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Miscibility of Poly(phenyl acrylate) with Acrylonitrile/Styrene Copolymers

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ABSTRACT: The glass transition and phase behavior of blends of poly(phenyl acrylate) with poly(acrylonitrile-*co*-styrene) was studied by differential scanning calorimetry. It was found that poly(phenyl acrylate) is miscible with poly(acrylonitrile-*co*-styrenes) within a specific range of copolymer composition. The segmental interaction parameters were estimated and found to be positive for all three pairs. The miscibility in this system appears to be the consequence of the intramolecular repulsion between styrene and acrylonitrile units.

Introduction

There is considerable interest in the study of polymer blends in recent years due to their wide technological importance. For high molecular weight polymers, the entropy contribution to the free energy of mixing is negligible, and hence, the miscibility is primarily governed by energetic considerations emanating from the secondary forces between the constituents of the blends.[1,2] It has, however, been demonstrated, in blend systems consisting of a homopolymer and a copolymer[3-5] or two different copolymers,[6-8] that the miscibility could occur in a range of copolymer compositions due to the so-called "copolymer effect". The copolymer effect arises when there is mutual repulsion between the constituents of the copolymers, that prevails over other interactions involved in the system.

There are several studies of the miscibility of homopolymer and copolymer systems,[9] but the effect of the systematic variation of the copolymer composition on the phase behavior of blends is not well-known, particularly where all the interactions are mutually repulsive. The miscibility of poly(acrylonitrile-*co*-styrene) (AS) with poly(methyl methacrylate)[10-12] and poly(ϵ-caprolactone)[13,14] has been reported. Their comixing may be due to the repulsion between acrylonitrile (AN) and styrene (St) comonomer units.

We report here the effect of systematic variation of AN in the copolymer AS on the phase behavior of their blends with poly(phenyl acrylate) (PPA). Attention may be drawn to the fact that both homopolymers of the comonomeric constituents are immiscible with PPA. The main focus in the present investigation is to identify the lower and upper bounds of the miscibility window and to calculate the interaction parameters by using a mean field approach.

Experimental Section

Poly(phenyl acrylate) and AS copolymers were prepared as described elsewhere.[14,15] The copolymer composition was determined by ^{1}H NMR. Table I summarizes the composition, viscosity, and density of the polymers used in the present study. The numeral of each copolymer indicates the rounded off weight percentage of AN in the sample.

The blends were prepared by dissolving appropriate quantities of the components in $CHCl_3$ followed by coprecipitation with methanol. The polymers were dried under vacuum to a constant weight. The blend films were prepared by casting them from $CHCl_3$ solutions and dried under vacuum at 80 °C for about a week.

Table I
Physical Properties of Homopolymers and Copolymers

	AN content				
sample	mol %	wt %	T_g, °C	$[\eta]$,[a] dL/g	density, g/cm^3
PS	0	0	100	0.431[b]	
AS4	7.3	3.86	106	0.553	
AS8	14.3	7.84	106.5	0.796	
AS11	20.4	11.55	107	0.567	
AS15	25.1	14.59	109	0.759	1.062
AS18	30.6	18.35	109.5	0.923	1.063
AS21	33.8	20.65	111	1.163	1.064
AS24	38.6	24.3	112	1.092	1.074
AS27	41.5	26.55	113	1.347	1.076
AS30	45.6	29.93	113	1.584	1.078
AS34	49.8	34.1	113	1.563	1.094
AS40	53.5	40	114	1.697	
PPA			55	1.208[b]	1.227

[a] Measured in DMF at 30 °C. [b] Measured in $CHCl_3$ at 25 °C.

The glass transition temperatures (T_g) were determined with a Du Pont DSC (Model 990) using about 25 mg of the sample in each run. For each T_g measurement, the sample was heated to 140 °C for 5 min to afford a good thermal contact between the sample and the pan and to exterminate the previous thermal history. It was then quenched and scanned from 0 °C with a heating rate of 10 °C/min. The T_g was taken as the extrapolated onset of the abrupt increase in the specific heat trace.

Phase separation studies were performed by annealing the homogeneous blend sample at a selected annealing temperature for 15 min (further annealing did not change the DSC trace). The sample was then quenched to liquid nitrogen temperature and scanned at 10 °C/min. The annealing temperature corresponding to the appearance of two T_g's is taken as the phase separation temperature.

Densities were measured at 25 °C by the floating method using $CdSO_4$ solutions.

Results and Discussion

Figure 1 shows the illustrative plot of the density and specific volume of PPA/AS21 blends against the weight fraction of AS21. The observed values (open circles) are in good agreement with the calculated values (solid line) from volume additivity. Identical results were obtained for other miscible blends as well, indicating that the excess volume of mixing is small.

The glass transition behavior of the blends of PPA with PS, AS4–11, is shown in Figure 2. All these blend films were cloudy. In PPA–AS11 blends, it was also found that the upper T_g is sufficiently lowered but the lower T_g is nearly the same. This behavior is attributed to the compositon fluctuation,[16] implying that AS11 copolymer is just at the threshold of miscibility.

