

Miscible Blends Containing Poly(tetrahydrofurfuryl methacrylate)

INTRODUCTION

The miscibility of various polymethacrylates with poly(styrene-co-acrylonitrile) (SAN) and poly(α -methyl styrene-co-acrylonitrile) (MSAN) is well documented.¹⁻⁸ The miscibility of some copolymers of methyl methacrylate with SAN and MSAN has also been reported.^{9,10} The miscibility of polymethacrylate with SAN and MSAN is affected by modification of the pendant alkyl group. We have reported that the incorporation of hydroxyl groups in the pendant alkyl groups enhances the miscibility of the polymethacrylate with SAN and MSAN, but the incorporation of sterically hindered amine groups reduces the miscibility.¹¹⁻¹³ The miscibility of poly(tetrahydrofurfuryl methacrylate) (PTHFMA) with SAN and MSAN is reported in this communication. The miscibility of polymethacrylates with poly(vinyl chloride) (PVC) has been studied.¹⁴⁻¹⁸ The miscibility of PTHFMA with PVC will also be reported.

EXPERIMENTAL

PTHFMA was obtained from Scientific Polymer Products, Inc. (SPP). Its intrinsic viscosity is 0.31 dL/g in toluene at 30°C. SAN was also obtained from SPP. It contains 30% by weight of acrylonitrile and its intrinsic viscosity is 0.61 dL/g in 2-butanone at 30°C. The MSAN used was Luran KR 2556U manufactured by BASF. It contains 30% by weight of acrylonitrile and its \bar{M}_w is 160,000.

Other polymers used in this study are PVC (SPP, $\bar{M}_w = 83,500$), polystyrene (BDH Chemicals Ltd., $\bar{M}_w = 150,000$), poly(α -methyl styrene) (SPP, $\bar{M}_w = 50,000$) and polyacrylonitrile (SPP, $\bar{M}_w = 150,000$).

Binary blends of PTHFMA with SAN, MSAN, polystyrene (PS), and poly(α -methyl styrene) (PMS) were solution-cast from tetrahydrofuran at room temperature. They were further dried in a vacuum oven at 120°C for 24 h. PTHFMA/polyacrylonitrile (PAN) blends were cast from dimethylformamide at 100°C, followed by drying *in vacuo* at 120°C for 24 h. PTHFMA/PVC blends were also cast from tetrahydrofuran at room temperature. To stabilize PVC against degradation during heating, a stabilizer (Advastab TM-181) was added in an amount of 5% by weight of PVC. The blends were further dried *in vacuo* at 100°C for 24 h.

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

All the miscible blends were examined for the existence of lower critical solution temperatures (LCST) using the method described previously.¹¹

RESULTS AND DISCUSSION

All the binary blends of PTHFMA/SAN and PTHFMA/MSAN were transparent. Each blend showed a single composition-dependent T_g as shown in Figure 1, indicating its single-phase nature. Thus PTHFMA is miscible with SAN and MSAN at all compositions. The T_g of the blend is approximately a weighted-average of the T_g 's of the two component polymers.

The transparent PTHFMA/SAN blends turned cloudy when heated to around 260–280°C, showing LCST behavior. The cloud point curve of PTHFMA/SAN blends is shown in Figure 2. Similarly, PTHFMA/MSAN blends also turned cloudy upon heating. However, the cloud points of these blends are about 60°C lower than the corresponding PTHFMA/SAN blends as shown in Figure 2. In our previous work, it has been observed that a SAN blend had a higher cloud point than the corresponding MSAN blend.^{9,11-13} If cloud point is used as a measurement of the

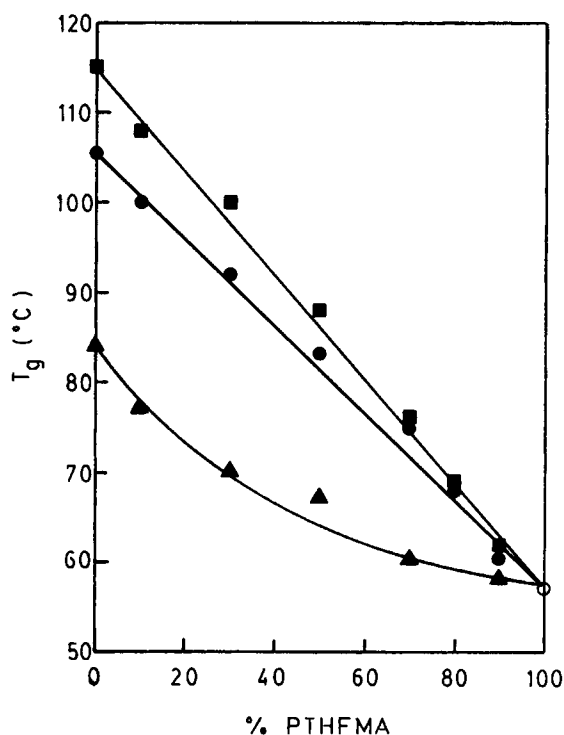


Fig. 1. T_g -composition curves of PTHFMA/SAN (●), PTHFMA/MSAN (■), and PTHFMA/PVC (▲) blends.

