Binary blends of poly(3-chloropropyl methacrylate) and poly(2-iodoethyl methacrylate) with aliphatic polyesters

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The miscibility behaviour of poly(3-chloropropyl methacrylate) (PCPMA) and poly(2-iodoethyl methacrylate) (PIEMA) with a series of aliphatic polyesters was investigated by differential scanning calorimetry. Binary blends of PCPMA and PIEMA with poly(butylene adipate), poly(2,2-dimethyl-1,3-propylene adipate), poly(ε-caprolactone) (PCL) and poly(hexamethylene sebacate) (PHS) exhibit single, composition-dependent glass transition temperatures, characteristic of miscible systems. However, PCPMA and PIEMA are immiscible with poly(ethylene succinate), poly(ethylene adipate) and poly(2,2-dimethyl-1,3-propylene succinate). Blends of PCPMA and PIEMA with poly(2,2-dimethyl-1,3-propylene sebacate) exhibit upper critical solution temperature behaviour. Interaction parameters for PCPMA/PHS, PIEMA/PHS, PCPMA/PCL and PIEMA/PCL blends were evaluated from melting-point depression analysis.

(Keywords: blend miscibility; poly(haloalkyl methacrylate)s; aliphatic polyesters)

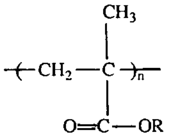
INTRODUCTION

Chlorine-containing polymers such as poly(vinyl chloride) (PVC)[1-5], polyepichlorohydrin (PECH)[6] and copolymers of vinylidene chloride[7-9] are miscible with polyesters having suitable CH_2/COO ratios. For example, PVC is miscible with polyesters having ratios between 4 and 12; and PECH is miscible with those having ratios between 3 and 8. Woo *et al.*[2] determined the interaction energy densities B of various PVC/polyester blends and found that the value of B goes through a minimum when CH_2/COO ratios are 6–7. Riedl and Prud'homme[5] studied PVC/polyester blends by inverse gas chromatography and found that the interaction parameter χ varies with CH_2/COO ratio and reaches a minimum when the ratio is 5.

The formation of miscible polymer blends generally requires some intermolecular interactions between component polymers. Fourier-transform infra-red (*FT*i.r.) spectroscopy is widely used to study the nature of intermolecular interactions in polymer blends[10-13]. For PVC/polyester blends, the interactions involve the carbonyl groups of the polyesters. However, it is difficult to detect which functional moiety in PVC is involved in intermolecular interactions. Based on the *FT*i.r. study on poly(ε-caprolactone) (PCL)/α-deuterated PVC blends, Varnell *et al.*[11] concluded that the principal mode of interaction between PCL and PVC is a hydrogen-bonding interaction between the carbonyl group of PCL and the C–H group of PVC. The miscibility of copolymers of vinylidene chloride with polyesters is attributed to hydrogen-bonding interactions between the carbonyl groups of polyesters and β-hydrogens of vinylidene chloride, and/or dipole–dipole interactions between the C–Cl and C=O groups[9,14].

Cousin and Prud'homme[15,16] studied the miscibility of poly(vinyl fluoride) (PVF) and poly(vinyl bromide) (PVB) with polyesters. Compared with PVC, PVB is miscible with a smaller number of polyesters, and PVF is immiscible with all the polyesters used. The immiscibility of PVF/polyester blends is attributed to strong intramolecular interaction between PVF segments.

In a recent series of papers[17-19], we reported the miscibility of poly(chloromethyl methacrylate) (PCMMA), poly(2-chloroethyl methacrylate) (PCEMA) and poly(2-bromoethyl methacrylate) (PBEMA) with various polyesters. We now report the miscibility of poly(3-chloropropyl methacrylate) (PCPMA) and poly(2-iodoethyl methacrylate) (PIEMA) with polyesters. The miscibility behaviour of PCPMA, when compared to PCMMA and PCEMA, provides information on the effect of increasing number of methylene units in the pendent group. The



$$-\!\left(CH_2-\overset{\displaystyle CH_3}{\underset{\displaystyle O{=}C-OR}{C}}\right)_{\!n}\!-$$

R = $-CH_2Cl$ (PCMMA)

$-CH_2CH_2Cl$ (PCEMA)

$-CH_2CH_2CH_2Cl$ (PCPMA)

$-CH_2CH_2Br$ (PBEMA)

$-CH_2CH_2I$ (PIEMA)

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results of PCEMA, PBEMA and PIEMA illustrate the effect of the nature of halogen on the miscibility behaviour.

