Effect of Copolymer Composition on the Compatibility of Blends of Styrene—Acrylonitrile Copolymers with Polymethacrylates

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Received 14 October 1993

Dedicated to Professor Dr. J. Schurz in honour of his 70th birthday

The miscibility of three polymethacrylates with poly(styrene—co—acrylonitrile) (SAN) has been studied. Poly(n-propyl methacrylate) is miscible with SAN copolymers having acrylonitrile contents between 9 mass % and 24 mass %, but poly(n-butyl methacrylate) and poly(n-octyl methacrylate) are immiscible with SAN. It was confirmed that the width of the miscibility window decreases with increasing size of the pendant alkyl group of the polymethacrylate.

Polymer blends have been of great interest particularly in the last ten years. The enhanced activities are related to both the hope of producing advanced high-performance materials and the need for basic knowledge on their phase behaviour. At one time the compatibility of two polymers was considered a rarity because the combinatorial entropy on mixing is very small and the miscibility of polymer pairs is most often the result of an exothermic heat of mixing due to specific interactions in the system.

In the last decade studies of polymer—polymer miscibility have focused on systems involving random copolymers. In contrast to polymer blends involving homopolymers only, it is believed that specific interactions are not a necessary requirement for miscibility, which may be enhanced by the interaction of dissimilar segments in the random copolymer chain [1—4]. The interaction parameter χ_{blend} for a blend of homopolymer A with copolymer BC is expressed by the equation

$$\chi_{\text{blend}} = y\chi_{\text{AC}} + (1 - y)\chi_{\text{AB}} - y(1 - y)\chi_{\text{BC}} \qquad (1)$$

where y is the volume fraction of C in the copolymer and χ_{AB}, χ_{AC}, and χ_{BC} are the segmental interaction parameters. If the interaction between segments B and C is sufficiently strong (*i.e.* sufficiently positive), a negative χ_{blend} can result even when χ_{AB} and χ_{AC} are positive. The χ parameters contain all the contributions to the Gibbs free energy of mixing except for the ideal entropy of mixing. Hence, not surprisingly, they are complicated functions of composition and temperature. One of the principal goals of these studies on random copolymer blends is to reach a stage where it is possible to predict polymer—polymer miscibility on the basis of a database of χ parameter values. Despite of limitations, the predictive scheme based on available χ parameter values has been quite successful so far, mainly because the values are apparently not too sensitive to the assumptions involved in their evaluation. The precise location of the so-called windows of miscibility may differ from the predicted location, but the effect is usually only a slight shift of the miscibility window borderline. This has been demonstrated convincingly by a large body of experimental results in recent review papers by *Cowie* [5] and *Kammer et al.* [6].

Statistical styrene—acrylonitrile copolymers are miscible with a variety of different homo- and copolymers [7], which gives a simple way for creating the database of χ-parameters. Systematically was studied their compatibility with halogen- (chloromethyl- [8], 2-chloroethyl- [9], 3-chloropropyl- [10], and 2-bromoethyl- [11]), n-alkyl- (methyl- [12—14] and ethyl- [7]), and hydroxyl-containing (hydroxyethyl and hydroxypropyl [15]) polymethacrylates. It was generally found that the width of the miscibility windows decreases with the increasing size of the pendant alkyl group of the polymethacrylate. Further the miscibility of poly(styrene—co—acrylonitrile) (SAN) copolymers with poly(tetrahydrofurfuryl methacrylate) [16], poly(cyclohexyl methacrylate) [17], poly(tetrahydropyranyl-2-methyl methacrylate) [18], and poly(acetonyl methacrylate) [19] was confirmed.

The aim of our contribution is to determine the binary segmental interaction parameters from the phase separation of poly(n-propyl, n-butyl, and n-octyl methacrylate)s with SAN copolymers and to compare the results obtained with the SAN copolymers—polymethacrylates systems studied.

EXPERIMENTAL

Materials

The SAN copolymers used were prepared by photo-initiated copolymerization at the presence of naphthalene [20] as low-conversion materials, thereby keeping the chemical heterogeneity very low. Molecular characteristics of the SAN copolymers are summarized in Table 1. Poly(n-propyl, n-butyl, and n-octyl methacrylate)s were unfractionated samples from Roehm and Haas Co., Darmstadt, FRG and their molecular parameters are also collected in Table 1.

Table 1. Molecular Characteristics of the Materials Used

Sample	w(AN)/mass %	$M_N \cdot 10^{-5}$ / g mol^{-1}	Conversion
1	6.4	1.75	5.6
2	8.5	0.64	7.3
3	12.9	3.49	7.5
4	15.5	4.00	4.5
5	20.4	2.85	5.0
6	23.4	4.26	7.1
7	29.4	6.26	7.8
8	31.1	4.33	7.0
9	33.8	5.32	6.8
	$M_m \cdot 10^{-5}$ / g mol^{-1}	$M_N \cdot 10^{-5}$ / g mol^{-1}	T_g/K
Poly(n-propyl-methacrylate)	5.85	3.66	320
Poly(n-butyl-methacrylate)	5.12	3.01	297
Poly(n-octyl-methacrylate)	7.26	2.85	227

Blend Characterization

Films of composition w_r = 50 : 50 were cast from butanone solutions (4—5 mass %) in a closed box under dry nitrogen atmosphere at room temperature. The films obtained were first dried under an infrared lamp and finally in a vacuum oven at 350 K for 3 d.

