

# Comparison of the Miscibility Strategies in Poly(benzyl methacrylate)–Polystyrene Blends

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## SYNOPSIS

Exothermic interactions like hydrogen bonding, ionic and charge transfer, etc., and “copolymer effect” are commonly used to induce miscibility in immiscible blends. The efficacy of these methods in promoting miscibility in poly(benzyl methacrylate) (PBMA)–polystyrene (PS) immiscible blends has been studied by suitably modifying the structure of the component polymers. It has been found that hydrogen bonding approach is most advantageous among these approaches as it involves the need for minimum interacting sites. It has also been shown that these results can be extended to the blends of poly(acrylate)s or poly(methacrylate)s with PS. © 1996 John Wiley & Sons, Inc.

## INTRODUCTION

Currently polymer blends are attracting considerable attention because they offer convenient and economic means of producing materials of varied properties, sometimes superior to their component polymers.<sup>1,2</sup> In spite of significant progress made in the last two decades, the molecular level understanding of the miscibility in polymer blends in its various facets is still lacking. Since most of the polymer pairs are generally not miscible because of the unfavorable entropy effects, one of the important features in this research has been focused on promoting the miscibility through specific interactions. Many miscibility enhancement strategies have been explored in the past. These include utilization of hydrogen bonding between the dissimilar chains,<sup>3–5</sup> formation of donor-acceptor complexes,<sup>6</sup> dipole-dipole,<sup>7</sup> ion-dipole, and ion-ion interactions,<sup>9</sup> and the use of block copolymeric emulsifiers.<sup>10</sup> Recently, it has been shown that the so-called ‘copolymer effect’ can also be made use of to promote miscibility in the immiscible polymer blends, where the strong mutual repulsion between the comonomeric constituents in the copolymer causes miscibility with the second component.<sup>11–15</sup> Since we do not have a clear comparative view on the relative advantages

of these approaches, the main focus of the present study is to compare the relative merits of the various methods. In order to do so, an immiscible polymer pair of poly(benzyl methacrylate)/polystyrene<sup>14</sup> was chosen and structural modifications on the constituent polymers were performed in order to induce miscibility using these approaches. The presence of single glass transition temperatures ( $T_g$ s) was used as a scale to determine the miscibility in these blends.

## EXPERIMENTAL

Poly(benzyl methacrylate-*co*-4-vinyl pyridine) (BVP) copolymers were prepared by bulk polymerization using benzoyl peroxide as initiator. The 4-vinyl pyridine contents in the BVP copolymers were determined by titrating with perchloric acid in acetic acid/acetonitrile mixtures using crystal violet as indicator.<sup>16</sup>

Poly(4-hydroxy styrene) (PSOH) and poly(styrene-*co*-4-hydroxy styrene) (PSOH-*x*) copolymers (where *x* represents the mol % of phenolic groups in the copolymers) were prepared from the precursor polymers of poly(4-acetoxy styrene) and poly(styrene-*co*-4-acetoxy styrene) copolymers and the compositions were determined from <sup>1</sup>H-NMR.<sup>17</sup>

Lightly sulfonated polystyrenes (PSSs) were prepared from polystyrene (PS) by the procedure described by Makowski et al.<sup>18</sup> and the sulfonation level was determined volumetrically by titrating the

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**Table I** Characteristics of the Polymers Used in the Study

Polymer	Copolymer Composition (mol %)		$[\eta]$ (dL g <sup>-1</sup> ) <sup>a</sup>	$T_g$ (°C)
BVP4	3.74	VP	0.37	68
BVP7	6.70		1.02	75
BVP11	11.23		0.96	77
PSS4	4.05	SS		109
PSS7	7.10			112
PSS10	10.24			116
PSOH3	2.8	PSOH	0.23	102
PSOH5	4.9		0.31	108
PSOH9	9.2		0.23	110
PSOH23	23.0		0.25	126
PSOH	100.0		0.29	161
PDMAST	—		0.25	138
PDNBOEM A	—		0.22	98