EXPERIMENTAL

PCPMA and PIEMA were prepared by free-radical polymerization as described previously[21,22]. The weight-average molecular weights of PCPMA and PIEMA are 138 and 100 kg mol^{-1}, respectively, as determined by gel permeation chromatography. The glass transition temperatures (T_g) of PCPMA and PIEMA are 52 and 55°C, respectively. The characteristics of the various polyesters used in this study are shown in *Table 1*.

All the blends were prepared by solution casting from tetrahydrofuran. The solvent was first allowed to evaporate slowly at room temperature. The residual solvent was then removed by further drying of the blends *in vacuo* at 70°C for 7 days.

Glass transition temperatures of various samples were determined with a Du Pont 910 differential scanning calorimeter using a heating rate of 20°C min^{-1}. Each sample was scanned several times between a temperature 50°C below the T_g of the polyester and 120°C. The T_g value was taken as the initial onset of the change of slope in the differential scanning calorimetry (d.s.c.) curve.

All the blends were examined for the existence of lower critical solution temperature (*LCST*) or upper critical solution temperature (*UCST*) behaviour using the method described previously[23].

The melting points of some samples were determined with a Perkin–Elmer DSC-4 differential scanning calorimeter. Each sample was heated to 100°C and held at that temperature for 10 min. The sample was then cooled to the desired crystallization temperature, where it was kept for 30 min. It was then scanned at 5°C min^{-1} to obtain the melting temperature (T_m), which was taken as the peak temperature of the melting endotherm.

RESULTS AND DISCUSSION

Poly(ethylene succinate) blends

Blends of PES with PCPMA and PIEMA were cloudy and remained so upon heating above the melting point of PES. The opacity of these blends arises from the crystallinity of PES and also the immiscibility of the blends. For both systems, a glass transition at −16°C corresponding to the T_g of PES was observed regardless of the composition. PES underwent cold crystallization and the crystallization peak obscured the glass transition of PCPMA and PIEMA in the respective blend. Nevertheless, the cloudiness of the melt indicates that PES is immiscible with PCPMA and PIEMA.

Poly(ethylene adipate) blends

For PCPMA/PEA and PIEMA/PEA blends, d.s.c. measurements showed a glass transition at −50°C corresponding to the T_g of PEA, regardless of the composition. The glass transitions of PCPMA and PIEMA were obscured by the melting of PEA. All the blends remained cloudy upon heating above the melting point of PEA. Based on the glass transition behaviour and the cloudiness of the melt, it is then concluded that PEA is immiscible with PCPMA and PIEMA.

Poly(2,2-dimethyl-1,3-propylene succinate) blends

Blends of PDPS with PCPMA and PIEMA were cloudy and remained so upon heating above the melting point of PDPS. D.s.c. measurements showed the existence of two T_g values in each blend. The T_g values correspond to those of the pure components, indicating immiscibility of these blend systems.

Poly(butylene adipate) blends

All the PBA/PIEMA blends were cloudy but they turned clear upon heating above the melting point of PBA. Blends containing 90 and 75 wt% PCPMA were clear, but the rest of PBA/PCPMA blends were cloudy. However, the cloudiness of these blends also disappeared upon heating above the melting point of PBA. The existence of a single T_g in each blend further confirms that the amorphous phase of PBA is miscible with PCPMA and PIEMA. The T_g *versus* composition curves are shown in *Figures 1a* and *1b*. Except for PBA/PCPMA blends having 75 and 90 wt% PCPMA, which are single-phase blends, the other blends are two-phase systems consisting of a crystalline PBA phase and an amorphous phase of PBA with PCPMA or PIEMA.

