Miscibility of poly(methyl methacrylate) blends with halogen-containing polycarbonates and copolymers

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Blends of poly(methyl methacrylate) (PMMA) and bisphenol-A polycarbonate (PC) having high molecular weights do not form homogeneous mixtures at equilibrium above the glass transition temperature. In this paper, the possibility of developing blends of PMMA with polycarbonates that can be melt processed into homogeneous materials was examined by adding a comonomer to the polycarbonate. Hexafluorobisphenol-A appears to be an extremely effective comonomer for this purpose. The phase behaviour of PMMA blends with hexafluorobisphenol-A polycarbonate (HFPC) and with PC–HFPC copolycarbonates containing various amounts of hexafluorobisphenol-A was determined. The blends of PMMA and HFPC are miscible and do not phase separate prior to thermal decomposition. The phase separation temperatures of PMMA blends with the copolycarbonates increase dramatically as the hexafluorobisphenol-A content increases. Blends of PMMA with copolycarbonates containing 15 wt% hexafluorobisphenol-A or higher have phase separation temperatures above the temperature range required for melt processing. Additionally, the interaction energies for blends of PMMA with PC, bisphenol chloral polycarbonate and PC–HFPC copolymers were calculated from the phase boundaries using the lattice fluid theory and binary interaction model.

(Keywords: blends; PMMA; copolycarbonates; LCST; equation of state)

INTRODUCTION

The equilibrium phase behaviour of polymer blends depends on the interactions between the monomer units present, equation of state effects and the molecular weights of the components[1–6]. When the net interaction is near the borderline of miscibility, the phase diagram becomes very sensitive to small modifications of the molecular structure. For this reason incorporation of relatively small amounts of a comonomer into one of the components can be very effective for converting an immiscible pair into a miscible one or for increasing the phase separation temperature of a miscible blend having a relatively low lower critical solution temperature (*LCST*)[7–12].

Recent observations suggested that bisphenol-A polycarbonate (PC)/poly(methyl methacrylate) (PMMA) blends are miscible but phase separate on heating at temperatures just above the glass transition[13–18]. A subsequent re-examination has shown that these reports overestimated the extent that PC and PMMA are miscible and that the previously published cloud points do not reflect an equilibrium phase diagram because of extremely slow kinetics of phase separation[19]. Nevertheless PC/PMMA blends appear to be right on the edge of miscibility. Thus, PC/PMMA blends present an interesting example to illustrate how the phase diagram can be manipulated by the copolymer approach. Previous experiments on blends of poly(methyl methacrylate-*co*-styrene) with PC also overestimated the cloud point temperature because of the same difficulty of slow kinetics of phase separation[20]. A more thorough search was made for a comonomer that in combination with methyl methacrylate would yield an acrylic polymer whose blends with PC would be fully miscible[21]. Of those examined, cyclohexyl methacrylate (CHMA) and phenyl methacrylate (PhMA) were found especially effective for this purpose. The *LCST* could be raised marginally enough to give melt processible blends by using large amounts of either CHMA or PhMA.

In this paper, the possibility of raising the *LCST* for this system by adding a comonomer to the polycarbonate is examined. During the course of a general investigation of blends of various polycarbonates with polymers based on styrene, methyl methacrylate, acrylonitrile, etc., it was found that hexafluorobisphenol-A polycarbonate, HFPC, is miscible with PMMA but immiscible with PC. Thus, hexafluorobisphenol-A emerged as a promising candidate for this purpose. We report here the changes in miscibility and phase boundaries for blends of PMMA with polycarbonate copolymers containing various amounts of hexafluorobisphenol-A. In addition, the effects of changing the structure of the polymethacrylate on miscibility with PC, bisphenol chloral polycarbonate (BCPC) and HFPC were also examined. Finally, the interaction energies for blends of PMMA with PC, BCPC and HFPC copolymers were evaluated from the equilibrium phase diagram using the lattice fluid theory of Sanchez–Lacombe[4,22–24].

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EXPERIMENTAL

Table 1 describes the polymers used in this study. The HFPC homopolymer and its copolymers, PC–HFPC, were synthesized using an interfacial polymerization technique[25–28]. The bisphenol monomers dissolved in the aqueous phase were reacted with bis(trichloromethyl) carbonate, or triphosgene, using triethylamine as phase transfer catalyst[29,30]. Triphosgene (Aldrich Chemical Co.) dissolved in methylene chloride was found to be a suitable substitute for phosgene. Triphosgene is a white crystalline solid that is safer and more convenient to handle than phosgene generally used for polycarbonate synthesis. In most cases, reaction required only one-third equivalent of triphosgene[31–33]. The HFPC homopolymer and HFPC–PC copolymers were optically transparent.

The numerical part of the code for these copolymers (see *Table 1*) indicates the weight per cent of hexafluorobisphenol-A monomer as reactant. The actual copolymer compositions used in the interaction parameter analysis were determined by elemental fluorine analysis (by Huffman Laboratories Inc., Golden, CO). The resulting weight per cent compositions are listed in *Table 1*. Molecular weights of commercial PC (Lexan 131-111) and polycarbonates synthesized were determined by g.p.c. using polystyrene standards. These results indicate that the synthesized polycarbonates have molecular weights at least as high as commercial PC.

