polymer communications

Observation of restricted miscibility in binary blends of poly(styrene-*stat*-acrylonitrile) and poly(α-methyl styrene-*stat*-acrylonitrile)

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Binary blends of two structurally similar copolymers poly(styrene-*stat*-acrylonitrile) and poly(α-methyl styrene-*stat*-acrylonitrile) were examined by differential scanning calorimetry. A miscibility map constructed for the system showed that the miscibility range was quite restricted and had a significant molecular weight dependence. The system was characterized by using segmental interaction energy densities calculated from earlier work and it was found that a satisfactory description of the miscibility range could only be obtained if a distinction was made between the 'intra' and 'inter' segmental interaction parameters. This sensitivity of the interchange energy to the environment of the segment has been observed in other systems. Consequently it may be an important feature in blends whose miscibility ranges are strongly molecular weight dependent, whereas in less sensitive blends the approximation $B_{ij}(\text{inter}) = B_{ij}(\text{intra})$ is adequate.

(Keywords: miscibility; blends; molecular weight dependence)

Introduction

Copolymers of poly(styrene-*stat*-acrylonitrile), SAN, have been found to be miscible with numerous other polymers and copolymers[1–6]. These blends are usually miscible within certain clearly defined composition ranges for the SAN, when mixed with a second component, and by establishing these miscibility limits experimentally it is possible to derive the segmental interaction energy density parameters B_{ij} for the system, provided at least one B_{ij} is known from other measurements. A structurally related copolymer is poly(α-methyl styrene-*stat*-acrylonitrile), MSAN, and it has been observed that if this is used as a component in blends the miscibility behaviour is often similar to that displayed when SAN is used. This is perhaps not too surprising as polystyrene can form miscible blends with poly(α-methyl styrene) if both the component molecular weights[7,8] are $< \sim 80000$, and acrylonitrile, AN, is the common unit in both copolymers. This might lead one to expect that SAN and MSAN will themselves mix over the entire composition range and can be interchanged in all blends with impunity, but this is not so. An examination of binary blends of these two copolymers reveals that only a limited composition range is available to SAN and MSAN if miscible blends are to be obtained. Details of this observation are given here.

Experimental

Copolymers. The synthesis of a wide range of SAN and MSAN samples has been described elsewhere[3,9]. Details of copolymer compositions, molecular weights, and glass transition temperatures, T_gs, for the samples used in this study are listed in *Table 1*.

Blend preparation. Blends were prepared by co-precipitation, using ethanol as a non-solvent, of 50/50 wt% mixtures of SAN and MSAN dissolved in methyl ethyl ketone (MEK). Blends were collected as powders and dried under vacuum for at least 2 days prior to use.

Blend miscibility. The criterion defining a miscible blend was taken to be the presence of only one T_g, whereas blends exhibiting the two T_g values characteristic of each component were deemed to be immiscible. The T_g for the blend was measured by differential scanning calorimetry (d.s.c.) using a Perkin Elmer DSC 4 and was taken to be the onset temperature of the base line shift in the thermogram, measured at a heating rate of 20 K min^{-1}. As the T_g values for some of the SAN/MSAN blends were quite close together, the physical ageing method suggested by Bosma *et al.*[10] was used to resolve the d.s.c. thermograms.

When necessary, physical ageing of the blends was accomplished by annealing the sample at 5 K below the lower T_g for times of up to 118 h. The longer times were required when the component T_gs were very close together (e.g. SAN 24 and SAN 30 blended with MSAN 46) and if immiscible, can only be resolved when long ageing times are used.

After annealing, the samples were quenched and a d.s.c. measurement was run again. As an enthalpy relaxation peak normally appears after ageing, the blend is considered miscible if only one such enthalpy relaxation peak is seen. If two peaks develop then the blend is immiscible.

Molecular weights. Number average molecular weights were measured using a Knauer membrane osmometer with MEK as solvent.

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Table 1 Compositions, molecular weights and glass transition temperatures for SAN and MSAN samples

Copolymer	AN (vol%)	$10^4 M_n$	T_g (K)
SAN 13	11.9	17.5	373
SAN 17	15.2	18.3	381
SAN 24	21.8	15.4	386
SAN 30	27.5	7.1	383
SAN 34	31.3	13.8	385
SAN 37	34.0	40.0	386
SAN 46	42.8	14.2	386
SAN 67	64.5	20.0	388
MSAN 12	10.9	3.65	431
MSAN 17	14.9	1.59	401
MSAN 24	20.8	2.60	399
MSAN 28	25.3	3.16	398
MSAN 33	29.0	7.85	397
MSAN 37	34.0	2.80	390
MSAN 46	42.3	6.07	388
MSAN 52	47.9	5.52	386

