

# Miscible Blends of Poly(styrene-co-Acrylonitrile) and Poly( $\alpha$ -Methyl Styrene-co-Acrylonitrile) with Poly(methyl Methacrylate) Containing Sterically Hindered Amine Group

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## Synopsis

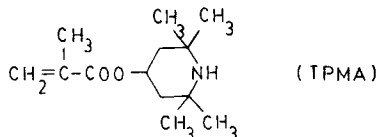
Poly(methyl methacrylate) containing a small amount of pendant 2,2,6,6-tetramethylpiperidiny group was found to be miscible with poly(styrene-co-acrylonitrile) and with poly( $\alpha$ -methyl styrene-co-acrylonitrile). The poly( $\alpha$ -methyl styrene-co-acrylonitrile) blends exhibited lower critical solution temperatures. Phase separation of the poly(styrene-co-acrylonitrile) blends could not be induced by heating up to 270°C.

## INTRODUCTION

Sterically hindered amines (SHA) from the 2,2,6,6-tetramethylpiperidine series represent a relatively new class of polymer stabilizers.<sup>1,4</sup> A notable example is bis-(2,2,6,6-tetramethyl-4-piperidiny) sebacate. SHA stabilizers are highly efficient as thermal and photostabilizers for polymers. The photostabilizing activity of SHA stabilizers for polymers such as polyolefins, polystyrene, and polydienes exceeds that of such well-known stabilizers like 2-hydroxy-benzophenone.

One problem commonly encountered in the stabilization of polymers using low-molecular weight stabilizers is the loss of the stabilizers due to their volatility. The problem can be overcome by the use of high-molecular weight stabilizers or by the incorporation of stabilizing groups into the base polymers. Polymers containing 2,2,6,6-tetramethylpiperidiny groups have also been used as stabilizers.<sup>5-8</sup>

The miscibility of poly(styrene-co-acrylonitrile) (SAN) and poly( $\alpha$ -methyl styrene-co-acrylonitrile) (MSAN) with various polymethacrylates has been studied.<sup>9-15</sup> 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 reported that both SAN and MSAN are miscible with some copolymers of methyl methacrylate.<sup>16</sup> It will be of interest to study if the miscibility of PMMA with SAN and MSAN is affected by the incorporation of a small amount of SHA group into the PMMA. Such miscible binary blends may be of practical importance as the SHA groups are expected to impart better thermal and photostability to the blends. This paper reports the miscibility of SAN and MSAN with PMMA containing 2,2,6,6-tetramethylpiperidiny group. The SHA group was incorporated into PMMA by copolymerizing 2,2,6,6-tetramethylpiperidiny methacrylate (TPMA) with methylmethacrylate (MMA).



## EXPERIMENTAL

### Materials

The MSAN polymer used was Luran KR 2556U 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 and its intrinsic viscosity is 0.54 dl/g in 2-butanone at 30°C.

TPMA was prepared by ester exchange reaction between 2,2,6,6-tetramethyl-4-piperidinol and MMA according to the method of Lu et al.<sup>8</sup> The MMA-TPMA copolymers were prepared by copolymerizing MMA and TPMA in bulk at 60°C for 18 h, using 0.3% by weight of azobisisobutyronitrile as initiator. The resulting copolymers were purified by precipitating the copolymers from 2-butanone solutions by *n*-hexane. Three MMA-TPMA copolymers of varying compositions were prepared. The TPMA contents as determined by elemental analysis, together with the glass transition temperatures ( $T_g$ ) and the intrinsic viscosities ( $[\eta]$ ) of the three copolymers are given in Table I.

**Preparation of Blends.** All the blends were prepared by solution casting using 2-butanone 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.

**Calorimetric Measurement.** The glass transition temperatures of the MMA-TPMA copolymers 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 onset of the change of slope in the heat capacity plot.

**Measurements of Lower Critical Solution Temperature (LCST).** All the blends were examined for LCST. The polymer film was sandwiched between two microscopic cover glasses and heated in a Fisher-Johns melting apparatus with a heating rate of about 20°C/min. The optical appearance of the film was observed with the aid of a magnifying glass attached to the apparatus. A transparent sample which turned cloudy on heating indicated the existence of LCST. The temperature at which the sample first showed cloudiness was recorded as the cloud point.

TABLE I  
Description of MMA-TPMA Copolymers

Copolymer	Wt% of TPMA	$T_g$ (°C)	$[\eta]$ (dl/g) <sup>a</sup>
MMA-TPMA-1	1.5	109	0.44
MMA-TPMA-2	7.8	118	0.16
MMA-TPMA-3	14.5	122	0.41

<sup>a</sup> In 2-butanone at 30°C.

## RESULTS AND DISCUSSION

## Blends Containing MSAN

All the binary blends of MSAN with various MMA-TPMA copolymers were transparent. The proximity of the  $T_g$ 's of MMA-TPMA and MSAN ( $T_g$ : 115°C) precluded the use of  $T_g$  measurement to ascertain the miscibility of the blends. An immiscible blend can be transparent if the difference between the refractive indices of the two component polymers is smaller than 0.01 or the domain size is smaller than the wavelength of the visible light. The refractive indices of MSAN, MMA-TPMA-1, MMA-TPMA-2, and MMA-TPMA-3 are estimated to be 1.566, 1.496, 1.498, and 1.500, respectively, by the Vogel method.<sup>17</sup> In the absence of experimental values, the Vogel method provides good estimations of the refractive indices of polymers. For example, the refractive index of PMMA is estimated to be 1.495 as compared to the literature value of 1.492.<sup>18</sup> Apparently, the transparency of the MSAN/MMA-TPMA blends is not the result of matching refractive indices of the two component polymers.

