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Miscibility of Poly(2-iodoethyl methacrylate) with Various Polymethacrylates

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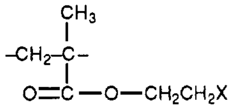
Introduction

Chlorine-containing polymers such as poly(vinyl chloride) (PVC),[1-4] poly(epichlorohydrin),[5] chlorinated polyethylene,[2,3] and poly(vinylidene chloride)[2,6] are miscible with a large number of polymethacrylates. We have recently found that chlorine-containing polymethacrylates such as poly(chloromethyl methacrylate) (PCMMA),[7] poly(2-chloroethyl methacrylate) (PCEMA),[8] and poly(3-chloropropyl methacrylate) (PCPMA)[9] are also miscible with some polymethacrylates, with the miscibility range decreasing in the order PCMMA > PCEMA > PCPMA.

A chlorinated polymer is more readily miscible with other polymers than its brominated counterpart. Cousin and Prud'homme found that PVC is miscible with a large number of polyesters, but poly(vinyl bromide) is miscible with a few polyesters.[10,11] We have also found that poly(2-bromoethyl methacrylate) (PBEMA) has a poorer miscibility with polymethacrylates as compared with PCEMA.[12]

The miscibility of iodine-containing polymers receives scant attention. Russell and Stein reported that polystyrene (PS) is immiscible with iodinated PS having a degree of iodination of 87.5%.[13] We found that PS is miscible with iodinated PS with degrees of iodination of 6 and 15%.[14] In this note, we report the miscibility of poly(2-iodoethyl methacrylate) (PIEMA) with various polymethacrylates, and the results are compared to those of PCEMA and PBEMA.



$$-CH_2-\overset{CH_3}{\underset{O=C-O-CH_2CH_2X}{C}}-$$

X = Cl (PCEMA), Br (PBEMA), I (PIEMA)

Experimental Section

The monomer IEMA was prepared from 2-chloroethyl methacrylate (CEMA) following the procedures reported by Brown et al.[15] IEMA was polymerized in 2-butanone at reflux temperature for 6 h with 0.25% by weight of azobis(isobutyronitrile) as initiator. The polymer was obtained by precipitation of the solution in excess methanol. The number-average and weight-average molecular weights of PIEMA determined by GPC are 30 600 and 100 400, respectively. The glass transition temperature (T_g) of PIEMA is 55 °C. The following commercially available polymethacrylates were used in the study: poly(methyl methacrylate) (PMMA) (Du Pont Elvacite 2010, $M_w = 120\,000$, $T_g = 100$ °C), poly(ethyl methacrylate) (PEMA) (Du Pont Elvacite 2042, $M_w = 310\,000$, $T_g = 65$ °C), poly(*n*-propyl methacrylate) (P*n*PMA) (Scientific Polymer Products, $M_w = 175\,000$, $T_g = 45$ °C), poly(isopropyl methacrylate) (P*i*PMA) (Scientific Polymer Products, $[\eta] = 0.33$ dL/g in 2-butanone at 30 °C, $T_g = 82$ °C), poly(*n*-butyl methacrylate) (P*n*BMA) (Du Pont Elvacite 2044, $M_w = 288\,000$, $T_g = 20$ °C), poly(tetrahydrofurfuryl methacrylate) (PTHFMA) (Scientific Polymer Products, $M_w = 240\,000$, $T_g = 57$ °C), and poly(cyclohexyl methacrylate) (PCHMA) (Scientific Polymer Products, $M_w = 66\,000$, $T_g = 95$ °C).

Blends of PIEMA 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 at least 3 days. To study a possible solvent effect on the miscibility, blends were also prepared by coprecipitation. THF solutions of the polymers were poured into excess methanol to obtain the blends.

The glass transition temperature (T_g's) of various samples were measured with a Du Pont 2910 differential scanning calorimeter using 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. All the miscible blends were examined for the existence of lower critical solution temperature (LCST) by using the method described previously.[7] The thermal stability of PIEMA in air was evaluated with a Du Pont 951 thermogravimetric analyzer. PIEMA starts to lose weight when heated to 240 °C, and it does not lose weight when held isothermally at 140 °C for 3 h.