Blends of the polycarbonates and PMMA were prepared by solution casting from tetrahydrofuran in a Petri dish. The cast films were dried at 70°C for 10 min in an air circulating oven until most of the solvent evaporated. The resulting films were further dried for a week in a vacuum oven at 20–30°C higher than the glass transition temperature (T_g). Some blends were prepared by melt mixing at 260°C in a Mini-Max moulder in order to examine melt processibility. All other blends were prepared by the solution method described above. When phase-separated mixtures were obtained, variations, such as hot casting from methylene chloride, precipitation methods, etc., were explored to ensure as nearly as possible that the results reported here correspond to equilibrium phase behaviour.

A Perkin-Elmer DSC 7 was used to measure the thermal behaviour of these blends. Values of T_g defined by the onset method were recorded during the second thermal scan, using a heating rate of 20°C min^{-1}, after the samples had been quenched from 200 to 25°C. On heating, some of the blend samples turned cloudy due to phase separation. Phase separation temperatures were determined in a manner designed to eliminate rate effects caused by slow phase separation kinetics. Blend samples were annealed on a hot stage (Mettler, FP 82 HT) equipped with a temperature controller (Mettler, FP 80 HT) at various constant temperatures around the phase separation temperature for a certain period of time. The phase separation temperature reported here was determined by a visual observation or by use of a d.s.c. technique[34,35].

The absolute densities of PC, BCPC and HFPC at 30°C were determined using a density gradient column. Changes in specific volume as a function of temperature and pressure were measured using a Gnomix PVT apparatus. Starting at 30°C, a sample was compressed along 31 isotherms, spaced ~15–20°C apart, up to ~280°C, with volume data recorded at pressure intervals of 10 MPa between 10 MPa and 200 MPa along each

Table 1 Polymers used

Abbreviation	Polymer	T_g (°C)	HFPC content (%)[a]	Molecular weight[b]	Source
PC	Bisphenol-A polycarbonate	148	–	$\bar{M}_n$ = 37 000[c] $\bar{M}_w$ = 76 500	General Electric Co. (Lexan 131-111)
BCPC	Bisphenol chloral polycarbonate	163	–	$\bar{M}_n$ = 51 100 $\bar{M}_w$ = 118 500	General Electric Co.
HFPC	Hexafluorobisphenol-A polycarbonate	169	100	$\bar{M}_n$ = 41 100 $\bar{M}_w$ = 107 000	Synthesized
PC–HFPC 5	Bisphenol-A polycarbonate-*co*-hexafluorobisphenol-A polycarbonate	152	4.5	$\bar{M}_n$ = 31 000 $\bar{M}_w$ = 80 300	Synthesized
PC–HFPC 6.5	Bisphenol-A polycarbonate-*co*-hexafluorobisphenol-A polycarbonate	152	5.3	$\bar{M}_n$ = 27 900 $\bar{M}_w$ = 72 200	Synthesized
PC–HFPC 8	Bisphenol-A polycarbonate-*co*-hexafluorobisphenol-A polycarbonate	154	7.9	$\bar{M}_n$ = 33 400 $\bar{M}_w$ = 85 400	Synthesized
PC–HFPC 10	Bisphenol-A polycarbonate-*co*-hexafluorobisphenol-A polycarbonate	155	9.6	$\bar{M}_n$ = 29 900 $\bar{M}_w$ = 103 100	Synthesized
PC–HFPC 15	Bisphenol-A polycarbonate-*co*-hexafluorobisphenol-A polycarbonate	157	14.0	$\bar{M}_n$ = 28 000 $\bar{M}_w$ = 83 900	Synthesized
PMMA	Poly(methyl methacrylate)	107	–	$\bar{M}_n$ = 52 900[d] $\bar{M}_w$ = 130 000[d]	Rohm & Haas Co. (V 811)
PEMA	Poly(ethyl methacrylate)	70	–	–	Dupont (Elvacite 2042)
PnPMA	Poly(n-propyl methacrylate)	50	–	–	Polysciences, Inc.
PiPMA	Poly(i-propyl methacrylate)	83	–	–	Polysciences, Inc.
PnBMA	Poly(n-butyl methacrylate)	19	–	–	Scientific Polymer Products

[a] Determined by elemental analysis
[b] Determined by g.p.c. using polystyrene standards
[c] $\bar{M}_w$ = 38 000 determined by light scattering in this laboratory; molecular weight information provided by supplier: $\bar{M}_n$ = 13 000; $\bar{M}_w$ = 34 200
[d] Data from Rohm & Haas using PMMA standards

isotherm. Samples were pressurized at a rate of ~20 MPa min^{-1}. The specific volume at zero pressure (or 1 atm) for each isotherm was obtained by extrapolation using the Tait equation[36].

