

Miscibility of polyarylate copolymers with poly(styrene-co-acrylonitrile)

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The miscibility of random copolymers of bisphenol-A polyarylate and tetramethyl bisphenol-A polyarylate (PAR-co-TMPAr) with poly(styrene-co-acrylonitrile) (SAN) was studied based on the glass transition behaviour measured by differential scanning calorimetry. Analysis of the miscibility map by using the mean field theory showed that the intramolecular repulsion between styrene and acrylonitrile units in SAN gives a large contribution to the miscibility of PAR-co-TMPAr and SAN. © 1997 Elsevier Science Ltd. All rights reserved.

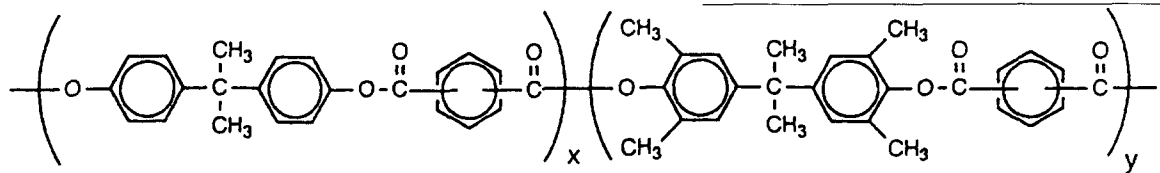
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INTRODUCTION

The exothermic heat of polymer blending can originate not only from intermolecular specific interactions, such as hydrogen bonding but also from intramolecular repulsions¹. A minor modification in chemical structure of polymer can cause the enhanced intermolecular or intramolecular interaction necessary to obtain a miscible system.

Polycarbonate (PC), polyarylate (PAR), and polysulfone are not miscible with poly(styrene-co-acrylonitrile) (SAN). However, when the bisphenol-A units of these polymers are substituted by tetramethyl bisphenol-A units, SANs are miscible with these tetramethyl bisphenol-A based polymers for certain ranges of acrylonitrile (AN) content²⁻⁵.

PC was reported to be miscible with tetramethyl bisphenol-A polycarbonate⁶. In our preliminary study, PAR was found to be immiscible with tetramethyl bisphenol-A polyarylate (TMPAr). Therefore there will be intramolecular repulsion in the random copolymer of PAR and TMPAr (PAR-co-TMPAr) with the following chemical structure:



In this paper, the miscibility behaviour of PAR-co-TMPAr/SAN blends is reported, and intermolecular or intramolecular interactions are analysed.

EXPERIMENTAL

Information about the polymers used in this study is given in Table 1. The TMPAr was prepared as described previously². Tetramethyl bisphenol-A synthesized⁷ in our laboratory and terephthaloyl chloride/isophthaloyl chloride (50/50) dissolved in dry chloroform were cooled down in an ice bath. As soon as triethylamine was added dropwise to the solution while stirring, an exothermic reaction took place. After 7 h, the reaction mixture was poured into 10-fold methanol, and the filtered precipitate was repeatedly refluxed in methanol to remove the triethylamine-hydrochloride salt complex formed during the reaction. The purified product was filtered and dried under reduced pressure at 80°C for 72 h. PAR-co-TMPAr was synthesized using the same method at various molar ratios of bisphenol-A and tetramethyl bisphenol-A. The TMPAr repeating unit content in PAR-co-TMPAr was determined by ¹H nuclear magnetic resonance (n.m.r.) analysis. SAN was prepared by the bulk radical copolymerization of freshly distilled styrene and acrylonitrile at 60°C using benzoyl peroxide as an initiator. The AN content in SAN was determined by elemental

analysis. The absolute weight average molecular weight of TMPAr determined by Zimm's plot method⁸ using light scattering data was 20 800, which was similar to the value obtained by gel permeation chromatography (g.p.c.). The other molecular weights were determined by g.p.c. and calibrated with polystyrene standards.

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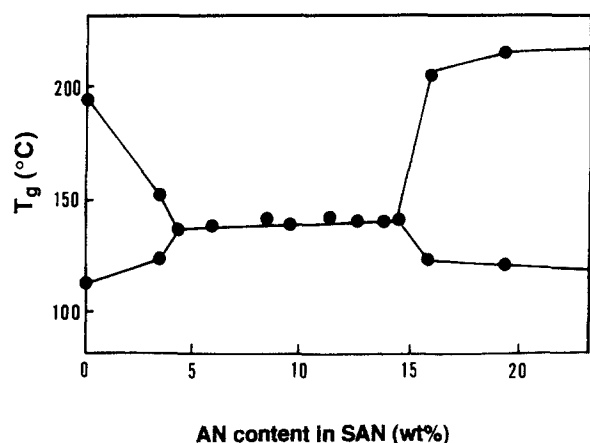
Table 1 Characteristics of polymers used in this study

