

Miscibility of Poly(styrene-co-Acrylonitrile) and Poly(α -Methyl Styrene-co-Acrylonitrile) with Polymethacrylates Containing Sterically Hindered Amine Groups

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Synopsis

Sterically hindered amine groups were incorporated into poly(methyl methacrylate) and poly(ethyl methacrylate) by copolymerizing 2,2,6,6-tetramethylpiperidinyll methacrylate (TPMA) with MMA and EMA. The replacement of the pendant alkyl groups of the polymethacrylates by SHA groups reduced their miscibility with poly(styrene-co-acrylonitrile) (SAN) and with poly(α -methyl styrene-co-acrylonitrile) (MSAN). The cloud points of the miscible blends indicated that the effective interaction parameter B of a blend became less negative with increasing TPMA content in the copolymer, and B was more negative for SAN blend than for a corresponding MSAN blend.

INTRODUCTION

Sterically hindered amines (SHA) are excellent photostabilizers for polyolefins.¹⁻⁴ Polymers containing SHA groups have also been used as stabilizers.⁵⁻¹¹ As compared with low molecular weight stabilizers, polymeric stabilizers are less volatile and extractable, and, therefore, their loss during fabrication and end use is reduced.^{12,13} However, the polymeric stabilizers must be completely soluble in the polymer at the concentration used. Thus a miscible polymer blend in which one of the component polymer contains stabilizing groups is expected to possess good thermal and photo-stability.

We have reported that both poly(styrene-co-acrylonitrile) (SAN) and poly(α -methyl styrene-co-acrylonitrile) (MSAN) are miscible with poly(methyl methacrylate) (PMMA) containing a small amount of SHA groups, namely, 2,2,6,6-tetramethylpiperidinyll groups.¹⁴ In this communication, we report the miscibility of SAN and MSAN with poly(ethyl methacrylate) (PEMA) containing 2,2,6,6-tetramethylpiperidinyll groups. In addition, the miscibility of SAN and MSAN with PMMA of higher SHA contents will also be reported. Since SAN and MSAN are miscible with PMMA and with PEMA,¹⁵⁻²¹ it will be of interest to study how the incorporation of SHA groups affects the miscibility of the polymethacrylates with the acrylonitrile-containing polymers. The SHA groups were incorporated into PMMA and PEMA by copolymerizing the methacrylates with 2,2,6,6-tetramethylpiperidinyll methacrylate (TPMA).

TABLE I
 Commercial Polymers Used in This Study

Polymer	Abbrev.	Source	T_g (°C)	Mol wt information
Poly(α -methyl styrene-co-acrylonitrile), 30% AN	MSAN	BASF (Luran KR 2556)	115	$\bar{M}_w = 160,000^a$
Poly(styrene-co-acrylonitrile), 30% AN	SAN	Scientific Polymer Products, Inc. (SPP)	106	$[\eta] = 0.61$ dL/g in 2-butanone at 30°C
Polyacrylonitrile	PAN	SPP	93	$\bar{M}_w = 150,000^a$
Poly(α -methyl styrene)	PMS	SPP	140	$\bar{M}_w = 50,000^a$
Polystyrene	PS	BDH Chemicals Ltd	100	$\bar{M}_w = 150,000^a$
Poly(methyl methacrylate)	PMMA	DuPont (Elvacite 2010)	100	$\bar{M}_w = 120,000^b$
Poly(ethyl methacrylate)	PEMA	DuPont (Elvacite 2042)	60	$\bar{M}_w = 310,000^b$

^a Provided by manufacturer.

^b Based on intrinsic viscosity measurement.

EXPERIMENTAL

Materials. The commercial polymers used in this study are listed in Table I. TPMA was prepared by ester exchange reaction between 2,2,6,6-tetramethyl-4-piperidinol and MMA according to the method of Lu and co-workers.⁸ The various MMA-TPMA and EMA-TPMA copolymers were prepared by copolymerizing TPMA with MMA and EMA in 2-butanone at 80°C for 48 h using 0.3% by weight of azobisisobutyronitrile (AIBN) as initiator. The resulting copolymers were obtained by precipitating the copolymers from 2-butanone solutions by *n*-hexane. The polymer of TPMA was similarly prepared by solution polymerization. The compositions of the copolymers as determined by ¹H-NMR, together with their glass transition temperatures (T_g) and intrinsic viscosities ($[\eta]$) are given in Table II.

Preparation of Blends. All the blends except PAN/PTPMA blends were prepared by solution casting using tetrahydrofuran as solvent. The solvent was allowed to evaporate slowly at room temperature. The blends were then dried in a vacuum oven at 110°C for 48 h. PAN/PTPMA blends were cast from dimethylformamide at 100°C, followed by drying in vacuum at 110°C for 48 h.