BACKGROUND

Binary interaction model

This model envisions each polymer as being composed of structural entities like monomer units in a copolymer but it is not restricted to this type of situation[1,2,37,38]. The interaction between unlike units *i* and *j* within the blend or in the polymer itself is characterized by the product of an interaction energy density B_{ij} and the volume fraction of these units. The heat of mixing a volume V_A of polymer A with volume V_B of polymer B may be written as:

$$\Delta H_m = (V_A + V_B)\sum_{i>j} B_{ij}\phi_i\phi_j - V_A \sum_{k>l} B_{kl}\phi'_k\phi'_l - V_B \sum_{m>n} B_{mn}\phi''_m\phi''_n \qquad (1)$$

For a binary blend of copolymer A composed of units 1 and 2 and a homopolymer B composed of units of 3, the interaction energy density between polymers A and B is given by:

$$B = B_{13}\phi'_1 + B_{23}\phi'_1 - B_{12}\phi'_1\phi'_2 \qquad (2)$$

Such parameters when deduced from a phase diagram include possible entropic contributions in addition to the enthalpic one implied by equation (1). In an attempt to avoid inclusion of contributions arising from equation of state effects, the lattice fluid theory of Sanchez–Lacombe[4,22–24] will be used for the calculation of interaction parameters from phase behaviour.

Lattice fluid theory

This theory expresses thermodynamic functions in terms of reduced variables $\tilde{P} = P/P^*$, $\tilde{T} = T/T^*$ and $\tilde{\rho} = 1/\tilde{v} = \rho/\rho^* = v^*_{sp}/v_{sp}$, where the asterisks denote characteristic parameters. The ΔH_m at low pressure for a binary mixture is given by:

$$\frac{\Delta H_m}{V} = \tilde{\rho}^2 \Delta P^* \phi_1\phi_2 + \tilde{\rho}[\phi_1 P^*_1(\tilde{\rho}_1 - \tilde{\rho}) + \phi_2 P^*_2(\tilde{\rho}_2 - \tilde{\rho})] \qquad (3)$$

The characteristic pressure for the mixture, P^*, is related to those of the pure components, P^*_i, and the bare (stripped of free volume effects) interaction energy, ΔP^*, by:

$$P^* = \phi_1 P^*_1 + \phi_2 P^*_2 - \phi_1\phi_2\Delta P^* \qquad (4)$$

where the ϕ_i are close-packed volume fractions. The reduced density $\tilde{\rho}$ refers to the mixture, whereas $\tilde{\rho}_i$ refers to the pure components. For a binary blend of a copolymer composed of 1 and 2 units and a homopolymer 3, the net interaction parameter by analogy with equation (2) is[34,39]:

$$\Delta P^* = \phi'_1 \Delta P^*_{13} + \phi'_2 \Delta P^*_{23} - \phi'_1\phi'_2 \Delta P^*_{12} \qquad (5)$$

where ϕ'_1 and ϕ'_2 are the close packed volume fraction of units 1 and 2 in the copolymer. The details of this theory have been described in our previous papers[34,35] and elsewhere[4,22–24].

Table 2 Miscibility of high molecular weight polycarbonates and polymethacrylates[a]

	PC	BCPC	HFPC
PC	–	Miscible	Immiscible
BCPC	Miscible	–	Immiscible
HFPC	Immiscible	Immiscible	–
PMMA	Immiscible[b]	Miscible	Miscible
PEMA	Immiscible	Immiscible	Miscible
PnPMA	Immiscible	Immiscible	Miscible
PiPMA	Immiscible	Immiscible	Partially miscible[c]
PnBMA	Immiscible	Immiscible	Immiscible

[a] Systems classified as miscible have equilibrium *LCST* above T_g for molecular weights typical of commercial polymers. All acrylics refer to free radical polymerized or atactic forms

[b] Blends of PMMA and PC are nearly miscible and become so when the molecular weight of either component is below values typical of commercial polymers

[c] This system shows miscibility for some ratios of blend components but not all

BLENDS OF POLYCARBONATE AND POLYMETHACRYLATE HOMOPOLYMERS

Table 2 summarizes the miscibility of each homopolymer pair. Both BCPC[40] and HFPC form thermodynamically miscible blends with PMMA. These blends were optically transparent and exhibited a single T_g that depends on composition. Depending on the method of preparation PC blends with PMMA may also be optically transparent and exhibit a single composition-dependent T_g; however, they undergo irreversible phase separation on heating at temperatures not far above the glass transition[13–19]. BCPC blends with PMMA show reversible *LCST* behaviour at relatively high temperatures, whereas HFPC blends with PMMA do not phase separate prior to decomposition. These results suggest that the polar connector groups between the phenyl rings of the bisphenol unit promote favourable interactions with PMMA and, thus, miscibility as found in many other pairs involving halogens in one component and carbonyls in the other[41–50]. The miscibility of poly(vinyl chloride) (PVC) with polyesters, polymethacrylates and polyacrylates has been suggested to involve hydrogen bonding between the α-hydrogen of PVC and the carbonyl groups[41–50], charge transfer between the ester group and the halogen[41,45] or electrostatic interaction caused by halogen-induced dipoles[41–44,47–50].

