Miscibility of Poly(styrene-co-Acrylonitrile) and Poly(α-Methyl Styrene-co-Acrylonitrile) with Copolymers of Methyl Methacrylate

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Synopsis

Poly(α-methyl styrene-co-acrylonitrile) was found to be miscible with poly(methyl methacrylate-co-ethyl methacrylate) and with poly(methyl methacrylate-co-*n*-butyl methacrylate). All these blends exhibited lower critical solution temperatures. Poly(styrene-co-acrylonitrile) was also found to be miscible with poly(methyl methacrylate-co-ethyl methacrylate) and with poly(methyl methacrylate-co-*n*-butyl methacrylate). However, phase separation of these blends could not be induced by heating up to 300°C.

INTRODUCTION

Blends containing poly(styrene-co-acrylonitrile) (SAN) have been widely studied. SAN is miscible with poly(methyl methacrylate)[1–5] (PMMA) and with poly(ethyl methacrylate)[6] (PEMA); but SAN is immiscible with the higher homologs of the polymethacrylate.[6] However, studies involving the closely related polymer, poly(α-methyl styrene-co-acrylonitrile) (MSAN) are scarce. It has been reported recently that MSAN is miscible with PMMA and with PEMA, but immiscible with the higher homologs.[7] Since the formation of a miscible blend requires some specific interaction between chemical moieties of the two polymers, these results suggest that SAN and MSAN interact most intensely with PMMA, and the intensity of interaction decreases as the size of the alkyl pendant group of the polymethacrylate increases. It will be of interest to study how the miscibility of SAN and MSAN with PMMA is affected by the incorporation of other methacrylate unit into PMMA. This paper reports the miscibility of SAN and MSAN with poly(methyl methacrylate-co-ethyl methacrylate) and with poly(methyl methacrylate-co-*n*-butyl methacrylate).

EXPERIMENTAL

Materials. The MSAN polymer used was Luran KR 2566U manufactured by BASF. It contains 30% by weight of acrylonitrile and it has a M_w of 160,000.

The SAN polymer was supplied by Monsanto. The polymer contains 22% by weight of acrylonitrile as shown by elemental analysis.

Two poly(methyl methacrylate-co-ethyl methacrylate) samples containing 60% and 30% by weight of methyl methacrylate, respectively, were obtained from

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Polysciences, Inc. The two copolymers are designated as MEMA-60 and MEMA-30, respectively.

The poly(methyl methacrylate-co-*n*-butyl methacrylate) sample, designated as MBMA, was also obtained from Polysciences, Inc. The composition of the copolymer was not available from the supplier. Based on the glass transition temperature of the copolymer (73°C) and the Fox equation, it is estimated that the copolymer contains 70% by weight of methyl methacrylate.

Sample Preparation. All the blends were prepared by solution casting using 2-butanone as solvent. After the evaporation of the solvent at room temperature, the blends were dried in a vacuum oven at 110°C for 48 h.

Calorimetric Measurements. The glass transition temperatures of the polymers and the blends were measured with a Perkin-Elmer DSC-1B Differential Scanning Calorimeter. A heating rate of 16°C/min was used. The T_g was taken as the onset of the change of slope in the heat capacity plot by extrapolating both slopes to the point of intersection.

Measurements of Lower Critical Solution Temperature (LCST). All the blends were examined for the existence of LCST. The polymer film was sandwiched between two microscopic cover glasses and heated in a Fisher-John melting apparatus with a heating rate of about 20°C/min. The temperature at which the transparent film first became cloudy was taken as the cloud point. To check the validity of the cloud point results, the cloud points of MSAN/PMMA blends were measured and were found to agree well with the reported values.[7]

RESULTS AND DISCUSSION

Blends Containing MSAN

All the binary blends of MSAN with MEMA-60, MEMA-30, or MBMA were transparent. Each of these blends showed only one T_g as shown in Table I. The transparency and the existence of one T_g of the blends show that they are miscible blends. In addition, all these blends turned cloudy when heated to high temperature, indicating the existence of LCST. The cloud points of the blends are given in Table II and also shown in Figure 1. The phase separation induced on heating was not reversed on cooling because of the low mobility of the polymer chains. Similar observation was also noted for MSAN/PMMA blends.[7]

The formation of a miscible blend is the result of an exothermic heat of mixing which requires specific interaction between the two components. For miscible

TABLE I
T_g (°C) of MSAN Blends

Wt % MSAN in blend	MSAN/MEMA-60	MSAN/MEMA-30	MSAN/MBMA
0	83	76	73
10	85	78	74
30	87	85	81
50	92	91	88
70	96	98	96
90	104	105	103
(T_g of MSAN = 115°C)			