Poly(2,2-dimethyl-1,3-propylene adipate) blends

PDPA is a low-molecular-weight waxy material. Once heated above its melting point, it remains transparent at room temperature even after one month. All the blends were transparent and remained so upon heating to 240°C. *Figures 2a* and *2b* demonstrate a single composition-dependent T_g for blends of PDPA with PCPMA and

Table 1 Characteristics of various aliphatic polyesters

Polymer	CH_2/COO	Abbreviation	Source[a]	$\bar{M}_w$ (kg mol^{-1})	T_m (°C)	T_g (°C)
Poly(ethylene succinate)	2	PES	SPP	9.00	101	−16
Poly(ethylene adipate)	3	PEA	SPP	8.70	46	−54
Poly(2,2-dimethyl-1,3-propylene succinate)	3.5	PDPS	SPP	16.0	75	−19
Poly(butylene adipate)	4	PBA	PS	11.3	49	−70
Poly(2,2-dimethyl-1,3-propylene adipate)	4.5	PDPA	RPC	3.90	40	−60
Poly(ε-caprolactone)	5	PCL	UC	15.0	70	−70
Poly(2,2-dimethyl-1,3-propylene sebacate)	6.5	PDPSb	Aldrich	5.80	11	−60
Poly(hexamethylene sebacate)	7	PHS	SPP	62.0	74	−70

[a] SPP = Scientific Polymer Products Inc.; PS = Polysciences Inc.; RPC = Ruco Polymer Corporation; UC = Union Carbide

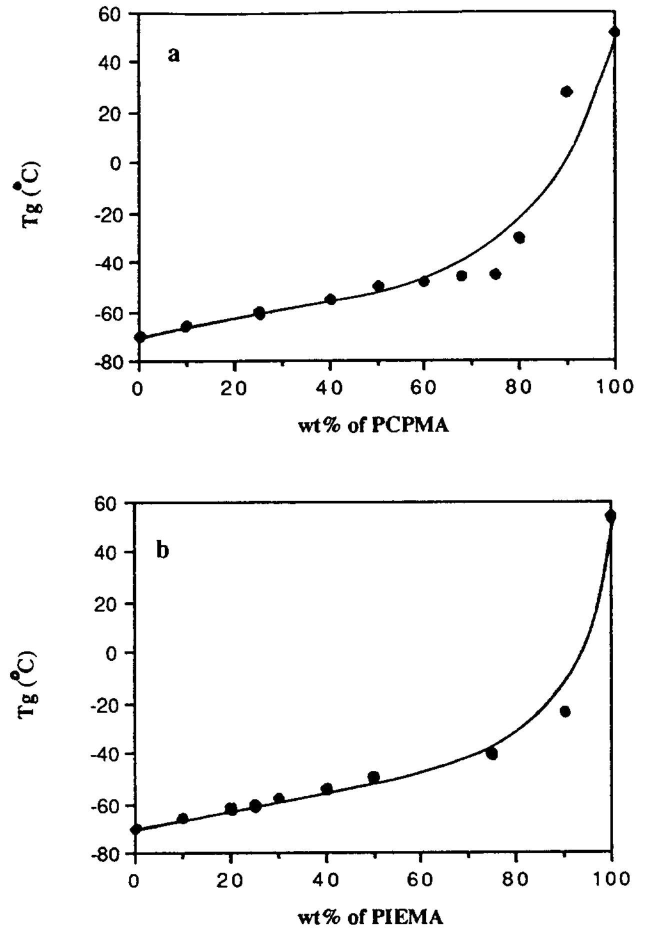

Figure 1 T_g *versus* composition curve for blends: (a) PBA/PCPMA; (b) PBA/PIEMA

PIEMA, respectively, which serve to show the miscibility of these binary polymer systems.

