Miscibility of Poly(chloromethyl Methacrylate) with Poly(styrene-co-Acrylonitrile)

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INTRODUCTION

In a recent series of papers,[1-3] we reported the miscibility behavior of poly(chloromethyl methacrylate) (PCMMA). The miscibility behavior of PCMMA is similar to that of poly(methyl methacrylate) (PMMA) in forming miscible blends with bisphenol-A polycarbonate[1] and poly(α-methylstyrene-co-acrylonitrile).[2] On the other hand, PCMMA also behaves like a chlorinated polymer in forming miscible blends with several polymethacrylates.[3] It is well known that PMMA is miscible with poly(styrene-co-acrylonitrile) (SAN) over a certain copolymer composition range.[4-7] It is envisaged that PCMMA may similarly be miscible with SAN. In this communication, we report the miscibility behavior of PCMMA/SAN blends.

EXPERIMENTAL

Chloromethyl methacrylate (CMMA) was prepared following the method reported by Ueda and coworkers.[8] CMMA was polymerized in 2-butanone at reflux temperature for 24 h using 0.25% by weight of azobisisobutyronitrile (AIBN) as initiator. The polymer was obtained by precipitation of the solution in excess methanol. The number-average molecular weight of PCMMA was 58,000 from intrinsic viscosity measurements using the appropriate Mark-Houwink equation.[8]

An SAN sample containing 30.0% by weight of acrylonitrile (AN) was obtained from Scientific Polymer Products, Inc. Another SAN sample containing 22.0 wt % AN was obtained from Monsanto. Other SAN samples were prepared by solution polymerization in 2-butanone at reflux temperature for 4 h using AIBN (0.3 wt % monomers) as initiator. The copolymers were obtained by precipitation of the solutions in excess methanol. The composition of SAN was determined by elemental analysis of nitrogen.

Various PCMMA/SAN blends were cast from tetrahydrofuran at room temperature. They were further dried *in vacuo* at 110°C for 3 days.

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.

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All the miscible blends were examined for the existence of lower critical solution temperature (LCST) behavior using the method described previously.[9]

RESULTS AND DISCUSSION

The optical appearance of a blend often provides the first clue of its miscibility. Blends of PCMMA with SAN containing 9.8 and 43.6 wt % AN were opaque, indicating the heterogeneous nature of these blends. Blends of PCMMA with an SAN containing 40.0 wt % of AN were hazy. However, blends of PCMMA with SAN containing 13.6, 22.0, 30.0, and 34.5 wt % AN were transparent, indicating that these blends might be miscible.

PCMMA has a T_g value of 87°C, which is about 15–20°C lower than those of various SAN samples. It is often difficult to resolve the two T_gs of an immiscible blend containing polymers with close T_gs by using the conventional DSC measurements. However, recent studies have demonstrated that the enthalpy recovery (or enthalpy relaxation) of an annealed blend can be used to ascertain miscibility.[10–12] The enthalpy recovery is manifested as an endothermic peak in the DSC curve when scanning through the glass transition zone. An immiscible blend is characterized by the appearance of two enthalpy recovery peaks.

To confirm the miscibility of various PCMMA/SAN blends, each blend was first heated to 150°C and kept at that temperature for 5 min. The blend was then rapidly cooled to room temperature, followed by annealing at 70°C for 10 days. The DSC curves of various annealed PCMMA/SAN (50/50) blends are

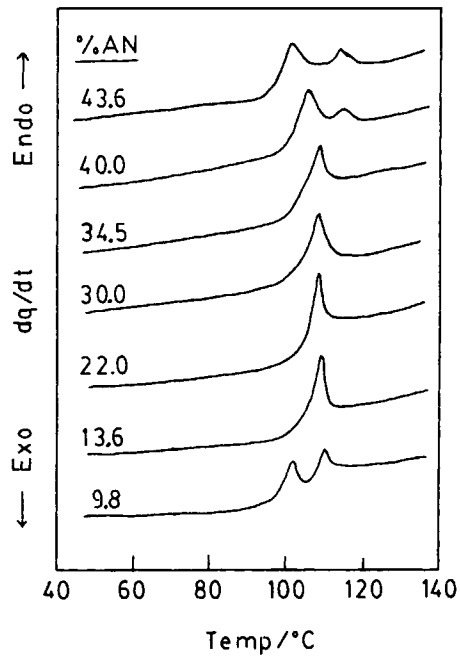

Fig. 1. DSC curves of various PCMMA/SAN (50/50) blends.

TABLE I
Miscibility Ranges of PCMMA/SAN and PMMA/SAN Blends

Blend	Miscibility range (wt % AN)	Ref.
PCMMA/SAN	12–37	This work
PMMA/SAN	9–35	5
PMMA/SAN	8–30	6
PMMA/SAN	9–39	7

shown in Figure 1. PCMMA is miscible with SAN containing 13.6, 22.0, 30.0, and 34.5 wt % AN as evidenced by the appearance of a single enthalpy recovery peak in each blend. Furthermore, these blends remained transparent when heated to about 280°C, where discoloration began to develop. PCMMA is immiscible with SAN containing 9.8 and 43.6 wt % AN as each of these blends is opaque and shows two distinct enthalpy recovery peaks. The enthalpy recovery peak of PCMMA in the blend with SAN containing 40.0 wt % AN is at a higher temperature than the corresponding PCMMA peaks in the immiscible blends with SAN containing 9.8 and 43.6 wt % AN. This observation, together with the hazy appearance of the blends, suggests that PCMMA is partially miscible with SAN containing 40.0 wt % AN.

Therefore, PCMMA is completely miscible with SAN over a copolymer composition range of about 12–37 wt % AN. The miscibility range is similar to that of PMMA/SAN blend system, as summarized in Table I.

For a homopolymer/copolymer blend, the miscibility depends on both intramolecular and intermolecular interactions between various segments in the blend.[13–16] For PCMMA/SAN blend, the interaction parameter χ is related to various segmental interaction parameters by the equation

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

where y is the volume fraction of AN in SAN. The segmental interaction parameter $\chi_{\text{S/AN}}$ is 0.829.[7] The other two parameters $\chi_{\text{CMMA/AN}}$ and $\chi_{\text{CMMA/S}}$ can be evaluated from the phase behavior of the blends. For a blend at the phase boundary,

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

where N_1 and N_2 are the degrees of polymerization of the two polymers. χ_{crit} approaches zero for polymers of sufficiently high molecular weight. In the present case, χ_{crit} is taken as 0.005, assuming N_1 and N_2 to be 400. The phase boundaries are at 12 and 37 wt % AN, which correspond to y values of 0.11 and 0.35. $\chi_{\text{CMMA/S}}$ and $\chi_{\text{CMMA/AN}}$ are then calculated to be 0.0369 and 0.485, respectively. These values are slightly larger than $\chi_{\text{MMA/S}}$ and $\chi_{\text{MMA/AN}}$, which are 0.030 and 0.461, respectively.[7]

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