intensity of intermolecular interaction,¹⁹ the results indicate a more intense interaction in a SAN blend than in the corresponding MSAN blend. The cloud points of PTHFMA/MSAN blends are about the same as those of poly(methyl methacrylate) (PMMA)/MSAN blends, but they are higher than those of poly(ethyl methacrylate) (PEMA)/MSAN blends.⁷ It is interesting to note that, in spite of the bulkiness of the tetrahydrofurfuryl group, the miscibility behavior of PTHFMA is about the same as that of PMMA, as indicated by the cloud point results.

The binary blends of PTHFMA/PS, PTHFMA/PMS and PTHFMA/PAN were opaque, indicating the heterogeneous nature of these blends. The immiscibility of these blends were further confirmed by T_g measurements which showed two T_g 's in each of the blends.

Thus while PTHFMA is immiscible with PS, PMS, and PAN, it is miscible with SAN and MSAN which contain 30% by weight of acrylonitrile. It is commonly observed that a copolymer A/B is miscible with a homopolymer C over a certain range of copolymer composition, but neither homopolymer A nor homopolymer B is miscible with homopolymer C. The thermodynamics of the miscibility of homopolymer/copolymer blends has been discussed in several recent papers.²⁰⁻²⁶ It has been pointed out that if the intramolecular repulsive interaction between monomer units A and B in the copolymer is large enough, the copolymer can be miscible with homopolymer C even in the absence of any favorable intermolecular interaction. Using the solubility parameter approach, Kammer and co-workers⁸ showed that there was a strong repulsive effect between S and AN in SAN/PMMA blend. In the present blend systems, the formation of miscible blends of PTHFMA/SAN and PTHFMA/MSAN is also helped by the repulsive intramolecular interactions between the two different monomer units in SAN and MSAN.

As mentioned earlier, the miscibility behavior of PTHFMA appears to be similar to that of PMMA. It is of interest to see if PTHFMA is miscible with PVC since PMMA is miscible with PVC.

The PTHFMA/PVC blends were transparent and each showed one T_g . The T_g -composition curve of the blends is shown in Figure 1. The optical clarity and the existence of a single

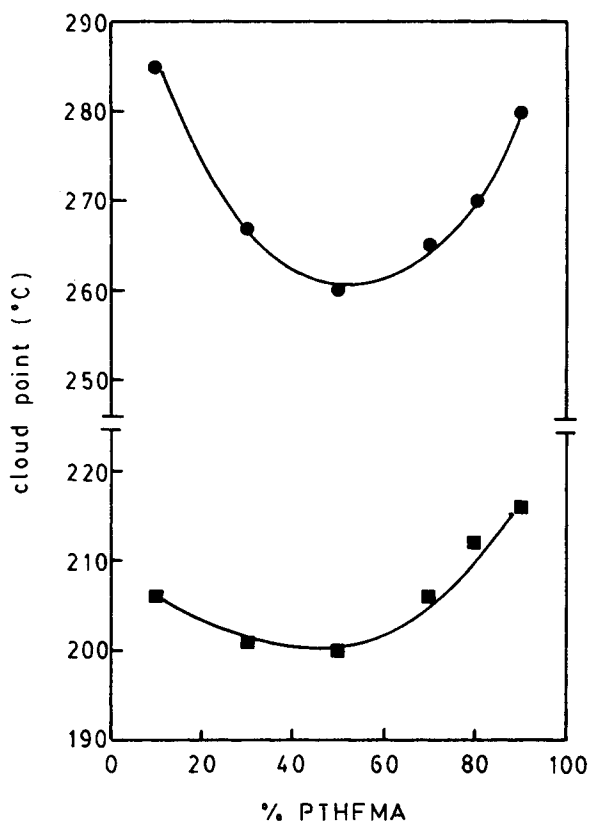


Fig. 2. Cloud point curves of PTHFMA/SAN (●) and PTHFMA/MSAN (■) blends.

composition-dependent T_g show that PTHFMA is miscible with PVC. All the blends remained transparent when heated up to 250°C. Further heating led to discoloration caused by degradation of the polymers.

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