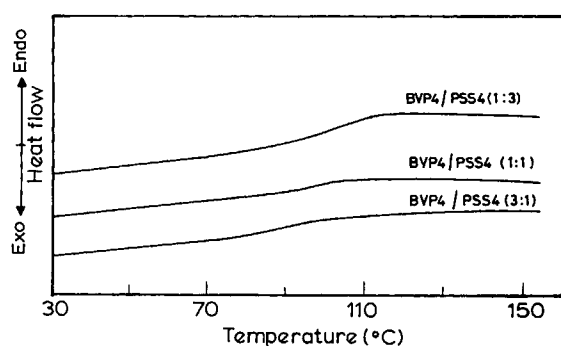
VP, 4-vinyl pyridine; SS, styrene sulfonic acid; PSOH, 4-hydroxy styrene.

<sup>a</sup> Samples were prepared from PS solutions whose  $[\eta] = 0.43$  dL g<sup>-1</sup> in the THF at 30°C except for PSS4, PSS7, and PSS10 whose PS solutions had  $[\eta] = 0.43$  dL g<sup>-1</sup> in CHCl<sub>3</sub> at 30°C.

solutions of PSS in toluene/methanol (9/1 v/v) with methanolic sodium hydroxide solutions using phenolphthalein indicator. Poly(*N,N'*-dimethyl amino styrene) (PDMAST) and poly(3,5-dinitro benzoyl oxy ethyl methacrylate) (PDNBOEMA) were prepared according to the literature procedures.<sup>19,20</sup>

BVP/PSS blends were prepared by mixing the THF/DMF solutions of the constituent polymers together with stirring. The resultant gels were isolated and dried. PBMA/PSOH-*x* blends were prepared by casting the films from THF solutions. Blends of PDMAST/PDNBOEMA were also prepared by solution casting from THF solutions and drying the samples.

The characteristics of the polymers used in the present study are given in Table I.

**Figure 1** DSC thermograms of BVP4/PSS4 blends.

The glass transition temperatures ( $T_g$ s) were determined with a Du Pont TA 9900 DSC instrument. The  $T_g$ s taken from the second scans as the onset of the change in the heat capacity curves. The width of the glass transition ( $TW$ ) is expressed as the temperature difference in the upper and lower points of deviation from extrapolated liquid and glassy baselines, respectively. The viscosity measurements were carried out using Scott-Gerrate Ubbelohde Viscometer. Fourier transform infrared (FTIR) spectra were recorded on Bio-Rad FTS7 FTIR spectrometer with the resolution of 2 cm<sup>-1</sup>.

## RESULTS AND DISCUSSION

### Ionic Interaction

To promote miscibility through ionic interactions, sulfonic acid groups in PS chains and pyridine basic groups in PBMA chains were introduced. The results obtained from the DSC measurements, viscosity, and the FTIR studies of these blends are discussed below.

### $T_g$ Measurements

The DSC thermograms of the BVP4/PSS4 blends are shown in Figure 1, which indicates that the blends with just 4 mol % of the acid and base units in the constituent polymers, respectively, exhibit miscibility. The acid-base neutralization in this

**Table II**  $T_g$ s of the Ionic Blends

Blends (1 : 1 w/w)	$T_g$ (°C) (exp)	$T_g$ (°C) (Fox)	$\Delta T_g$ (= $T_g \text{ exp} - T_g \text{ Fox}$ ) (°C)
BVP4/PSS4	88.5	83.4	5.1
BVP7/PSS7	95.8	89.7	6.1
BVP11/PSS10	102.0	92.7	9.3

system as a result of the proton transfer from the acid to the basic groups leads to the association of the polymers with the formation of the ionic crosslinks<sup>9</sup> between them. The formation of ionic crosslinks is evident from the gel formation during the mixing of THF solutions of BVP4 and PSS4 together. These gels are soluble only in strongly polar solvents like DMF, forming highly viscous solutions. When the concentrations of the acid and basic groups in the constituent polymers are more than 4 mol %, insoluble gels are obtained even in DMF. For example, when DMF solutions of BVP7 or BVP11 are mixed with PSS7 or PSS10, respectively, insoluble gels are obtained.

