

Miscibility of Terpolymer/Copolymer and Terpolymer/Homopolymer Blend Systems

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ABSTRACT: Miscibility of binary blends of terpolymer of methyl methacrylate (MMA), acrylonitrile (AN) and styrene (MAS) and copolymer of St and AN (SAN), or MAS and PMMA was studied by light scattering experiments and optical microscope observation. Miscibility windows were calculated from solubility parameter on the basis of mean field approximations. The experimental results showed a good coincidence with the theoretical predictions of the miscibility window.

KEY WORDS Miscibility / Blend / Styrene and Acrylonitrile / Poly(methyl methacrylate) / Terpolymer /

Several studies¹⁻⁴ were reported on the miscibility of blends of copolymer, poly(A-co-B) with homopolymer, poly(C). It is known from preceding studies that the blend is miscible only in certain restricted composition ranges of the copolymer. These are systems in which the component homopolymers corresponding to the constituents of the copolymer, *e.g.*, poly(A) and poly(B), are not miscible with each other and neither with the homopolymer, poly(C), but when copolymerized there appears miscibility between copolymer and homopolymer. Mean field approximation by ten Brinke *et al.*⁵ succeeded in explaining this behavior quantitatively.

In this paper we investigated the miscibility of the blends of terpolymer of methyl methacrylate, acrylonitrile, and styrene (MAS) with copolymer of styrene and acrylonitrile (SAN), and with homopolymer of methyl methacrylate (PMMA), and tried to apply the mean field theory to the blends containing the terpolymer.

EXPERIMENTAL

MAS was synthesized by a bulk and an emulsion polymerization in our laboratory. PMMA and SAN were commercial grades of Sumitomo Chemical Co., Ltd. and Sumitomo Naugatuck Co., Ltd., respectively. Details of the samples were shown in Table I.

Compositions were determined by ¹³C NMR and molecular weight of samples were determined by a size exclusion chromatography equipped with a refractometer and a UV meter as detectors. Blends were prepared by dissolving two polymers into 1,2-dichloroethane and casting onto a slide glass at ambient temperature. Concentration of solution was 2% by weight. For cloud point measurement, casted films were pressed at 135°C and annealed at 135°C further for 1 day. The sample thickness was 0.1 mm for MAS/PMMA blends and 0.5 mm for MAS/SAN blends.

Both a Nikon Optiphotopol for the macroscopic observation and light scattering system equipped with a gonio-photometer (Optec Co.,

Table I. Characteristics of samples

Sample	Polymer composition/mol% ^a			Molecular weight ^b	
	AN	St	MMA	M_n	Q
MAS1	6.4	34.4	59.2	126000	3.6
MAS2	11.1	60.7	28.3	62200	5.5
MAS3	11.9	7.7	80.4	87900	2.0
MAS4	14.6	30.3	55.1	96800	4.5
MAS5	17.1	74.8	8.1	84200	4.3
MAS6	18.0	66.8	15.2	45600	2.0
MAS7	23.6	17.4	59.0	68700	2.0
MAS8	33.9	35.0	31.3	81500	1.9
MAS9	34.1	15.9	50.0	15700	6.7
MAS10	34.6	54.4	11.0	146000	4.5
MAS11	35.1	9.8	55.1	85900	1.9
MAS12	50.4	18.4	31.2	—	—
MAS13	37.2	—	62.8	—	—
MAS14	—	17.8	82.2	49.200	1.8
MAS15	—	49.6	50.4	43600	1.8
MAS16	—	81.3	18.7	27700	1.9
SAN1	45.0	55.0	—	48400	3.5
SAN2	46.5	53.5	—	68600	2.1
PMMA	—	—	100	72900	1.8

^a Calculated from ¹³C NMR spectrum.

^b Determined by size exclusion chromatography.

Ltd.) were used to judge the miscibility of blends. Order of observable immiscibility by these systems was 0.4–500 μm . Phase diagrams were obtained from the cloud point (CP) measurement using thermal optical analysis (TOA). CP was determined from the temperature at which decrease of transmitted intensity occurs during the temperature elevation. CP was measured at various rates of temperature elevation (1, 2, and 5°C min⁻¹), and phase separation temperature was obtained by the extrapolation to zero temperature elevation.

RESULTS AND DISCUSSION

First, phase diagrams were investigated for 50/50 blends of MAS/SAN and MAS/PMMA. It was found that MAS was miscible with SAN and with PMMA in certain MAS composition ranges as shown in Figures 1 and 2. Miscible ranges obtained experimentally for MAS/SAN1 blends became wider with increasing

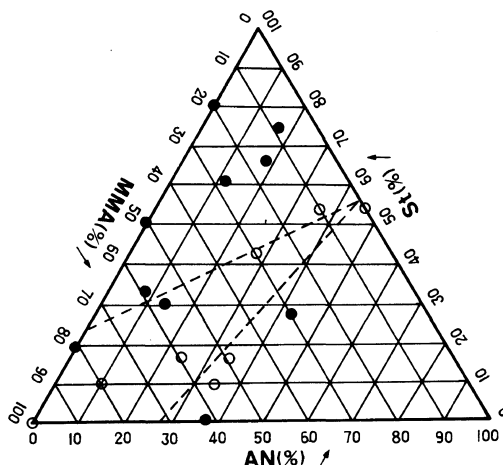


Figure 1. Influence of terpolymer composition on the miscibility of MAS/SAN1 blends at room temperature. The lines were calculated with values reported by Kammer *et al.* (see the text). Blend ratio was 50/50 by weight. O, miscible; ●, immiscible.