Figure 1 shows charge distributions on the atoms of the repeat units of PC, BCPC, HFPC and PMMA calculated by the Gast–Huck method using SYBYL Software from TRIPOS Associates Inc. The Gasteiger–Marsili method[51,52] was used to calculate the σ component of the atomic charge while the Hückel method[53] was used to calculate the π component of the atomic charge. The partial charge on each atom is the sum of these two calculations. As shown in *Figure 1*, the most obvious changes in the electronic structure of HFPC and BCPC relative to PC are in the connector groups themselves. Addition of halogens convert the exterior surface of these groups from positive (+0.007 partial charges on the H in PC) to negative (−0.198 for F in HFPC and −0.043 for Cl in BCPC) while the interior carbons go from negative in PC to strongly positive in HFPC and a weaker, mixed situation in BCPC. Thus, the directions of the individual bond dipoles are reversed

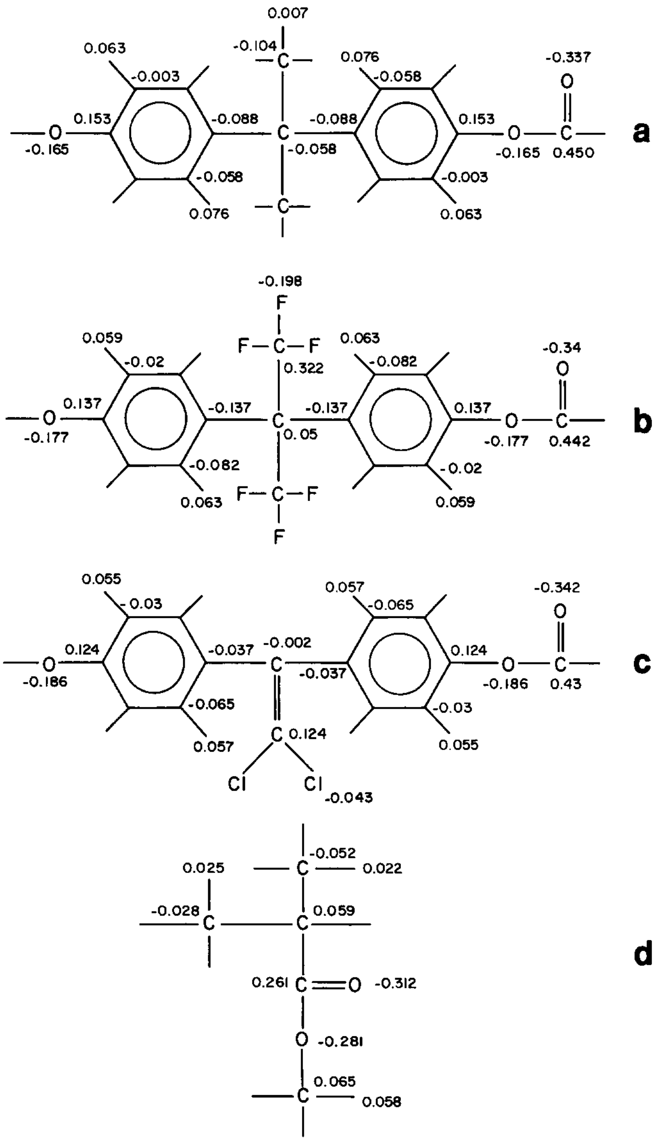
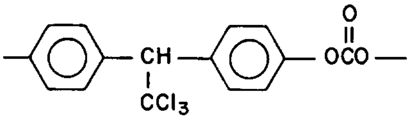


Figure 1 Atomic charge distribution for the repeat units of (a) PC, (b) HFPC, (c) BCPC and (d) PMMA calculated by the Gast–Huck method

and the magnitudes are strengthened. In addition, the phenyl rings become significantly more polarized in HFPC and less so in BCPC. There is little change in the calculated electronic distribution in the more distant carbonate linkage. Evidently, these changes drive the interactions with PMMA from weakly unfavourable for PC to more favourable for BCPC and strongly favourable for HFPC, since *LCST* behaviour suggests that the miscibility of blends follows the sequence HFPC > BCPC > PC, which is more or less the order of the effects seen in *Figure 1*. It is interesting to note, however, that evidently the halogenated polycarbonate containing 50% PC units and 50% of units with the structure



does not form miscible blends with PMMA based on results presented by Eastmond *et al.*[54].

Table 3 compares solubility parameters (δ values) obtained from various sources of a number of polymers including those of direct interest here. Those listed in the first two columns were calculated by group contribution methods developed by Small[55] and by Coleman *et al.*[56]. The next column lists experimental values from various sources summarized by Van Krevelen[55]. Those given in the final column were estimated from P^* (see *Table 4*) obtained by fitting the Sanchez–Lacombe equation of state to experimental *PVT* data above the T_g of each polymer. According to the theory, the cohesive energy density, *CED*, is:

$$CED = \tilde{\rho}^2 P^* \qquad (6)$$

For simplicity, $\tilde{\rho} \sim 1$ is used to obtain

$$\delta \equiv CED \approx \sqrt{P^*} \qquad (7)$$

Assignment of precise values to $\tilde{\rho}$ is difficult since the other estimates of δ presumably apply to room temperature where all these polymers are glassy and the

Table 3 Comparison of solubility parameters (in $J^{1/2}\,cm^{-3/2}$)

	Small[55]	Coleman *et al.*[56]	Experimental sources	$\sqrt{P^*}$
PMMA	18.6	18.6	18.6–26.2	22.5
Polystyrene (PS)	18.6	19.4	17.4–19.0	19.2
PC	21.7	21.7	20.3	22.3
Tetramethylbisphenol-A polycarbonate (TMPC)	21.4	19.4	–	20.9
BCPC	23.0	25.0	–	23.0
HFPC	20.5	–	–	20.9
Polyacrylonitrile (PAN)	26.6	28.2	25.6–31.5	–
Poly(maleic anhydride)	–	36.4	–	–