The  $T_g$  values of the dried gels of BVP7/PSS7 and BVP11/PSS10 blends of 1 : 1 compositions are shown in Table II. The blends exhibit a single  $T_g$  with the positive deviation from the  $T_g$  defined by Fox equation<sup>21</sup> ( $+\Delta T_g$ , where  $\Delta T_g = T_g \text{ exp} - T_g \text{ Fox}$ ). Maximum deviation was obtained for BVP11/

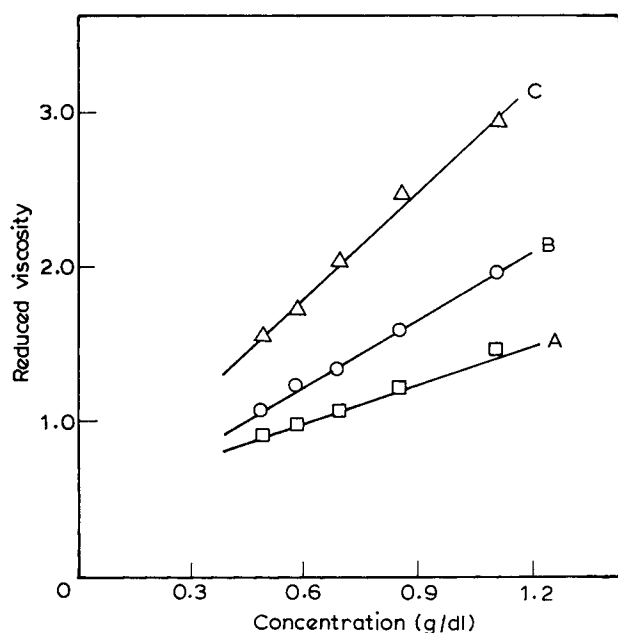
PSS10 blends as a result of highest extent of crosslinking in this blend leading to reduced segmental mobility and hence high  $T_g$ .

### Viscosity Measurements

The formation of molecular associations of the heterochains of the acid-base neutralized blends is supported by the solution viscosity measurements. Since the blends were insoluble when the acid and base units were greater than 4 mol %, viscosity measurements were carried out only for BVP4/PSS4 (1 : 1 w/w) blends in DMF at 30°C. The  $\eta_{\text{red}}$  values of the blends (1 : 1 w/w compositions of BVP4/PSS4) at different concentrations of the solutions are shown in Figure 2, which indicates that the 1 : 1 blend of BVP4/PSS4 exhibits higher viscosity than its component polymers in the limits of the concentrations studied, suggesting that the heterochains are associated together through the formation of ionic crosslinks. It is also clear from Figure 2 that the deviation of the viscosity of the blends is maximum in concentrated solutions.

### FTIR Studies

The proposed mechanism of the proton transfer from sulfonic acid units in PSS to vinyl pyridine units in BVP copolymers is supported by FTIR analysis of the blends. Figure 3 shows the FTIR spectrum (in the range of 1700–1500  $\text{cm}^{-1}$ ) of a thin film of BVP11/PSS10 blend of 1 : 1 composition made from drying the gel obtained from DMF solutions and subsequently by hot pressing. The appearance of a new band at 1640  $\text{cm}^{-1}$ , which is absent in both BVP11 and PSS10 is attributed to the pyridinium cation formed by the proton transfer from sulfonic acid to the pyridine group upon blending.<sup>22</sup> The appearance of the sharp peak at 1640  $\text{cm}^{-1}$  without any broadening indicates the proton transfer mechanism.



