Study on polymer blends of poly(styrene-*co*-acrylonitrile) and poly(styrene-*co*-maleic anhydride)

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Polymer blends of poly(styrene-*co*-acrylonitrile) and poly(styrene-*co*-maleic anhydride) have been investigated by differential scanning calorimetry and light scattering measurements. Depending on the copolymer compositions it is possible to obtain miscible and immiscible blends and blends with lower critical solution temperature behaviour. In this way a miscibility channel can be designed. Fourier transform infrared spectroscopy suggests that the miscibility is caused chiefly by intramolecular interactions, and intermolecular interactions can be partially neglected.

(Keywords: blends; copolymers; miscibility; Fourier transform infra-red spectroscopy; differential scanning calorimetry measurements)

INTRODUCTION

It is well known that random copolymers of poly(styrene-*co*-acrylonitrile) (SAN) and poly(styrene-*co*-maleic anhydride) (SMA) are miscible within a certain range of copolymer composition[1-3]. Hall *et al.*[1] found miscibility of the two copolymers, as evidenced by a single glass transition temperature, if the SAN and SMA contain approximately equal amounts of styrene (in wt%). Kato *et al.*[2] observed miscibility of cast films by visual inspection of the turbidity if the styrene contents are nearly equal (in mol%). Aoki[3] studied the rheological properties of miscible SAN/SMA blends. Using the data of Hall *et al.*[1], Paul and Barlow estimated segmental interaction energy densities E_{ij} on the basis of a simple thermodynamic binary interaction model[4]. If one denotes styrene by 1, acrylonitrile by 2 and maleic anhydride by 3, for the binary interaction energy densities Paul and Barlow arrived at the following result:

$$E_{12} \sim E_{13} > 0 \qquad (1)$$

$$E_{23} < 0 \qquad (2)$$

According to the general thermodynamic theory of polymer miscibility[5], the overall interaction parameter X_{AB} in a blend containing two random copolymers A and B is a linear combination of individual interaction parameters corresponding to each non-identical segmental interaction. For a blend of two random copolymers containing a common segment it reads:

$$X_{AB} = (\alpha - \beta)[(1-\beta)\chi_{13} - (1-\alpha)\chi_{12}] + (1-\alpha)(1-\beta)\chi_{23} \qquad (3)$$

where χ_{ij} are the segmental interaction parameters proportional to E_{ij} and α and β refer to the respective copolymer compositions (mole fractions). Inserting (1) and (2) in equation (3) one obtains:

$$X_{AB} = (\alpha - \beta)^2\chi_{13} + (1-\alpha)(1-\beta)\chi_{23} \qquad (4)$$

As a consequence, miscibility of the two copolymers is caused by specific interactions of acrylonitrile (AN) and maleic anhydride (MA) leading to an exothermic heat of mixing or to $X_{AB} < 0$.

The phase behaviour of these blends has been investigated by glass transition measurements and laser light scattering. As the assumption inherent in equation (1) is not straightforward, we studied the interactions by Fourier transform infra-red (*FT*i.r.) spectroscopy. This paper reports the results of these investigations.

EXPERIMENTAL

Polymers

The SAN was polymerized at 60°C in ethylbenzene with $0.02\,\mathrm{mol\,l^{-1}}$ AIBN (azobisisobutyronitrile) and a monomer concentration of $8\,\mathrm{mol\,l^{-1}}$. The maximum degree of conversion was about 6%. The copolymer composition was determined by the Kjeldahl method. The molecular weights of the SAN were estimated by g.p.c. The $\bar{M}_w$ values are between 128 000 and $179\,000\,\mathrm{g\,mol^{-1}}$ and $\bar{M}_w/\bar{M}_n$ is about 2. The SMA was prepared in a continuously stirred tank reactor. The $\bar{M}_w$ values for the SMA samples were determined by light scattering to be in the range from 120 000 up to $145\,000\,\mathrm{g\,mol^{-1}}$. The SAN samples have an acrylonitrile content from 5.4 to 55.6 wt% and the maleic anhydride content of the SMA varies from 8.5 up to 50 wt%.

Blend preparation

Up to 19.6 wt% MA in SMA, both copolymers, the SAN and the SMA were dissolved in 1,2-dichloroethane (total 5 wt% polymer in the solution). From 26.7 up to 50 wt% MA in SMA, all blends were dissolved in butan-

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2-one. For light scattering experiments the solution was cast onto a cover glass and the solvent evaporated room temperature and dried in a vacuum oven at 90°C. The samples for d.s.c. measurements were precipitated into methanol for blends containing up to 19.6 wt% MA in SMA. If the MA content was higher, the blends were precipitated into petroleum ether.

