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MISCIBILITY OF POLY(CHLOROMETHYL METHACRYLATE) WITH POLY(p-METHYLSTYRENE-CO-ACRYLONITRILE)

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ABSTRACT

The miscibility of poly(chloromethyl methacrylate) (PCMMA) with poly(p-methylstyrene-co-acrylonitrile) (pMSAN) of various compositions was studied by differential scanning calorimetry. PCMMA is miscible with pMSAN over a composition range of 13-42 wt% AN. The phase behaviour allows evaluation of two segmental interaction parameters.

INTRODUCTION

The miscibility of poly(methyl methacrylate) (PMMA) with poly(styrene-co-acrylonitrile) (SAN) has been much investigated (1-9). PMMA is immiscible with polystyrene (PS) and with polyacrylonitrile (PAN) but miscible with SAN over a certain range of copolymer composition. The miscibility of such a blend system is explained by the binary interaction model which takes into consideration the intramolecular interactions between the two types of segments in the copolymer (10-12). Likewise, poly(ethyl methacrylate) and poly(n-propyl methacrylate) are also miscible with SAN over a limited range of copolymer compositions (8). In recent papers, we considered the case of poly(chloromethyl methacrylate) (PCMMA) (13-16). It is miscible with SAN over a copolymer composition range of 12-37 wt% of AN (16). We now report the miscibility of PCMMA with poly(p-methylstyrene-co-acrylonitrile) (pMSAN).

EXPERIMENTAL

Chloromethyl methacrylate (CMMA) was prepared by the procedure of Ueda et al. (17). It was polymerized in 2-butanone at reflux temperature for 24 hr using 0.25 wt% of azobisisobutyronitrile (AIBN) as initiator. The resulting PCMMA had $\bar{M}_\eta$ of 58,000, as determined by intrinsic viscosity measurements using the equation $[\eta]$ (ml/g) = $1.0\times10^{-2}\ \bar{M}_\eta^{0.725}$ (tetrahydrofuran, 30°) (17).

Various pMSAN samples were prepared by solution polymerization in 2-butanone at reflux temperature for 4 hr using AIBN (0.3 wt% of monomers) as initiator. The copolymers were precipitated in excess methanol. Their AN contents were determined by elemental analyses for nitrogen. Their intrinsic viscosities were in the order of 0.25 dl/g in 2-butanone at 30°.

Except for pMSAN containing 45.3 wt% of AN, other PCMMA/pMSAN blends in ratios of 1:3, 1:1 and 3:1 were cast from tetrahydrofuran (THF) at room temperature. Blends of PCMMA with pMSAN containing 45.3 wt% of AN were cast from dimethylformamide at 100° because the pMSAN sample was insoluble in THF. All the blends were further dried in vac. at 110° for 48 hr.

A Perkin-Elmer DSC-4 differential scanning calorimeter was used to study the glass transition behaviour of the blends. The heating rate was 20°/min. All the miscible blends were examined for the existence of lower critical solution temperature (LCST) behaviour using the method described previously (18).

RESULTS AND DISCUSSION

Blends of PCMMA with pMSAN containing 21.3, 26.5, 32.3 and 39.6 wt% of AN were transparent and remained so upon heating to about 280° where discolouration began. The optical clarity of the blends indicated that they were likely to be miscible blends. Blends of PCMMA with pMSAN containing 7.7 and 45.3 wt% of AN were opaque, indicating their heterogeneous nature.

Blends of PCMMA with pMSAN containing 13.6 wt% of AN were transparent when cast from THF at room temperature but they turned cloudy during drying. It appears that these blends have rather low LCSTs so that phase separation occurs during drying at 110°. A new batch of blends was prepared and dried in vacuum at 70° for one week. When examined for LCST behaviour, these transparent blends became cloudy at 135-140°. The low cloud points indicate that these blends are near the verge of immiscibility.

