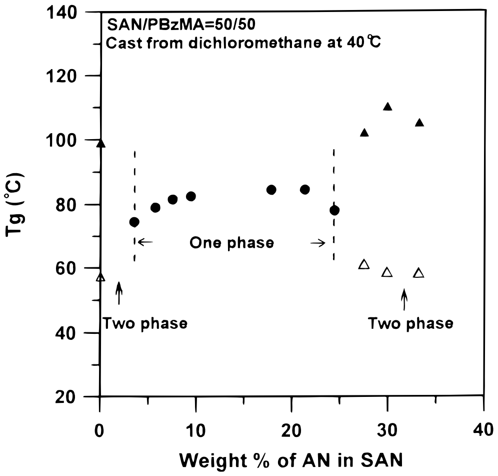


Figure 1. Effect of systematic variation of AN contents (in SAN copolymers) on the phase behavior of all SAN-*x*/PBzMA systems (for the fixed 50/50 composition).

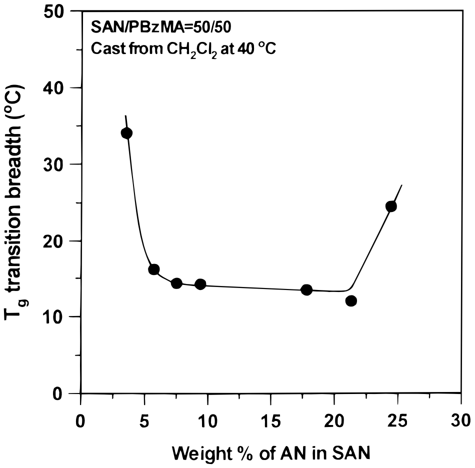


Figure 2. Dependence of T_g transition breadth on AN content in SAN for the SAN/PBzMA (for fixed 50/50 composition) blend systems.

investigated blend systems are too numerous to be shown here fully and completely.

As a representative illustration, the T_g behavior of a fixed 50/50 SAN-*x*/PBzMA blend composition was examined. The T_g behavior for other compositions (in full range) was found to be similar and for brevity is not all shown here. Figure 1 shows the effect of systematic variation of AN contents (in SAN copolymers) on the phase behavior (single T_g vs separated T_g's) of SAN-*x*/PBzMA (50/50) blend systems. The figure clearly illustrates that the lower bound for miscibility (single T_g) of SAN/PBzMA blend whose AN content in SAN is 3.5 wt % and the upper bound is 24.4 wt % AN in the copolymer. Beyond these two bounds, the SAN-*x*/PBzMA blends are clearly phase-separated (two T_g's and obviously immiscible).

Although only one composition (SAN-*x*/PBzMA of 50/50) is demonstrated in the above plot, the same dependence of phase behavior on the copolymer AN content was observed for all other blend compositions (80/20, 60/40, 40/60, 20/80, etc.) in full range. It would be too numerous to show all of them here. For brevity, the results for the 50/50 composition are illustrated and discussed, but other compositions are not all shown. Note that the single T_g's of the miscible SAN/PBzMA (50/50) near the lower and upper bounds (i.e., SAN3/PBzMA and SAN24/PBzMA, respectively) are noticeably lower in comparison to those closer to the middle of the window. This is so because the miscible blends near the bounds of window approaches a marginal state of miscibility, and the T_g exhibited a greater extent of broadening as a result of increasing heterogeneity vs homogeneity. The T_g broadening lowered the value of T_g as in this study the onset value of T_g was used. The phenomenon of T_g broadening as affected by AN weight percent in SAN will be discussed in the next paragraph.