Laser light scattering

The cover glass was placed into a high-temperature cell and the intensity of the scattered light was measured vertically with respect to the incident beam. The cloud points were determined at three different heating rates. For the design of the binodals the values were extrapolated to a zero heating rate. The same method was used as previously described[6].

D.s.c. measurements

A Perkin-Elmer DSC-4 equipped with a data station was used. Measurements were made under N_2 with a heating rate of 10°C min^{-1} and the mass of the samples was about 10 mg. The specimens were annealed at about 200°C for 2 min before the measurements were carried out.

FTi.r. measurements

The *FT*i.r. spectra were obtained using an IRF 180 (ZWG of the Academy of Science of GDR) equipped with a Ge/KBr beam splitter, triglycine sulphate (TGS) detector and a dry nitrogen purge. Spectra were recorded at a resolution of 2 cm^{-1} and a mirror velocity of 0.126 cm s^{-1}. A minimum of 100 scans were accumulated for each spectrum. The samples were prepared by casting the polymer solutions (1 wt% of total polymer in 1,2-dichloroethane) onto a KBr plate.

RESULTS AND DISCUSSION

Firstly, the area of miscibility of the copolymers as a function of the copolymer compositions of SAN and SMA was established. A broad range of copolymer compositions was used to prepare 50:50 (wt%) blends.

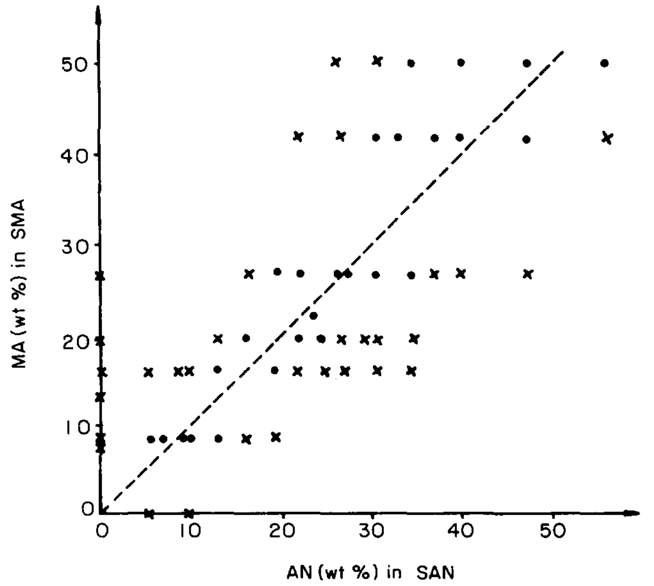

Figure 1 Occurrence of one or two glass transitions depending on the copolymer composition: (●) one glass transition; (×) two glass transitions; (---) 45° line

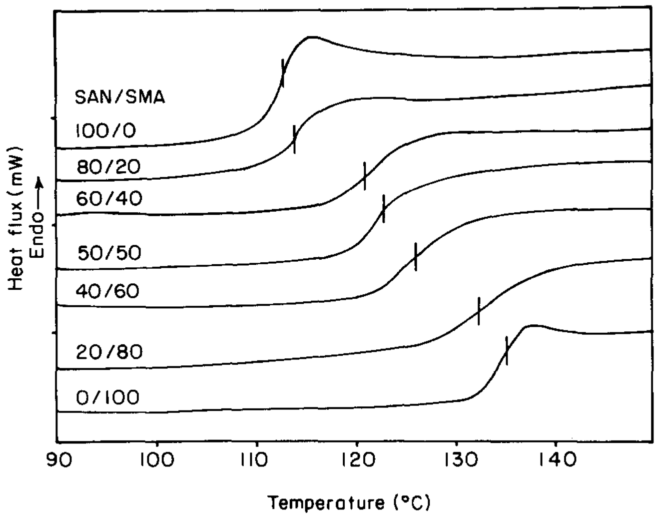

Figure 2 The shape of the glass transition of blends of SAN-16.2 and SMA-16.0 as a function of the blend ratio