All these blends turned cloudy upon heating, indicating the existence of LCST. However, the phase separation induced on heating was not reversed on cooling to room temperature because of the low mobilities of these high  $T_g$  mixtures. Such behaviors have also been observed for other blends of MSAN and SAN with various polymethacrylates.<sup>14-16, 19</sup> When the phase-separated blend was treated with a drop of 2-butanone and then placed in an oven at 130°C, it reverted to transparency. Upon the addition of solvent and heating, the polymers have sufficient mobilities to mix again. These results indicate that complete miscibility exists below the LCST. The cloud points of the blends are given in Table II and also shown in Figure 1. The cloud point decreases as the TPMA content in the MMA-TPMA copolymer increases.

The formation of a miscible blend is generally attributed to a negative heat of mixing arising from some specific interaction between the two component polymers. The nature of specific interaction in miscible blends of MSAN and SAN with PMMA has not been identified. In a recent study on the miscibility of styrene/*p*-(hexafluoro-2-hydroxyl isopropyl)styrene copolymer with SAN and with PMMA,<sup>20</sup> a shift in the nitrile absorption peak of SAN and the carbonyl absorption peak of PMMA in the blend was observed, indicating the interaction of nitrile groups and carbonyl groups with the hydroxyl groups of the styrene copolymer. It is possible that nitrile-carbonyl interaction could take place in the SAN/PMMA and MSAN/PMMA blends.

TABLE II  
Cloud Points (°C) of MSAN Blends

Wt% MSAN in blend	MSAN/MMA-TPMA-1	MSAN/MMA-TPMA-2	MSAN/MMA-TPMA-3
10	215	207	205
25	208	200	189
50	200	197	187
75	213	203	190
90	220	208	200

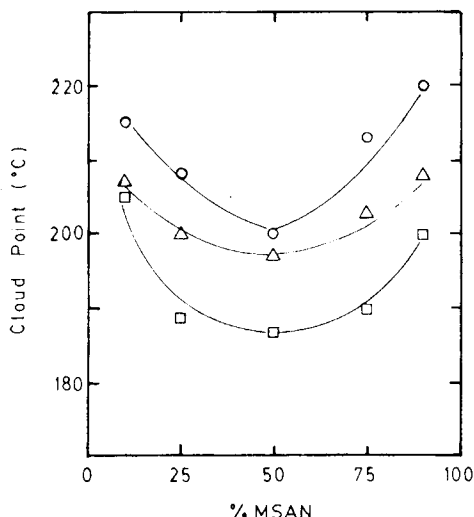


Fig. 1. Cloud point curves for MSAN blends: (○) MSAN/MMA-TPMA-1 blends; (△) MSAN/MMA-TPMA-2 blends; (□) MSAN/MMA-TPMA-3 blends.

It has been found that for blends of poly(vinylidene fluoride) with some polymethacrylates and polyacrylates, there was a good correlation between the interaction parameters and the cloud points of the blends, and hence the cloud points provided a simple means to compare the interaction parameters of the blends.<sup>21</sup> As shown in Figure 1, the cloud point of MSAN/MMA-TPMA blend decreases as the TPMA content in MMA-TPMA increases. This can be taken as an indication that the interaction between MSAN and PMMA is reduced when the pendant methyl group is replaced by 2,2,6,6-tetramethylpiperidinyll group. Nevertheless, even when 14.5% of the MMA is replaced by TPMA, the blend is still miscible.

Several recent papers<sup>22-24</sup> pointed out that for blend containing a copolymer, intramolecular interaction between the two monomer units in the copolymer could be important in determining the miscibility of the blend. Such theories adequately explain the "miscibility window" of the copolymer. In the present case, both MSAN and MMA-TPMA are copolymers, and therefore two intramolecular and four intermolecular interactions among the four monomer units in the blend have to be considered. A complete picture on the miscibility behavior of this blend system will then require a thorough study using various MSAN and MMA-TPMA covering a wide copolymer composition range, and this has not been done in the present case as we only seek to study the miscibility of a commercial MSAN with PMMA containing a small amount of SHA group.

### Blends Containing SAN

The proximity of the  $T_g$ 's of MMA-TPMA and SAN ( $T_g = 100^\circ\text{C}$ ) also precluded the use of  $T_g$  measurement to ascertain the miscibility of the blends. All the binary blends of SAN with MMA-TPMA were transparent, and they remained transparent when heated up to  $270^\circ\text{C}$  where the blends showed sign of decomposition. The transparency of the blends is not due

to the matching of refractive indices of the two component polymers, as SAN has an estimated refractive index of 1.577 (refractive index of SAN containing 25% AN is reported to be 1.570.<sup>18</sup>)

In our previous study on the miscibility of MSAN and SAN with MMA/ethyl methacrylate (MMA/EMA) and MMA/*n*-butyl methacrylate (MMA/BMA) copolymers, the MSAN blends showed phase separation upon heating but not the SAN blends.<sup>16</sup>  $T_g$  measurements by DSC had conclusively shown the miscible nature of those blends.

In the present study, although  $T_g$  measurements cannot be used to help ascertain the miscibility, the existence of LCST in the MSAN blends and the transparency of the SAN blends even on heating can be taken as sufficient evidence to show the miscible nature of these blends.

If the cloud point is used as a measurement of polymer-polymer interaction in the blend as mentioned earlier, the present result suggests that the intensity of interaction in the SAN blend is stronger than that in the corresponding MSAN blend.

In summary, PMMA containing a small amount of 2,2,6,6-tetramethylpiperindinyl group is still miscible with MSAN and SAN. It will be worthwhile to study the stability of these blends in view of the stabilizing nature of the SHA group.

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