Miscibility Behavior of Halogen-Containing Polymethacrylates: Poly(2,2-dichloroethyl methacrylate) and Poly(2,2,2-trichloroethyl methacrylate) with Various Polymethacrylates

S. M. Low, S. H. Goh,* and S. Y. Lee

Department of Chemistry, National University of Singapore,
Singapore 0511, Republic of Singapore

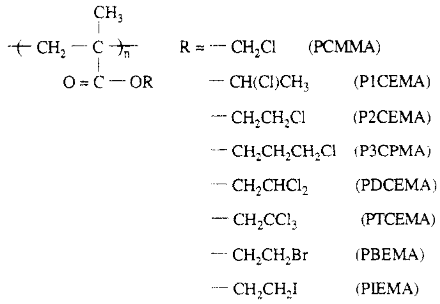
Received December 17, 1993; Revised Manuscript Received April 7, 1994[⊛]

ABSTRACT: The miscibility behavior of poly(2,2-dichloroethyl methacrylate) (PDCEMA) and poly(2,2,2-trichloroethyl methacrylate) (PTCEMA) with various polymethacrylates was examined using differential scanning calorimetry. PDCEMA and PTCEMA are both miscible with poly(methyl methacrylate), poly(ethyl methacrylate), poly(*n*-propyl methacrylate) (PnPMA), poly(isopropyl methacrylate) (PiPMA), poly(tetrahydrofurfuryl methacrylate), and poly(cyclohexyl methacrylate) but immiscible with poly(*n*-hexyl methacrylate). They differ in those cases involving poly(*n*-butyl methacrylate) (PnBMA), poly(*n*-amyl methacrylate) (PnAMA), and poly(isoamyl methacrylate) (PiAMA). PDCEMA, but not PTCEMA, is miscible with PnBMA and PiAMA. PDCEMA has a limited miscibility with PnAMA, but PTCEMA is immiscible with PnAMA. Miscible blends of PDCEMA with PnPMA, PiPMA, PnBMA, and PiAMA showed lower critical solution temperature behavior. PDCEMA shows a wider range of miscibility with polymethacrylates than PTCEMA and other chlorine-containing polymethacrylates such as poly(chloromethyl methacrylate), poly(1-chloroethyl methacrylate), poly(2-chloroethyl methacrylate), and poly(3-chloropropyl methacrylate). The good miscibility of PDCEMA appears to be correlated to the acidic hydrogen in the pendant $-CHCl_2$ group.

Introduction

There have been many studies on the effects of structural changes of polymers on the miscibility behavior. The incorporation of halogens into a polymer can effectively change its miscibility behavior. Chlorinated polymers often show wider ranges of miscibility than the corresponding nonchlorinated,[1-12] brominated,[13-15] and iodinated counterparts.[16-18] In a recent series of papers, we reported the miscibility behavior of various halogen-containing polymethacrylates with poly(alkyl methacrylate)s. The ability of poly(2-haloethyl methacrylate) to be miscible with poly(alkyl methacrylate)s is in the order poly(2-chloroethyl methacrylate) (P2CEMA) > poly(2-bromoethyl methacrylate) (PBEMA) > poly(2-iodoethyl methacrylate) (PIEMA). The miscibility appears to be correlated to the acidity of the hydrogen atoms in the pendant $-CH_2X$ group.

We have recently reported that poly(1-chloroethyl methacrylate) (P1CEMA) shows a much wider range of miscibility with poly(alkyl methacrylate)s than P2CEMA.[19]



The differences in the miscibility behavior between P1CEMA and P2CEMA have been attributed to the more acidic methine hydrogen in the $-CH(Cl)CH_3$ group of P1CEMA as compared with the methylene hydrogens in the $-CH_2Cl$ group of P2CEMA. We have extended our study to poly(2,2-dichloroethyl methacrylate) (PDCEMA) and poly(2,2,2-trichloroethyl methacrylate) (PTCEMA). It is of interest to study how the miscibility is affected by the incorporation of additional chlorine atoms in the pendant ethyl group.

