Miscibility of Poly(2-Chloroethyl Methacrylate) with Various Polymethacrylates

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SYNOPSIS

The miscibility behavior of poly(2-chloroethyl methacrylate) (PCEMA) with various polymethacrylates was investigated by differential scanning calorimetry. PCEMA is miscible with poly(methyl methacrylate) (PMMA), poly(ethyl methacrylate) (PEMA), and poly(tetrahydrofurfuryl methacrylate) (PTHFMA), but is immiscible with poly(*n*-propyl methacrylate), poly(isopropyl methacrylate), poly(*n*-butyl methacrylate), and poly(cyclohexyl methacrylate). PCEMA/PEMA blends showed lower critical solution temperature (LCST) behavior but PCEMA/PMMA and PCEMA/PTHFMA blends degraded before phase separation could be induced. The miscibility behavior of PCEMA is similar to that of a chlorinated polymer.

INTRODUCTION

The role of specific interactions on the miscibility of polymer blends is well established.[1-3] The presence of specific intermolecular interactions such as hydrogen bonding, ion–dipole, dipole–dipole, π-bonding or charge transfer, and so forth, produces a favorable heat of mixing and hence leads to the formation of miscible blends. Therefore, suitable functional groups capable of forming specific interactions can be incorporated into one or both of the component polymers to improve the miscibility of immiscible blends. For example, copolymerization of styrene with *p*-(hexafluoro-2-hydroxylpropyl)styrene yields polystyrene containing hydroxyl groups.[4] While polystyrene is immiscible with poly(*n*-butyl methacrylate) (PnBMA), the incorporation of 1.8% of the hydroxyl moiety to polystyrene is sufficient to achieve miscibility with PnPMA.

We have recently studied the miscibility behavior of poly(chloromethyl methacrylate) (PCMMA).[5-9] The miscibility behavior of PCMMA was found to be similar to that of poly(methyl methacrylate) (PMMA) in forming miscible blends with poly(styrene-*co*-acrylonitrile) (SAN),[5] poly(α-methylstyrene-*co*-acrylonitrile) (αMSAN)[6] and poly(*p*-methylstyrene-*co*-acrylonitrile) (*p*MSAN).[7] The miscibility behavior of PCMMA/bisphenol-A polycarbonate (PC) blend was also found to be similar to those of PMMA/PC blends.[8] On the other hand, PCMMA also behaves like a chlorinated polymer in forming miscible blends with PMMA, poly(ethyl methacrylate) (PEMA), poly(isopropyl methacrylate) (PiPMA), poly(*n*-propyl methacrylate) (PnPMA), and poly(tetrahydrofurfuryl methacrylate) (PTHFMA).[9] It is interesting to note that while PMMA is immiscible with other polymethacrylates,[10] PCMMA is readily miscible with several polymethacrylates. In this communication, we report the miscibility of poly(2-chloroethyl methacrylate) (PCEMA) with various polymethacrylates.

EXPERIMENTAL

Materials

The monomer CEMA was obtained from Polysciences. After purification by fractional distillation under reduced pressure (60–62°C/7 mm Hg), CEMA was polymerized in 2-butanone at reflux temperature for 6 h using 0.25% by weight of azobisisobutyronitrile as initiator. The polymer was obtained by precipitation of the solution in excess

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Table I Characteristics of Polymethacrylates

Polymer	Abbreviation	Source	Mol Wt	T_g/°C
Poly(methyl methacrylate)	PMMA	Du Pont (Elvacite 2010)	$\bar{M}_w$ = 120,000	100
Poly(ethyl methacrylate)	PEMA	Du Pont (Elvacite 2042)	$\bar{M}_w$ = 310,000	65
Poly(*n*-propyl methacrylate)	PnPMA	Scientific Polymer Products	$\bar{M}_w$ = 175,000	45
Poly(isopropyl methacrylate)	PiPMA	Scientific Polymer Products	[a]	82
Poly(*n*-butyl methacrylate)	PnBMA	Du Pont (Elvacite 2044)	$\bar{M}_w$ = 288,000	20
Poly(tetrahydrofurfuryl methacrylate)	PTHFMA	Scientific Polymer Products	$\bar{M}_w$ = 240,000	57
Poly(cyclohexyl methacrylate)	PCHMA	Scientific Polymer Products	$\bar{M}_w$ = 66,000	95
Poly(2-chloroethyl methacrylate)	PCEMA	This Laboratory	$\bar{M}_n$ = 142,000	80

[a] $[\eta]$ = 0.33 dL/g in 2-butanone at 30°C.

methanol. The polymer PCEMA has a number-average molecular weight of 142,000 as determined by intrinsic viscosity measurement using the appropriate Mark–Houwink equation.[11] The main characteristics of various polymethacrylates used in this study are given in Table I.

