Miscibility Studies of Poly(Styrene—co—Acrylonitrile) with Methyl Methacrylate Based Copolymers: Phase Behaviour and Interaction Parameters

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The compatibility of statistical styrene—acrylonitrile copolymers with methyl methacrylate—butyl methacrylate and methyl methacrylate—dodecyl methacrylate copolymers has been studied. It was confirmed that the miscibility in the system decreases with increasing size of the pendant alkyl group of the methacrylate in methyl methacrylate based copolymers.

There has been a strong interest in the miscibility of blends based on random copolymers [1—11], which often have more interesting phase behaviour than those formulated from corresponding homopolymers. Simple binary interaction models [12—15] provide a way to rationalize these effects through the concept of intramolecular interactions within these copolymers. The models also provide a useful framework for predicting blends with controlled phase structure [6]. An important step towards this is quantification of the various binary interaction parameters between the monomer units involved. A fruitful way of obtaining this information is to experimentally construct a map of the miscibility region as a function of copolymer composition which can be fitted to the model equation [6, 10] to give the segmental interaction parameters. *Cowie* and *Lath* [6] demonstrated the usefulness of a quantitative interaction parameters database in searching for miscible binary and ternary blends from homopolymers and copolymers made from the monomers styrene (S), acrylonitrile (AN), and methyl methacrylate (MMA).

In a number of papers, the phase behaviour of poly(styrene—co—acrylonitrile) (SAN) blended with poly(methyl methacrylate) (PMMA) and other poly(n-alkyl methacrylate)s has been studied and the miscibility up to poly(propyl methacrylate) was found [5]. The segmental interaction parameters of higher n-alkyl methacrylates with styrene, acrylonitrile, and methyl methacrylate can be determined from the observed miscibility between SAN and copolymers of methyl methacrylate with n-alkyl methacrylates by fitting the data to the model equations. In this contribution, we report on the phase diagrams for blends of SAN with statistical poly(MMA—co—butyl methacrylate (BMA)) and poly(MMA—co—dodecyl methacrylate (DoMA)) within wide ranges of copolymer compositions. Using the above-mentioned proce-dure we calculate the individual interaction parameters of the systems studied.

EXPERIMENTAL

The SAN copolymers used in this work are described in Table 1, while the MMA-based copolymers are listed in Table 2. The former were prepared in this laboratory and the details of the preparation are described in [16], while the latter were prepared by the copolymerization of appropriate monomers at 60 °C as low conversion products (conversion up to 5 %) using α,α'-azobisisobutyronitrile initiator. Both higher n-alkyl methacrylates (C_4, C_{12}) are from Aldrich, Steinheim (Germany), methyl methacrylate is the product of Chemical Works Žilina (Slovak Republic).

The copolymer compositions shown in Tables 1 and 2 were determined by elemental analysis. Copolymer

Table 1. Styrene—Acrylonitrile Copolymers Used

Copolymer		w_{AN}	$[\eta]$	$M_N \ 10^{-5}$
		mass %	cm^3 g^{-1}	g mol^{-1}
Poly(S—co—AN)	−5	5.5	—	1.10
	−10	9.6	59	—
	−13	12.9	—	3.49
	−15	14.4	—	—
	−16	15.5	—	4.00
	−18	18.8	60	—
	−20	20.4	—	1.34
	−30	28.6	49	—
	−31	30.2	—	—
	−40	39.1	50	—
	−55	52.9	39	
	−60	59.8	—	2.80
	−70	67.2	—	3.27

Table 2. Methyl Methacrylate Copolymers Used

Copolymer		w_{BMA} resp. w_{DoMA}	Conversion	$[\eta]$	M_N 10^{-5}
		mass %	%	cm^3 g^{-1}	g mol^{-1}
Poly(MMA—co—BMA)	−15	13.8	4.0	123	—
	−20	20.3	4.0	141	—
	−25	26.5	2.3	132	3.02
	−30	32.4	4.2	122	2.82
	−35	38.0	2.6	154	4.12
	−45	48.9	3.1	127	—
	−55	58.9	4.1	87	3.10
	−65	68.4	3.9	205	—
	−75	75.8	4.0	113	—
	−85	85.1	4.2	—	2.51
	−95	92.7	4.8	147	2.12
Poly(MMA—co—DoMA)	−10	11.7	3.4	—	2.72
	−15	17.9	3.4	—	—
	−20	22.2	4.1	132	2.83
	−30	30.9	4.2	—	2.12
	−40	38.7	4.8	150	—
	−50	52.1	5.4	158	—
	−60	62.8	5.0	162	3.10
	−70	71.5	6.8	139	2.71
	−80	79.3	6.0	140	—
	−85	85.6	5.2	110	—
	−90	90.1	5.7	93	2.85
	−95	95.7	5.6	70	2.72