To confirm the miscibility of blends, the glass transition behaviour was studied by DSC. The T_g of PCMMA is 87° i.e. about 15-20° below those of various pMSAN samples. It has been shown that, for a blend containing two polymers with rather close T_gs, the enthalpy recovery of the blend provides a useful means to ascertain miscibility (19-21). To erase the previous thermal history, all the blends except PCMMA/pMSAN (13.6 wt% AN) were first heated to 150° and kept at that temperature for 5 min before being quenched to room temperature. PCMMA/pMSAN (13.6 wt% AN) blends, in view of their low cloud points, were thermally treated at 110° for 5 min before being quenched to room temperature. The blends were then annealed at 70° for 10 days. The DSC curves of annealed PCMMA/pMSAN (50/50) blends are shown in Fig. 1.

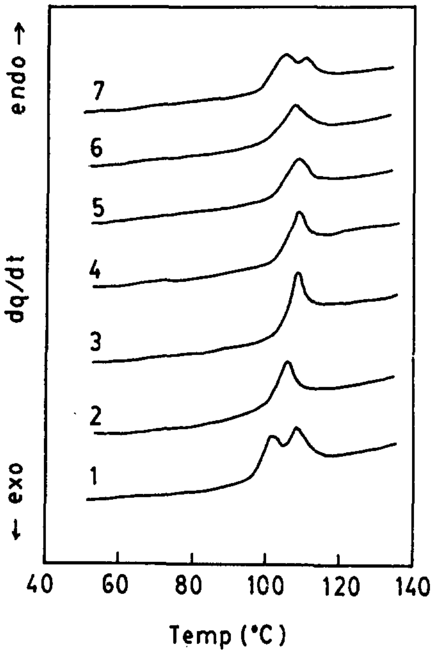

Figure 1. DSC curves of annealed PCMMA/pMSAN (50/50) blends. Wt% AN in pMSAN; (1) 7.7; (2) 13.6; (3) 21.3; (4) 26.5; (5) 32.3; (6) 39.6; (7) 45.3.

PCMMA is miscible with pMSAN containing 13.6, 21.3, 26.5, 32.3 and 39.6 wt% of AN, as shown by the appearance of a single enthalpy recovery peak for each blend. PCMMA is immiscible with pMSAN containing 7.7 and 45.3 wt% of AN, as judged by the appearance of two enthalpy recovery peaks for each blend. Therefore, PCMMA is miscible with pMSAN over a copolymer composition range of about 13-42 wt% of AN.

The segmental interaction parameter between CMMA and AN segments, $\chi_{CMMA/AN}$, is 0.49 (16). This value, together with the information obtained from the PCMMA/pMSAN blends, is used to evaluate other segmental interaction parameters. For PCMMA/pMSAN blends, the interaction parameter χ is given by the equation

$$\chi = y\chi_{CMMA/AN} + (1 - y)\chi_{CMMA/pMS} - y(1 - y)\chi_{pMS/AN}$$

where y is the volume fraction of AN in pMSAN. For a blend at the point of phase separation

$$\chi_{crit} = 1/2(N_1^{-\frac{1}{2}} + N_2^{-\frac{1}{2}})^2$$

where N_1 and N_2 are the degrees of polymerization of the two polymers. The value of χ_{crit} depends mainly on the polymer with the lower degree of polymerization. Although information on the molecular weights of the pMSAN samples is not available, the fairly high intrinsic viscosities indicate that they are sufficiently high. χ_{crit} is then assumed to be governed by the degree of polymerization of PCMMA which is about 400. χ_{crit} is then 0.005 by assuming N_1 and N_2 to be 400. The phase boundaries are at 13 and 42 wt% of AN, corresponding to y values of 0.12 and 0.40. $\chi_{CMMA/pMS}$ and $\chi_{pMS/AN}$ are then found to be 0.049 and 0.91 respectively. These values are larger than those of 0.037 and 0.83 for $\chi_{CMMA/S}$ (16) and $\chi_{S/AN}$ (9) respectively. The results indicate that the repulsive interactions between styrene (S) and AN and between S and CMMA segments are enhanced by methyl substitution in the benzene ring of S.

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