Interestingly, the transition breadth of T_g of SAN/PBzMA was found to be influenced by the AN content in SAN copolymers. For example, the T_g transition breadth for the SAN3/PBzMA system appeared to be comparatively more significant than that for SAN5/PBzMA. As the AN content increases in SAN, the T_g transition in the SAN/PBzMA blend (compared for the same composition) was found to become sharper and narrower, indicating better segmental-scale mixing between the SAN and PBzMA chains. The trend of sharper T_g transition for the SAN/PBzMA blends with increasing AN in the SAN copolymer appeared to be valid until AN content reached the upper bound (AN = 24.8 wt %) for blend miscibility, where for the SAN24/PBzMA blend, the T_g transition once again became more broadened. Note that beyond the upper bound of 24.4 wt % AN in SAN the SAN/PBzMA was found to be immiscible, as discussed earlier. For miscible blend systems, the T_g transition breadth was not all the same for all compositions, but generally for the intermediate compositions (near 50/50 for example) the T_g transition breadth was usually the most significant. Thus, examination of effect of AN weight percent on the T_g breadth must be compared among the same composition, say for example 50/50. Figure 2 shows that the dependence of T_g transition breadth on AN content in SAN for the SAN-*x*/PBzMA (50/50) miscible blend systems. Apparently, for AN contents within 5 and 20 wt %, the T_g transition breadth remains quite constant (~15 °C). However, the T_g breadth quickly broadens (to breadth of ~30 °C or broader) for the SAN/PBzMA blend (50/50 composition) whose SAN constituent contains AN lower than 5 wt % or greater than 20 wt %. Again, same behavior was observed for all blend compositions (e.g., 90/10−10/90); but for brevity, only the 50/50 SAN-*x*/PBzMA composition is illustrated and discussed here.

The broadening of T_g for the blends may be an indication of gradual shifting from a state of some extent of homomolecular aggregation prior to an outright phase separation. Thus, a transition of phase behavior of SAN/PBzMA within a window of AN content is apparent. Miscibility in general criteria, with various scale of phase homogeneity, was proved in the SAN/PBzBA blends whose SAN copolymer contains AN within 3.5 and 24.8 wt %. On one end of the extreme where AN content is nil in the copolymer (i.e., SAN-0 = polystyrene), immiscibility in the copolymer/PBzMA blend is known to be true. On the other extreme of the window where AN content equals or exceeds 27 wt %, phase separation was also demonstrated in this study. Near the border of window, the extent of intermolecular interactions might be only barely sufficient to ensure a homogeneous mixture of SAN/PBzMA, which exhibited a limited scale of intermolecular mixing vs increased extents of aggregation of the same molecules, leading to the observed T_g broadening phenomenon.

The quantitative trend of T_g dependence on blend composition was analyzed for the SAN-*x*/PBzMA blend systems in order to understand the effect of AN weight percent in SAN copolymers on the blend phase behavior. Fitting of the T_g data with several common models for miscible polymer systems was examined. The classical Fox expression or the Gordon–Taylor equation has been commonly used to measure quantitative fitness of T_g with composition.[15]

$$T_g = (\omega_1 T_{g1} + k\omega_2 T_{g2})/(\omega_1 + k\omega_2) \qquad (1)$$

where ω_i is the mass (weight) fraction of polymer component *i* and *k* is a fitness parameter. Note that *k* can be viewed as an adjusting parameter, where $k = 1$ results in an additive relationship of blend T_g vs composition. If *k* approaches unity, the G–T model basically predicts the same behavior as the Fox equation $[1/T_g = (\omega_1/T_{g1} + \omega_2/T_{g2})]$, which is commonly a good fit for the T_g's of copolymers comprising two different repeat units statistically and randomly linked by covalent bonds. On the other hand, low values of *k* may hint at an increasing extent of phase heterogeneity and/or broadening of T_g transitions before eventual phase separation. Thus, although the value of *k* cannot be viewed as thermodynamic interactions between the constituent polymer chains, high values of *k* do hint at a state of statistical well mixing at molecular chain/segment scales that approach the phase homogeneity commonly seen in most random copolymers.