Experimental Section

Monomeric 2,2-dichloroethyl methacrylate (DCEMA) was prepared by esterification of methacrylic acid with 2,2-dichloroethanol. A mixture of 37.0 g of methacrylic acid (0.43 mol) and 50.0 g of 2,2-dichloroethanol (0.43 mol) was refluxed in 250 mL of benzene for 7 h in the presence of 1.50 g of hydroquinone and 2.50 mL of concentrated H_2SO_4. The reaction flask was then fitted with a Dean and Stark trap, and the mixture was refluxed until no more water was observed in the trap. The mixture was neutralized with a 5% K_2CO_3 solution, washed with H_2O, and dried over anhydrous Na_2SO_4. The dried organic layer was concentrated at reduced pressure, and the residue was distilled at 52 °C/2 mmHg: ^1H NMR ($CDCl_3$) δ 2.00 (s, $-CH_3$), 4.55 (d, $-OCH_2-$), 5.70 (s, $-CH=$), 5.90 (t, $-CHCl_2$), and 6.20 (s, $-CH=$).

The monomer 2,2,2-trichloroethyl methacrylate (TCEMA) was prepared by trans-esterification of methyl methacrylate (MMA) with 2,2,2-trichloroethanol (TCEOH), catalyzed by acid. A mixture of 75.1 g of MMA (0.75 mol), 89.6 g of TCEOH (0.60 mol), 2.50 g of hydroquinone, and 0.75 g of toluene-*p*-sulfonic acid was placed in a two-neck round-bottom flask which was attached to an all-glass fractionating column. The solution was heated to boiling in an oil bath. The column was operated under total reflux until the temperature of the vapors at the still head dropped to 63–64 °C, which is the boiling point of the methanol–methyl methacrylate azeotrope. This azeotrope was then distilled as rapidly as it was formed. When the production of methanol became very slow (after 8 h), the remaining excess MMA was removed by distillation. The 2,2,2-trichloroethyl methacrylate was then fractionally distilled, bp 48 °C/1.5 mmHg: ^1H NMR ($CDCl_3$) δ 2.00 (s, $-CH_3$), 4.20 (s, $-OCH_2-$), 5.60 (s, $-CH=$), and 6.15 (s, $-CH=$).

Polymerizations of DCEMA and TCEMA were carried out in 2-butanone at reflux temperature for 20 h using 0.25% by weight of 2,2′-azobis(isobutyronitrile) as initiator. Both PDCEMA and PTCEMA were obtained by precipitation of the solution in excess methanol. The weight-average ($\bar{M}_w$) and number-average ($\bar{M}_n$) molecular weights of PDCEMA determined by gel permeation chromatography using polystyrene as standard are 84 000 and

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* Author to whom correspondence should be addressed.

[⊛] Abstract published in *Advance ACS Abstracts,* May 15, 1994.

0024-9297/94/2227-3764$04.50/0

Table 1. Characteristics of Polymethacrylates

polymer[a]	abbrev	source	$\bar{M}_w$ (kg mol^{-1})	T_g (°C)
poly(methyl methacrylate)	PMMA	DuPont (Elvacite 2010)	120	100
poly(ethyl methacrylate)	PEMA	DuPont (Elvacite 2042)	310	65
poly(*n*-propyl methacrylate)	PnPMA	Scientific Polymer Products	180	45
poly(isopropyl methacrylate)	PiPMA	this laboratory	170	92
poly(*n*-butyl methacrylate)	PnBMA	DuPont (Elvacite 2044)	290	20
poly(*n*-amyl methacrylate)	PnAMA	this laboratory	92	10
poly(*n*-hexyl methacrylate)	PnHMA	this laboratory	44	-21
poly(isoamyl methacrylate)	PiAMA	this laboratory	150	38
poly(tetrahydrofurfuryl methacrylate)	PTHFMA	Scientific Polymer Products	240	57
poly(cyclohexyl methacrylate)	PCHMA	Scientific Polymer Products	66	95
poly(2,2-dichloroethyl methacrylate)	PDCEMA	this laboratory	84	73
poly(2,2,2-trichloroethyl methacrylate)	PTCEMA	this laboratory	8.4	83

[a] All of the polymers are atactic.