Polymer Blends

Blends of PCEMA with various polymethacrylates were prepared by solution casting from tetrahydrofuran (THF). Solvent was allowed to evaporate slowly over a period of 1–2 days at room temperature. The cast films were then dried *in vacuo* at 90°C for 3 days.

T_g Measurements

The glass transition temperatures (T_gs) of various samples were measured with a Perkin–Elmer DSC-4 differential scanning calorimeter using a heating rate of 20°C/min. The T_g value was taken as the initial onset of the change of slope in the DSC curve. The reported T_g is the average value based on the second and subsequent runs.

Cloud Point Measurements

All the miscible blends were examined for the existence of lower critical solution temperature (LCST) using the method as described previously.[9] The temperature at which the film first showed cloudiness was taken as the cloud point.

RESULTS AND DISCUSSION

PCEMA/PMMA Blends

All the blends of PCEMA with PMMA were transparent. Each of the blends showed a single composition-dependent T_g as shown in Figure 1. It is concluded that PCEMA is miscible with PMMA. Phase separation of the PCEMA/PMMA blends could not be induced by heating up to 280°C where discoloration began to develop.

PCEMA/PEMA Blends

All the blends were transparent. Each blend showed a single composition-dependent T_g as shown in Figure 2. Blends containing 25, 50, 75, and 90% of PCEMA turned cloudy when heated to 200–220°C, showing LCST behavior. The development of cloudiness for the blend containing 10% of PCEMA

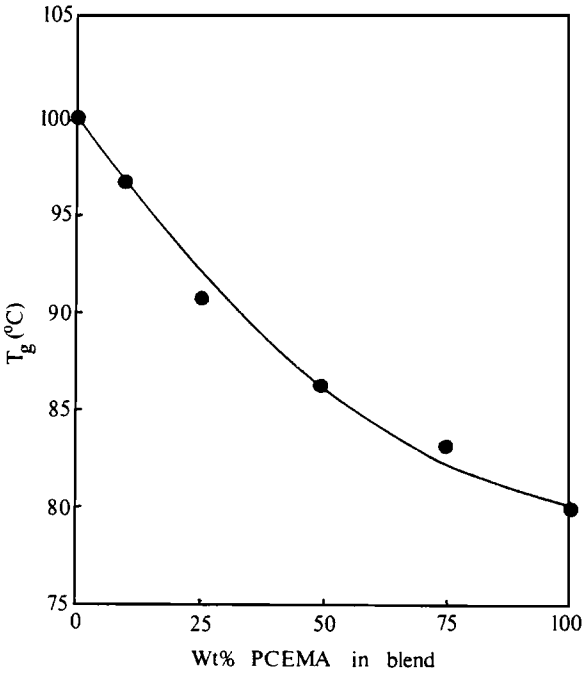

Figure 1 T_g-composition curve for PCEMA/PMMA blends.

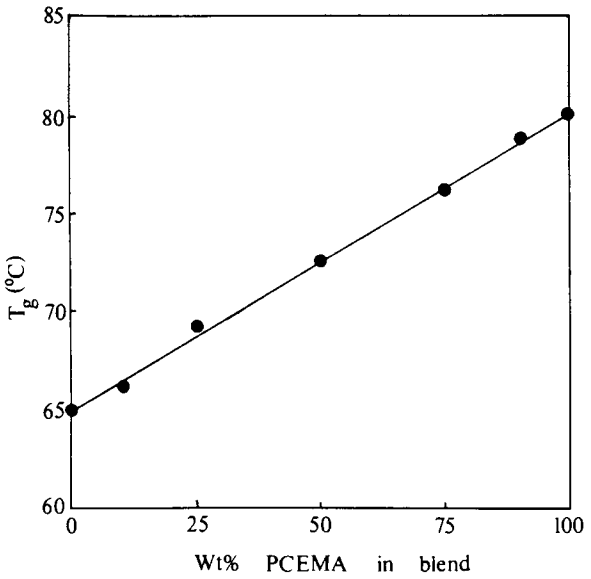

Figure 2 T_g-composition curve for PCEMA/PEMA blends.