Poly(ε-caprolactone) blends

Blends of PCL with PCPMA and PIEMA were cloudy. However, they turned clear upon heating above the melting point of PCL. The cloudiness of PCPMA/PCL and PIEMA/PCL blends arises from PCL crystallites. D.s.c. measurements revealed a single T_g for each of these blends. The T_g *versus* composition curves are shown in *Figures 3a* and *3b*. It is concluded that the amorphous phase of PCL is miscible with both PCPMA and PIEMA. All the blends are semicrystalline, consisting of a crystalline PCL phase and an amorphous phase of PCL with PCPMA or PIEMA.

Poly(2,2-dimethyl-1,3-propylene sebacate) blends

All the PDPSb/PIEMA and PDPSb/PCPMA blends were cloudy and each blend showed the existence of two glass transitions. However, the cloudy PDPSb/PCPMA blends turned clear when heated to the region of 70–108°C, while the PDPSb/PIEMA blends turned clear in the region of 84–104°C, showing the existence of *UCST* behaviour. The cloud-point curves are shown in *Figure 4*. Upon cooling to room temperature, cloudiness developed within a day. The cloudiness is not a result of crystallization of PDPSb, as its melting point is below room temperature. Blends of PDPSb with PCEMA and PBEMA also showed *UCST* behaviour[18,19].

Poly(hexamethylene sebacate) blends

All the blends of PCPMA and PIEMA with PHS were cloudy, but they turned clear upon heating above the melting point of PHS. As shown in *Figures 5a* and *5b*, a single composition-dependent T_g was observed for each of the blends. The transparency of the melt and the glass transition behaviour show that the amorphous phase of PHS is miscible with PCPMA and PIEMA.

Melting-point depression analysis

For a miscible blend containing a crystallizable component, the melting-point depression of the crystalline polymer by the miscible diluent is used to evaluate the polymer–polymer interaction parameter, χ, using the equation[24]:

$$(1/T_m)-(1/T_m^\circ) = -(RV_{2u}/V_{1u}\Delta H_{2u})\chi\phi_1^2$$

where the subscripts 1 and 2 refer to the amorphous polymer and the crystalline polymer, respectively; ΔH_{2u} is the heat of fusion per mole of crystalline repeating units; V_{1u} and V_{2u} are the molar volumes of repeating units; ϕ_1 is the volume fraction of component 1 in the blend; and T_m and T_m° are the equilibrium melting points of the blend and the pure crystalline polymer, respectively.

The equilibrium melting point of a sample is determined by the Hoffman–Weeks method[25] in which the observed melting points (T_m) are plotted as a function of crystallization temperatures (T_c) and extrapolated to intersect with the $T_m = T_c$ line to obtain the equilibrium