Polymer	Copolymer designation	Copolymer composition ^a (wt% AN or mol% TMPAr)	T_g^b (°C)	Molecular weight ^c	Source
Tetramethyl bisphenol-A polyarylate	TMPAr	100.0	225	$M_n = 11\,100$	Synthesized
Polystyrene	PS	0.0	104	$M_n = 85\,000$	Synthesized
Poly(styrene-co-acrylonitrile)	SAN 3	3.5	106	$M_n = 96\,500$	Synthesized
Poly(styrene-co-acrylonitrile)	SAN 4	4.2	108	$M_n = 92\,000$	Asahi Chemical Co.
Poly(styrene-co-acrylonitrile)	SAN 6	5.7	109	$M_n = 77\,300$	Dow Chemical Co.
Poly(styrene-co-acrylonitrile)	SAN 7	7.1	108	$M_n = 72\,000$	Synthesized
Poly(styrene-co-acrylonitrile)	SAN 9	8.6	107	$M_n = 98\,000$	Asahi Chemical Co.
Poly(styrene-co-acrylonitrile)	SAN 10	9.5	109	$M_n = 94\,700$	Synthesized
Poly(styrene-co-acrylonitrile)	SAN 12	11.5	108	$M_n = 87\,700$	Asahi Chemical Co.
Poly(styrene-co-acrylonitrile)	SAN 13	12.7	108	$M_n = 87\,000$	Synthesized
Poly(styrene-co-acrylonitrile)	SAN 14	13.9	107	$M_n = 74\,000$	Synthesized
Poly(styrene-co-acrylonitrile)	SAN 15	14.7	109	$M_n = 83\,400$	Synthesized
Poly(styrene-co-acrylonitrile)	SAN 16	15.5	111	$M_n = 87\,100$	Dow Chemical Co.
Poly(styrene-co-acrylonitrile)	SAN 18	17.8	112	$M_n = 71\,100$	Monsanto Co.
Poly(styrene-co-acrylonitrile)	SAN 20	19.5	111	$M_n = 84\,300$	Dow Chemical Co.
Poly(styrene-co-acrylonitrile)	SAN 25	25.0	113	$M_n = 73\,700$	Dow Chemical Co.
Poly(styrene-co-acrylonitrile)	SAN 30	30.0	122	$M_n = 121\,000$	Monsanto Co.
PAr-co-TMPAr	TMPAr 95	92.2	224	$M_w = 23\,400$	Synthesized
PAr-co-TMPAr	TMPAr 90	86.5	223	$M_w = 24\,100$	Synthesized
PAr-co-TMPAr	TMPAr 85	80.0	221	$M_w = 22\,900$	Synthesized
PAr-co-TMPAr	TMPAr 80	77.3	220	$M_w = 23\,500$	Synthesized
PAr-co-TMPAr	TMPAr 70	66.7	219	$M_w = 24\,500$	Synthesized
PAr-co-TMPAr	TMPAr 50	43.5	216	$M_w = 26\,800$	Synthesized
PAr-co-TMPAr	TMPAr 30	27.1	208	$M_w = 26\,200$	Synthesized
PAr-co-TMPAr	TMPAr 10	8.0	202	$M_w = 28\,400$	Synthesized
Bisphenol-A polyarylate	PAr	0.0	199	$M_w = 29\,600$	Synthesized

^a Determined by CHN analysis or ¹H n.m.r. analysis

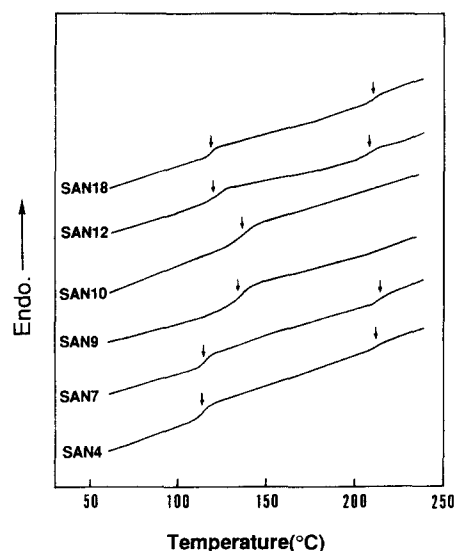
^b Measured by d.s.c.