Results and Discussion

THF-cast blends of PIEMA with various polymethacrylates except PTHFMA were cloudy. Two distinct glass transitions were observed for blends of PIEMA with PMMA, P*i*PMA, P*n*BMA, and PCHMA. The T_g values of the blends are close to the respective component polymers. The results show that PIEMA is immiscible with these four polymethacrylates. Blends prepared by coprecipitation were also found to be immiscible, as shown by the existence of two T_g's in each blend.

Due to the close proximity of T_g values of PIEMA with PTHFMA, P*n*PMA, and PEMA, conventional DSC measurements cannot be used to ascertain the miscibility of these blends. For a blend of two polymers with similar T_g values, the enthalpy recovery peak of an annealed blend can be used to ascertain its miscibility.[16,17] A single enthalpy recovery peak is indicative of a miscible blend.

All the THF-cast PIEMA/PTHFMA blends were transparent and turned cloudy when heated to 155–190 °C, indicating the existence of LCST behavior. The cloudy blends can revert to transparency upon cooling, albeit slowly. For example, a phase-separated blend became transparent when held at 100 °C for about 90 min. A 1:1 physical mixture of PIEMA and PTHFMA was heated to 70 °C and kept at that temperature for 20 min, followed by annealing at 40 °C for 14 days. As shown in Figure 1, the annealed mixture showed two distinct enthalpy recovery peaks, indicating the applicability of the method to ascertain the miscibility of PIEMA/PTHFMA blends. Various blends were similarly annealed and the DSC curves of the annealed blends are also shown in Figure 1. Each annealed sample showed a single enthalpy recovery peak, which moved progressively to a higher temperature with increasing PTHFMA content. Thus, the optical clarity and the existence of a single enthalpy recovery peak in each blend show that PIEMA is miscible with PTHFMA. Blends prepared by coprecipitation were also found to be miscible and showed LCST behavior. PCEMA and PBEMA are also miscible with PTHFMA, but these blends do not exhibit LCST behavior.[8,12]

The enthalpy recovery method is also useful in ascertaining the miscibility of the PIEMA/P*n*PMA blends. All the blends were annealed at 70 °C for 20 min and aged at 40 °C for 14 days. The two distinct enthalpy recovery peaks of each blend correspond to those peaks of the annealed physical mixture of PIEMA/P*n*PMA, indicating the immiscibility of PIEMA with P*n*PMA.

The enthalpy recovery method is not applicable to ascertain the miscibility of PIEMA/PEMA blends, as an

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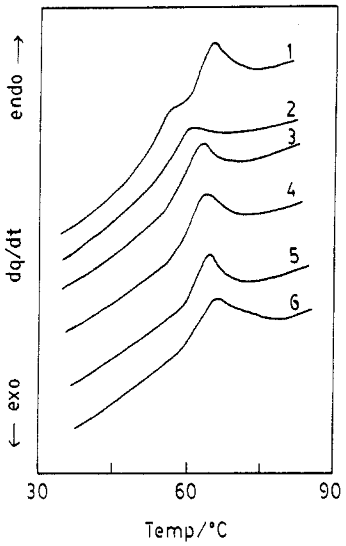

Figure 1. DSC curves for annealed PIEMA/polymethacrylate blends: (1) 1:1 physical mixture of PIEMA/PTHFMA; (2) 10% PTHFMA; (3) 25% PTHFMA; (4) 50% PTHFMA; (5) 75% PTHFMA; (6) 90% PTHFMA.

Table I. Miscibility Behavior of Blends

	PCEMA	PBEMA	PIEMA
PMMA	miscible[a]	immiscible	immiscible
PEMA	miscible[b]	immiscible	immiscible
P*n*PMA	immiscible	immiscible	immiscible
P*i*PMA	immiscible	immiscible	immiscible
P*n*BMA	immiscible	immiscible	immiscible
PCHMA	immiscible	immiscible	immiscible
PTHFMA	miscible[a]	miscible[a]	miscible[c]

[a] Miscible up to decomposition temperature. [b] Miscible up to 200 °C. [c] Miscible up to 155 °C.

annealed physical mixture of the two polymers shows only one enthalpy recovery peak. Nevertheless, the cloudy appearance of THF-cast PIEMA/PEMA blends suggests that PIEMA is immiscible with PEMA.