Table 4 Tait equation[a] and Sanchez–Lacombe equation of state parameters[b] for PC, BCPC and HFPC

	PC	BCPC	HFPC
a_0 ($cm^3\,g^{-1}$)	0.7888	0.6737	0.6111
a_1 ($cm^3\,g^{-1}\,°C^{-1}$)	3.432×10^{-4}	3.634×10^{-4}	4.898×10^{-4}
a_2 ($cm^3\,g^{-1}\,°C^{-2}$)	4.5710×10^{-7}	2.3698×10^{-7}	1.7301×10^{-7}
C_0 (bar)	3489	3634	2366
b_1 ($°C^{-1}$)	4.921×10^{-3}	4.921×10^{-3}	5.156×10^{-3}
T^* (K)	802	802	723
P^* (bar)	4961	5238	4331
ρ^* ($g\,cm^{-3}$)	1.2764	1.4795	1.6119

[a] $V(p,t) = V(0,t)\{1 - 0.0894\ln[1 + p/C(t)]\}$ where $V(0,t) = a_0 + a_1 t + a_2 t^2$ and $C(t) = C_0 \exp(-b_1{}^* t)$

[b] Characteristic parameters obtained over the range 0–50 MPa and 220–280°C

volumetric state is not well-defined from the point of view of an equilibrium equation of state. In any case the approximation $\tilde{\rho} \sim 1$ is not too serious. The agreement between δ values from the various sources is fairly good. Recently, Coleman *et al.*[56] suggested a method for predicting the phase behaviour of polymer blends using δ values. They assume the enthalpy of mixing can be separated into additive contribution from dispersive and specific interaction terms and that the former can be calculated from δ value information. If the contributions of entropy and specific interactions are absorbed into a $(\Delta\delta)_{\text{critical}}$ value, according to this approach two polymers A and B will be miscible if

$$|\bar{\delta}_A - \bar{\delta}_B| < (\Delta\delta)_{\text{critical}} \qquad (8)$$

where $\bar{\delta}_A$ and $\bar{\delta}_B$ are the volume averaged solubility parameters of polymers A and B. The binary interaction model[1,2,37,38] used here formulates the problem somewhat more generally. It includes the dispersive interactions but is not limited by the assumption of strict adherence to the geometric mean assumption inherent in a δ value formulation. Solubility parameter differences may not describe dispersive interactions in polar systems for either intermolecular or intramolecular interacting pairs. Even this more general mean field approach is likely to be inadequate when the system behaviour is dominated by strongly directional interactions like hydrogen bonds[57–59].

The approach suggested by Coleman *et al.*[56] can be useful for identifying potentially miscible systems. Like the binary interaction model, it formally predicts the possibility of miscibility windows for copolymer systems. However, the binary interaction model does not lead to *a priori* predictions unless the applicable B_{ij} values have been determined previously in some manner. The approach of Coleman *et al.* implies a route that by-passes the need for this information, but this can result in some quite misleading predictions. For example, based on the results in *Table 3*, the probability for miscibility of PMMA with the various polycarbonates listed would be in the order HFPC > TMPC > PC > BCPC. The *LCST* for PMMA blends with HFPC is in fact higher than that for BCPC in accord with this ranking, but neither TMPC nor PC are miscible with PMMA. The latter lack halogens which clearly promote interactions with PMMA that are favourable for miscibility. In fact PC is closer to miscibility with PMMA than is TMPC. A part of the difficulty may stem from insufficient accuracy in the available estimates for δ, but the limitations of such predictions go beyond this as seen next. The δ for PC is clearly intermediate between those for PS and PAN. Thus, a copolymer of styrene and acrylonitrile, or SAN, will have *exactly* the same δ as PC at some composition (~26–39 vol% depending on the homopolymer δ values used). Similarly, a styrene–maleic anhydride copolymer, SMA (at ~14 vol% MA) will have a δ value that exactly matches that of PC. However, neither SAN nor SMA copolymers are miscible with PC[60–62].

Both PC and BCPC form immiscible blends with polymethacrylates having larger pendant groups, e.g. PEMA, PnPMA, PiPMA and PnBMA. It appears that the interaction with polymethacrylates becomes increasingly unfavourable as the size of the alkyl pendant group increases. This point becomes clearer for HFPC blends with polymethacrylates. For PMMA, PEMA and PnPMA the blends with HFPC are optically clear and have a single T_g at all compositions as shown in *Figure 2*. Whereas HFPC blends with PMMA do not phase separate on heating prior to decomposition, its blends with the other polymethacrylates exhibit *LCST* behaviour at temperatures that become progressively lower as the alkyl group becomes longer or more bulky as shown in *Figure 3*. Solvent cast blends with PiPMA have complex phase behaviour. As shown in *Figure 2*, blends containing <70 wt% HFPC showed relatively narrow T_gs that depend on composition. These blends were always optically transparent. On the other hand, blends containing >80 wt% HFPC were cloudy and showed a broad glass transition region believed to be caused by two overlapped T_gs. HFPC blends with PnBMA were cloudy and showed two well-separated T_gs at all compositions. The higher phase separation temperature for blends with PnPMA compared to those of PiPMA suggests that bulky pendent groups, isopropyl or isobutyl, are unfavourable for miscibility. The phase boundaries shown in *Figure 3* and the blend T_g behaviour suggest that polymethacrylate interaction with HFPC lies in the order PMMA > PEMA > PnPMA > PiPMA > PnBMA. Similar results have been observed for other systems[50,63].