42 000, respectively; the $\bar{M}_w$ and $\bar{M}_n$ of PTCEMA are 8400 and 6500, respectively. The main characteristics of other polymethacrylates used in this study are given in Table 1.

Blends of PDCEMA and PTCEMA with various polymethacrylates in weight ratios of 1:9, 1:3, 1:1, 2:3, 3:1, and 9:1 were prepared by solution casting from tetrahydrofuran (THF). Solvent was allowed to evaporate slowly at room temperature for 1–2 days. The cast films were then dried *in vacuo* at 90 °C for another 9 days.

The glass transition behavior of various samples was measured with a TA Instruments 2910 differential scanning calorimeter using a heating rate of 20 °C min^{-1}. The glass transition temperature (T_g) 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. For a blend of two polymers with close T_g values ($\Delta T_g < 20$ °C), the physical annealing technique was used to ascertain its miscibility.[20] Sample was first kept at a temperature $T_0 > T_g$ for 10 min to erase previous thermal history. The sample was then quench cooled in liquid nitrogen followed by annealing at a temperature $T_a < T_g$ for an extended period before the subsequent DSC scan was taken. A single enthalpy relaxation peak is indicative of a miscible blend, while double enthalpy relaxation peaks indicate an immiscible blend.

All of the miscible blends were examined for the existence of lower critical solution temperature (LCST) behavior using the method as described previously.[10] The temperature at which the film first showed cloudiness was taken as the cloud point.

Self-consistent-field molecular orbital calculations were performed at the semiempirical level using AMPAC program version 1.0[21], model AM1, which was installed on a Silicon Graphic Model 4D/20 Iris personal computer. In this calculation, internal coordinates, i.e., interatomic bond lengths, bond angles, and dihedral angles, were used to define the molecular geometries. Standard bond lengths and angles of similar structures[22] were used as initial estimates to obtain information of a minimum-energy molecular structure.

Results and Discussion

All of the PDCEMA/PMMA and PTCEMA/PMMA blends were transparent and remained so upon heating to 240 °C, where discoloration began to develop. The transparency of these blends is not likely due to the matching of the refractive indices of the two polymers. As the differences in refractive indices between PDCEMA, PTCEMA (n = 1.505 and 1.515 for PDCEMA and PTCEMA, respectively, estimated using the Vogel method[23]), and PMMA (n = 1.490)[24] is larger than 0.01, the clarity of the blends may serve as an indication of miscibility. Figure 1 shows the T_g-composition curves of the two blend systems. The existence of a single composition-dependent T_g further confirms the miscibility of PDCEMA/PMMA and PTCEMA/PMMA blends.

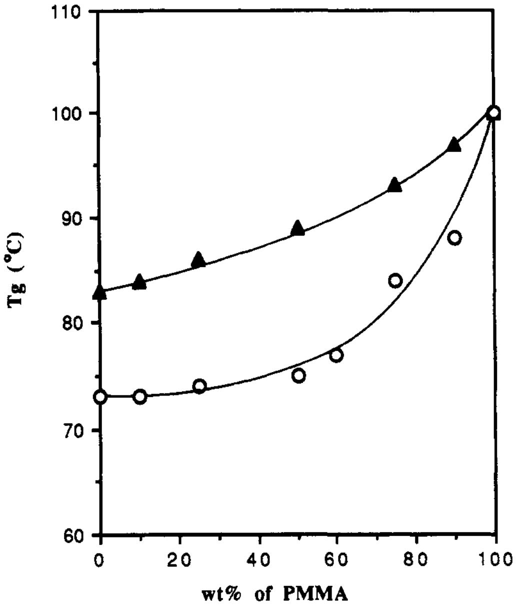

Figure 1. T_g-composition curves for blends: (○) PDCEMA/PMMA; (▲) PTCEMA/PMMA.