The T_g–composition relationships for all miscible SAN/PBzMA blends systems were analyzed by comparing with these T_g models. As discussed earlier, the miscibility window of AN contents in SAN was found to be within 3.5–24.4 wt %. A total of eight miscible blends of the SAN-*x*/PBzMA system were examined in this study. It would be too numerous to show all of them here; thus, only three representative blend cases are shown here for a brief discussion. The rest of the miscible systems investigated in this study exhibited a similar T_g–composition dependence. Figure 3A–C shows clear evidence of single-T_g miscibility criteria and the quantitative trend of T_g variation with composition, where the T_g of three representative SAN/PBzMA blend systems (where AN content in SAN = 3.5, 7.5, and 24.4 wt %) was plotted as a function of composition. In each of the plots, fitness of the experimental T_g's with the Fox or G–T model was shown for comparison. The three diagrams (a, b, c) represent the three miscible SAN/PBzMA blends whose SAN structures are located at the lower, center, and upper bound, respectively, of the miscibility window.

To understand the effect of AN on window miscibility between SAN and PBzMA, the transition trend of miscibility/immiscibility behavior of the SAN/PBzMA systems was plotted as a function of the AN content in SAN copolymers. Figure 4 shows a plot of scale of "phase homogeneity" (maximum scale = 1) as a function of AN weight percent in the SAN copolymers. The qualitative fit with the T_g–composition models was taken only as an indication of scales of phase homogeneity in the miscible blends. The effect of AN weight percent on the window miscibility is apparent for each of the miscible SAN/PBzMA blend systems (AN content ranging from 3.5 to 25 wt %) showing various scales of phase homogeneity within the window. Outside the window, outright phase separation (also evidenced by two T_g's) was observed. This fact suggests that, for a SAN whose AN content is near the center of window, SAN7/PBzMA blend exhibits much better physical mixing (in absence of chemical bonding or other primary forces), reflecting a state of good scale of intermolecular mixing. The window is located near AN = 7–10 wt %, while outside this window (AN < 3.5 wt % or AN > 25 wt % in SAN) the SAN/PBzMA blends were found to be immiscible (i.e., phase-separated) and their T_g's are distinctly separated and not predicted by any models. Quantitative fitness of blend's T_g with the models was taken as indication of miscibility with reasonable homogeneity.

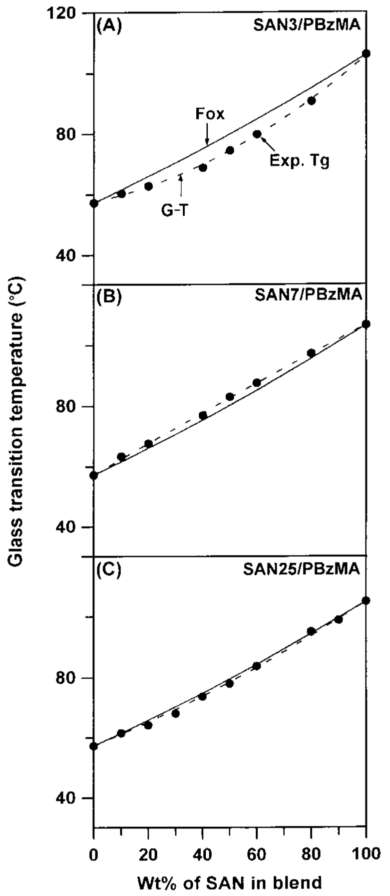


Figure 3. T_g of three representative SAN/PBzMA blend systems plotted as a function of composition: (a) AN content in SAN = 3.5, (b) 7.5, and (c) 24.4 wt %.

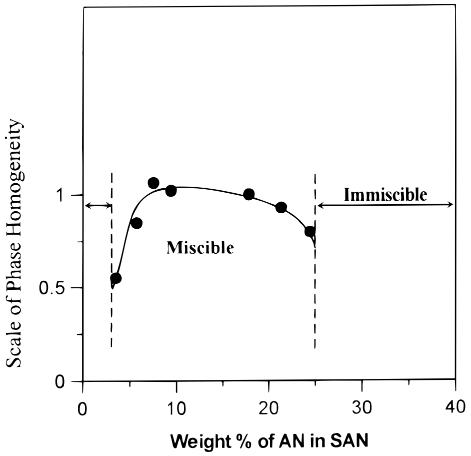


Figure 4. Scale of phase homogeneity as a function of AN weight percent in the SAN copolymers for the miscible SAN/PBzMA blend systems (AN content ranging from 3.5 to 25 wt %).