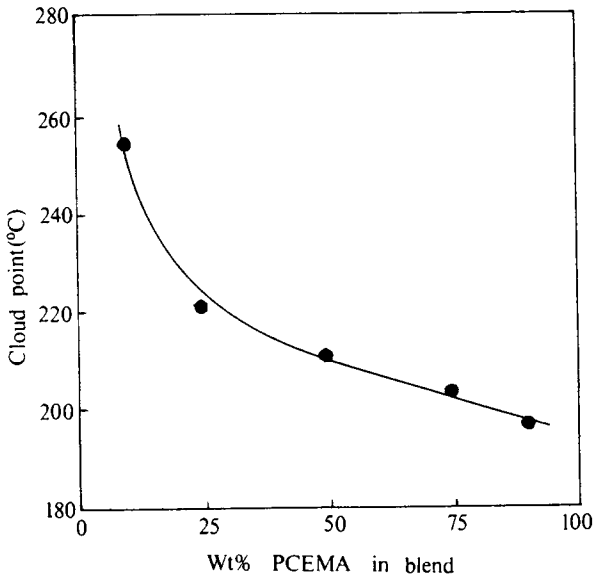

Figure 3 Cloud point curves for PCEMA/PEMA blends.

was not distinct. The cloud point curve is skewed towards PCEMA as shown in Figure 3. The skewness of cloud point curves has been observed for other blends[12–14] and may arise from molecular weight effect or composition-dependent interaction.[12] It is concluded that PCEMA is miscible with PEMA.

PCEMA/PnPMA Blends

The blends were cloudy. DSC measurements show the existence of two T_gs in each blend. The T_g values correspond to those of PCEMA and PnPMA. A typical DSC curve is shown in Figure 4. It is concluded that PCEMA is immiscible with PnPMA.

PCEMA/PiPMA Blends

The blends were cloudy. Due to the close proximity of the T_g values of the two polymers ($\Delta T_g \cong 2°C$), it is difficult to use the conventional DSC measurements to ascertain the miscibility of the blends. It was reported recently that for a blend of two polymers with similar T_g values, the enthalpy recovery of an annealed blend can be used to ascertain its miscibility.[15–16] Annealing of polymers below the glass transition temperature results in a decrease in enthalpy that is recovered during heating. The enthalpy recovery is seen as a rather sharp endothermic peak when the annealed sample is scanned through the glass transition. An annealed immiscible blend would show two distinct endothermic peaks while a single peak is indicative of a miscible blend. To test the applicability of the method, PCEMA and PiPMA were physically mixed and annealed at 70°C for 10 days. However, the annealed mixture showed only one enthalpy recovery peak. In this case, the T_g values of PCEMA and PiPMA were too close to be resolved. As such, annealing of the blends was not done. Nevertheless, the cloudy appearance of the blends suggests that PCEMA is immiscible with PiPMA.

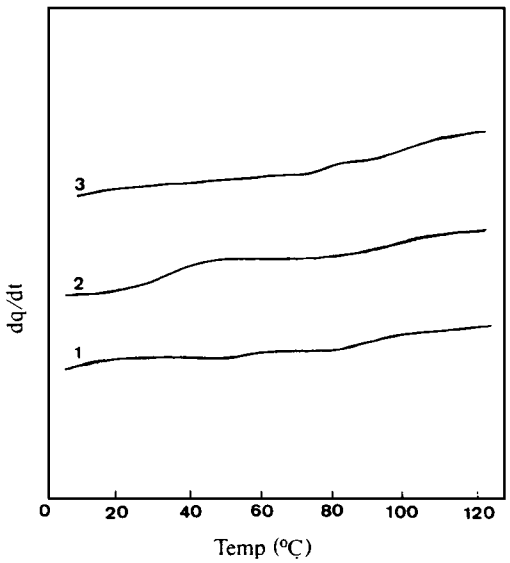

Figure 4 DSC curves for 50/50 blends of (1) PCEMA/PnPMA; (2) PCEMA/PnBMA and (3) PCEMA/PCHMA.