All of the PDCEMA/PEMA and PTCEMA/PEMA blends were transparent and remained so upon heating to 240 °C, where discoloration began to develop. Due to the close proximity of the T_g values of PDCEMA and PEMA ($\Delta T_g \simeq 8$ °C), the conventional T_g measurement was not used to ascertain miscibility. Instead, the enthalpy relaxation behavior of an annealed blend was used to ascertain its miscibility. To study the enthalpy relaxation of PDCEMA/PEMA blends, each blend was first heated to 130 °C and kept at that temperature for 10 min to erase its thermal history. The sample was then quench cooled in liquid nitrogen followed by annealing at room temperature for 6 weeks. A 1:1 physical mixture was similarly treated. As shown in Figure 2, the annealed physical mixture showed two distinct enthalpy relaxation peaks, indicating the applicability of this method to ascertain the miscibility of this blend system. Each of the various annealed blends showed a single enthalpy relaxation peak, which moved progressively to a higher temperature with increasing PDCEMA content. Thus, PDCEMA is judged to be miscible with PEMA.

PTCEMA/PEMA blends were not annealed as the two T_g values of a two-phase physical mixture could be observed by conventional DSC measurement. Each blend showed a single glass transition, which moved progressively to a higher temperature with increasing PTCEMA content. These observations suggest that PTCEMA forms miscible blends with PEMA.

PDCEMA and PTCEMA were also found to be miscible with PnPMA as each of the blends was transparent and showed a single T_g. PDCEMA/PnPMA blends exhibit LCST behavior in the region 230–265 °C, and the cloud point curve is shown in Figure 3. The dashed line indicates cases where it was not possible to discern a reliable cloud point.

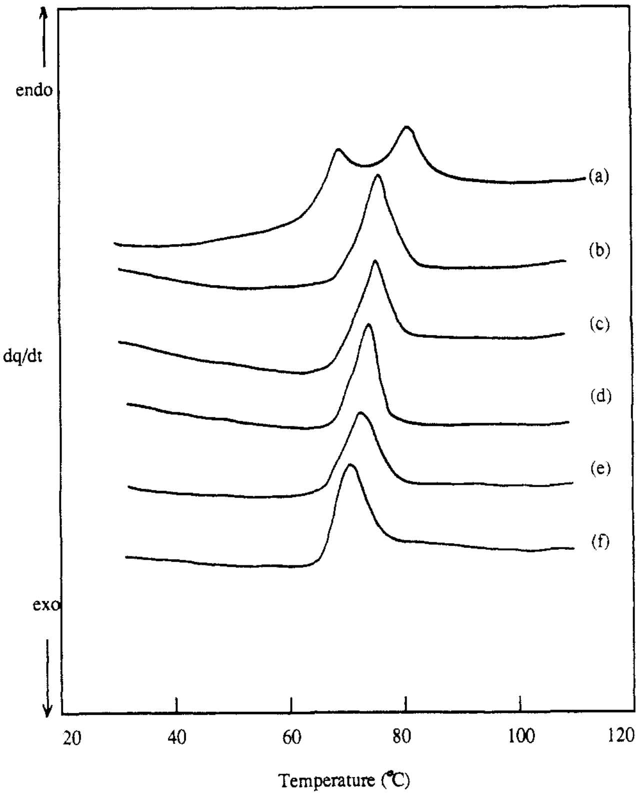

Figure 2. DSC curves for annealed PDCEMA/PEMA blends: (a) 1:1 physical mixture of PDCEMA/PEMA; (b) 10% PEMA; (c) 25% PEMA; (d) 50% PEMA; (e) 75% PEMA; (f) 90% PEMA.