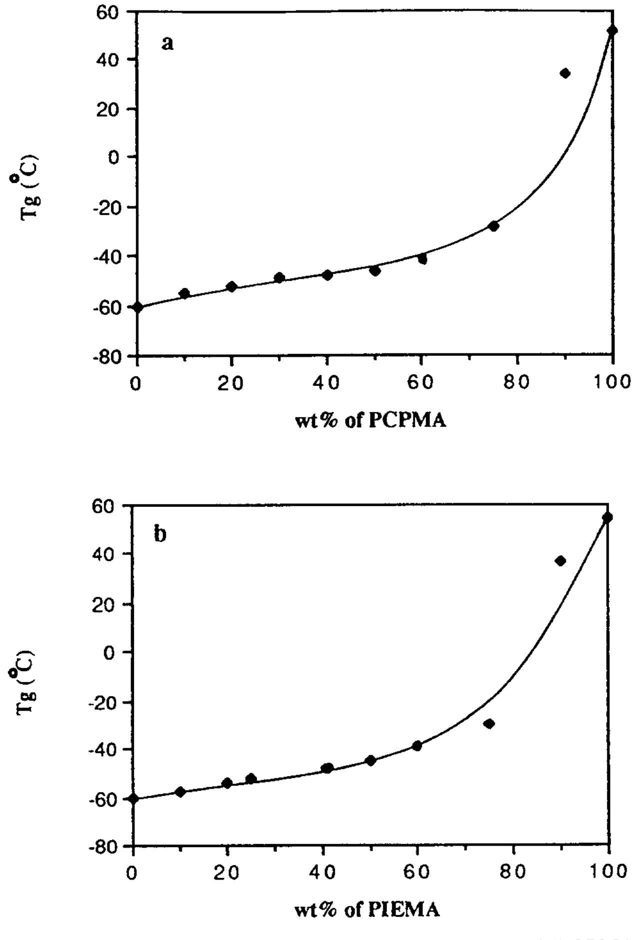

Figure 2 T_g *versus* composition curve for blends: (a) PDPA/PCPMA; (b) PDPA/PIEMA

