Notes

Three Miscible Blends Containing an α-Methylstyrene/Acrylonitrile Copolymer

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Received February 21, 1990;
Revised Manuscript Received July 5, 1990

Introduction

The miscibility of an α-methylstyrene/acrylonitrile copolymer containing 30% by weight of acrylonitrile (αMSAN30) with various polyacrylates and polymethacrylates was studied by Goh et al.[1] αMSAN30 is miscible with poly(methyl methacrylate) (PMMA) and poly(ethyl methacrylate) (PEMA) but is immiscible with higher members of the polymethacrylates. Suess et al.[2] later extended the study to blends of αMSAN samples of varying compositions with PMMA. In recent years, we have found that αMSAN30 is miscible with several polymethacrylates containing other functional moieties in their pendant groups.[3-5] These polymethacrylates include poly(hydroxyethyl methacrylate), poly(hydroxypropyl methacrylate), poly(tetrahydrofurfuryl methacrylate), poly(chloromethyl methacrylate), and poly(methoxymethyl methacrylate). In addition to polymethacrylates, αMSAN30 is also miscible with poly(vinyl chloride)[6] and bisphenol-A polycarbonate.[7] In this paper, we report three new miscible binary blends of αMSAN30 with poly(2-chloroethyl methacrylate) (PCEMA), poly[(methylthio)methyl methacrylate] (PMTMA), and poly(acetonyl methacrylate) (PACMA).

$$-CH_2C(CH_3)(COOR)-$$

PCEMA, R = CH_2CH_2Cl
PMTMA, R = CH_2SCH_3
PACMA, R = CH_2COCH_3

Experimental Section

The monomer CEMA was obtained from Polysciences, Inc., and it was purified by fractional distillation. PCEMA was prepared by solution polymerization in 2-butanone at reflux temperature for 6 h using 0.25 wt % of azobisisobutyronitrile as initiator. The M_n of PCEMA is 142 000 as determined by intrinsic viscosity measurement using the appropriate Mark-Houwink equation.[8] The monomers MTMA and ACMA were prepared following the procedures reported by Ueda et al.[9,10] PMTMA and PACMA were prepared by solution polymerization as described elsewhere.[11,12] The M_w of PMTMA is 48 000 as determined by intrinsic viscosity measurement.[10] PACMA has an intrinsic viscosity of 0.99 dL/g in tetrahydrofuran (THF) at 30 °C. The following commercial polymers were used: αMSAN30 (BASF, M_w = 150 000), poly(α-methylstyrene) (PαMS) (Aldrich, M_w = 113 000), and polyacrylonitrile (PAN) (Scientific Polymer Products, Inc., M_w = 150 000).

Except for blends containing PAN, other binary blends were cast from THF at room temperature. Blends containing PAN were cast from dimethylformamide at 100 °C. The cast films were then dried in vacuo at 90 °C for 72 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. Each sample was scanned several times between 30 and 150 °C to check the consistency of the T_g values. T_g was taken as the initial onset of the change of slope in the DSC curve.

All the blends were examined for the existence of lower critical solution temperature (LCST) behavior. A film was sandwiched between two microscopic glasses and heated in a Fisher-John melting point apparatus with a heating rate of ca. 10 °C/min. The optical appearance of the film was observed with a magnifying glass attached to the apparatus. A transparent film that turns cloudy upon heating indicates the existence of LCST. The temperature at which the film first showed cloudiness was taken as the cloud point. The reported cloud point is the average of several measurements with a reproducibility of ±2 °C.

Results and Discussion

All the binary blends of αMSAN30 with PCEMA, PMTMA, and PACMA were transparent. The optical clarity indicates that the blends are likely miscible blends. DSC measurements showed that each of the blends had one composition-dependent T_g, confirming that αMSAN30 is miscible with the three polymethacrylates. The DSC curves of αMSAN30/PCEMA blends are shown in Figure 1. The T_g-composition curves of the three blend systems are shown in Figures 2-4. The three T_g-composition curves can be fitted by the Gordon-Taylor equation[14]

$$T_g = (w_1T_{g1} + kw_2T_{g2})/(w_1 + kw_2)$$

as well as the Utracki equation[15]

$$w_1 \ln (T_g/T_{g1}) + kw_2 \ln (T_g/T_{g2}) = 0$$

where T_g, T_{g1}, and T_{g2} are the glass transition temperatures of the blend, polymer 1, and polymer 2, respectively; w_1 and w_2 are the weight fractions of polymer 1 and polymer 2 in the blend, respectively; and k is an adjustable parameter. The Gordon-Taylor k parameters are 0.10, 0.20, and 0.60 for αMSAN/PCEMA, αMSAN/PMTMA, and αMSAN/PACMA blends, respectively, and the corresponding Utracki k parameters are 0.12, 0.25, and 0.65. The T_g-composition curves in Figures 2-4 are based on the Gordon-Taylor equation. The curves based on the Utracki equation are not shown as they are close to those based on the Gordon-Taylor equation.