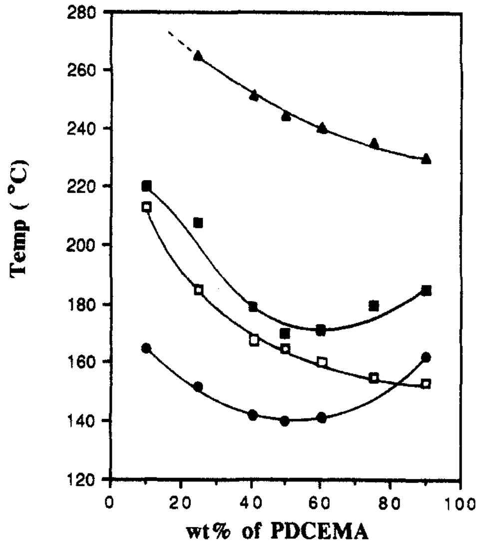

Figure 3. Cloud point curves for PDCEMA/polymethacrylates blends: (▲) PDCEMA/PnPMA; (■) PDCEMA/PiPMA; (□) PDCEMA/PnBMA; (●) PDCEMA/PiAMA.

All of the PDCEMA/PiPMA blends were transparent, but they turned cloudy when heated to 170–220 °C, showing the existence of LCST behavior. As shown in Figure 3, the cloud point values are lower than those of the PDCEMA/PnPMA blends. Annealing of PDCEMA/PiPMA blends was not required as the two T_g values of a two-phase physical mixture could be observed by conventional DSC measurement. Each blend showed a single glass transition, which moved progressively to a higher temperature with increasing PiPMA content. These observations suggest that PDCEMA is miscible with PiPMA but the blends become phase separated on heating to temperature above 170 °C.

PTCEMA/PiPMA blends were transparent and remained so on heating to 270 °C. Various blends were annealed for 21 days at 70 °C. A single enthalpy relaxation peak, which moved progressively to a higher temperature with increasing PiPMA content, was observed, indicating the miscibility of PTCEMA with PiPMA.

The good optical clarity of PDCEMA/PnBMA blends suggested the miscibility of these two polymers. Each blend exhibited a single composition-dependent T_g and showed LCST behavior in the region 153–213 °C. The cloud point curve is shown in Figure 3. On the basis of the single glass transition temperature criterion and the LCST behavior, we conclude that PDCEMA is miscible with PnBMA.

PTCEMA/PnBMA blends were transparent and remained so upon heating to 270 °C. However, DSC measurements revealed two glass transitions which correspond to those of the pure components, suggesting the two-phase nature of PTCEMA/PnBMA blends. The clarity of the immiscible blends may arise from the matching refractive indices of the two polymers or a small domain size.

PDCEMA/PnAMA blends containing 25, 50, 75, and 90 wt % PDCEMA were hazy. DSC measurements showed the existence of two T_g values in each blend. The upper T_g value is close to that of PDCEMA, while the lower T_g value is about 20 °C higher than that of PnAMA, indicating the presence of PDCEMA in the PnAMA-rich phase. However, a blend containing 10 wt % PDCEMA was transparent but turned cloudy at 142 °C, indicating the existence of LCST behavior, and the blend had a single T_g. Thus, PDCEMA is miscible with PnAMA at low PDCEMA content. Figure 4 shows the T_g-composition plot of this blend system.

Two distinct glass transition temperatures corresponding to those of the pure components were observed for each of the PTCEMA/PnAMA blends, as shown in Figure 4. It is concluded that PTCEMA is immiscible with PnAMA.

DSC measurements revealed two distinct glass transition temperatures, which correspond to those of the pure components, for both PDCEMA/PnHMA and PTCEMA/PnHMA blend systems. PDCEMA and PTCEMA are then judged to be immiscible with PnHMA.

All of the PDCEMA/PiAMA blends were transparent and turned cloudy when heated to 140–165 °C, indicating the existence of LCST behavior. The cloud point curve is shown in Figure 3. Each PDCEMA/PiAMA blend exhibited a single T_g, suggesting the miscibility of PDCEMA with PiAMA. These results indicate that PDCEMA/PiAMA blends are miscible at all compositions but undergo phase separation at rather low temperatures. On the other hand, the existence of two glass transition temperatures in each of the PTCEMA/PiAMA blends shows that PTCEMA is immiscible with PiAMA.