MMA content in MAS, in contrast to narrowing for MAS/PMMA blends. The results were considered to be mainly due to a

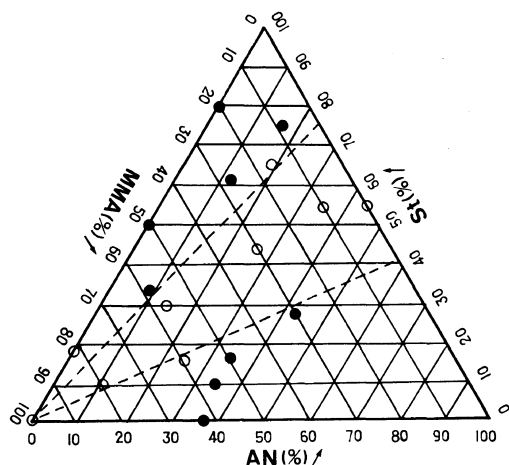


Figure 2. Influence of terpolymer compositions on the miscibility of MAS/PMMA blends at room temperature. The lines were calculated with values reported by Kammer *et al.* (see the text). Blend ratio was 50/50 by weight. ○, miscible; ●, immiscible.

relative strength in polarity among monomer segments. Theoretical calculations of polymer/polymer interaction parameter, χ , was tried according to ten Brincke's method.⁵⁾ In general, parameter of two random copolymers, [(A1)_{x1}(A2)_{x2}... (An)_{xn}] and [(B1)_{y1}(B2)_{y2}... (Bm)_{ym}], was calculated as follows,⁶⁻⁸

$$\chi = \sum_{i=1}^n \sum_{j=1}^m x_i y_j \chi_{A_i, B_j} - \sum_{i=1}^{n-1} \sum_{j=i+1}^n x_i x_j \chi_{A_i, A_j} - \sum_{i=1}^{m-1} \sum_{j=i+1}^m y_i y_j \chi_{B_i, B_j} \quad (1)$$

where x_i , y_j are volume fractions of segments, i and j , and $\chi_{i,j}$ is segmental interaction parameter between segments, i and j . Extending eq 1, χ parameter for MAS/SAN and MAS/PMMA were derived as follows.

$$\chi_{\text{MAS/PMMA}} = \chi_{13}\phi_1^2 + (\chi_{13} + \chi_{23} - \chi_{12})\phi_1\phi_2 + \chi_{23}\phi_2^2 \quad (2)$$

$$\chi_{\text{MAS/SAN}} = \chi_{23}\phi_1^2 + (\chi_{23} + \chi_{12} - \chi_{13})\phi_1\phi_2 + (0.55\chi_{13} - 1.45\chi_{23} - 0.55\chi_{12})\phi_1 + (0.45\chi_{13} - 1.55\chi_{12} - 0.45\chi_{23})\phi_2 + \chi_{12}\phi_2^2 - 0.428\chi_{13} + 0.45\chi_{23} + 0.55\chi_{12} \quad (3)$$

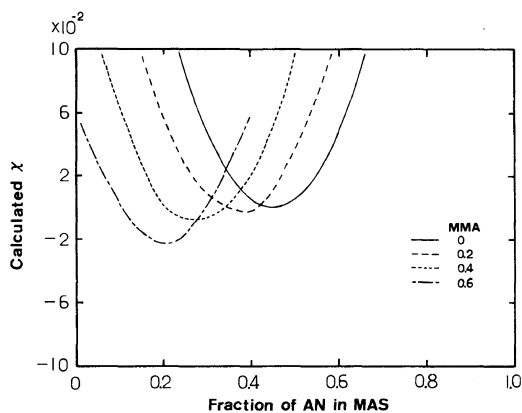


Figure 3. Calculated χ parameter dependence on MAS composition for MAS/SAN1 blends at room temperature.

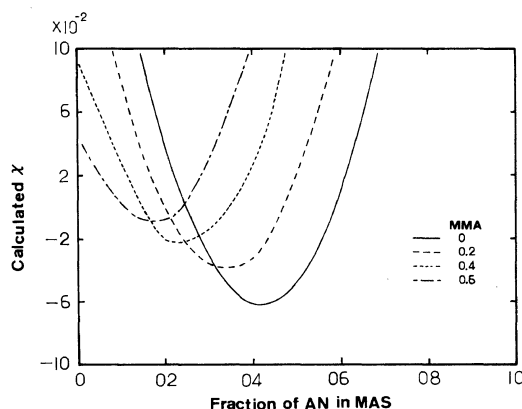


Figure 4. Calculated χ parameter dependence on MAS composition for MAS/PMMA blends at room temperature.

