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Miscibility of poly(styrene-co-acrylonitrile) with random copolymers of tetramethyl bisphenol-A polyarylate and tetrabromo bisphenol-A polyarylate

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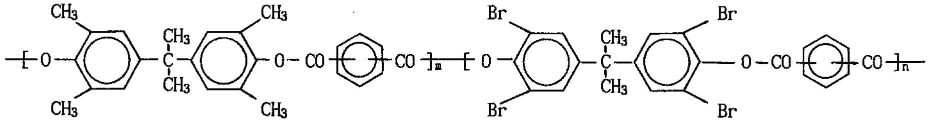
Summary

Tetramethyl bisphenol-A polyarylate(TMPAR) was miscible with poly(styrene-co-acrylonitrile)'s(SANs) containing 4, 7, 10, and 13wt% of acrylonitrile(AN) repeating unit. As the content of tetrabromo bisphenol-A polyarylate(TBPAR) repeating unit in the random copolymer of TMPAR and TBPAR was increased, the miscibility window in the blends with SANs was narrowed. The intramolecular repulsion between styrene and AN repeating units in SAN was suggested to be the main driving force for the miscibility of SANs with the random copolymers of TMPAR and TBPAR.

Introduction

The prediction of miscibility behavior of polymer blends has been a continuous subject of interest for researchers during the past two decades from both industrial and academic viewpoints. There has been much interest in polymer blends in which one or both of the component polymers are random copolymers(1,2), because the effect of the variation of the copolymer composition on the miscibility behavior of blends can be studied systematically. For blends based on copolymers, it has been reported that intramolecular repulsive interaction as well as intermolecular specific interaction play an important role in determining miscibility behavior(3,4).

In our previous paper(5), we reported that tetramethyl bisphenol-A polyarylate(TMPAR) showed somewhat different miscibility behavior from that of polyarylate in blends with poly(styrene-co-acrylonitrile)(SAN). That is, TMPAR was miscible with SANs for a certain range of acrylonitrile(AN) content. In this paper, we report the results from our study on the blends of SANs with the random copolymers of TMPAR and tetrabromo bisphenol-A polyarylate(TBPAR). The schematic structure of the random copolymer of TMPAR and TBPAR(TMPAR-co-TBPAR) is shown below:



Experimental

TMPAR-co-TBPAR was synthesized in chloroform in the presence of acid acceptor, triethylamine at 15℃. That is, 1:1 mixture of terephthaloyl chloride and isophthaloyl chloride was reacted with tetrabromo bisphenol-A for 2hr, and further reacted for 4hr after the addition of tetramethyl bisphenol-A to complete copolymerization. The reaction mixture was poured into 10-fold of methanol and the filtered precipitate was refluxed for 20hr to remove the triethylamine hydrochloride(salt complex) formed during the reaction. The purified product was filtered and dried under vacuum at 80℃.

The SANs were synthesized at 60℃ by bulk radical copolymerization of freshly distilled styrene monomer with a known amount of AN comonomer(6). The intrinsic viscosity, [η] of the synthesized polymers was measured in chloroform at 25℃.

The TMPAR-co-TBPAR/SAN blends were prepared by a dissolution-precipitation method. The polymers(50/50 by weight) were dissolved in methylene chloride for 1hr to give a concentration of 5%(w/v). These solutions were added to an excess(10-fold) amount of methanol, causing a rapid precipitation. The precipitates were filtered off and dried under vacuum at 65℃.

Glass transition temperature(T_g) was measured by differential scanning calorimetry (Dupont DSC-910) and defined as the temperature at the half height of heat capacity change. Sample weights were 10.0±0.5mg. Samples were heated to 280℃ from 50℃ followed by cooling down to 10℃. T_g was determined in the next heating cycle to 280℃. Heating and cooling rates were both 20℃/min.

Table 1 shows the characteristics of the TMPAR-co-TBPARs and SANs.

Results and Discussion

The results from T_g measurements are shown in Table 2. TMPAR blends with SAN4, SAN7, SAN10, and SAN13 show single T_g's located at midway between those of homopolymers, indicating miscibility between constituent polymers. However TMPAR blends with PS and SAN16 show two separate T_g's being inner shifted compared with the T_g's of the two pure components. This show that there exists phase separation with partial miscibility in these blends(7). As the content of TBPAR repeating unit in TMPAR-co-TBPAR increases, the number of miscible pair reduces. TBPAR40 is miscible only with SAN7 and all TBPAR60 blends with SANs have two separate T_g's. The miscibility map of TMPAR-co-TBPAR/SAN blends from T_g behavior is summarized in Figure 1.