Unfortunately, the copolymer SMA can only be prepared up to about 50 mol% maleic anhydride in the copolymer[7]. These 50:50 blends were used for glass transition measurements. The results are reported in *Figure 1*. It can be seen that miscibility, indicated by one glass transition, occurs near the 45° line, i.e. at nearly equal amounts of styrene in SAN and SMA (in wt%). For zero content of AN or MA, respectively, two glass transitions are always detected. It follows that neither SMA nor SAN is miscible with polystyrene, even if the copolymer contains only small amounts of the second component. By variation of the blend ratio in miscible blends, one observes that the glass transition is broadened with increasing SMA content. An example for SAN-16.2/SMA-16.0 blends is depicted in *Figure 2*. The code SAN-16.2 means an SAN with an AN content of 16.2 wt% and analogously SMA-16.0 means an SMA with 16.0 wt% MA. The dependence of the glass transition temperature on the blend ratio can be approximated by the Fox equation[8] (cf. *Figure 3*). As depicted in *Figure 1* a certain SMA blended in a 50:50 ratio with different SAN copolymers results in immiscible, miscible and again immiscible blends with increasing AN content. This behaviour is analogous to the occurrence of a miscibility window in copolymer/homopolymer blends[9]. In regions near the crossing from miscible to immiscible blends, a lower critical solution temperature (*LCST*) is usually found. A widely used method for the detection of *LCST* behaviour is the following. A blend with a single glass transition is heated above the *LCST* and afterwards rapidly quenched. In the case of *LCST* behaviour two glass transitions occur in the d.s.c. trace[10]. Using this method we found only a noticeable broadening of the glass transition but a quantitative determination of two glass transition temperatures was impossible, owing to the small difference in the glass transition temperatures of the two components (about 40 K). Therefore, measurements with laser light scattering and optical microscopy observations were carried out. Two examples are depicted in *Figure 4*. This method was applied for the determination of the binodal points of several 50:50 blends. Keeping the composition of SMA constant and varying the composition of SAN, a miscibility window can be designed (cf. *Figure 5*). Variation of the

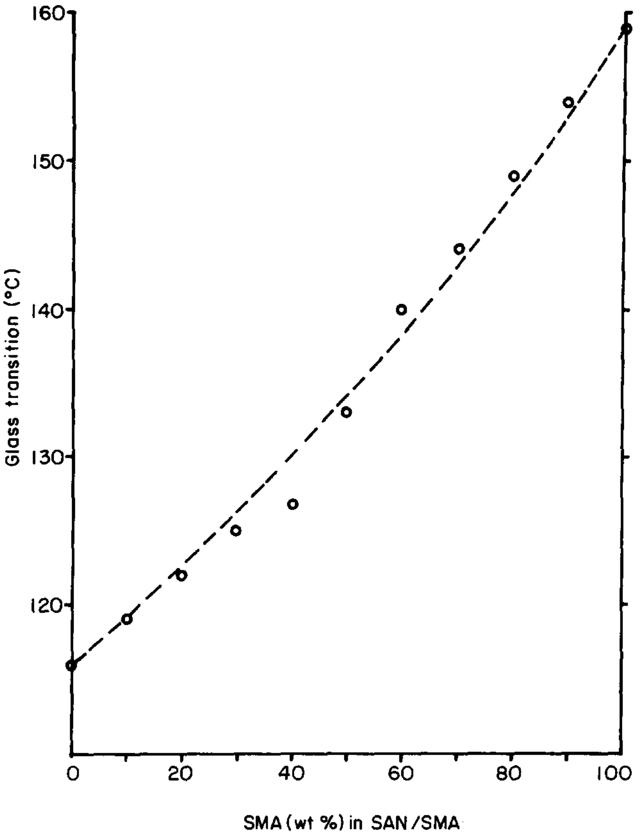

Figure 3 Dependence of the glass transition temperature on the blend ratio for SAN-23.8/SMA-21.6 blends: (O) measured values; (---) calculated by Fox equation