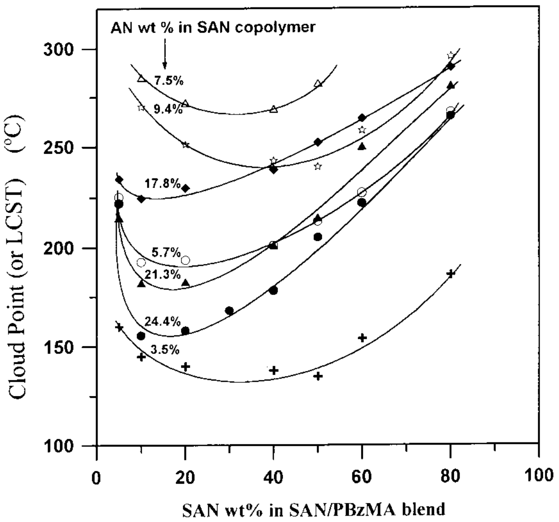


Figure 5. Phase diagrams showing cloud point (or LCST) as a function of blend composition (SAN weight percent) for all miscible SAN/PBzMA systems.

The plot in this figure shows that the behavior of miscibility is located at a window of copolymer (SAN-*x*) structure whose AN = 3.5−24.4 wt %, and the scale of phase homogeneity in the miscible SAN-*x*/PBzMA blends exhibits a convex trend within the window.

Dependence of LCST Behavior on Copolymer Structure. Figure 5 shows the phase diagrams and cloud point along with LCST (the minimum) as a function of blend composition (SAN weight percent) for all miscible SAN-*x*/PBzMA blend systems. A total of seven curves are shown in this figure, with each corresponding to one of the SAN/PBzMA blends whose AN content (3.5, 5.7, 7.5, 9.4, 17.8, 21.3, and 24.4 wt %) in the SAN copolymer is as labeled in the figure. All cloud-point curves are concave-shaped and slightly asymmetric with respect to blend composition but apparently differed in their temperature location. When compared at the same blend compositions, the cloud-point temperatures (or LCST's) for the seven miscible SAN-*x*/PBzMA systems are apparently influenced by the AN contents in the SAN copolymers. The variation and off-center of the minimum of the LCST curve are noted in the figure. Note that theories usually predict LCST minimum being at 50/50 by volume in the blends. The data in Figure 5 were plotted on weight percent (not volume) of SAN-*x* in the blends. After adjustment to plots in volume fractions, the *x*-axis of the minimum would move a bit toward the center (50/50) but is still off-centered. Molecular weights of the constituents and factors other than M_w may be involved. The M_w's of SAN-*x* and PBzMA differ by about three times. The M_w of PBzMA is 5.4×10^4 g/mol, while those for SAN are in the range $(1.6-2.5) \times 10^5$ g/mol (see Table 1). M_w of PBzMA is in general lower than any of SAN-*x*, and there is some variation in the M_w's of SAN. The LCST mimimum is usually shifted toward the axis of the low-M_w polymer (i.e., PBzMA), which is what was observed in the data. However, the main objective of this study was not investigating effects of M_w on cloud point (or LCST) behavior, but on the window miscibility phenomenon. Thus, other than pointing out the apparent shift of the LCST minimum in the plots, we focused on examining the dependence of the window behavior of LCST with respect to the variation in the copolymer structure.