 TABLE II
 Description of Copolymers

Copolymer	TPMA (wt %)	T_g (°C)	$[\eta]$ (dL/g) ^a
EMA-TPMA5	5.0	65	0.22
EMA-TPMA13	13.3	73	0.067
EMA-TPMA16	16.3	77	0.11
EMA-TPMA30	30.4	85	0.14
MMA-TPMA24	23.8	113	0.087
MMA-TPMA31	31.4	117	0.15
MMA-TPMA56	56.1	120	0.015
PTPMA	100.0	135	0.023

^a In 2-butanone at 30°C.

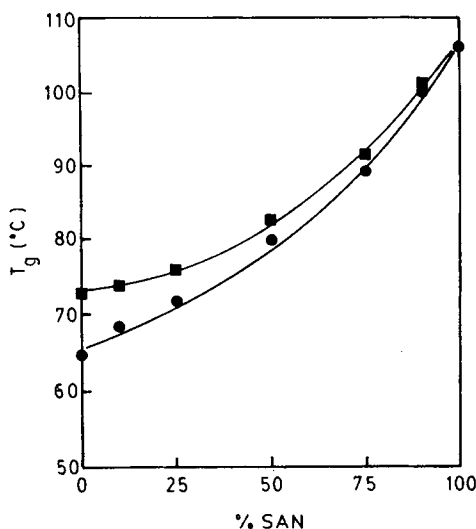


Fig. 1. T_g -composition curves of SAN/EMA-TPMA5 (●) and SAN/EMA-TPMA13 (■) blends.

Calorimetric Measurements. The glass transition temperatures of various samples were measured with a Perkin-Elmer DSC-4 differential scanning calorimeter using a heating rate of 20°C/min. The T_g was taken as the initial onset of the change of slope in the heat capacity plot.

Measurements of Lower Critical Solution Temperature (LCST). All the miscible blends were examined for the existence of LCST using the method described previously.¹⁴

RESULTS

SAN/EMA-TPMA Blends

SAN/EMA-TPMA5 blends containing 10, 25, 50, 75, and 90% by weight of SAN were transparent. Each of these blends showed only one composition-dependent T_g , indicating the miscible nature of the blend. The T_g -composition curve of this blend system is shown in Figure 1.

Similarly, all the SAN/EMA-TPMA13 blends were transparent and each of them showed one T_g as shown in Figure 1. Thus SAN is also miscible with EMA-TPMA13 at all proportions.

All the transparent SAN/EMA-TPMA5 and SAN/EMA-TPMA13 blends turned cloudy upon heating, showing LCST behavior. The cloud point curves of these two blend systems are shown in Figure 2. It is apparent that, at a given blend composition, the cloud point of SAN/EMA-TPMA5 blend is higher than that of the SAN/EMA-TPMA13 blend.

SAN/EMA-TPMA16 blends were transparent when cast at room temperature. However, they became cloudy during the drying process. It was thought that the LCST was sufficiently low such that phase separation occurred during drying at 110°C. A new batch of blends was prepared. After the evaporation of solvent at room temperature, the blends were examined for

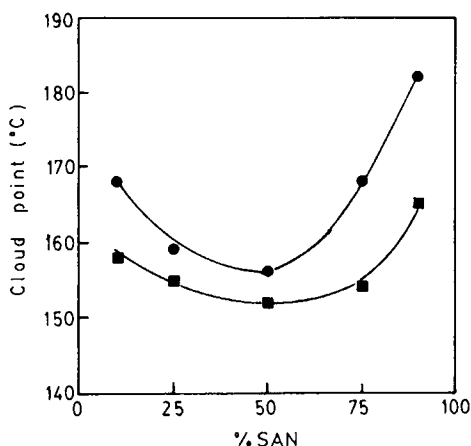


Fig. 2. Cloud point curves of SAN/EMA-TPMA5 (●) and SAN/EMA-TPMA13 (■) blends.

LCST without further drying. Bubble formation was seen starting at 70°C due to vaporization of the residual solvent in the blends. The blends then turned cloudy over the temperature range of 95–105°C. Thus the cloudiness of the blends developed during drying was a result of phase separation because of the low LCST. Since the LCST was quite low, it would be difficult to remove completely the residual solvent by drying at a low temperature in order to obtain true T_g values of the blends. No further attempts were made to dry these blends. It was then envisaged that further increase of TPMA content in EMA-TPMA copolymer would lead to immiscibility with SAN.

SAN/EMA-TPMA30 blends were opaque, indicating the heterogeneous nature of the blends. The immiscibility of SAN with EMA-TPMA30 was further confirmed by DSC measurements which showed two T_g 's for each of the blends.