^c Measured by g.p.c. relative to PS standards


Figure 1 T_g s of TMPAr/SAN (50/50 by weight) blend

Polymer blends were prepared by a dissolution-precipitation method. The polymers were dissolved in methylene chloride at a concentration of 5% (w/v). This solution was added to an excess (10-fold) amount of methanol, causing a rapid precipitation. The precipitate was filtered and dried under vacuum at 80°C for 72 h.

Thermal analysis was performed at a heating rate of 20°C min⁻¹ with samples weighing 10–15 mg, using a Perkin-Elmer DSC-4 differential scanning calorimeter


Figure 2 D.s.c. thermograms of TMPAr 85 blends (50/50 by weight) with various kinds of SANs

(d.s.c.). Before each scan all the samples were annealed for 3 min at 250°C to erase previous thermal histories, and cooled down to 50°C at a cooling rate of 20°C min⁻¹. The glass transition temperature (T_g) was taken at the

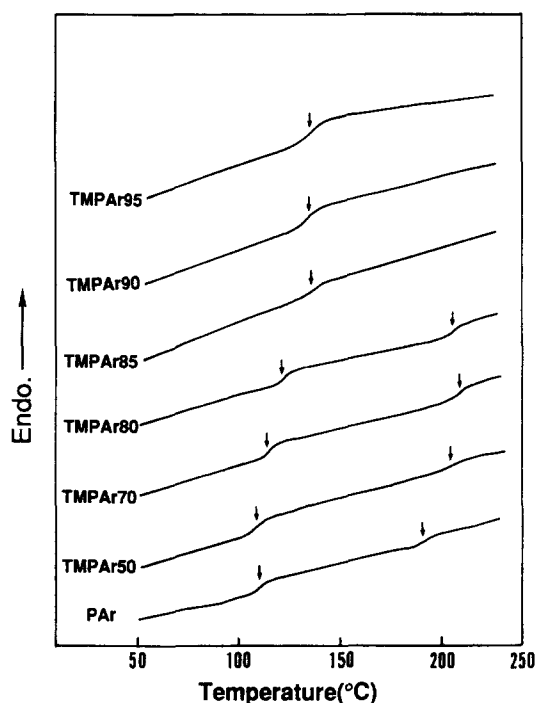


Figure 3 D.s.c. thermograms of SAN 10 blends (50/50 by weight) with various kinds of PAR-co-TMPAr

half-weight of the heat capacity change during the next heating from 50°C to 250°C.

RESULTS AND DISCUSSION

T_g s measured by d.s.c. for TMAPr blends with various kinds of SANs (50/50 by weight) are shown in Figure 1. The TMAPr/PS blend has two separate T_g s being inner shifted toward each other compared with the T_g s of the two pure components. This inner shift is more evident in the TMAPr/SAN 3 blend, showing an enhanced partial miscibility. When the AN content in SAN is in the range of 4–15 wt%, the TMAPr/SAN blend has a single glass transition, at a temperature between the T_g s of the component polymers, indicating miscibility of the two

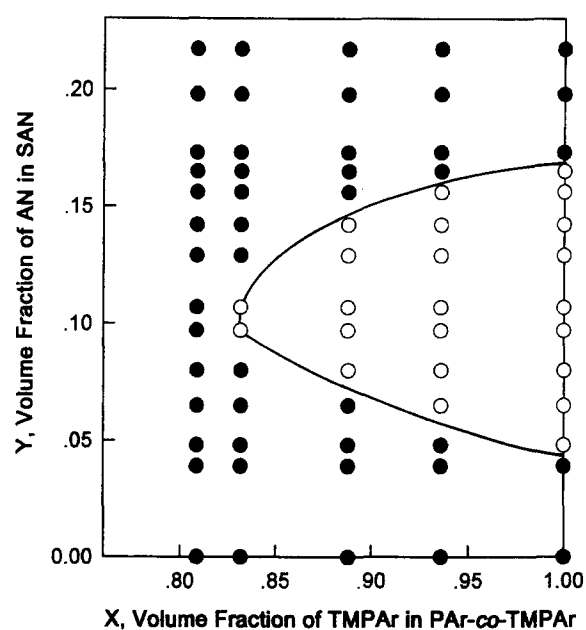


Figure 4 Miscibility map of PAR-co-TMPAr/SAN blends (50/50 by weight): ●, double T_g ; ○, single T_g