samples were characterized by membrane osmometry (M_N) with N,N-dimethylformamide and toluene as solvents and by viscometry in butanone at 25 °C (limiting viscosity number $[\eta]$). Blends of the copolymers were prepared by solution casting from butanone onto glass plates and the cast films were dried under a stream of dry nitrogen at ambient temperature, followed by further drying at 120 °C for 2 days under vacuum. Depending on the composition of the copolymers, films cast from their blends were either transparent or opaque. Films which became opaque were judged as phase-separated blends due to the blend components incompatibility.

RESULTS AND DISCUSSION

The Flory—Huggins theory provides a simple expression for the free energy of mixing of two polymers. Two polymers are miscible if the interaction parameter χ_{blend} is less than a critical value defined as

$$\chi_{crit} = 1/2(1/N_1^{1/2} + 1/N_2^{1/2})^2 \qquad (1)$$

which is zero in the limit of high molecular masses, N_i is the degree of polymerization.

The interaction parameter for mixing of two statistical copolymers $A_{\varphi_A} B_{1-\varphi_A}$ and $C_{\varphi_C} D_{1-\varphi_C}$ is

$$\chi_{blend} = \varphi_A\varphi_C\chi_{AC} + (1 - \varphi_A)\varphi_C\chi_{BC} +$$
$$+\varphi_A(1 - \varphi_C)\chi_{AD} + (1 - \varphi_A)(1 - \varphi_C)\chi_{BD} -$$
$$-\varphi_A(1 - \varphi_A)\chi_{AB} - \varphi_C(1 - \varphi_C)\chi_{CD} \qquad (2)$$

where φ_i describes the copolymer composition in volume fractions and χ_{ij} are the segmental interaction parameters between the copolymer monomer units.

The boundary dividing copolymer compositions that form miscible blends from immiscible ones, i.e. when $\chi_{blend} = \chi_{crit}$ can be used to obtain information about the χ_{ij}. Table 3 shows χ_{ij} values for binary pairs of S, MMA, and AN calculated from the data of *Cowie* and *Lath* [6], obtained from the measured miscibility window of the system PMMA—SAN statistical copolymers.

Lath et al. [17, 18] determined χ_{ij} values for styrene and acrylonitrile with methacrylate monomer having various alkyl groups (up to propyl). These results revealed that the size and structure of the methacrylate alkyl group affects the interaction parameters with other monomer units. Here we are interested in the effect of longer n-alkyl groups (C_4, C_{12}) on interaction parameters with S, MMA, and AN using the val-

Table 3. Segmental Interaction Parameters χ_{ij} of Various Monomer Pairs

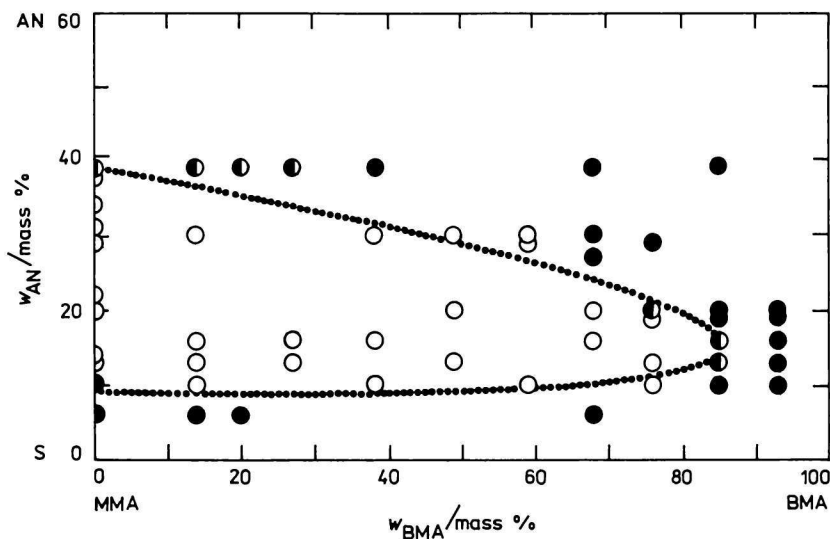| Monomer pair	χ_{ij}
S—AN	0.829
MMA—AN	0.46
S—MMA	0.03

Fig. 1. Miscibility map of $w_r = 50/50$ blends of MMA—BMA copolymers with SAN copolymers at room temperature: ○ miscible, ● phase-separated, ◐ partially miscible. The line represents the position where $\chi_{blend} = \chi_{crit}$, calculated by using χ_{ij} given in Tables 3 and 4.

ues of interaction parameters in Table 3 for the fitting procedure.