The films of the blends of PPA with AS15–34 were transparent bespeaking the miscibility, which is further supported by the manifestation of single T_g's (Figure 3a,b). However, the blends of PPA with AS40 exhibited two T_g's (Figure 3c). It is clear from Figure 3c that the lower T_g

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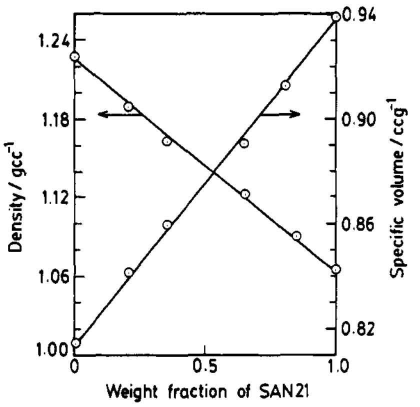


Figure 1. Dependence of densities and specific volumes on the weight fraction of AN21 in PPA/AS21 blends.

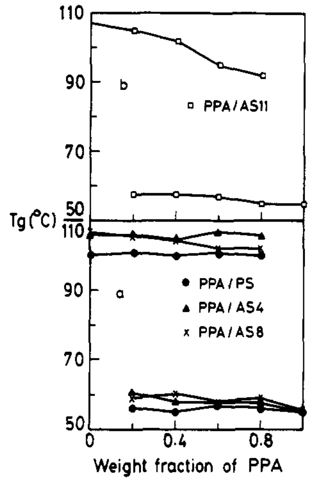


Figure 2. Glass transition behavior of blends of PPA with PS and AS4–11 copolymers.

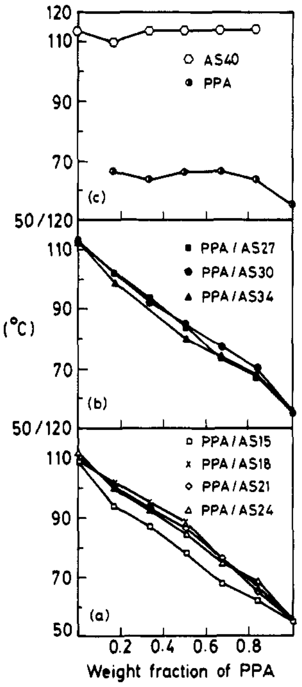


Figure 3. Glass transition behavior of blends of PPA with AS15–40 copolymers.

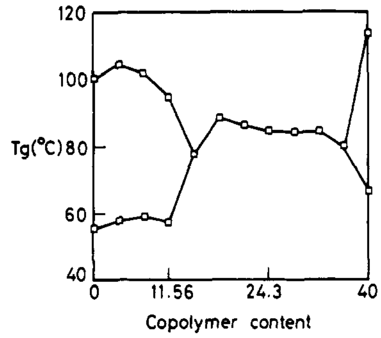


Figure 4. Dependence of T_g on the AN content in the blends of AS copolymers with PPA.

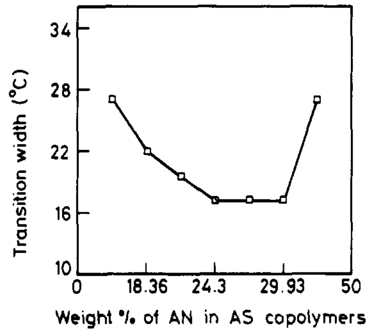


Figure 5. Dependence of glass transition width on the AN content in the PPA–AS miscible blends.

is raised but the upper T_g is nearly the same; this is the converse of the behavior of PPA–AS11 blends. It may be concluded that the AS11 and AS40 copolymers are lying at the brink of the miscibility window. This is clearly delineated in Figure 4 where the T_g behavior of blends containing 50% by weight PPA is plotted against AS copolymers of varying AN content. It may be conjectured that the PPA–AS blend system exhibits a miscibility window between 15 and 35 wt % AN in the AS copolymer.

The width of the glass transition, defined as the temperature interval between the onset and completion of the heat capacity change at T_g, is a measure of the extent of heterogeneity in the blend.[17] Figure 5 shows that this glass transition width for miscible PPA–AS blends (containing 50% PPA) as a function of AN content in the AS copolymer. Much broader transitions are observed in the case of PPA–AS15 and PPA–AS34 blends. This broadening eventually widens further as the interaction between the blend components weakens, leading to immiscibility.

The phase diagram (Figure 6) was constructed from the phase separation temperatures obtained from DSC.[18,19] From Figure 6, it is clear that the boundaries of the miscibility window correspond to 0.15 and 0.34 fractions of AN units in the AS copolymers. Phase separation temperatures were not, however, observed for the blends that lie well inside the miscibility window. In such cases, the phase separation temperature may exist above their decomposition temperature.