Table I summarizes the miscibility of PCEMA, PBEMA, and PIEMA with various polymethacrylates. The results clearly demonstrate that PCEMA shows a wider miscibility range with polymethacrylates as compared with PBEMA and PIEMA. The observed LCST behavior of PIEMA/PTHFMA blends also suggests that PIEMA interacts with PTHFMA less intensely as compared with PCEMA and PBEMA.

As suggested in an earlier communication,[7] the miscibility of a chlorine-containing polymethacrylate with other polymers may arise from an acid–base interaction involving the hydrogen atoms of the CH_2Cl group. The presence of electron-withdrawing chlorine and ester carboxyl group makes the hydrogen atoms of the CH_2Cl group acidic. Since the electronegativity decreases in the order Cl > Br > I, the acidity of hydrogen atoms of the CH_2X group also decreases in the order PCEMA > PBEMA > PIEMA. Thus, the differences in the acidity of hydrogen may account for the observed trend of the miscibility of the three halogen-containing polymethacrylates (PXEMA).

Coleman et al.[18] recently proposed a guide to predict polymer miscibility based on a non-hydrogen-bonded solubility parameter (δ_{nh}) approach. According to this approach, miscibility between two polymers is favored if their δ_{nh} values are close to each other and the intermolecular interactions between them are strong. For two polymers which interact with weak dispersive forces only, the δ_{nh} values of the two polymers must be closely matched [$\Delta\delta_{nh} < 0.2$ $(J/cm^3)^{1/2}$] in order for them to mix. A larger mismatch in δ_{nh} can be tolerated if there exist stronger interactions such as dipole–dipole and hydrogen-bonding interactions. From the group molar attraction constants (F) and group molar volumes (V) given by Coleman et al.,[18] the δ_{nh} value for PCEMA is calculated to be 20.0 $(J/cm^3)^{1/2}$. However, F and V values for Br and I are not provided by Coleman et al. Noting that the F value for Cl given by Coleman et al.[18] is very close to that given by Small,[19] we use Small's F values of 696 and 870 $(J/cm^3)^{1/2}$ mol^{-1} for Br and I, respectively.[19] In addition, we use Fedor's V values of 30.0 and 31.5 cm^3/mol for Br and I, respectively.[19] The δ_{nh} values for PBEMA and PIEMA are then estimated to be 20.3 and 21.6 $(J/cm^3)^{1/2}$, respectively. These values are larger than that of PCEMA. The δ_{nh} values for PMMA, PEMA, and P*n*BMA are 18.4, 18.2, and 17.8 $(J/cm^3)^{1/2}$, respectively.[18] Therefore, the difference in δ_{nh} values between PXEMA and a given polymethacrylate increases in the order PCEMA < PBEMA < PIEMA. Thus, a poorer miscibility of PIEMA is expected on the basis of the δ_{nh} approach.

It is noted that the δ_{nh} value for PBEMA is only 0.3 $(J/cm^3)^{1/2}$ larger than that for PCEMA. Yet, PCEMA is miscible with PMMA and PEMA but PBEMA is not. This behavior can be accounted for by the weaker interactions involving PBEMA because of the lower acidity of hydrogen atoms of the CH_2Br group. The δ_{nh} approach stipulates that more closely matched δ_{nh} values are required for a weaker intermolecular interaction. The narrower range of miscibility of PBEMA with polymethacrylates as compared with PCEMA can then be attributed to the more stringent δ_{nh} requirement.

The F and V values are not available for the THF ring from Coleman's work. We use Coleman's F and V values for $-CH_2-$, $>CH-$, and $-O-$ in our calculation and obtain a δ_{nh} value of 19.4 $(J/cm^3)^{1/2}$ for PTHFMA. The difference in δ_{nh} values between PXEMA and PTHFMA is significantly smaller than those involving other polymethacrylates. Accordingly, PTHFMA is more likely to be miscible with PXEMA.

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