Here, 1, 2, and 3 denote AN, St, and MMA segments in MAS, respectively. ϕ_1 , and ϕ_2 are AN, and St segments in MAS, redefined as mole fraction. SAN1 composition were already taken into eq 3 as numeric values.

Chemical compositions of MAS at which χ parameter is equal to zero were calculated from eq 2 and 3, and shown in Figures 1 and 2 as broken lines. The region inside the broken lines, where χ values are negative, is thus considered to be the miscible region. Good agreement was obtained between the calculated region and the experimental one in case of using the segmental χ parameters proposed by Kammer *et al.*⁹

($\chi_{12}=2.13$, $\chi_{13}=0.66$, $\chi_{23}=0.31$). The effects of MAS composition on χ parameter were calculated for blends of MAS/SAN and MAS/PMMA and shown in Figures 3 and 4. It was observed that minimum of χ parameter for MAS/SAN blend became smaller with increasing MMA content in MAS, but larger for MAS/PMMA. This suggests that miscibility between MAS and SAN increases with incorporation of MMA segment into MAS, contrary to the blend of MAS and PMMA. Considering from eq 1, χ parameter between two kinds of polymers is determined by relative intensity of intermolecular and intramolecular interactions between two segments. Among three kinds of segmental interaction, the segment pair of AN–St has the most significant interaction ($\chi_{12}=2.13$) compared to those of St–MMA and AN–MMA ($\chi=0.31$ and 0.66 , respectively). Therefore, in the case of MAS/PMMA blend, the intramolecular interaction in MAS terpolymer is considered to have dominant influence on the miscibility because there is no significant intermolecular segment pair. The favourable interaction between AN and St in MAS is reduced with the increase of MMA content in MAS, resulting in the increase of χ parameter between MAS and PMMA. On the other hand, in the case of MAS/SAN blend, the unfavourable intermolecular segmental interaction between AN and St is reduced with the increase of MMA content in MAS, which makes this blend system stable. Although, the favourable interaction in MAS is reduced, too, this might not contribute so much as intermolecular one because of relatively small fraction of AN–St pair in MAS.

Phase diagrams for MAS8/SAN2 and MAS8/PMMA blend were depicted in Figure 5, together with SAN2/PMMA blend. All blends exhibited LCST-type phase behaviour. Phase separation temperatures of MAS8/SAN2 blends were higher than these of PMMA/SAN2 blends. Those of MAS8/PMMA blends were also higher than those of PMMA/SAN2 blends. This behaviour seems

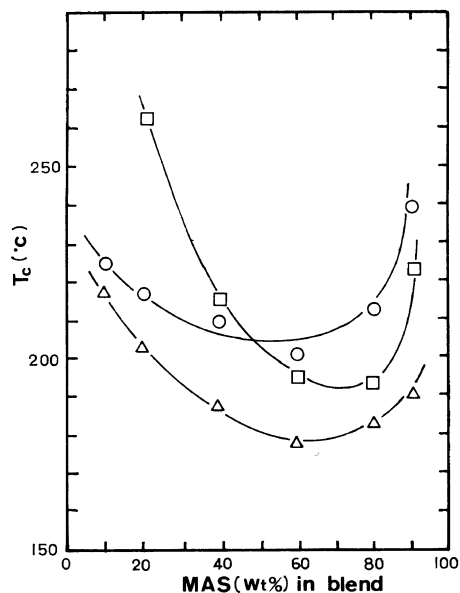


Figure 5. Phase diagrams of MAS8/SAN2 (○), MAS8/PMMA (□), and PMMA/SAN2 (△), determined by TOA method. ϕ denotes MAS % in MAS/SAN and MAS/PMMA blends, and SAN % in PMMA/SAN blend.

to be in conflict with the calculated results shown in Figures 3 and 4 if the temperature dependence of χ parameter for each blend was the same. The reason of this phenomenon seems to be the difference of the reduced free volume between MAS blend (MAS8/SAN2, MAS8/PMMA) and PMMA/SAN2 blend, which consequently influence χ parameter through the equation $\chi = \chi_H + \chi_F$. Here, χ_H and χ_F are enthalpic and the free volume difference terms, respectively. The latter term is considered to have larger contribution relative to the former term at high temperature,¹⁰ which might cause the difference in the temperature dependence of χ parameter. Actually PMMA and SAN would have different thermal expansion coefficient. To discuss this problem quantitatively, phase diagram at equilibrium is necessary as indicated in recent reports.^{11,12} Further works from this viewpoint is in progress now and will be published elsewhere.

CONCLUSION

1) Phase diagrams of the blends of terpolymer (MAS) with copolymer (SAN) and terpolymer with homopolymer (PMMA) were investigated, and the effect of terpolymer composition on the miscibility was studied both experimentally and theoretically.

2) Applicability of mean field approximation to the blends containing the terpolymer was successfully demonstrated.

3) Phase separation temperature of the blend containing the terpolymer was higher than that of the blend containing homopolymer. This phenomenon may be due to the reduced free volume difference between these blends.

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