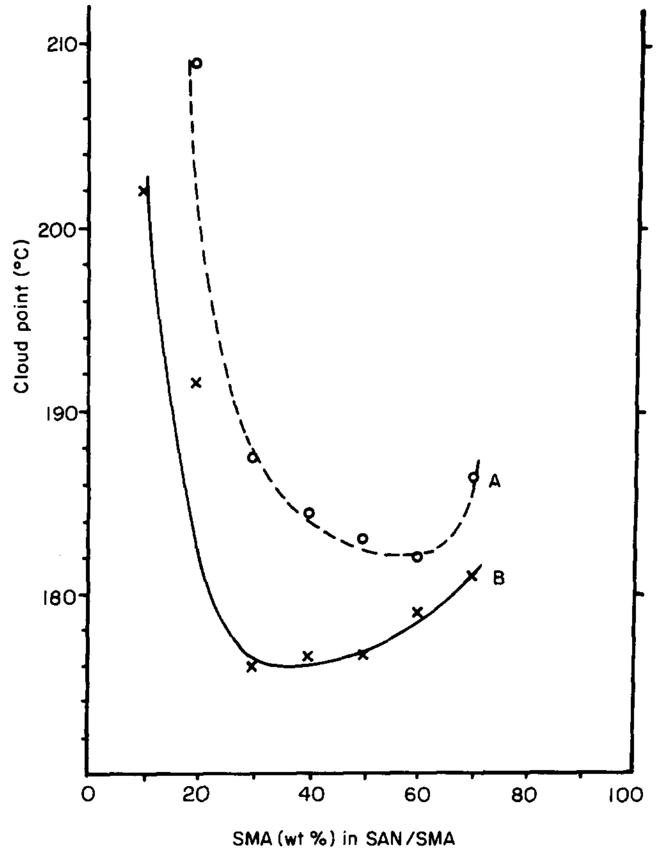

Figure 4 Binodals for SAN-31.5/SMA-19.6 (curve A) and SAN-24.0/SMA-16.0 (curve B) blends determined by light scattering

composition of SMA results for different MA contents in similar windows of miscibility. The left-hand curve is estimated considering one blend that is completely immiscible at room temperature and a second blend completely miscible without demixing up to the decomposition. The right-hand curve reflects a relatively wide range of copolymer compositions with *LCST* behaviour. Using all critical data from light scattering measurements, a three-dimensional diagram for 50:50 blends can be designed (cf. *Figure 6*).

Above the binodal temperature a regularly highly interconnected two-phase structure occurs[6]. The occurrence of these structures was only observed for

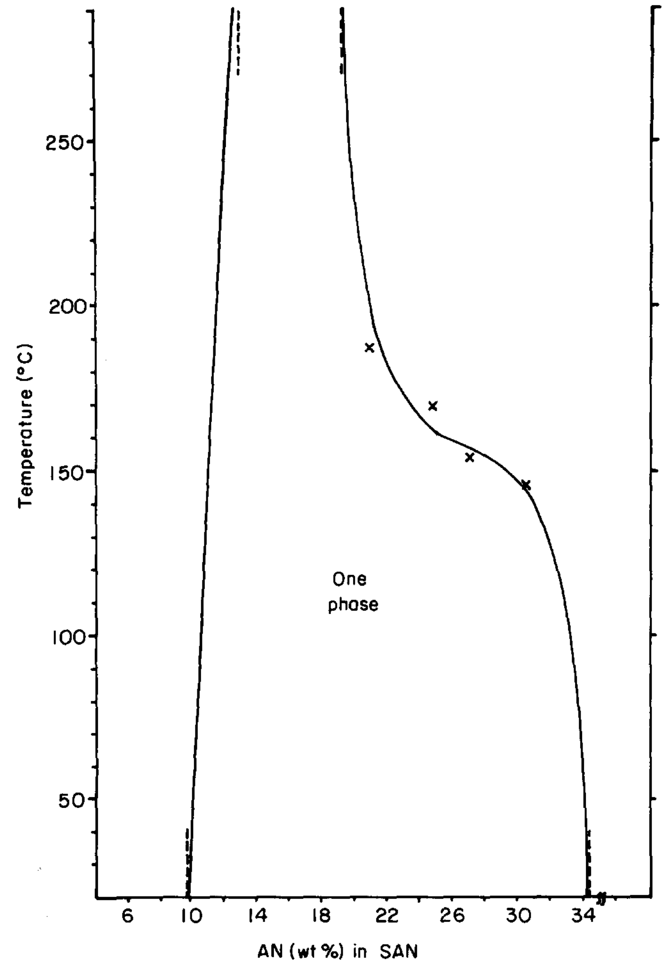

Figure 5 Miscibility window of 50:50 blends of SMA-16.0 and different SAN copolymers. The centre region between the curves is the area of miscibility

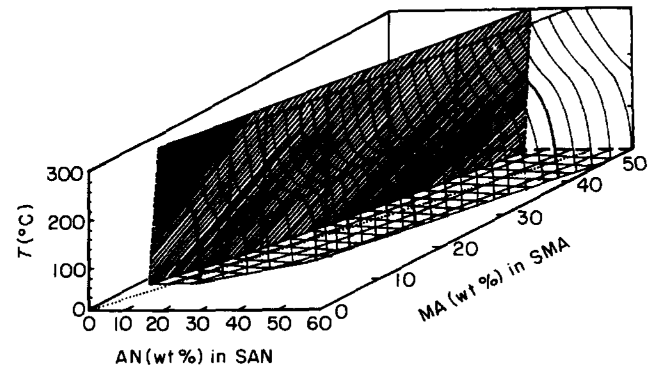

Figure 6 Miscibility channel of SAN/SMA polymer blends as a function of temperature and copolymer composition

blends exhibiting a very broad glass transition in the d.s.c. traces.