αMSAN30/PCEMA blends remained transparent upon heating to 280 °C, where discoloration began to develop. This shows that the blends degrade before phase separation could occur. A similar behavior has also been observed for αMSAN30/poly(chloromethyl methacrylate) blends.[13] All the αMSAN30/PMTMA and αMSAN30/PACMA blends turned cloudy upon heating, showing LCST behavior. The cloud point curves of the two blend systems are shown in Figures 3 and 4.

For a homopolymer/copolymer blend, the miscibility behavior depends on the composition of the copolymer and the signs and magnitudes of various segmental interaction parameters.[16-18] For the present systems, the net interaction parameter, χ_{blend}, is given by

$$\chi_{blend} = y\chi_{MA/AN} + (1-y)\chi_{MA/\alpha MS} - y(1-y)\chi_{\alpha MS/AN}$$

where y is the volume fraction of acrylonitrile (AN) in αMSAN30, and $\chi_{MA/AN}$, $\chi_{MA/\alpha MS}$, and $\chi_{\alpha MS/AN}$ are the

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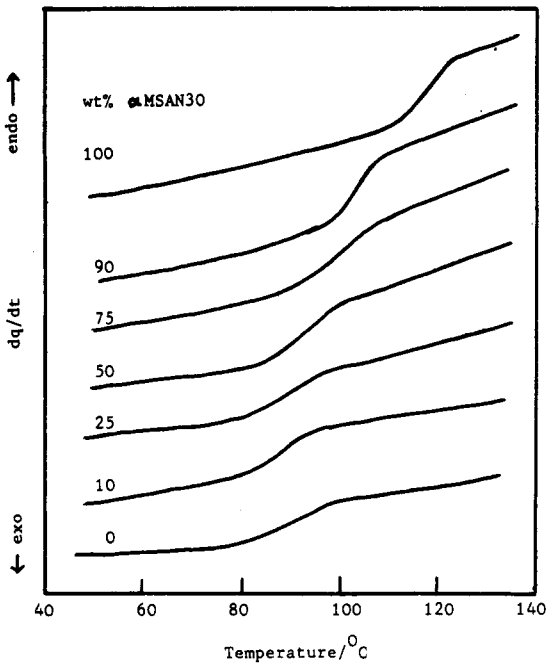

Figure 1. DSC curves of αMSAN30/PCEMA blend.

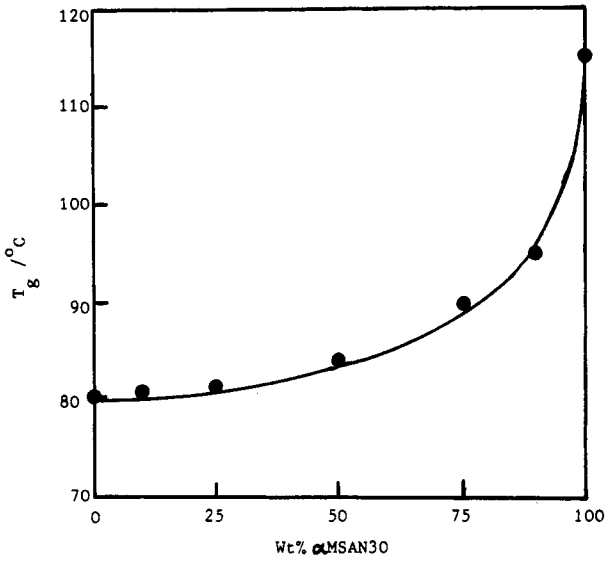

Figure 2. T_g–composition curve of αMSAN30/PCEMA blends.

various segmental interaction parameters. PαMS and PAN were found to be immiscible with PCEMA, PMTMA, and PACMA as shown by the opacity of the blends and the existence of two glass transitions in each blend. This implies that all the $\chi_{MA/AN}$ and $\chi_{MA/\alpha MS}$ are positive. Furthermore, the heat of mixing of *tert*-butylbenzene and 2-methylglutaronitrile, low molecular weight analogues for PαMS and PAN, respectively, is endothermic.[6] Thus, $\chi_{\alpha MS/AN}$ is also positive. The observed miscibility of the present blend systems confirms that a net exothermic heat of mixing for achieving miscibility can exist when none of the segmental interaction parameters is negative.[18]

In general, lower members of the polymethacrylates such as PMMA and PEMA have wide miscibility ranges than those polymethacrylates with bulkier pendant groups.[1,19] An earlier study has shown that αMSAN30 is immiscible with poly(*n*-propyl methacrylate) (PnPMA) and poly(isopropyl methacrylate) (PiPMA).[1] However, αMSAN30 is miscible with PMTMA and PACMA, whose pendant groups are of similar sizes as those of PnPMA and PiPMA. This indicates that the presence of additional functional