TABLE II
Cloud Points (°C) of MSAN Blends

Wt % MSAN in blend	MSAN/MEMA-60	MSAN/MEMA-30	MSAN/MBMA
10	228	222	170
30	215	214	165
50	208	208	161
70	204	205	169
90	206	211	175

polymer blend containing a crystallizable component, the melting point depression of the crystalline polymer by miscible diluent is frequently used to calculate the interaction parameter B, which is related to the heat of mixing by

$$\Delta H_{mix} = B\phi_1\phi_2$$

where ϕ_1 and ϕ_2 are the volume fractions of the two polymers in the blend.[8,9] It has been shown that the cloud point increases as the interaction parameter B becomes more negative.[10] Thus the cloud points provide a simple means to compare the interaction parameters of various blends.

Based on the cloud points of the blends, it has been suggested that the interaction between MSAN and polymethacrylate decreases as the size of the alkyl pendant group of the polymethacrylate decreases.[7] One would then expect that MEMA and MBMA would interact less intensely with MSAN as compared with PMMA. In other words, the interaction parameters B of the MEMA/MSAN and MBMA/MSAN blends would be less negative than that of PMMA/MSAN blend. The cloud points of the two MSAN/MEMA blends are close to each other

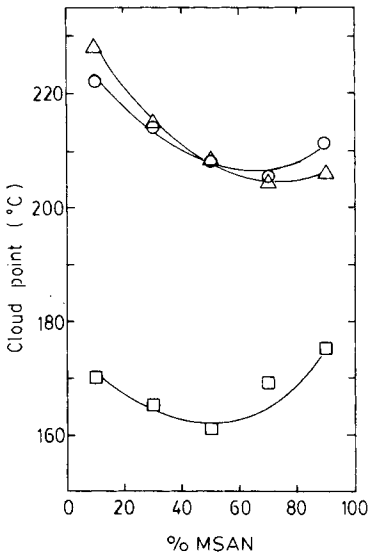

Fig. 1. Cloud point curves of MSAN blends: (△) MSAN/MEMA-60 blends; (○) MSAN/MEMA-30 blends; (□) MSAN/MBMA blends.

TABLE III
T_g (°C) of SAN Blends

Wt % SAN in blend	SAN/MEMA-60	SAN/MEMA-30	SAN/MBMA
0	83	76	73
10	83	77	75
30	86	79	80
50	88	82	83
70	94	86	86
90	94	90	90
(T_g of SAN = 100°C)			

and also close to the MSAN/PMMA blends. It has been shown that the cloud points are dependent on the molecular weights of the polymers.[7,11] If the cloud points are used as a measurement of interaction parameter B, it is necessary that the molecular weights of the polymers in various blends are similar unless the cloud points differ so substantially that the difference in cloud points cannot be solely attributed to the difference in molecular weights of the polymers. In the present case, the molecular weights of the two MEMA copolymers are not available. It is therefore difficult to compare the interaction parameters based on the cloud points.

On the other hand, the cloud points of MSAN/MBMA blends are 40–50°C lower than the corresponding MSAN/MEMA blends. For MSAN/PMMA blends, it was reported that except for PMMA of very high molecular weight, a change in the molecular weight of PMMA produced a change in cloud points by not more than 20°C.[7] In the present study, since the cloud points of MSAN/MBMA blends are much lower than those of MSAN/PMMA blends, it can be concluded that the interaction parameter B becomes less negative when n-butyl methacrylate units are incorporated into PMMA. It is also noted that, although poly(n-butyl methacrylate) is immiscible with MSAN,[7] a copolymer of MMA/nBMA containing 30% of n-butyl methacrylate and MSAN still have a negative interaction parameter to produce a miscible blend.

Blends Containing SAN

All the binary blends of SAN with MEMA-60, MEMA-30, or MBMA were transparent. Each of these blends also showed one T_g as shown in Table III. It is concluded that all these blends are miscible blends. The blends remained transparent when heated up to 300°C. The results suggest that the interaction parameters of SAN/MEMA and SAN/MBMA blends are more negative than those of MSAN/MEMA and MSAN/MBMA blends such that the cloud points of the SAN blends are not observed below 300°C.

It is also interesting to note that by substituting the α-hydrogen of styrene in SAN with methyl group, the resulting MSAN interacts less intensely with the copolymers of PMMA. On the other hand, previous studies[6,7] have shown that poly(methyl acrylate) and poly(ethyl acrylate) are immiscible with SAN and with MSAN, but by substituting the α-hydrogen in the polyacrylates with methyl group, the resulting polymethacrylates are miscible with SAN and with MSAN.

These results illustrate the complexity of the relationship between polymer structure and miscibility.

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