BLENDS OF PMMA WITH HFPC–PC COPOLYMERS

Table 2 indicates that HFPC is miscible with PMMA but immiscible with PC. These results suggest that the net interaction of PMMA with PC–HFPC copolycarbonates containing small amounts of HFPC should be favourable for miscibility. The effects of copolymerization on the interaction energy density, B, can be quantitatively expressed by the binary interaction model mentioned earlier[1,2,37,38]. For a blend of a copolymer composed of units 1 and 2 with a homopolymer composed of units of 3, the net interaction energy density is expressed by equation (2). Here we let 1 = PC, 2 = HFPC and 3 = PMMA. In this case, B_{13} is near zero and the current experimental results indicate that $B_{12} > 0$ and $B_{23} < 0$. Thus, B becomes more favourable for miscibility when HFPC (2) units are incorporated into the copolymer.

Hot cast blend films of PC–HFPC copolymers with PMMA were transparent and exhibited a single, composition-dependent T_g as expected for homogeneous blends. *Figure 4* shows the T_g behaviour of the blends as a function of the amount of HFPC units in the copolymers. Generally, the *LCST* behaviour of these blends was determined by measuring the optical cloud point while heating at finite rates. However, as reported by Nishimoto *et al.*[19] and Maruta *et al.*[64], when the phase boundary is near the blend T_g, the kinetics of the phase separation process may be very slow and this method is not appropriate because of rate effects. In order to avoid overestimation of the phase boundary, isothermal annealing was used. To illustrate this rate effect, the phase boundary for PC-HFPC 5/PMMA blends was determined using a light transmission method at a finite heating rate[19,35] and by isothermal annealing. The upper curve in *Figure 5* represents the 'phase boundary' observed at a heating rate of 2°C min^{-1}. Below this line are the results obtained by isothermal annealing. Solid symbols indicate blends that turned cloudy within the times shown while the open symbols indicate those