All of the PDCEMA/PCHMA, PDCEMA/PTHFMA, and PTCEMA/PTHFMA blends were transparent and did not undergo phase separation on heating prior to decomposition. However, PTCEMA/PTHFMA blends decomposed at 240 °C. Annealing of PTCEMA/PCHMA blends was not required as the two T_g values of a two-phase physical mixture could be observed by conventional DSC measurements. The existence of a single T_g suggests that both PTHFMA and PCHMA are miscible with PDCEMA and with PTCEMA.

Miscibility Behavior. Table 2 summarizes the miscibility of PDCEMA, PTCEMA, PCMMA, P1CEMA, P2CEMA, and P3CPMA with various polymethacrylates. Apparently, among the six chlorine-containing polymethacrylates, PDCEMA shows the widest range of miscibility with polymethacrylates. One notable point is that PDCEMA is miscible with both PiAMA and PCHMA,

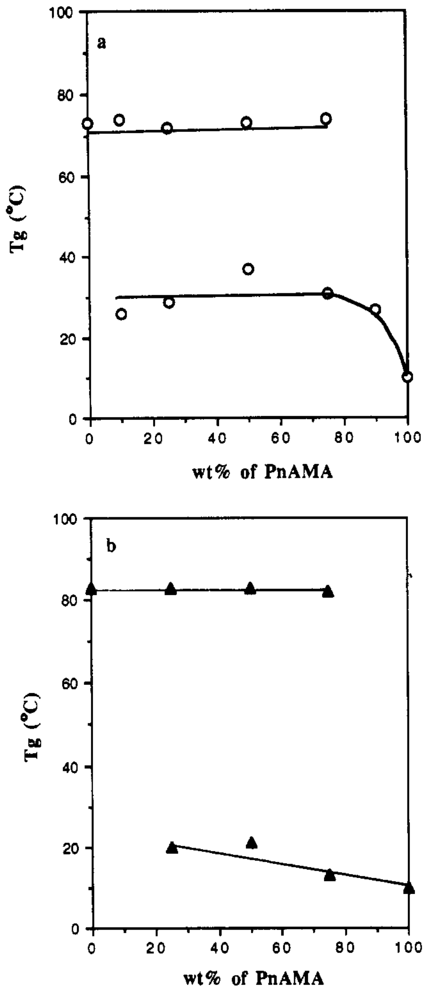

Figure 4. T_g-composition curves for blends: (a) PDCEMA/PnAMA; (b) PTCEMA/PnAMA.

while PTCEMA is miscible only with PCHMA, but the other chlorine-containing polymethacrylates are immiscible with PCHMA. We have earlier suggested that the miscibility of chlorine-containing polymethacrylates with various homologous polymethacrylates may arise from interactions involving the α-hydrogens of the pendant chloroalkyl group.[10,11] Our recent studies further support this suggestion. As shown in Table 2, the ability of a chlorine-containing polymethacrylate to be miscible with polymethacrylates decreases in the order PCMMA > P2CEMA > P3CPMA. The presence of electron-withdrawing chlorine and the ester carboxyl group makes the hydrogen atom of the $-CH_2Cl$ group acidic, and the acidity decreases in the order PCMMA > P2CEMA > P3CPMA because of the intervening methylene group(s). The observed order of miscibility, P2CEMA > PBEMA > PIEMA, also follows the same order of the acidity of the hydrogen atoms of the $-CH_2X$ group. The differences in the miscibility between P1CEMA and P2CEMA further illustrate the importance of the acidity of hydrogen atoms in achieving miscibility and also indicate that interactions involving C–Cl groups may not be important.