MSAN/EMA-TPMA Blends

MSAN/EMA-TPMA5 blends were opaque. DSC measurements showed two T_g 's for each of the blends as shown in Figure 3. Thus for EMA-TPMA copolymer containing 5% by weight of TPMA, it is already immiscible with MSAN.

Blends of MSAN with EMA-TPMA13, EMA-TPMA16, and EMA-TPMA30 were also judged to be immiscible based on the opaque appearance and the existence of two T_g 's for each of the blends.

SAN/MMA-TPMA Blends

It has been reported that both SAN and MSAN are miscible with MMA-TPMA copolymer containing 14.5% of TPMA.¹⁴ The miscibility of SAN and MSAN with MMA-TPMA of the higher TPMA content is now reported.

All the SAN/MMA-TPMA24 and SAN/MMA-TPMA31 blends were transparent. The proximity of the T_g 's of the two component polymers precluded the use of DSC measurements to ascertain the miscibility of the

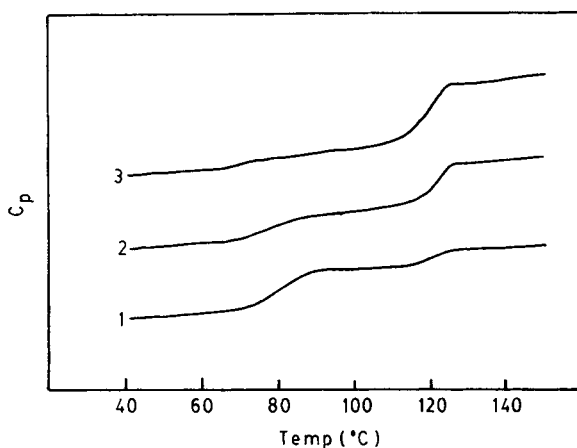


Fig. 3. DSC curves of MSAN/EMA-TPMA5 blends: (1) 25% MSAN; (2) 50% MSAN; (3) 75% MSAN.

blends. As discussed in an earlier paper,¹⁴ the transparency of SAN/MMA-TPMA blends is not a result of matching refractive indices of the two component polymers.

For blends of SAN with MMA-TPMA of a low TPMA content, they remained transparent when heated up to 270°C where they began to show sign of degradation.¹⁴ However, all the SAN/MMA-TPMA24 and SAN/MMA-TPMA31 blends developed cloudiness when heated, indicating the existence of LCST. The cloud point curves of these two blend systems are shown in Figure 4. Apparently, the LCSTs are high for blends of SAN with MMA-TPMA of low TPMA content such that they degrade before LCSTs are reached. As the TPMA content in MMA-TPMA increases, the LCSTs of the blends decrease and phase separation induced by heating can be observed.

All the SAN/MMA-TPMA56 blends were opaque, indicating the immiscible nature of these blends.

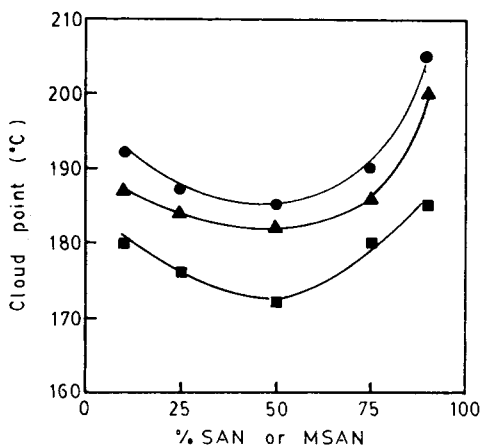


Fig. 4. Cloud point curves of SAN/MMA-TPMA24 (●), SAN/MMA-TPMA31 (■), and MSAN/MMA-TPMA24 (▲) blends.

MSAN/MMA-TPMA Blends

All the MSAN/MMA-TPMA24 blends were transparent but they became cloudy when heated. The cloud point curve of this blend system is shown in Figure 4. The cloud points of these blends are lower than those MSAN/MMA-TPMA blends of a lower TPMA content.¹⁴ Although DSC measurements cannot be used to confirm the miscibility of MSAN/MMA-TPMA24 blends, the transparency of the blends which is not a result of matching refractive indices and the existence of LCST are sufficient evidence to conclude the miscible nature of these blends.

On the other hand, all the MSAN/MMA-TPMA31 and MSAN/MMA-TPMA56 blends were opaque, showing that they were immiscible blends.

DISCUSSION

We have shown that while both PMMA and PEMA are miscible with SAN and with MSAN, the replacement of the pendant alkyl groups of the polymethacrylates by SHA groups reduces their miscibility with the acrylonitrile-containing copolymers.