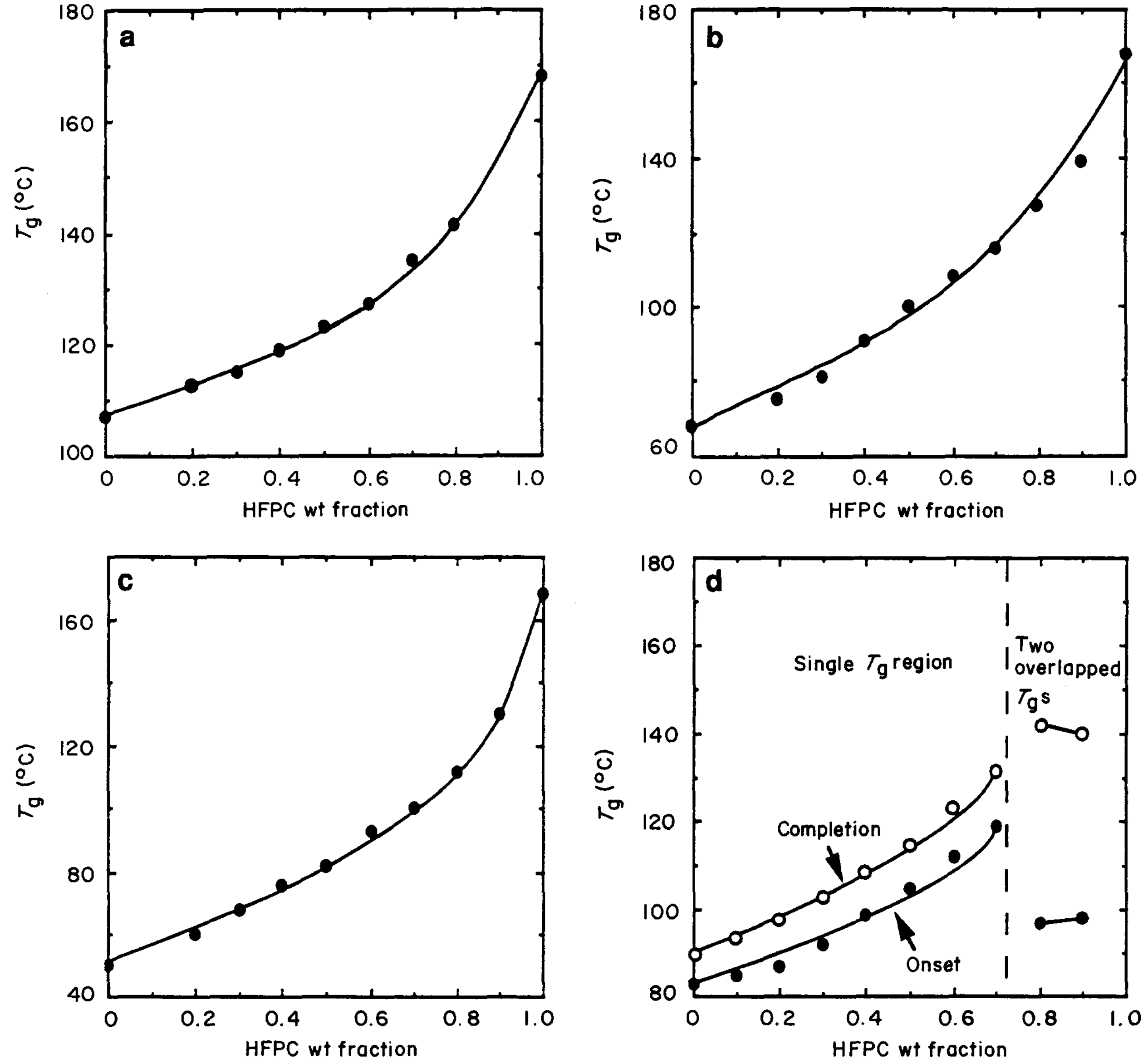


Figure 2 T_g behaviour of HFPC blends with various polymethacrylates: (a) PMMA; (b) PEMA; (c) PnPMA; (d) PiPMA

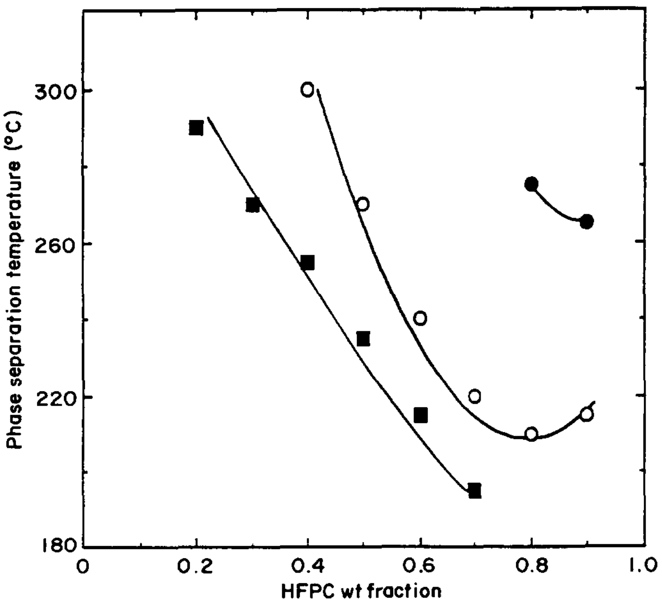


Figure 3 Phase separation temperatures for HFPC blends with various polymethacrylates: (●) PEMA; (○) PnPMA; (■) PiPMA

that remained transparent. The isothermal observations better reflect the equilibrium phase diagram. These results indicate that PC–HFPC 5/PMMA blends are miscible at all compositions but their phase boundary is only slightly above T_g. *Figure 6* shows phase boundaries determined by annealing blends of PMMA with copolycarbonates having HFPC levels in the range of 6.5–15 wt%. Blends were maintained at various constant temperatures near the phase separation temperature for up to 20 min. Longer annealing times could not be used because of thermal degradation at these high temperatures. Thermal decomposition at high temperature (~310°C) mainly comes from the thermal instability of PMMA (note this is a commercial acrylic that is heat stabilized by a comonomer) as shown in *Figure 7*. The phase separation temperature curves have a minimum at ~80 wt% copolycarbonate. Similar results have been reported for PC/methyl methacrylate copolymer blends[21] and PMMA/low molecular weight PC blends[19]. These phase boundaries are replotted in *Figure 8 versus* the percentage of HFPC units in the copolymer for fixed PMMA content in the blends. From these results, it is quite clear that the phase separation temperature