**Figure 2** Plot of reduced viscosity vs. polymer concentration (A) BVP4, (B) PSS4, and (C) 1 : 1 mixture of BVP4 and PSS4 in DMF at 30°C.

### Hydrogen Bonding

As the hydrogen bonding acceptor ester groups are already present in the PBMA component, to achieve

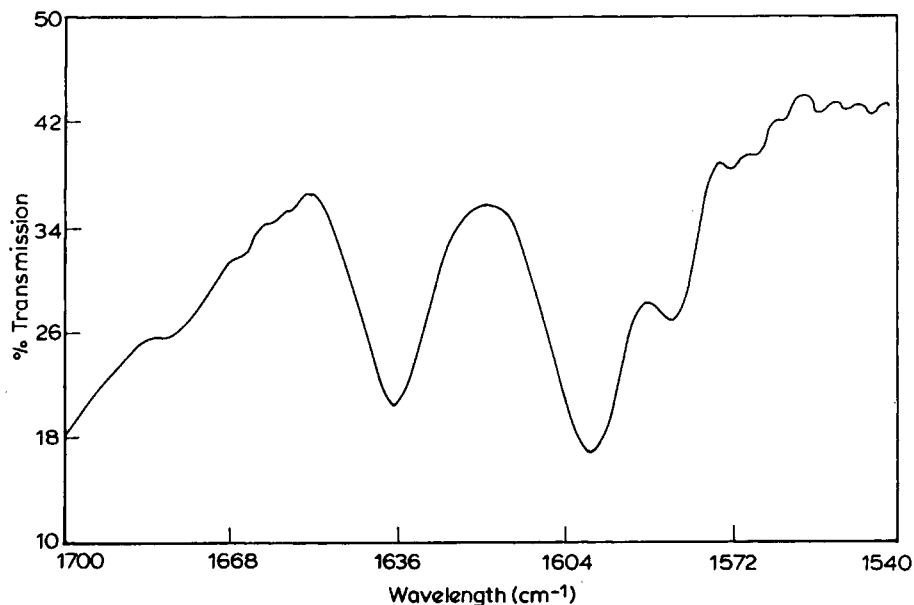


Figure 3 FTIR spectrum of BVP11/PSS10 copolymer blends.

miscibility in PBMA/PS blends through hydrogen bonding, the donor groups of phenolic units were incorporated in PS. To find the amount of phenolic groups needed to be incorporated in PS for making the system miscible, different amounts of phenolic groups were incorporated in the PS chain. The PSOH-*x* copolymers and PSOH homopolymer were blended with PBMA by solution casting of the films in THF solutions. The DSC thermograms for these blends are shown in Figure 4. The  $T_g$ s of PBMA/PSOH and PBMA/PSOH-*x* blends and the width of the  $T_g$ s ( $TW$ s) are shown in Table III, which indicates that when the concentration of phenolic groups 3 mol %, two  $T_g$ s are observed for its blend with PBMA. However, the lower  $T_g$  of the PBMA component is almost the same as the pure compo-

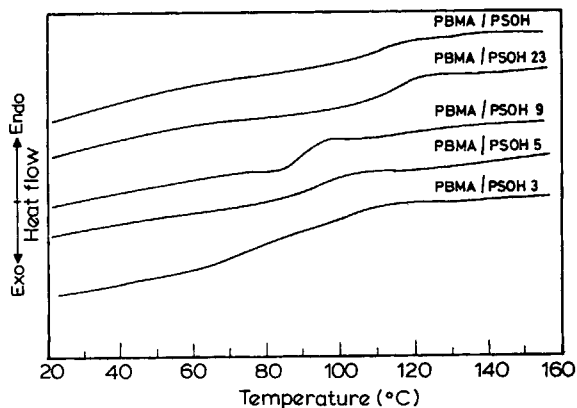


Figure 4 DSC thermograms of PBMA/PSOH and PBMA/PSOH $x$  blends (1 : 1 w/w).

nent. The upper  $T_g$  of the PSOH3 component, however, is decreased, indicating partial miscibility of the components. When the phenolic groups in the PSOH-*x* copolymers are more than 5 mol %, single  $T_g$ s were obtained indicating miscibility.