System SAN/P(MMA—BMA)

Fig. 1 illustrates how the miscibility of blends of SAN and P(MMA—BMA) depends on the composition of the two copolymers at room temperature. Fig. 1 includes also the SAN—PMMA blend results, along the zero BMA axis as presented in [6]. The blend composition used in this study to calculate χ_{ij} values is $w_r = 50/50$. This condition should be adopted for the blends of polymers having the same molecular mass. However, as shown in [10] these blends present reasonable results when the χ_{crit} value is small enough compared to the χ_{ij} values, which is the case of our study ($\chi_{crit} = 0.00075$ was calculated according to eqn (1), using copolymer molecular masses of samples close to the miscibility boundary). Recently *Nishimoto et al.* [10] published a miscibility boundary of the blends of SAN and P(MMA—*tert*-butyl MA) copolymer. Its comparison with Fig. 1 shows that the exchange of BMA with *tert*-butyl MA reduces the miscibility in the system: only statistical copolymers MMA—*tert*-butyl MA with *tert*-butyl MA content up to 50 mass % are miscible with SAN copolymers.

Because eqn (2) is elliptic function and provides only five independent equations, to estimate χ_{ij} values we need at least one χ_{ij} parameter from another source and then the other five parameters can be estimated by the curve-fitting method. In our case we applied the three segmental interaction parameters (Table 3) and following procedure was taken to determine segmental interaction parameters. The miscibility border is drawn by computer using the appropriate χ_{ij} values and the discrepancy between calculated misci-

Table 4. Determined Segmental Interaction Parameters χ_{ij} for Different Monomer Pairs

Methacrylates	χ_{ij}		
	MMA	S	AN
MMA	----	0.030	0.46
EMA	—	0.026	0.50
PrMA	—	0.017	0.57
BMA	0.01	0.020	0.62
DoMA	0.02	0.050	0.72

bility border and experimental results is shown, then the χ_{ij} values are readjusted finely to minimize the discrepancy. Because the densities of our copolymer samples were close to 1.0 g cm^{-3} in fitting procedure the mass fractions instead of volume ones were applied. The segmental interaction parameters optimally fitting the measured data are presented in Table 4.

System SAN/P(MMA—DoMA)

Fig. 2 presents the miscibility in the blends of SAN and P(MMA—DoMA) copolymers at room temperature. The comparison with Fig. 1 shows that the introduction of DoMA into the copolymer instead of BMA reduces the miscibility of the system significantly. The segmental interaction parameters were calculated by curve fitting and are listed in Table 4 together with segmental interaction data obtained from miscibility studies of poly(ethyl methacrylate (EMA)) and poly(propyl methacrylate (PrMA)) with statistical SAN copolymers [17, 18].

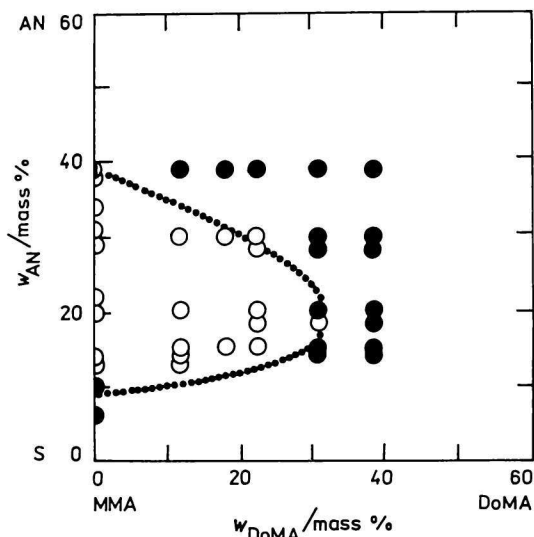All interaction parameters are repulsive and increase in magnitude with increasing the size of the

Fig. 2. Miscibility map of $w_r = 50/50$ blends of MMA—DoMA copolymers with SAN copolymers at room temperature. The denotations of points and the meaning of the line is the same as in Fig. 1.

pendant alkyl group of the methacrylate. Both interactions among various methacrylates with styrene and methyl methacrylate are only weakly repulsive as shown by their small positive χ values. On the other hand, the repulsive interactions between various methacrylates and acrylonitrile are much stronger and become more intense with increasing bulkiness of the methacrylate. These interactions together with strong repulsion within the SAN copolymer favour the appearance of the miscibility maps of SAN copolymers with methyl methacrylate based copolymers.

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