As mentioned above, according to the calculations of Paul and Barlow[4] polyacrylonitrile and a hypothetical poly(maleic anhydride) should be miscible, since specific intermolecular interactions lead to a negative contribution to the enthalpy of mixing. Therefore, the role of specific inter- and intramolecular interactions was studied by *FT*i.r. spectroscopy. Small shifts of the bands can be detected if one digitally subtracts the infra-red spectrum of the pure copolymer from that of the blend[11]. It should be emphasized that the relative absorbances of the two spectra must be comparable. *Figure 7* shows the carbonyl stretching of an SMA copolymer, an SAN/SMA 50:50 blend and a residual spectrum obtained by subtracting the spectra of the copolymer and the blend. The derivative-type difference band in *Figure 7* is very small but always reproducible. The residual observed here is somewhat similar to that of the carbonyl stretching of poly(β-propyllactone)/poly(vinyl chloride) blends[12]. The small shift may be caused by dispersion effects[11]. That this effect originates from specific intermolecular interactions as reported elsewhere[4] cannot be confirmed. But another interesting effect is observable. The γ-CH vibration of the styrene shows a significant shift as depicted in *Figure 8*. The residual spectrum obtained by subtracting the spectra of the pure copolymers SAN-19.2 and SMA-19.6 from the spectrum of the SAN/SMA 50:50 blend shows a peak at about 700 cm^{-1}. It follows that the styrene units in SMA and SAN, respectively, are influenced differently by the respective comonomers.

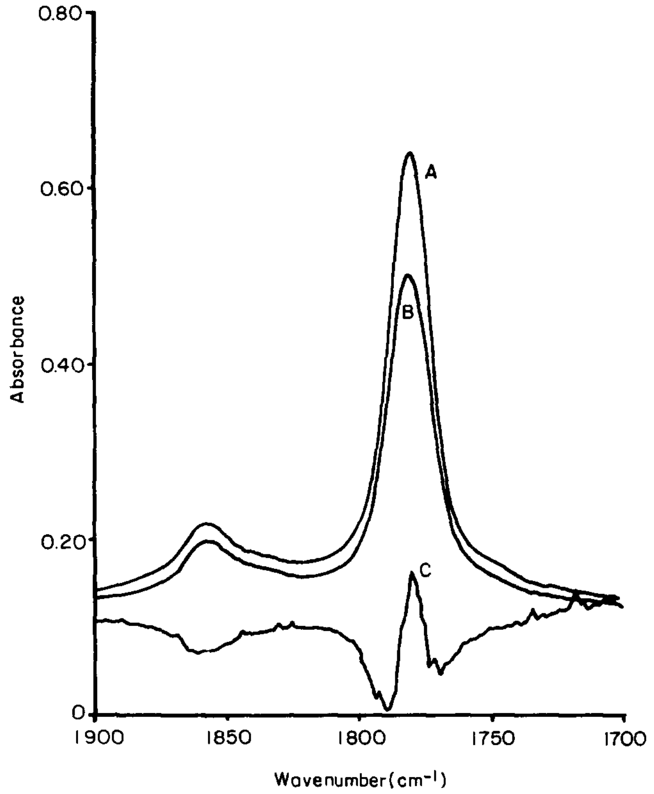

Figure 7 Carbonyl stretching at 1780 cm^{-1} for a miscible 50:50 blend of SMA-19.6/SAN-19.2 (curve A), for SMA-19.6 (curve B), and the residual spectrum (C) obtained by subtracting B from A (expanded by factor 4)