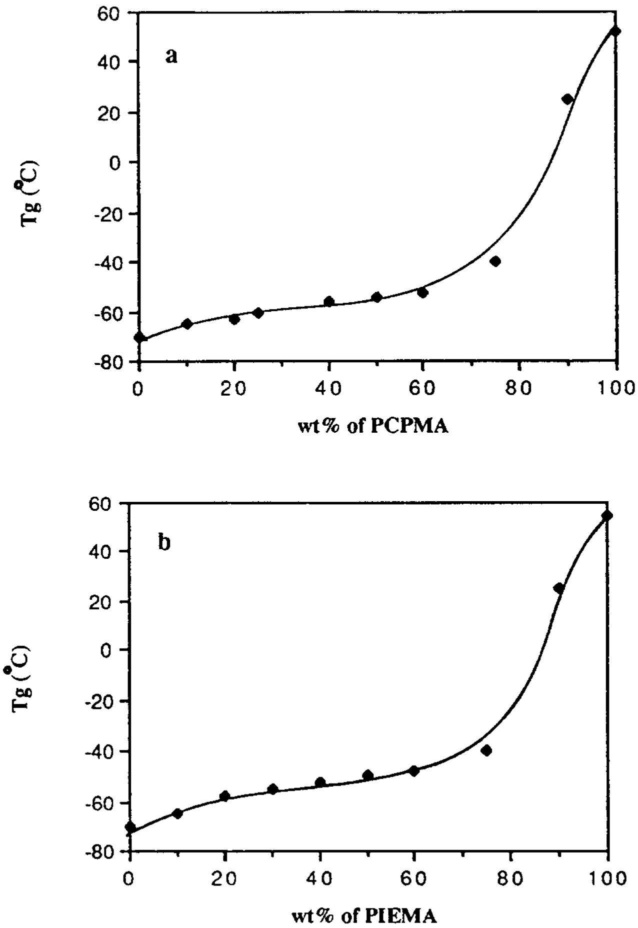

Figure 3 T_g *versus* composition curve for blends: (a) PCL/PCPMA; (b) PCL/PIEMA

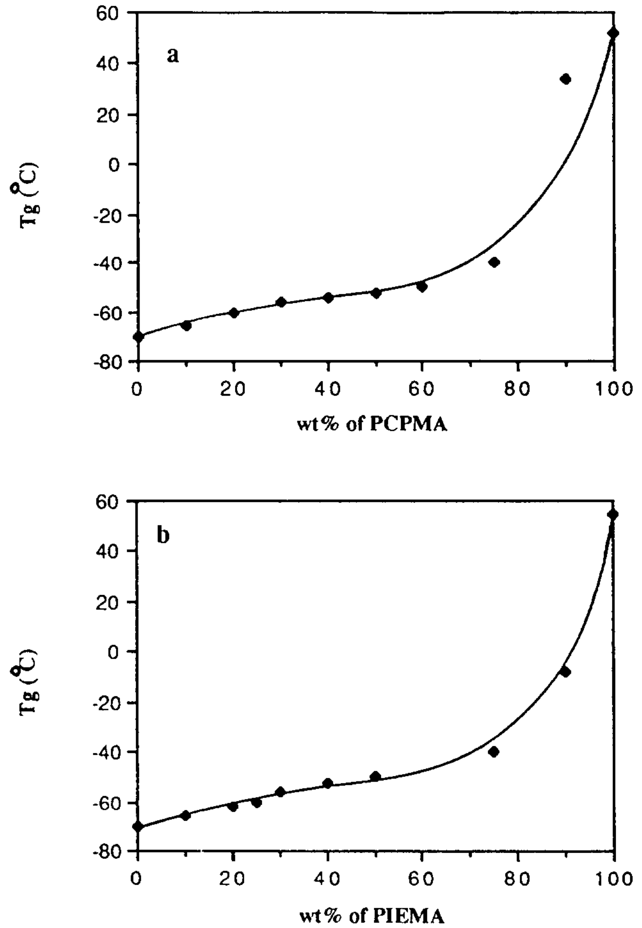

Figure 5 T_g *versus* composition curve for blends: (a) PHS/PCPMA; (b) PHS/PIEMA

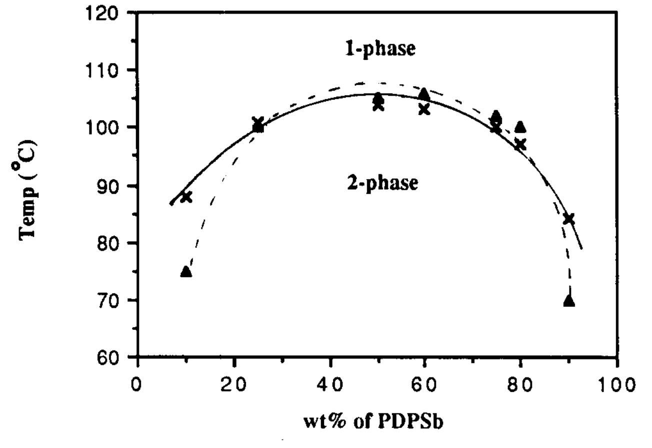

Figure 4 Cloud-point curve for PDPSb/PCPMA (×) and PDPSb/PIEMA (▲) blends

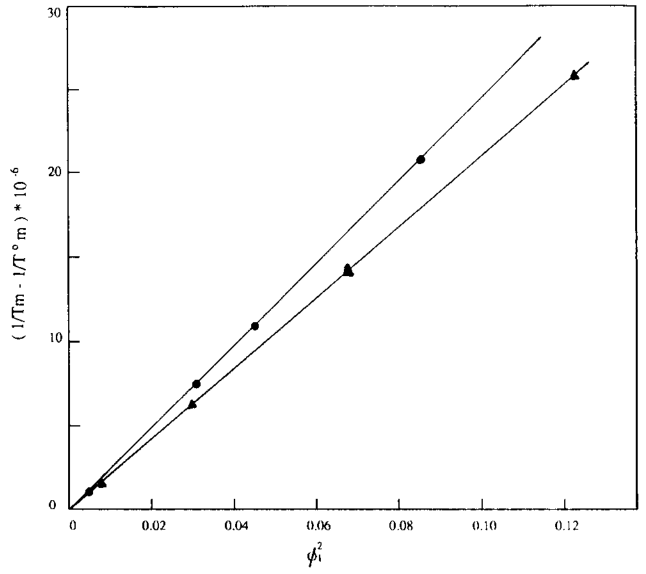

Figure 6 Melting-point depression plots for PCL/PCPMA (▲) and PCL/PIEMA (●) blends

melting point. *Figure 6* shows the melting-point depression plots for the two PCL blend systems. Using $(\Delta H_{2u}/V_{2u})=146.4\ \mathrm{J\,cm^{-3}}$ for PCL[20], V_{1u}(PCPMA)$=124.0\ \mathrm{cm^3\,mol^{-1}}$, V_{1u}(PIEMA)$=139.5\ \mathrm{cm^3\,mol^{-1}}$, density $\rho_{PCPMA}=1.31\ \mathrm{g\,cm^{-3}}$ and $\rho_{PIEMA}=1.72\ \mathrm{g\,cm^{-3}}$, the χ values were found to be -0.47 and -0.60 for PCPMA/PCL and PIEMA/PCL blends, respectively.