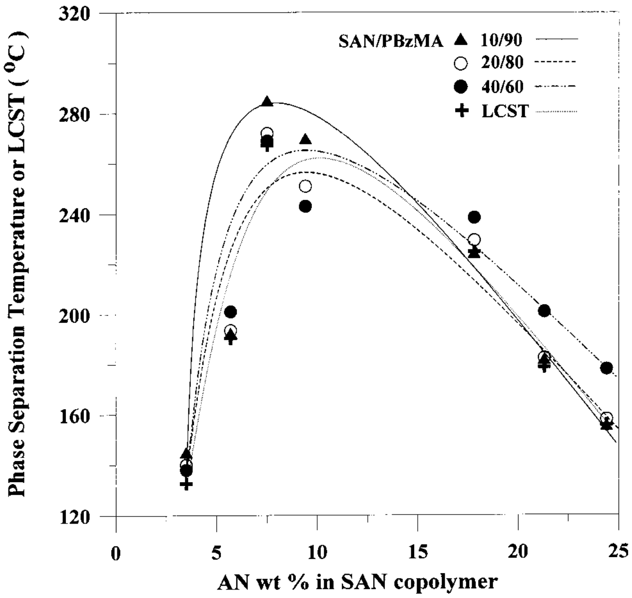


Figure 6. Phase separation temperature as a function of SAN copolymer structure (AN weight percent in SAN) in the miscible SAN/PBzMA systems at three fixed blend compositions. For comparison, trend of variation of the LCST point is also plotted.

To more clearly reveal the trend of variation of cloud-point temperatures (and LCST) with respect to the systematic changes of SAN copolymer structure (AN content), the cloud point (phase separation temperature) at a fixed blend composition was compared within the miscibility window. Figure 6 shows plots of phase-separation temperature variation with AN weight percent in the SAN copolymers. The phase separation temperatures are shown as functions of SAN structure (AN weight percent) for the SAN-*x*/PBzMA blend systems at three fixed compositions (as parameters): 10/90, 20/80, and 40/60. For comparison, the trend of variation of the LCST (data symbol "+") for each of the blend systems is also plotted in the same figure. The LCST's are 125 and 150 °C for the SAN/PBzMA blends whose AN is 3.5 and 24.4 wt %, respectively, while the highest LCST (near 275 °C) was found to exist in the SAN/PBzMA blend whose SAN copolymer comprises 7.5 wt % AN. Note that the LCST for different SAN's/PBzMA may not occur at the same blend composition primarily due to variation of SAN's M_w. The comparison shows that the trend of variation for LCST is similar or almost identical to those for the phase separation temperatures. Apparently, the figure shows that the SAN/PBzMA whose AN content near the miscibility border (AN = 3.5 and 24.4 wt %) possesses the lowest LCST temperature or lowest phase separation temperature in general. The trend of variation of either phase separation or LCST for the miscible SAN's/PBzMA blends also exhibits a window behavior with respect to AN weight percent in SAN's. Thus, similar to the earlier discussed trend of T_g breadth (broadening) in the miscible SAN/PBzMA blend systems with respect to the AN content in SAN, an apparent trend of LCST was observed in the SAN/PBzMA blends within a window of AN content. While higher LCST in a miscible blend may suggest a better scale of mixing in the blend, a lower LCST most likely indicates a state of phase behavior approaching the border of miscibility−immiscibility transition. Near the border of the window, the scale of phase homogeneity may be close to a transition from miscibility into phase segregation.

Evidence of Morphology and IR Characterization. Both optical microscopy and scanning electron microscopy characterization were performed on samples for revealing the phase homogeneity. Both optical and SEM micrographs of the SAN-*x*/PBzMA blend samples revealed no discernible phase domains. For brevity, the SEM result and numerous micrographs are not shown here. The SEM result provided additional supportive evidence on phase homogeneity in the eight miscible blend systems within the window. In addition, IR characterization was performed in order to probe molecular interactions through any sites. Specifically, two functional groups were of interest: −CN in SAN copolymer and C═O in PBzMA. As the miscible blend systems investigated in this study were numerous, only one miscible system (SAN25/PBzMA) was chosen for representative discussion. For brevity, the spectra are not shown here. The carbonyl group of the SAN/PBzMA blend of various compositions (90/10, 80/20, 60/40, 50/50, 40/60, 20/80, 10/90, 0/100) exhibited a C═O absorbance peak, whose position is stationary at 1728.6 cm^{-1} with respect to the composition. No noticeable shift of C═O peak with respect to composition was noted, suggesting no specific interactions (or other strong secondary forces) through the C═O group. Similarly, the −CN peak was monitored with respect to changes in the blend compositions. It was found that the absorbance peak of −CN was located at 2237 cm^{-1} and remained at the same frequency for all compositions. In summary, no evidence of specific interactions through possible functional groups in AN, St, or BzMA units was observed. This is an indication that the miscibility in the SAN/PBzMA blend depends only on "physical" van der Waals-type interactions or weakly interacting polar forces, but other stronger specific interactions are generally not available.