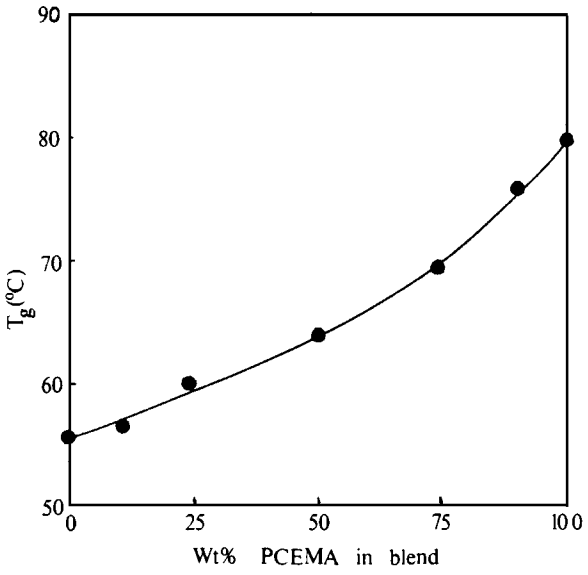

Figure 5 T_g-composition curve for PCEMA/PTHFMA blends.

PCEMA/PnBMA and PCEMA/PCHMA Blends

All the blends were cloudy and the DSC measurements showed two glass transitions for each blend. The T_g values are also close to those of the component polymers. Typical DSC curves are shown in Figure 4. It is concluded that PCEMA is immiscible with PnBMA and with PCHMA.

PCEMA/PTHFMA Blends

All the blends were transparent and remained so on heating to 260°C where discoloration began to develop. Each blend had a single composition-dependent T_g, as shown in Figure 5. Hence PCEMA is miscible with PTHFMA.

Miscibility Behavior

The present study shows that PCEMA is miscible with PMMA, PEMA and PTHFMA but immiscible with PnPMA, PiPMA, PnBMA, and PCHMA. This is consistent with the general observation that the miscibility of homologous polymethacrylates with other chlorine-containing polymers, such as PVC,[17-18] PCMMA,[9] chlorinated polyethylene,[19-20] and polyepichlorohydrin,[21] decreases with increasing bulkiness of the pendant groups of the polymethacrylates. While the lower members of the polymethacrylates, such as PMMA and PEMA, are readily miscible with other polymers, the higher members are not.

It has been reported earlier that PTHFMA is miscible with several polymers in spite of the bulkiness of its pendant groups.[9,22-24] It is interesting to note that both PCHMA and PTHFMA have pendant groups of similar sizes, yet PCEMA is miscible with PTHFMA but immiscible with PCHMA. The presence of ether oxygen atoms in the pendant groups of PTHFMA appears to play an important role in the miscibility behavior of PTHFMA.

The good miscibility of PTHFMA is also shown by the LCST behavior of the blends. PCEMA/PMMA and PCEMA/PTHFMA blends degrade before phase separation could be induced by heating, but PCEMA/PEMA blends show LCST behavior around 200–220°C. As discussed in an earlier communication, the free volume effects in various PCMMA/polymethacrylate blends are considered to be approximately the same. Hence the LCSTs provide a means to compare the intensities of enthalpic interactions in the blends.[8] The present results indicate that the interactions in PCEMA/PTHFMA are more intense than those in PCEMA/PEMA blends.

As compared with PCMMA, the miscibility of PCEMA with polymethacrylates is more limited. PCMMA is miscible with PnPMA and PiPMA,[8] but PCEMA is not. The LCST behavior of PCMMA/PEMA and PCEMA/PEMA blends is also informative. The cloud point curve of PCEMA/PEMA blends is about 30°C lower than that of PCMMA/PEMA blends.[8] If the free-volume effects in the two blend systems are similar, then the result indicates less intense interactions in PCEMA/PEMA blends than those in PCMMA/PEMA blends. This finding indicates that the miscibility of a chlorine-containing polymethacrylate also depends on the size of its pendant groups. Future study will be extended to poly(chloropropyl methacrylate) in order to study this effect.

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