Table 2 summarizes the χ values of various PCL blends. The results suggest that the interaction of a chlorine-containing polymethacrylate with PCL decreases in the order PCMMA > PCEMA > PCPMA. The χ value for PCEMA blends is more negative than those for PBEMA and PIEMA blends, suggesting a more intense interaction between PCEMA and PCL.

Figure 7 shows the melting-point depression plots for the two PHS blend systems. Using $\Delta H_{2u}/V_{2u}=156.4\ \mathrm{J\,cm^{-3}}$

for PHS[6], $\rho_{PHS} = 1.03\,\mathrm{g\,cm^{-3}}$, together with the above data, the χ values were found to be -0.51 and -0.46 for PCPMA/PHS and PIEMA/PHS blends, respectively. Similar to the PCL system, the χ values also suggest that the interaction decreases in the order PCMMA > PCEMA > PCPMA, and PHS interacts more intensely with PCEMA than with PBEMA and PIEMA.

The melting-point depression analysis was not carried out for other blends as the other polyesters crystallize very slowly or show complex melting endotherms.

Miscibility behaviour

Table 3 summarizes the miscibility behaviour of various blends. For the three chlorine-containing polymethacrylates, the miscibility with polyesters having small CH_2/COO ratios becomes poorer as the size of the pendent group increases from chloromethyl to chloropropyl. PIEMA has a poorer miscibility with polyesters having small CH_2/COO ratios as compared with PCEMA and PBEMA.

Table 2 Various χ values of halogen-containing polymethacrylates with PCL and PHS[a]

System	PCL	PHS
PCMMA	-0.82^{17}	-1.20^{18}
PCEMA	-0.76^{17}	-0.76^{18}
PCPMA	-0.47	-0.51
PBEMA	-0.62^{19}	-0.52^{19}
PIEMA	-0.60	-0.46

[a] Superscripts denote reference numbers

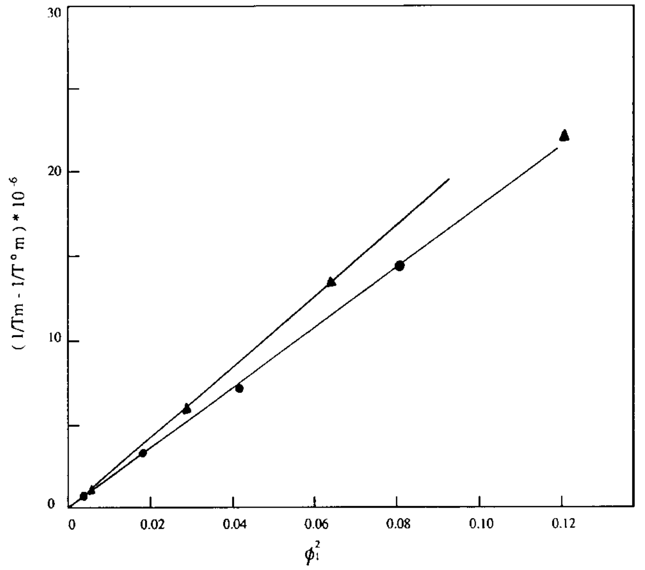

Figure 7 Melting-point depression plots for PHS/PCPMA (▲) and PHS/PIEMA (●) blends

In addition to chlorine-containing polymers, other polymers such as bisphenol A polycarbonate[26], tetramethylbisphenol A polycarbonate[27] and poly(hydroxy ether of bisphenol A) (Phenoxy)[20] have also been found to be miscible with polyesters having suitable CH_2/COO ratios. Several groups of investigators discussed the observed miscibility range in terms of CH_2/COO ratio in polyester blends. Woo *et al.*[2] considered polyester as a copolymer consisting of $-CH_x-$ and $-COO-$ segments. A strong unfavourable intramolecular interaction between the two types of segments is an important factor in determining miscibility. Coleman *et al.*[28,29] showed that the miscibility ranges for blends of polyesters could be satisfactorily explained by a 'non-hydrogen-bonded solubility parameter (δ_{nh})' approach. David and Sincock[30] examined polyester/Phenoxy blends using a 'miscibility parameter' approach.