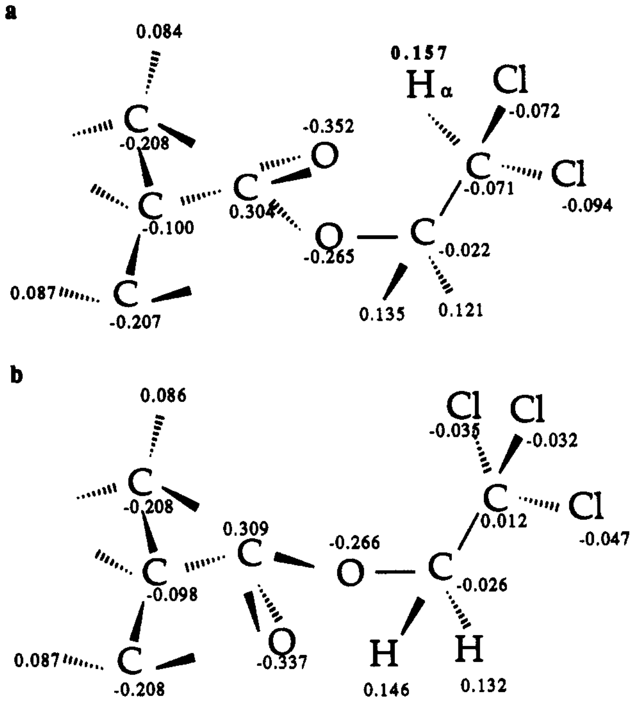

Figure 5. Atomic charge distributions for the repeat units of (a) PDCEMA and (b) PTCEMA.

It has been shown that information about atomic charge distributions in the polymer segment can serve as a very useful guide about possible polar interactions between polymers.[25,26] Figure 5 shows the atomic charge distributions for the repeat units of PDCEMA and PTCEMA. The hydrogen of the $-CHCl_2$ group in PDCEMA has a larger atomic charge and, therefore, is more acidic than the hydrogens in the $-CH_2CCl_3$ group in PTCEMA. The computation results of the atomic charges of α-hydrogens for other chlorine-containing polymethacrylates are given in Table 3. Except for PTCEMA, the α-hydrogen refers to the hydrogen with the largest atomic charge on the carbon atom bearing chlorine. The order of atomic charges of α-hydrogens, PDCEMA > PTCEMA > PCMMA $\cong$ P1CEMA > P2CEMA > P3CPMA, is the same as for our experimentally observed miscibility ranges of these chlorine-containing polymethacrylates.

Miscible blends often undergo phase separation on heating. The temperature at which phase separation occurs can be taken to indicate, at least qualitatively, the strength of interactions between the binary components.[27,28] The cloud point curves for blends of PDCEMA,

Table 2. Miscibility Behavior of Chlorine-Containing Polymethacrylates with Various Homologous Polymethacrylates[a]

	PDCEMA	PTCEMA	P1CEMA[19]	PCMMA[10]	P2CEMA[11]	P3CPMA[12]
PMMA	miscible	miscible	miscible	miscible	miscible	immiscible
PEMA	miscible	miscible	miscible (L)[b]	miscible (L)	miscible (L)	immiscible
PnPMA	miscible (L)	miscible	miscible (L)	miscible (L)	immiscible	immiscible
PiPMA	miscible (L)	miscible	miscible (L)	miscible (L)	immiscible	immiscible
PnBMA	miscible (L)	immiscible	miscible (L)	immiscible	immiscible	immiscible
PnAMA	miscible at low PDCEMA content	immiscible	immiscible[c]	nd[d]	nd	nd
PnHMA	immiscible	immiscible	nd	nd	nd	nd
PiAMA	miscible (L)	immiscible	immiscible[c]	nd	nd	nd
PCHMA	miscible	miscible	immiscible	immiscible[12]	immiscible	immiscible
PTHFMA	miscible	miscible	miscible	miscible	miscible	miscible

[a] Superscript numbers denote reference numbers. [b] (L), lower critical solution temperature behavior. [c] J. Peng, unpublished results. [d] nd, not determined.