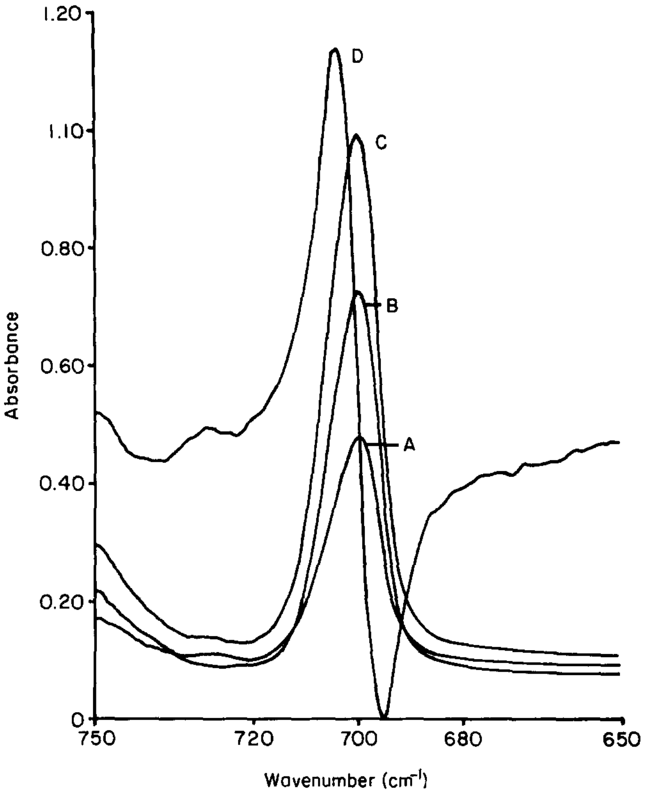

Figure 8 *FT*i.r. spectra overlay plot of the CH out-of-plane deformation region of styrene: curve A, SAN-19.2/SMA-19.6 50:50 blend; curve B, SAN-19.2; curve C, SMA-19.6; curve D, residual spectrum obtained by subtracting B and C from A (expanded by factor 20)

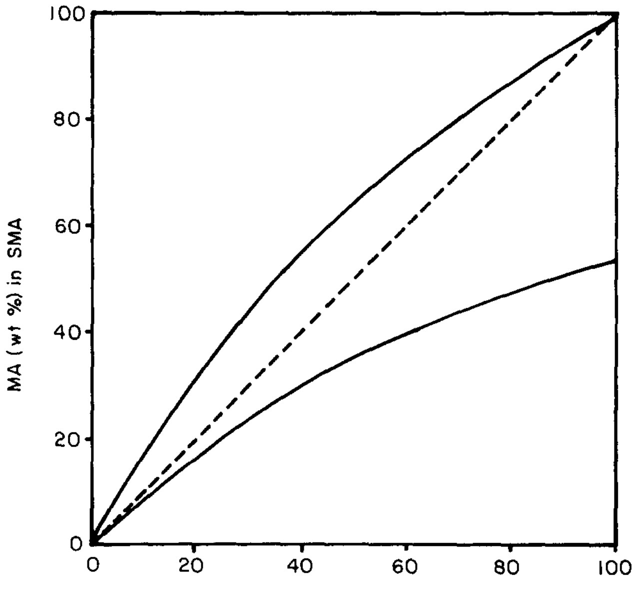

Figure 9 Miscibility map for the SAN/SMA blend. The curves were calculated with $\chi_{SAN} = 0.1$, $\chi_{ANMA} = 4 \times 10^{-4}$ and $\chi_{SMA} = 0.18$ in the infinite molecular limit

To estimate the individual segmental interaction parameters, we pursued the following course. According to *Figure 4* the *LCST*s occur to a good approximation at $\phi_c = 0.5$ (ϕ being the volume fraction). Furthermore, the combinatorial entropy of mixing is negligible. Then the stability limit for miscibility is characterized by $X_{AB} = 0$ (see equation (3)). In a previous paper[13] we reported a window of miscibility in blends of poly(methyl methacrylate) and SAN. From the binodals the interaction parameter of the S/AN pair, χ_{12}, has been estimated as 0.1. Using the copolymer compositions indicated in *Figure 4* and applying $\chi_{12} \approx 0.1$ equation (3) provides simultaneously the parameters χ_{13} and χ_{23}, viz.:

$$\chi_{13} = 0.18 \qquad \chi_{23} = 4 \times 10^{-4} \qquad (5)$$

This result deviates largely from that of Paul and Barlow[4]. However, it basically agrees with our spectroscopic studies that there are no specific interactions leading to $\chi_{23} < 0$. The parameters of equation (5) can be used to construct a map of miscibility of the two copolymers. This is shown in *Figure 9* as a function of the copolymer compositions (in wt%). The domain of miscibility is bounded by curves intersecting at the origin.

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