Discussion of Copolymer Structural Effect on Miscibility. According to the Flory−Huggins relationship for polymer blends,[17] the free energy of mixing ΔG at a temperature T is given by

$$\Delta G/RT = (\phi_1/r_1)\ln\phi_1 + (\phi_2/r_2)\ln\phi_2 + \chi_{12}\phi_1\phi_2 \qquad (2)$$

where R is the universal gas constant, ϕ_1 and ϕ_2 are the volume fractions of polymers 1 and 2, and r_1 and r_2 are the degree of polymerization. χ_{12} is the segmental interaction parameter between the two polymers in the mixtures. The combinatorial entropy term in eq 2 can be neglected for high-molecular-weight polymers; thus, the miscibility only depends on the sign and magnitude of the χ_{12}. If χ_{12} is negative, these two polymers can be miscible; but if positive, then they are likely not. Thermodynamic interpretation of the miscibility behavior of the SAN/PBzMA blends, a copolymer/homopolymer system, was attempted. As discussed earlier, within a window of SAN structure as governed by AN weight percent, the SAN copolymers (AN and St units) are miscible with PBzMA homopolymer (BzMA unit only). For the blends of a copolymer and a homopolymer, χ_{12} can be expressed as a general quadratic equation, whose variable is volume fraction composition (y) of the copolymer. ten Brinke et al.[13] have proposed that, for a blend consisting of homopolymer A and copolymer C_yD_{1-y}, χ_{12} is defined as

$$\chi_{12} = y^2 + y(\chi_{AC} - \chi_{AD} - \chi_{CD})/\chi_{CD} + \chi_{AD}/\chi_{CD} \qquad (3)$$

where χ_{AC}, χ_{AD}, and χ_{CD} are the segmental interaction parameters between the different monomer units as indicated by their subscripts. In this study, the subscripts A, C, and D are as follows: A = BzMA unit, C = AN unit, and D = styrene (St) unit. At the boundary condition (miscibility−immiscibility), χ_{12} can be assigned to zero. If $\chi_{12} = 0$ is used as a boundary condition in eq 3, two roots y_1 and y_2 can be obtained:

$$y_1 + y_2 = (\chi_{BzMA-St} + \chi_{AN-St} - \chi_{BzMA-AN})/\chi_{AN-St} \qquad (4)$$

$$y_1 y_2 = \chi_{BzMA-St}/\chi_{AN-St} \qquad (5)$$

Thus, χ_{AC}, χ_{AD}, and χ_{CD} are the parameters for the BzMA−AN, BzMA−St, and AN−St pair, respectively. To find the values for all χ_{ij}, the following approach was used, which have also been used by many other authors.[10,18] The miscibility window values for the volume fractions of AN unit in the SAN copolymers was experimentally observed in this system. By setting y_1 = lower bound (AN = 3.5 wt % or 0.0312 volume fraction) and y_2 = upper bound (AN = 24.4 wt % or 0.223 volume fraction), eqs 4 and 5 can be solved. These two equations have three unknown χ_{ij} parameters. If one of the three is known, the other two can be calculated. Aoki[18] has calculated $\chi_{AN-St} = 0.98$ using the solubility parameters of PAN and PS assuming that there is no specific interaction between the AN−St pair. Alternatively, Cowie and Lath[19] determined a value of $\chi_{AN-St} = 0.83$ from their miscibility studies of blends of PMMA and SAN. In addition, Nishimoto et al.[6] have reported the interaction energy density (B_{ij}) for the AN−St pairs from several different copolymer blends, and the values for B could be readily converted to give $\chi_{AN-St} = 0.80$ from the known relation $\chi = B(V/RT)$, where V is the geometric mean of the molar volumes of PAN and PS as used by Kressler et al.[8] In this study, eqs 4 and 5 were solved for $\chi_{BZMA-St}$ and $\chi_{BzMA-AN}$ by using the literature values for χ_{AN-St}.[6,19] The estimated values and the average of $\chi_{BZMA-St}$ and $\chi_{BZMA-AN}$ are given in Table 2. The order of calculated χ values for the respective pairs of units was found to be

$$\chi_{AN-ST}\,(0.85) \doteq \chi_{BzMA-AN}\,(0.65) \gg \chi_{BzMA-St}\,(0.0064\text{, or nearly zero})$$