In the present work, we examine the miscibility behaviour using the δ_{nh} approach because of its simplicity. The δ_{nh} approach considers a balance between unfavourable physical forces and favourable specific interaction. The unfavourable physical forces are minimized by a close match of δ_{nh} values of the two polymers. The δ_{nh} values of linear aliphatic polyesters decrease with increasing CH_2/COO ratios, ranging from 21.8 $(\mathrm{J\,cm^{-3}})^{1/2}$ for PES to 18.5 $(\mathrm{J\,cm^{-3}})^{1/2}$ for PHS calculated from group molar constants (F) and group molar volumes (V) given by Coleman *et al.*[28,29]. The δ_{nh} values of PCMMA, PCEMA and PCPMA are 20.7, 20.0 and 19.6 $(\mathrm{J\,cm^{-3}})^{1/2}$, respectively. The CH_2/COO ratio range in which polyesters are expected to be miscible with a halogen-containing polymethacrylate can be calculated using computer software developed by Coleman *et al.* The ranges are 1.2–4.7, 1.7–6.8 and 2.1–8.4 for PCMMA, PCEMA and PCPMA, respectively, assuming a moderately low interaction. Compared to our experimental results, the δ_{nh} approach underestimates the miscibility range for PCMMA/polyester blends. Since the largest CH_2/COO ratio is 7 for the polyesters used in our study, we cannot check how well the δ_{nh} approach could predict the miscibility ranges for PCEMA and PCPMA blends. However, the δ_{nh} approach predicts that the lower end of the CH_2/COO ratio range moves to a larger values when the pendent group is changed from

Table 3 The miscibility behaviour of halogen-containing polymers with polyesters[a]

	PVC	PCMMA	PCEMA	PBEMA	PCPMA	PIEMA
PES	I	M	I	I	I	I
PEA	I	M	M	M	I	I
PDPS	M	M	M	M	I	I
PBA	M	M	M	M	M	M
PDPA	M	M	M	M	M	M
PCL	M	M	M	M	M	M
PDPSb	M	M	*UCST*	*UCST*	*UCST*	*UCST*
PHS	M	M	M	M	M	M

[a] M = miscible; I = immiscible; *UCST* = upper critical solution temperature behaviour

chloromethyl to chloropropyl, and the prediction is consistent with our experimental observation.

The 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.* is very close to that given by Small[31], we use Small's F values and Fedor's V values for Br and I. The δ_{nh} values for PBEMA and PIEMA are then estimated to be 20.3 and 21.6 $(\mathrm{J\,cm^{-3}})^{1/2}$, respectively. PBEMA and PIEMA are then predicted to be miscible with polyesters having CH_2/COO ratios of 1.4–6.0 and 1.1–4.0, respectively. Thus, the δ_{nh} approach predicts that, as the halogen in the pendent group of the polymethacrylate changes from chlorine to iodine, the miscibility range with polyesters becomes narrower, and the lower end of the miscibility range moves to a smaller CH_2/COO ratio. However, our experimental results show that the lower end of the miscibility range moves to a larger CH_2/COO ratio when the pendent group changes from chloroethyl to iodoethyl.

Nevertheless, the present study shows that PIEMA is miscible with several aliphatic polyesters. To our knowledge, there are only two other miscible blends involving iodine-containing polymers, namely, PIEMA/poly(tetrahydrofurfuryl methacrylate)[22] and iodinated polystyrene/poly(2,6-dimethyl-1,4-phenylene oxide)[32] blends. Future study will be extended to fluorine-containing polymethacrylates.

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