According to the mean field thoery,[20] the free energy of mixing ΔG at temperature T is given by

$$\frac{\Delta G}{RT} = \frac{\phi_1}{r_1}\ln\phi_1 + \frac{\phi_2}{r_2}\ln\phi_2 + \chi_{\text{blend}}\phi_1\phi_2 \qquad (1)$$

where R is the gas constant, ϕ_1 and ϕ_2 are volume fractions of polymers 1 and 2, and r_1 and r_2 are their respective degrees of polymerization. For high molecular weight polymers, the combinatorial entropy can be neglected in eq 1. The free energy of mixing then depends upon the sign of the interaction parameter χ_{blend}. For the blend consisting of a homopolymer A and copolymer C_yD_{1-y} (y in terms of volume fraction), χ_{blend} is defined by the following quadratic equation as[4]

$$f(y) = \chi_{\text{blend}} = y^2 + y(\chi_{AC} - \chi_{AD} - \chi_{CD})/\chi_{CD} + \chi_{AD}/\chi_{CD} \qquad (2)$$

We make the following assignments for the present case:

Table II
Interaction Parameter for the AN-St Pair

$\chi_{AN\text{-}St}$	ref	$\chi_{AN\text{-}St}$	ref
0.98	7	0.97	29
0.8	27	0.83	31
0.81	28		

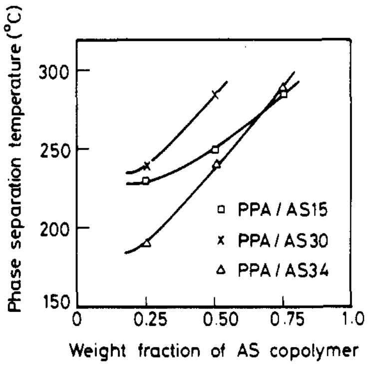
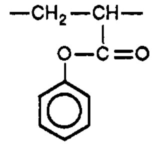


Figure 6. Phase separation temperature versus weight fraction of AS in the blend.



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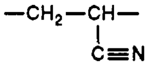

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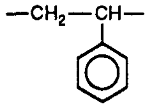

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At the boundary condition, χ_{blend} becomes zero in eq 2. It was then solved to obtain roots

$$Y_1 + Y_2 = (\chi_{PA\text{-}St} + \chi_{AN\text{-}St} - \chi_{PA\text{-}AN})/\chi_{AN\text{-}St} \quad (3)$$

$$Y_1 Y_2 = \chi_{PA\text{-}St}/\chi_{AN\text{-}St} \quad (4)$$

In order to find the three $\chi_{i\text{-}j}$'s, the following approach has been adopted.[7] By considering the fact that the interaction parameter is composed of additive parts arising from dispersive and nondispersive or specific interactions,[21,22] the dispersive part can be calculated from the solubility parameters of the components.[23,24] Assuming the absence of any specific interactions for the AN-St pair, Akoi[7] has calculated the interaction parameter $\chi_{AN\text{-}St}$ as 0.98 using the solubility parameters of polyacrylonitrile and polystyrene. Employing this value and applying boundary conditions, $Y_1 = 0.132$ and $Y_2 = 0.316$ (experimentally observed) in terms of volume fractions of AN units in the AS copolymers, eqs 3 and 4 were solved. The values of $\chi_{PA\text{-}St}$ and $\chi_{PA\text{-}AN}$ were found to be 0.041 and 0.582, respectively.

Recently, Nishimoto et al.[27] have tabulated various literature values of the interaction energy density ($B_{i\text{-}j}$) for the AN-St pair obtained from different copolymer blends. We have converted these values into their corresponding interaction parameters ($\chi_{AN\text{-}St}$) by using the relationship

$$\chi_{AN\text{-}St} = \frac{V}{RT} B_{AN\text{-}St} \quad (5)$$

where V is the reference volume, which is taken at the geometric mean of the molar volumes of PAN and PSt as used by Akoi[7] and Kressler et al.[25] The $\chi_{AN\text{-}St}$ values are given in Table II.

Though we have used the value 0.98 for $\chi_{AN\text{-}St}$ to derive $\chi_{PA\text{-}AN}$ and $\chi_{PA\text{-}St}$, these two parameters were also obtained by considering the least value of 0.8 (Table II) for $\chi_{AN\text{-}St}$ to estimate the maximum deviation. By using $\chi_{AN\text{-}St} = 0.8$ and applying boundary conditions, the above two interaction parameters were calculated to be $\chi_{PA\text{-}St} = 0.03$ and $\chi_{PA\text{-}AN} = 0.48$; they deviate 17–37% from the corresponding values when using $\chi_{AN\text{-}St} = 0.98$. However, the order of the magnitude is well maintained.

Inspection of the magnitude of the above interaction parameters reveals that there is a close resemblance of these values with that reported for methacrylates with AS copolymer systems;[27] they also pursue the following order we have observed in our system

$$\chi_{AN\text{-}St} > \chi_{PA\text{-}AN} > \chi_{PA\text{-}St}$$

The miscibility window in our systems is the consequence of the high value of $\chi_{AN\text{-}St}$, which precedes over the other two interaction parameters as shown above. A calorimetric study[30] on AS copolymers with PMMA using model systems also supports this trend.

Conclusion

The existence of the miscibility window in PPA–AS blend systems, due to the "copolymer effect" in the AS copolymer, has been demonstrated. The segmental interaction parameters were calculated and found to follow the order $\chi_{AN\text{-}St} > \chi_{PA\text{-}AN} > \chi_{PA\text{-}St}$.

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