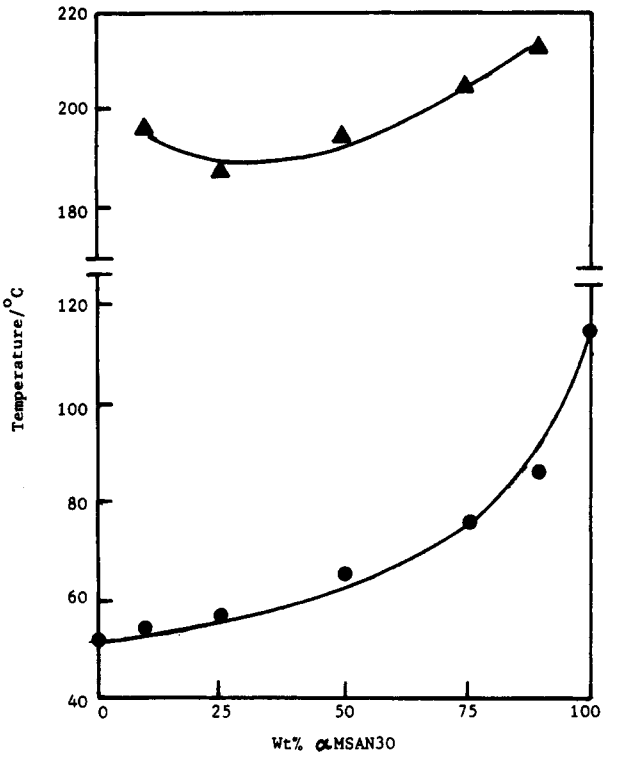

Figure 3. (●) T_g–composition and (▲) cloud point curves of αMSAN30/PMTMA blends.

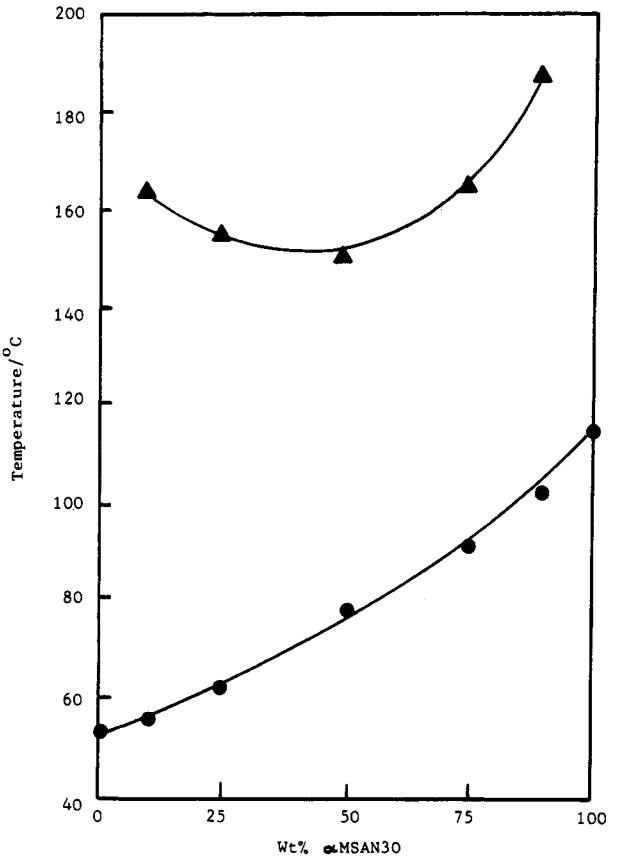

Figure 4. (●) T_g–composition and (▲) cloud point curves of αMSAN30/PACMA blends.

moieties such as sulfur and carbonyl reduces the values of $\chi_{MA/AN}$ and/or $\chi_{MA/\alpha MS}$, resulting in negative values for χ_{blend}.

The LCST behavior of miscible polymer blends has often been explained by the free-volume effects.[20,21] Phase separation occurs at a temperature where the unfavorable

free-volume effects outweigh the favorable interactional (enthalpic) effects. The LCST data are often used to indicate the intensities of interactions in blends.[6,22] αMSAN30/PCEMA blends degrade before phase separation can take place, but αMSAN30/PEMA blends undergo phase separation around 170–205 °C.[1] The much higher cloud points of the αMSAN30/PCEMA blends than those of αMSAN30/PEMA blends may be taken to indicate a more negative χ_{blend} in the former blends arising from the lower $\chi_{MA/AN}$ and/or $\chi_{MA/\alpha MS}$ values. On the other hand, the cloud points of αMSAN30/PMTMA blends are only 30 °C higher than those of αMSAN30/PACMA blends. This may be taken to indicate that the interactions in αMSAN30/PMTMA blends are slightly more intense than those in αMSAN30/PACMA blends.

In summary, the present study shows that αMSAN30 is miscible with PCEMA PMTMA, and PACMA. Blends of αMSAN30 with PMTMA and PACMA show LCST behavior. The presence of other functional moieties in the pendant groups of polymethacrylates affects the miscibility behavior.

Acknowledgment. We thank the National University of Singapore for financial support of this research.

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Registry No. αMSAN30, 25747-74-4; PCEMA, 26937-47-3; PMTMA, 107761-14-8; PACMA, 44901-95-3.