Miscible Blends of Poly(styrene-co-Acrylonitrile) and Poly(α-Methyl Styrene-co-Acrylonitrile) with Hydroxyl-Containing Polymethacrylates

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Synopsis

Poly(styrene-co-acrylonitrile)(SAN) and poly(α-methyl styrene-co-acrylonitrile)(MSAN) are miscible with poly(2-hydroxyethyl methacrylate) (PHEMA) and with poly(2-hydroxypropyl methacrylate) (PHPMA). That SAN and MSAN are immiscible with poly(n-propyl methacrylate) and with poly(isopropyl methacrylate) but miscible with PHPMA indicates the enhancement of polymer miscibility due to hydroxyl groups. The miscibility of these blends is explained in terms of recent theories for copolymer/homopolymer blends.

INTRODUCTION

The enhancement of polymer miscibility through hydrogen-bonding interaction is well documented. Hydroxyl-containing polymers such as poly(hydroxyether of bisphenol-A),[1-6] poly(styrene-co-allyl alcohol),[7,8] poly(p-vinyl phenol),[9,10] poly(styrene-co-p-vinyl phenol),[11] and poly(styrene-co-p-(hexafluoro-2-hydroxyl isopropyl) styrene)[11-14] are miscible with a large variety of polymers which contain proton acceptor groups. Hydrogen-bonding interactions in many of these blends have been detected by Fourier transform infrared (FTIR) spectroscopy.

The miscibility of poly(styrene-co-acrylonitrile)(SAN) and poly(α-methyl styrene-co-acrylonitrile)(MSAN) with various polymethacrylates have also been studied.[15-21] Both SAN and MSAN are miscible with poly(methyl methacrylate)(PMMA) and with poly(ethyl methacrylate) (PEMA), but immiscible with the higher homologs. We have studied the miscibility of SAN and MSAN with some copolymers of methyl methacrylate[22] and with PMMA containing sterically hindered amine groups.[23] The miscibility of SAN and MSAN with two hyroxyl-containing polymethacryates, namely poly(2-hydroxyethyl methacrylate) and poly(2-hydroxypropyl methacrylate), is reported in this communication.

EXPERIMENTAL

The sources, the glass transition temperatures (T_g) and the molecular weight information of the polymers used in this study are given in Table I.

Blends were prepared by solution casting using the following solvents: tetrahydrofuran (THF) for blends containing PHPMA, and dimethylformamide (DMF) for blends containing PHEMA and also blends containing

TABLE I
Polymers Used in This Study

Polymer	Abbreviation	Source	T_g (°C)	Mol. wt. information
Poly(α-methyl styrene-co-acrylonitrile), 30% AN	MSAN	BASF (Luran KR 2556)	115	$\bar{M}_w = 160,000$
Poly(styrene-co-acrylonitrile), 22% AN	SAN	Monsanto	100	$[\eta] = 0.54$ dL/g in 2-butanone at 30°C
Poly(2-hydroxyethyl methacrylate)	PHEMA	Scientific Polymer Products, Inc. (SPP)	101	$[\eta] = 0.54$ dL/g in DMF at 30°C
Poly(2-hydroxypropyl methacrylate)	PHPMA	SPP	93	$[\eta] = 0.31$ dL/g in THF at 30°C
Poly(α-methyl styrene)	PMS	SPP	140	$\bar{M}_w = 50,000$
Polyacrylonitrile	PAN	SPP	103	$\bar{M}_w = 150,000$
Polystyrene	PS	BDH Chemicals Ltd.	100	$\bar{M}_w = 150,000$

PAN. Solvent evaporation was conducted at room temperature for THF and at 100°C for DMF. The resulting films were then dried under vacuum at 110°C for 48 h.

T_g's of the polymers and blends were measured using a Perkin-Elmer DSC-4 Differential Scanning Calorimeter. A heating rate of 20°C/min was used. T_g was taken at the onset of the change of slope in the heat capacity plot.

All the transparent blends were examined for the existence of lower critical solution temperatures (LCST) using the method as described previously.[23]

RESULTS AND DISCUSSION

Blends Containing PHEMA

The closeness of the T_g's of SAN, MSAN, and PHEMA prevents the use of T_g measurement to ascertain the miscibility of the blends. SAN/PHEMA and MSAN/PHEMA blends containing 10, 30, 50, 70, and 90% by weight of PHEMA were transparent. All these blends remained transparent when heated up to 270°C where they began to show signs of degradation. In contrast, SAN/PEMA and MSAN/PEMA blends showed LCST behavior between 170°C and 220°C.[20,21] An immiscible blend can be transparent if the difference between the refractive indices of the two polymers is smaller than 0.01 or the domain size is smaller than the wavelength of the visible light. The refractive index of PHEMA is 1.5119[24] and those of SAN and MSAN are estimated to be 1.577 (reported refractive index of SAN containing 25% AN: 1.570[24]) and 1.566, respectively, by the Vogel method.[25] The transparency of these blends is not a result of matching refractive indices of the polymers and can be taken as an indication of their miscible nature.

Although PHEMA is miscible with SAN and MSAN, it is immiscible with PS, PMS, and PAN as evidenced by the heterogeneous appearance of these blends. It is commonly observed that a copolymer 1/2 is miscible with a homopolymer 3 over a certain range of copolymer composition, but neither homopolymer 1 nor homopolymer 2 is miscible with homopolymer 3. Such behavior is explained by several recent theories[26-28] as discussed in a later section.