The glass transition temperatures, T_g, of the samples and blends were determined using a Perkin—Elmer DSC-2 differential scanning calorimeter, scanning at 20 K min^{-1}.

The blend miscibility was monitored using the criteria that a miscible blend exhibited one T_g and was prepared as a transparent film (determined visually) whereas a phase-separated blend showed the T_g for both components and the film was cloudy.

The temperature at which phase separation occurred on heating (cloud point) for blends exhibiting lower critical solution temperature (LCST) behaviour was detected visually on the microscope hot stage using a heating rate of 10 K min^{-1} as the temperature, where the first milky turbidity of the original transparent film appeared.

RESULTS AND DISCUSSION

SAN—Poly(n-Propyl Methacrylate) Blends

From miscibility measurements using the T_g values and optical properties it was found that only poly(n-propyl methacrylate) (PnPMA) forms miscible blends with SAN copolymers. Both poly(n-butyl methacrylate) and poly(n-octyl methacrylate) with SAN copolymers gave hazy films and DSC measurements showed two T_g's, indicating the two-phase nature of these blends, for all copolymer samples studied.

From the miscibility data for SAN—poly(n-propyl methacrylate) blends, a miscibility window was determined and the phase boundary compositions were established. The results are presented in Table 2. This table shows that poly(n-propyl methacrylate) forms one-phase blends with SAN copolymers in the copolymer composition range of 9 to 24 mass % acrylonitrile; the copolymer composition range in both binary blends SAN—poly(methyl methacrylate) and SAN—poly(ethyl methacrylate) is much broader (up to 39 mass % AN and 34 mass % AN, respectively) [12, 7]. Also the shape of the miscibility window is different from both of the above-mentioned systems; in binary blend SAN—poly(n-propyl methacrylate) miscibility "chimney" is absent. Both findings confirm that poly(n-propyl methacrylate) interacts less strongly with SAN copolymers than poly(methyl methacrylate) and poly(ethyl methacrylate).

The comparison with the results of the SAN—poly(n-propyl methacrylate) blends [21] shows that the width of our miscibility windows is slightly narrower. The differences in boundary composition (low acrylonitrile content SAN copolymers) are probably due to the differences in chemical polydispersity and the use of tetrahydrofuran, which is a thermodynamically less favourable solvent than butanone, due to its hygroscopicity [22].

Table 2. Cloud Points Used for the Determination of the Miscibility Window

w(AN in SAN) / mass %	T_g/K	Cloud point/K
6.4	378 + 321	Cloudy
8.5	347	520
12.9	345	528
15.5	349	483
20.4	350	458
23.4	346	443
29.4	377 + 322	Cloudy
31.1	374 + 318	Cloudy
33.8	378 + 320	Cloudy

Segmental Interaction Parameters

The miscibility behaviour of homopolymer—copolymer blends depends on various segmental interactions. Based on the binary interaction model, the interaction parameter χ_{blend} for the present system is given by eqn (*1*). The criterion for miscibility is that $\chi_{\text{blend}} < \chi_{\text{crit}}$ where

$$\chi_{\text{crit}} = \frac{1}{2}\left(\alpha_1^{-1/2} + \alpha_2^{-1/2}\right)^2 \qquad (2)$$

with α_1 and α_2 being the degrees of polymerization of the two polymers. For the binary blend studied $\chi_{\text{crit}} = 0.00075$ and since $\chi_{\text{S—AN}}$ is 0.829 [12], other χ values can be evaluated. For the SAN—poly(n-propyl methacrylate) system and phase boundaries determined, the values of $\chi_{\text{S—nPMA}}$ and $\chi_{\text{nPMA—AN}}$ are then 0.017 and 0.57, respectively.

For the sake of comparison, the χ values and miscibility ranges for the SAN blends with various n-alkyl- and chlorine-containing methacrylates are shown in Table 3. The interactions among various methacrylates with styrene are only weakly repulsive as shown by the small positive χ values, being slightly higher for chlorine-containing methacrylates and the interaction decreases slightly in magnitude with increasing size of the pendant group of the methacrylate. On the other hand, the repulsive interactions between various methacrylates and acrylonitrile are much stronger, and the interaction becomes more intense with increasing bulkiness of the methacrylate. Both interactions are relatively small, so the appearance of a miscibility window for SAN copolymers with polymethacrylates is favoured by strong repulsion within the SAN copolymer.

Table 3. Segmental Interaction Parameters for the Systems SAN—Polymethacrylates

Methacrylate	Miscibility range	χ	
	w(AN)/mass %	with styrene	with acrylonitrile
Methyl	9—39 [12]	0.030	0.46
Ethyl	9—34 [7]	0.026	0.50
n-Propyl	9—24	0.017	0.57
n-Butyl	Immiscible	–	–
n-Octyl	Immiscible	–	–
Chloromethyl	12—37 [8]	0.037	0.49
2-Chloroethyl	12.5—43 [9]	0.045	0.43
3-Chloropropyl	12—35 [10]	0.034	0.53

Acknowledgements. The authors are grateful to the Slovak Grant Agency for Science (Grant No. 2/999052/93) for partial supporting of this work.

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Translated by D. Lath