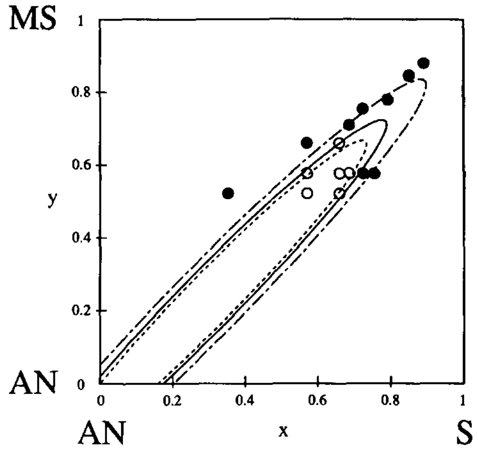

Figure 1 Miscibility map for various blends of SAN and MSAN plotted as a function of the volume fraction of styrene (x) and α-methyl styrene (y) in the copolymers. Miscible blends (○); immiscible blends (●); B_{crit} values of (····) 0.0, (——) 0.061, and (·–·) 0.1 J cm^{-3}

Results and discussion

The system under discussion is an example of a blend of two copolymers with a common monomer, i.e. (A_xB_{1-x}) mixed with (C_yB_{1-y}), and the experimental data plotted on the x–y composition plane as shown in *Figure 1* show the range of miscible and immiscible blends obtained. The miscibility limits can be defined using a conic section to fit the miscibility area as described elsewhere[11] and the relevant equation for systems with a common monomer is given by

$$ax^2 + by^2 + cxy - B_{\text{crit}} = 0 \qquad (1)$$

Here $B_{\text{AB}} = a$, $B_{\text{BC}} = b$, $B_{\text{AC}} = a + b + c$ and B_{crit} is defined as

$$B_{\text{crit}} = \frac{RT}{2}(V_1^{-0.5} + V_2^{-0.5})^2 \qquad (2)$$

where V_i is the molar volume of component i.

The interaction between the copolymer segments i and j can be expressed as the interaction energy density B_{ij} which is related to the Flory–Huggins interaction parameter χ_{ij} by

$$B_{ij} = \frac{RT\chi_{ij}}{V_r} \qquad (3)$$

where V_r is a reference segment volume that can be defined as a fixed value chosen to be comparable to a polymer repeat unit.

Equation (1) corresponds to an ellipse whose centre is at the origin of the x–y coordinates, but curves restricted in this way could not be used to give a sensible fit to the perceived miscibility boundary when using the previously determined values of $B_{\text{S-AN}} = 22.8$ J cm^{-3} and $B_{\text{MS-AN}} = 22.3$ J cm^{-3}. One must then resort to the equation for a full ellipse, namely

$$ax^2 + by^2 + cxy + dx + ey + f = 0 \qquad (4)$$

and the relevant identities for the system are

$$B_{\text{S-AN}}(\text{intra}) = a; \qquad B_{\text{MS-AN}}(\text{intra}) = b$$

$$B_{\text{AN-AN}} = f + B_{\text{crit}} = 0$$

$$B_{\text{S-AN}}(\text{inter}) = a + d + f + B_{\text{crit}}$$

$$B_{\text{MS-AN}}(\text{inter}) = b + e + f + B_{\text{crit}}$$

$$B_{\text{S-MS}} = a + b + c + d + e + f + B_{\text{crit}}$$

An acceptable fit, as shown in *Figure 1* as the solid line curve, can be obtained for an appropriate $B_{\text{crit}} = 0.061$, but in order to obtain this it is necessary to distinguish between 'inter' and 'intra' segmental interactions. These were calculated to be $B_{\text{S-AN}}(\text{inter}) = 19.2$ J cm^{-3} and $B_{\text{MS-AN}}(\text{inter}) = 25.2$ J cm^{-3}, which are sufficiently different to be required by the 'fitting' procedure but not too different from the intersegmental parameters calculated previously. This differentiation has been found to be necessary for B_{ij} parameters describing other blends[12] and may be more important when the blends are not strongly miscible, i.e. if the miscibility region is sensitive to changes in the molecular weights of the components.

The idea that the segment interaction energies can depend on their environment has been propounded by others. Balazs *et al.*[13,14] have considered the effect of comonomer sequence distribution on the interaction parameters, similarly Cantow and Schulz[15,16] suggested that the configurational sequence distribution in a polymer could also influence the miscibility, whereas Ellis[17] found that the interactions of methylene groups in nylons depended on their location in the polymer chain. Thus the assumption of a unique value for pair wise segmental interaction energy is an approximation, which may not be valid in all cases, and may have to be refined when the environment of the segment becomes an important factor.

It should also be noted that there is a molecular weight dependence of the calculated miscibility boundary. Again referring to *Figure 1*, the dotted curve is calculated for infinitely large molecular weight samples and the miscibility range is reduced, whereas the chain line which predicts and encloses a larger miscibility area was calculated for a B_{crit} of 0.1 J cm^{-3}. Thus the component molecular weights could make a significant difference in the miscibility range observed in this system though this is mainly when the molecular weights are low.

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