Blends Containing PHPMA

SAN/PHPMA and MSAN/PHPMA blends containing 10, 30, 50, 70, and 90% by weight of PHPMA were transparent and remained so when heated up to 270°C where they began to show signs of degradation. The transparency of these blends is not a result of matching refractive indices of the polymers as the refractive index of PHPMA is estimated to be 1.494 by the Vogel method. The T_g of PHPMA is sufficiently far apart from that of MSAN to allow the use of T_g measurement to ascertain the miscibility of the MSAN/PHPMA blends. As shown in Figure 1, each of these blends shows a single composition-dependent T_g indicating its miscible nature.
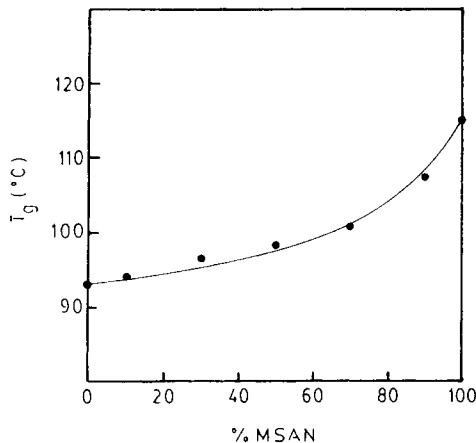
Fig. 1. T_g composition curve for MSAN/PHPMA blends.

Similar to the PHEMA blends, PHPMA is miscible with SAN and MSAN, but immiscible with PS, PMS, and PAN. Furthermore, while SAN and MSAN are immiscible with poly(n-propyl methacrylate)(PnPMA) and poly(isopropyl methacrylate)(PiPMA),[20,21] they are miscible with PHPMA. Apparently, the presence of hydroxyl groups in PHPMA enhances the miscibility.

Several theories[26-28] have been developed to account for the miscibility of polymer blends containing copolymers. These theories pointed out the importance of intramolecular interaction between the two different monomer units in the copolymer. According to the binary interaction model of Paul and Barlow,[28] the effective interaction parameter B for mixing a copolymer 1/2 and a homopolymer 3 is given by

$$B = B_{13}\Phi_1' + B_{23}\Phi_2' - B_{12}\Phi_1'\Phi_2'$$

where Φ_1' and Φ_2' are the volume fractions of monomer units 1 and 2 in the copolymer, and B_{12}, B_{13}, and B_{23} are the interaction parameters between various units. If homopolymer 3 is immiscible with homopolymer 1 and homopolymer 2, (i.e., both B_{13} and B_{23} are positive), B can be negative if B_{12} is a large enough positive value, leading to the formation of a miscible blend.

Based on this model, the immiscibility of blends of SAN and MSAN with PnPMA and PiPMA, and blends of PS/PAN and PMS/PAN indicates that B_{13}, B_{23}, and B_{12} are positive, but B_{12} is not large enough to give a negative B as shown schematically in Figure 2(a). The miscibility of SAN/PHPMA and MSAN/PHPMA blends is a result of a smaller positive B_{13} and/or B_{23} to give a negative B over a certain range of copolymer composition as shown in Figure 2(b). In a recent study on the miscibility of SAN with poly(styrene-co-p(hexafluoro-2-hydroxyl isopropyl)styrene) (PS/HFIPS),[14] shifts in the nitrile absorption peak of SAN and the hydroxyl absorption peak of the styrene copolymer were observed by FTIR, indicating the interactions between these groups. It is, therefore, tempting to attribute the miscibility of
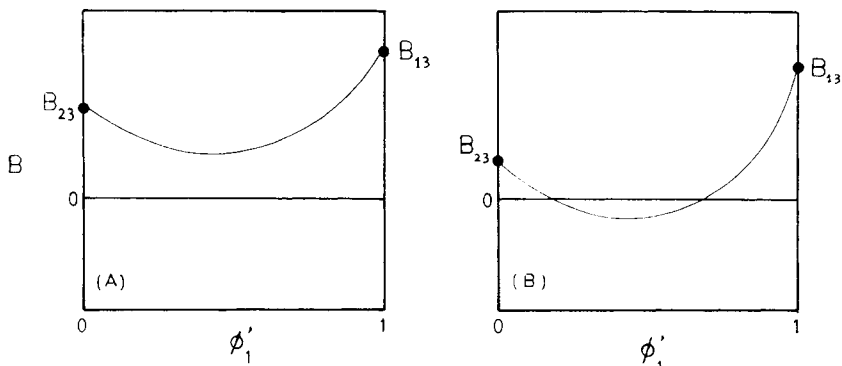
Fig. 2. Schematic diagram of polymer–polymer interaction parameter B.

SAN/PHPMA and MSAN/PHPMA blends to a smaller B_{23} through hydrogen-bonding intreaction of the hydroxyl groups in PHPMA and the nitrile groups in SAN and MSAN. However, one should note that the hexafluoroisopropanol (HFIP) moiety in PS/HFIPS is very acidic and is probably the main reason for the hydrogen-bonding interaction. Would the hydroxyl groups in PHPMA which are not as acidic as the HFIP groups also be involved in hydrogen-bonding interaction with the nitrile groups? It will be of interest in future work to study the interaction between PHPMA and SAN/MSAN by other technique such as FTIR spectroscopy. Nevertheless, the present study shows that the incorporation of hydroxyl groups in polymethacrylate enhances its miscibility with SAN and MSAN with a AN content around 20–30%.

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