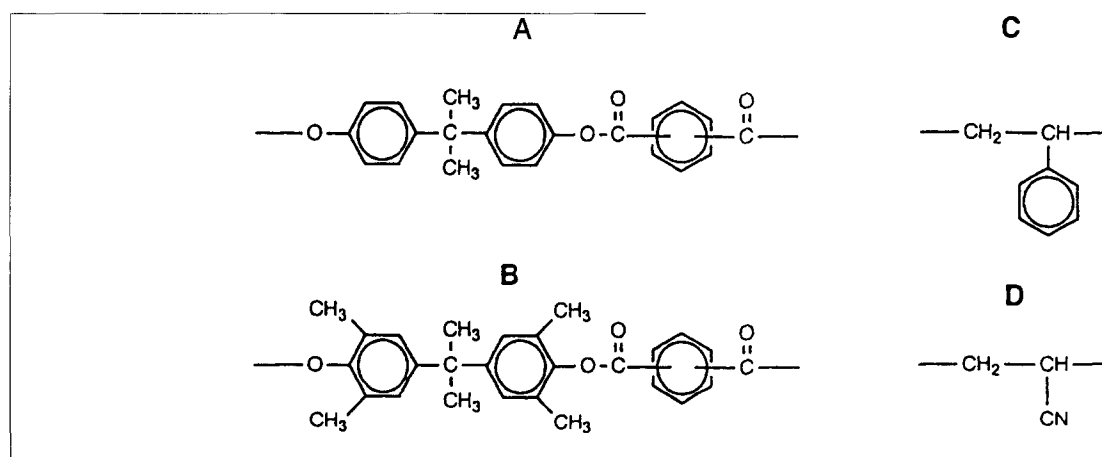
than 85 wt%. The miscibility behaviour based on T_g measurements of PAR-co-TMPAr/SAN blends (50/50 by weight) are summarized in Figure 4.

According to the mean field approximation^{9–11}, in binary miscible blends of random copolymers represented by $(A_{1-x}B_x)_n$ and $(C_{1-y}D_y)_m$, the net interaction energy parameter, B_{blend} is given by the following equation

$$B_{blend} = (1-x)(1-y)B_{AC} + y(1-x)B_{AD} + x(1-y)B_{BC} + xyB_{BD} - x(1-x)B_{AB} - y(1-y)B_{CD} \quad (1)$$

where the six interaction parameters, B_{ij} s, are the binary interaction parameters for the various units, and x and y are the volume fractions of constituent repeating units in the copolymers¹².

For the present case, we make the following assignments:



polymers. In Figure 2 we can observe that TMAPr 85 is miscible only with SAN 9 and SAN 10. In Figure 3, it can be seen that SAN 10 is miscible with PAR-co-TMPAr only when the content of TMAPr repeating units is more

At the miscibility–immiscibility boundary¹³, the following equation can be applied

$$B_{blend} = B_{crit} = 0 \quad (2)$$

Table 2 Interaction parameters between various repeating units

Interaction pair	B_{ij} (J cm ⁻³)
TMPAr-PAr	1.28
TMPAr-St	0.52
TMPAr-AN	23.64
PAr-St	2.51
PAr-AN	20.55
St-AN	28.14 ^a

^a Ref. 14

where B_{crit} is the conformational entropy contribution and is expressed in terms of the copolymer molar volumes V_{AB} and V_{CD} by

$$B_{\text{crit}} = (1/2)RT(V_{\text{AB}}^{-1/2} + V_{\text{CD}}^{-1/2})^2 \quad (3)$$

Using equation (1), equation (2) can be transformed to the following equation

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

where $a = B_{\text{AB}}$, $b = B_{\text{CD}}$, $f = B_{\text{AC}} - B_{\text{crit}}$, $a + d + f = B_{\text{BC}} - B_{\text{crit}}$, $b + e + f = B_{\text{AD}} - B_{\text{crit}}$, and $a + b + c + d + e + f = B_{\text{BD}} - B_{\text{crit}}$. In Figure 4, the curve at the miscibility-immiscibility boundary can be described by the following equation

$$1.28x^2 + 28.14y^2 - 5.08xy + 0.71x - 5.02y + 0.22 = 0 \quad (5)$$

B_{ij} values determined by comparing equations (4) and (5) are given in Table 2. In this procedure, the reported interaction energy parameter B_{ij} value between styrene and AN repeating units, 28.14 J cm⁻³, and the calculated (ref. 14) value of B_{crit} 0.3024 J cm⁻³ were used.

From Table 2, we can see that the repulsion between

repeating units increases in the following order:

$$\text{TMPAr-St} < \text{TMPAr-PAr} < \text{PAr-St} \\ < \text{PAr-AN} < \text{TMPAr-AN} < \text{St-AN}$$

The miscibility window in our system is thought to be the consequence of the high value of $B_{\text{St-AN}}$, which exceeds the other interaction parameters, and of the low value of $B_{\text{TMPAr-St}}$, which may be due to four substituted methyl groups in TMPAr.

ACKNOWLEDGEMENT

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