According to the mean field approximation of miscibility in binary mixtures of random copolymers represented by $(A_xB_{1-x})_n$ and $(C_yD_{1-y})_m$, the net interacion energy parameter, B_{blend} is given by the following equation (1):

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

where B_{ij} are interaction parameters for repeating unit i and j, and x and y are the volume fractions of constituent repeating units in the copolymers(8,9).

The miscibility-immiscibility boundary is determined by the condition:

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

where B_{crit} is the conformational entropy contribution and is expressed in terms of the copolymer molar volumes V_i by:

$$B_{crit} = \frac{1}{2} RT \left(V_1^{-0.5} + V_2^{-0.5} \right)^2 \qquad (3)$$

Using equation (1), equation (2) can be transformed as follows:

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

where $a=B_{AB}$, $b=B_{CD}$, $f=(B_{BD}-B_{crit})$, $(a+d+f)=(B_{AD}-B_{crit})$, $(b+e+f)=(B_{BC}-B_{crit})$, and $(a+b+c+d+e+f)=(B_{AC}-B_{crit})$.

The B_{ij} values that fit rightly miscibility-immiscibility boundary shown in Figure 1 were determined by trial-error method and are shown in Table 3. In this procedure, we

Table 1. Characteristics of polymers used

TMPAR-co-TBPAR				SAN			
Designation	TMPAR content^a (wt%)	[η] (dL/g)	T_g (℃)	Designation	AN content^b (wt%)	[η] (dL/g)	T_g (℃)
TMPAR	0	0.274	215	PS	0	0.423	104
TBPAR10	10	0.272	206	SAN4	4	0.688	106
TBPAR20	20	0.357	220	SAN7	7	1.115	98
TBPAR30	30	0.347	224	SAN10	10	1.294	100
TBPAR40	40	0.301	212	SAN13	13	1.276	110
TBPAR60	60	0.278	205	SAN16	16	1.339	110
TBPAR80	80	0.250	220				
TBPAR	100	0.256	252				

^{a}determined by NMR
^{b}determined by elemental analysis

Table 2. T_g of TMPAR-co-TBPAR/SAN(50/50) blend

TMPAR-co-TBPAR	T_g(℃)					
	TMPAR-co-TBPAR blends with					
	PS	SAN4	SAN7	SAN10	SAN13	SAN16
TMPAR	109, 211	135	140	134	122	115, 206
TBPAR10	111, 215	127	133	138	120, 210	114, 212
TBPAR20	108, 218	136	143	139	120, 215	114, 218
TBPAR30	105, 210	119, 214	132	133	117, 216	114, 218
TBPAR40	107, 217	117, 215	130	123, 215	122, 212	115, 211
TBPAR60	106, 212	112, 220	118, 220	120, 215	117, 216	114, 213
TBPAR80	102, 220	116, 215	116, 213	118, 218	117, 214	119, 212
TBPAR	105, 252	107, 252	106, 252	106, 252	110, 251	111, 250

Table 3. Values of B_{ij}

ij	B_{ij}(J/cm^3)
TMPAR-styrene	0.22
TMPAR-AN	22.34
TBPAR-styrene	0.75
TBPAR-AN	24.32
TMPAR-TBPAR	0.32
styrene-AN	28.14

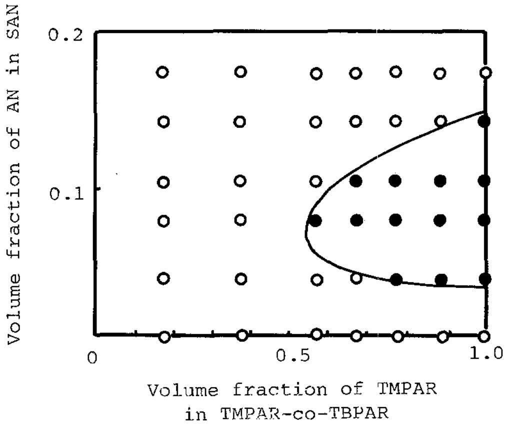


Fig. 1. Miscibility map of TMPAR-co-TBPAR/SAN blends(50/50), (○);double T_g, (●);single T_g.

used the reported B_{ij} value between styrene and AN repeating units, 28.14J/cm^3(9). B_{crit} was roughly estimated to be 0.302J/cm^3 by assuming the molecular weight of TMPAR-co-TBPAR and SAN to be 10000 and 100000, respectively.

The results in Table 3 show that the intramolecular repulsion between styrene and AN segments in SAN is the main driving force for the miscibility of TMPAR-co-TBPAR and SAN.

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