For SAN containing 30% of acrylonitrile, it is miscible with MMA-TPMA copolymer if the TPMA content is less than about 40%. The miscibility range of SAN with EMA-TPMA copolymer is smaller. It is miscible with EMA-TPMA copolymer when the TPMA content is less than 16%.

For MSAN containing 30% of acrylonitrile, its miscibility with MMA-TPMA and EMA-TPMA copolymers is more limited. MMA-TPMA copolymer containing 31% of TPMA and EMA-TPMA copolymer containing 5% of TPMA are already immiscible with MSAN.

Based on the above results, it was expected that both SAN and MSAN would be immiscible with PTPMA where all the pendant alkyl groups had been replaced by SHA groups. Both SAN/PTPMA and MSAN/PTPMA blends showed gross phase separation. The two-phase nature of these blends

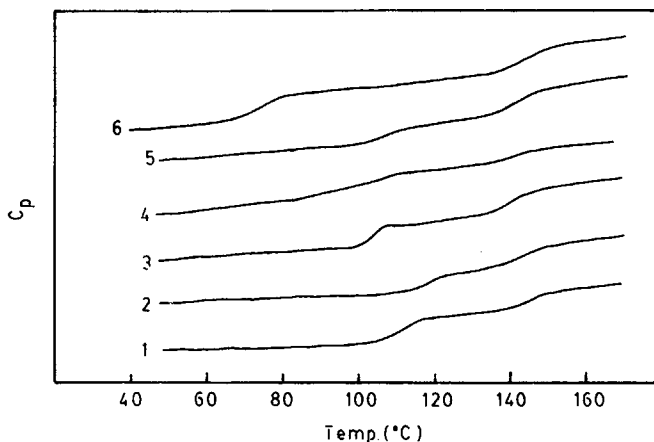


Fig. 5. DSC curves of binary blends containing 50% PTPMA: (1) PTPMA/SAN; (2) PTPMA/MSAN; (3) PTPMA/PS; (4) PTPMA/PAN; (5) PTPMA/PMMA; (6) PTPMA/PEMA.

was also confirmed by DSC. Figure 5 shows the DSC curves of 50/50 blends of SAN/PTPMA and MSAN/PTPMA.

Several recent theories²²⁻²⁴ point out that for polymer blends containing a copolymer, the intramolecular interaction between the two different monomer units in the copolymer is important in determining the miscibility of the blends. In the present study, both the component polymers are copolymers. The effective interaction parameter B for a blend of two copolymers C_x/D_{1-x} and M_y/N_{1-y} is given by

$$B = xyB_{CM} + (1-x)yB_{DM} + x(1-y)B_{CN} + (1-x)(1-y)B_{DN} \\ - x(1-x)B_{CD} - y(1-y)B_{MN}$$

where x and y denote the copolymer compositions; B_{CM} , B_{DM} , B_{CN} , and B_{DN} are the intermolecular interaction parameters, and B_{CD} and B_{MN} are the intramolecular interaction parameters.²³ Even if all the segment-segment interactions are unfavorable, i.e., positive, the effective interaction parameter B can still be negative, depending on the copolymer compositions and the magnitudes of the various interactions.²⁵

It has been noted that PS/PMMA, PS/PEMA, PAN/PMMA, PAN/PEMA, PS/PAN, PMS/PAN, PMS/PMMA, and PMS/PEMA are immiscible blends, indicating that the interaction parameters B for these blends are positive.²⁴ In addition, the binary blends of PTPMA with PMMA, PEMA, PS, PMS, and PAN were found to be immiscible. All these blends showed gross phase separation. The DSC curves of 50/50 blends of PTPMA/PMMA, PTPMA/PEMA, PTPMA/PS and PTPMA/PAN are shown in Figure 5, confirming that these blends are immiscible. The T_g 's of PMS and PTPMA are quite close to each other, but the heterogeneous appearance of the blends is sufficient to conclude that the blends are also immiscible.

Therefore, for each of the four blend systems studied in the present work, all the four intermolecular interactions parameters and two intramolecular interaction parameters are positive, and yet some of the blends are miscible. The results agree with the above-mentioned theories that, although none of the homopolymers are miscible with each other, the copolymer/copolymer blend can be miscible under certain conditions, and intramolecular repulsive interaction in copolymer is important in achieving miscibility.

It has been shown that cloud points of miscible polymer blends provide a simple means to compare interaction parameters.^{26,27} The cloud point increases as the interaction parameter B becomes more negative. The cloud point results indicate that the effective interaction parameter B of a blend becomes less negative with increasing TPMA content in MMA-TPMA and EMA-TPMA copolymers. The results also suggest that B is more negative for a SAN blend than for a corresponding MSAN blend.

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