The low value of $\chi_{BzMA-St}$ is in agreement of the prediction by the solubility parameter approach, which suggests that PBzMA and polystyrene possess a nearly matched polarity or solubility parameter. The values are then compared to other systems. The $\chi_{BZMA-St}$ (for BzMA−St) is significantly lower than the value reported for the PhA−St pair[10,11] or the MMA−ST pair,[19] while the value of $\chi_{BzMA-AN}$ is higher than the value of χ_{PhA-AN} and χ_{MMA-AN} reported in the literature.[10,11,19] These trends are in general agreement with the solubility parameter difference between the corresponding pairs.

It is worth noting here that similar treatments on the window miscibility have been extensively utilized in analyzing a wide variety of blends of a copolymer with a homopolymer. For example, Cowie et al.[20−22] have examined blends of poly(vinyl methyl ether)/poly(styrene-*co*-nitrostyrene), poly(butadiene-*co*-acrylonitrile)/chlorinated polymer, and poly(butadiene-*co*-acrylonitrile)/poly(styrene-*co*-methacrylate) systems, etc. They used

Table 2. Segmental Interaction Parameter for Binary Pairs of AN, St, or BzMA Repeat Units

χ_{AN-ST}	$\chi_{BzMA-ST}$	$\chi_{BzMA-AN}$
0.98[a]	0.0070	0.73
0.83[b]	0.0058	0.62
0.80[c]	0.0056	0.6
av 0.85	0.006	0.65

[a] Taken from ref 18. [b] Reference 19. [c] Reference 6.

a mean-field approach[12−14,20−22] to account for possible minor deviation from the simpler solubility parameter theory. By comparison, Gan and Paul et al.[23−25] have successfully investigated the phase behavior and explained window miscibility in various polymer/copolymer or copolymer/copolymer blends by using the classical Flory−Huggins theory and Sanchez−Lacombe equation-of-state theory[26] in combination with a binary interaction-density model. By deducting the binary interaction (B_{12}) in a copolymer of units 1 and 2, the net interaction in a polymer/copolymer (or copolymer/copolymer) is described with a pseudobinary model: $B = B_{13}\phi_1' + B_{23}\phi_2' - B_{12}\phi_1'\phi_2'$, where the volume fraction of ϕ_i' denotes volume fraction of units 1 or 2 in the copolymer.[23−25] It would be of great interest to continue future work in line with this study by attempting a more detailed analysis using those methodologies.

Conclusion

For the first time, this study has demonstrated that SAN copolymers and PBzMA can be miscible; furthermore, miscibility occurs in the SAN/PBzMA blends if AN weight percent in SAN is within a window range of 3−25 wt % (or 3.5−24.4 wt % to be more exact). Near the border of the window (AN = 3−5 or 20−25 wt %), the T_g broadens for the SAN/PBzMA blend; however, the phase homogeneity apparently decreases as a result of increasing scale of aggregation among the same molecules. Outside the window (AN <3.5 or >25 wt %), the SAN/PBzMA blends are phase-separated with two T_g's. Interestingly, similar shifting trends with respect to variation of SAN structure (in terms of AN weight percent) were also seen in the T_g−composition relationship. The scale of intermolecular mixing in the SAN/PBzMA blends approached a condition of maximum homogeneity when the AN unit accounted for 7−10 wt % in SAN. With decrease or increase of AN content away from the center of the window (i.e., AN = 7 wt %), the miscible SAN/PBzMA blends gradually assumed a greater scale of heterogeneity until eventually the blends became phase-separated outside the window bounds. In addition, all miscible SAN/PBzMA blends were found to display an LCST phenomenon and that the temperature of LCST also exhibited a window behavior with respect to AN weight percent in SAN's.

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