Table 3. Atomic Charges of α-Hydrogens of Chlorine-Containing Polymethacrylates

	polymer					
	PDCEMA	PTCEMA	PCMMA	P1CEMA	P2CEMA	P3CPMA
atomic charge	0.157	0.146	0.136	0.135	0.127	0.107

as shown in Figure 3, suggest that the intensity of interactions decreases in the order PMMA, PEMA > PnPMA > PiPMA > PnBMA > PiAMA. Similar trends were observed for blends of PCMMA and P1CEMA.[10,19] Thus, the lower members of the homologous polymethacrylates are more readily miscible with chlorine-containing polymethacrylates as compared with the higher members. It is noted that some miscible PDCEMA blends show LCST behavior but not the miscible PTCEMA blends. It is conceivable that the absence of LCST behavior for the PTCEMA blends may arise from the rather low molecular weight of PTCEMA as compared with PDCEMA.

The present work also illustrates a subtle steric effect on miscibility. PDCEMA is completely miscible with PiAMA, but it has a very limited miscibility with PnAMA. Furthermore, PDCEMA is miscible with PCHMA but not with PnHMA. Cowie and Reilly[28] have found that poly(*tert*-butyl methacrylate), but not poly(*n*-butyl methacrylate), is miscible with modified poly(α-methylstyrene) (PαMS). They proposed that the *n*-butyl chain was long, preventing the carbonyl group from coming close enough to interact with the hydroxyl group of the modified PαMS. On the other hand, the bulky *tert*-butyl group was only as long as an ethyl chain, and so a close contact between carbonyl and hydroxyl groups could be achieved. The results appear to suggest that polymethacrylates with long pendant linear alkyl chains are less likely to be miscible with other polymers than those polymethacrylates with branched alkyl chains. However, there are examples contrary to the suggestion. For example, PnPMA, but not PiPMA, is miscible with poly(vinyl chloride),[20,29] polyepichlorohydrin,[9] and poly(vinylidene chloride-*co*-vinyl chloride).[31] Thus, there is no general rule to predict the steric effect of the pendant group on the miscibility behavior of polymethacrylates.

We have previously examined the miscibility of various chlorine-containing/polymethacrylate blends using a non-hydrogen-bonded solubility parameter (δ_{nh}) approach proposed by Coleman *et al.*[31,32] The δ_{nh} approach considers that polymer–polymer miscibility depends on a balance between unfavorable physical forces and favorable specific interactions. The unfavorable physical forces can be minimized by a close match of δ_{nh} values of the two polymers. For two polymers that are able to undergo specific interactions, a large mismatch in the δ_{nh} values can be tolerated. The δ_{nh} values of polymethacrylates decrease from 18.4 $(\mathrm{J\,cm^{-3}})^{1/2}$ for PMMA to 17.5 $(\mathrm{J\,cm^{-3}})^{1/2}$ for PnHMA; the δ_{nh} values of PDCEMA, PTCEMA, PCMMA, P1CEMA, P2CEMA, and P3CPMA are 21.1, 22.3, 20.7, 19.5, 20.0, and 19.6 $(\mathrm{J\,cm^{-3}})^{1/2}$, respectively. The δ_{nh} values of PDCEMA and PTCEMA are quite different from those of the polymethacrylates, and yet they show good miscibility with these polymethacrylates. In terms of the δ_{nh} approach, the unfavorable physical forces arising from the large mismatch of δ_{nh} values must then be more than outweighed by the strong ability of PDCEMA and PTCEMA to undergo specific interactions with the polymethacrylates. Nevertheless, the use of δ_{nh} values alone cannot account for the differences in the miscibility behavior of various chlorine-containing polymethacrylates.

In summary, PDCEMA and PTCEMA are readily miscible with poly(alkyl methacrylate)s. The good miscibility of PDCEMA appears to be a result of the very acidic hydrogen in the $-\mathrm{CHCl_2}$ group.

Acknowledgment. We thank the National University of Singapore for financial support of this research. We also thank Dr. W. S. Chin and Dr. A. Rai-Chaudhuri for assistance in the calculation of atomic charge distributions.

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