A closer look at  $TW$  of the miscible blends in Table III reveals that it is narrow for PBMA/PSOH9 blends. Increase of the phenolic groups more than this level results in wider transitions of the blends, though single  $T_g$ s were observed. The  $TW$  is maximum for PBMA/PSOH blend, which may be attributed to the self-association of the phenolic groups, which dominates over the phenolic-ester associations. The intermolecular hydrogen bonding in PSOH-*x* copolymers at low concentrations of the phenolic groups is minimum, and hence the intermolecular hydrogen bonding between the heterochains of PBMA and PSOH-*x* is facilitated, leading to miscibility.

### Charge Transfer Interaction Studies

Attempts were also made to achieve miscibility in these systems through charge transfer interactions. PS chains with electron donating *N,N*-dimethyl amino groups and the electron acceptor 3,5 dinitro benzoyl oxyethyl groups in the methacrylate chains were prepared. The  $T_g$  values of the blends of PDNBOEMA with PDMAST (1 : 1 w/w) from the DSC measurements, indicates that the blends were immiscible as they exhibit two  $T_g$ s corresponding to the pure components (99 and 138°C). Hence, the

**Table III**  $T_g$  and TW of PBMA/PSOH- $x$  Blends of 1 : 1 Composition

Blend	$T_g$ (°C)	TW (°C)
PBMA/PSOH3	65, 97	—
PBMA/PSOH5	78	21.0
PBMA/PSOH9	84	11.5
PBMA/PSOH23	104	17.0
PBMA/PSOH	119	28.1

charge-transfer interaction in these systems is not strong enough to bring about the miscibility.

### Copolymer Effect

Recently we have demonstrated<sup>15</sup> that PBMA exhibits a miscibility window with styrene-acrylonitrile copolymers with acrylonitrile contents between 14.3 and 38.6 mol % of acrylonitrile units in the copolymers. The miscibility in these systems was attributed to the presence of strong mutual repulsion between the styrene and acrylonitrile units in the copolymers that outweighed all the other interactions present in the system.

### CONCLUSIONS

Miscibility in poly(benzyl methacrylate)/PS blends can be achieved through copolymer effect when a minimum of 14 mol % of acrylonitrile units are incorporated in PS. Though ionic interaction requires only 4 mol % of the interacting sites in both the components for miscibility, both their structures ought to be modified. Besides, at higher concentrations of the interacting sites, insoluble cross-linked gels are obtained. Miscibility through hydrogen bonding mechanism requires only 5 mol % of the phenolic units to be incorporated in PS. Our results on poly(benzyl methacrylate)/PS blends can be extended for other poly(acrylate)/PS or poly(methacrylate)/PS blends as these systems broadly behave in the same fashion. For example, poly(ethyl methacrylate) has been shown to be miscible with PS when the vinyl pyridine units and the sulfonic acid groups of 5 mol % concentrations are incorporated in the respective polymers.<sup>9</sup> Similarly, it has been shown that the presence of 1 mol % of phenolic groups in PS is sufficient to cause miscibility with poly(methyl methacrylate) (PMMA) and its ethyl analogue, whereas for poly(butyl methacrylate)<sup>2</sup> mol % of phenolic groups are needed.<sup>23</sup> PMMA requires nearly 17.5 mol % of acrylonitrile units to be

incorporated in PS chains to induce miscibility through the copolymer effect mechanism.<sup>24</sup> Interestingly, polyacrylates are not miscible with styrene-acrylonitrile copolymers. Finally, comparison of the above results edifies that hydrogen bonding approach is the most convenient and potent way to induce miscibility.

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Received June 27, 1995

Accepted January 25, 1996