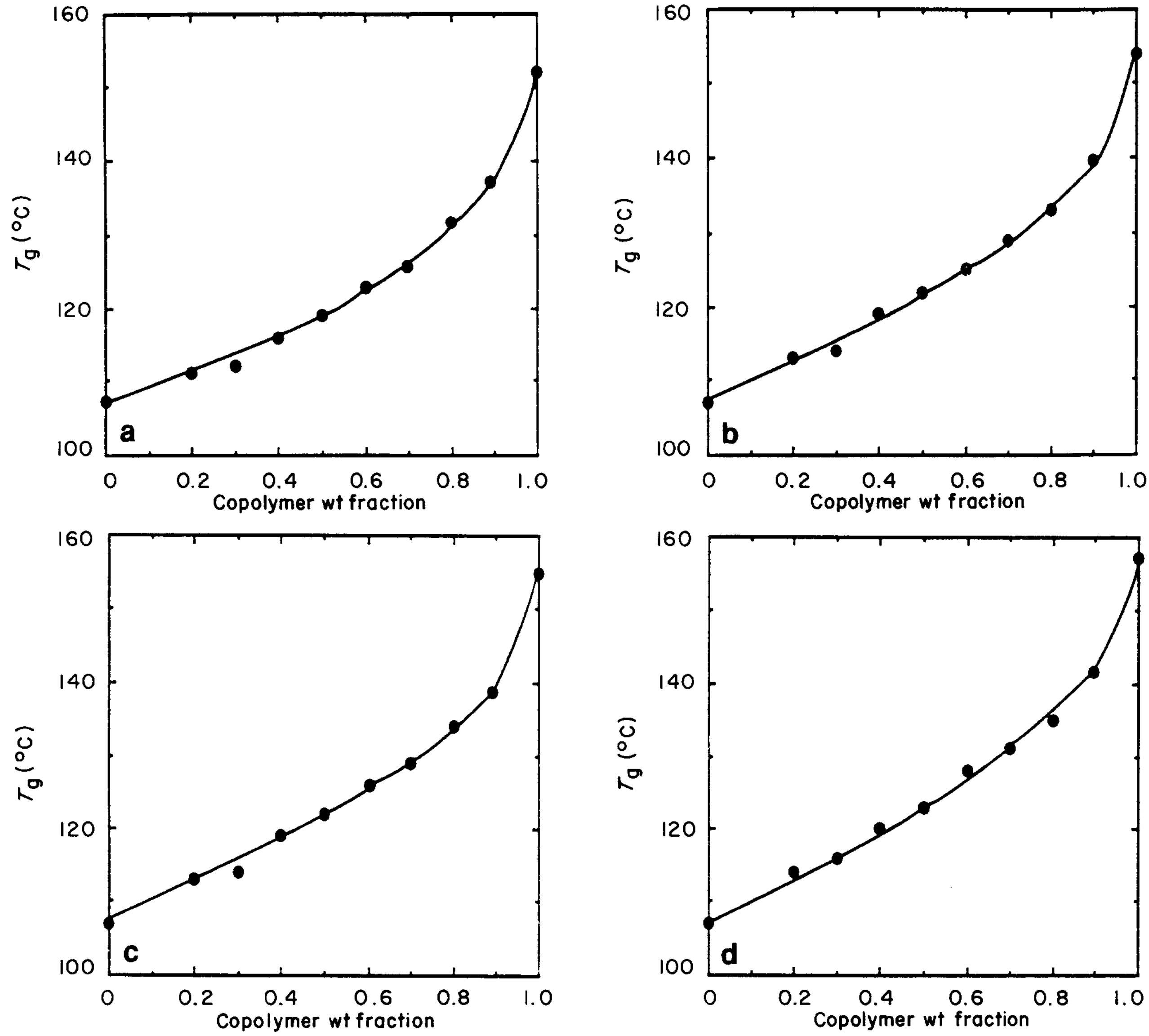


Figure 4 T_g behaviour of blends of PC–HFPC copolymers with PMMA: (a) PC–HFPC 5/PMMA; (b) PC–HFPC 8/PMMA; (c) PC–HFPC 10/PMMA; (d) PC–HFPC 15/PMMA

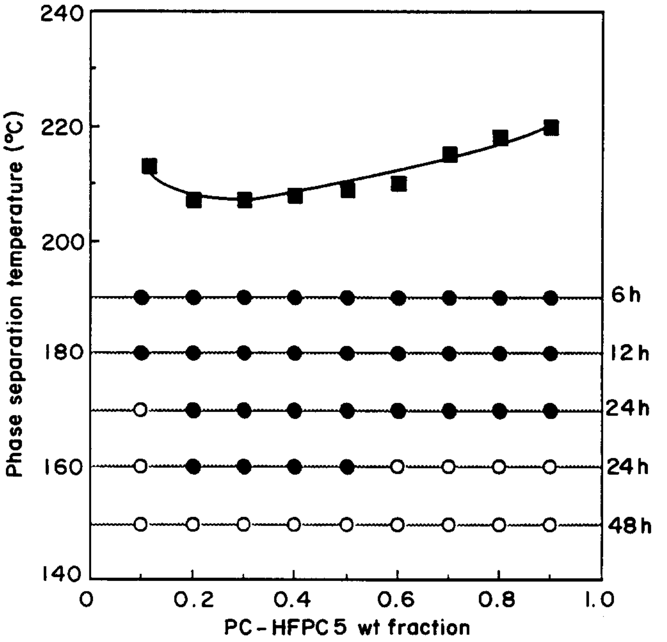


Figure 5 Phase behaviour of PC–HFPC 5/PMMA blends determined by light transmission at a heating rate of 2°C min^{-1} (■) and after annealing at various temperatures: (○) clear; (●) opaque

increases rapidly with HFPC content in the copolycarbonate. To examine melt processibility, a PMMA blend with PC–HFPC 15 containing 50 wt% PMMA was mixed in a Mini-Max moulder at 260°C. The resulting blend was transparent and had a single T_g.

EQUATION OF STATE ANALYSIS FOR INTERACTION ENERGIES

To extract information about the interaction energies for blends of PMMA with PC, BCPC and copolymers of PC and HFPC from their experimental liquid–liquid phase boundaries, the lattice fluid theory of Sanchez–Lacombe was used. As before[34,35], the two key assumptions employed were that the experimental phase boundary corresponds to the spinodal curve and the 'bare' interaction energy density, ΔP^*, does not depend on temperature. The latter will be true if the interaction between components involves only an energetic contribution. One may expect a strong specific interaction to involve an entropic component as well[65,66].

To obtain characteristic parameters of each pure component, experimental *PVT* data were fitted to the theoretical equation of state by non-linear regression.

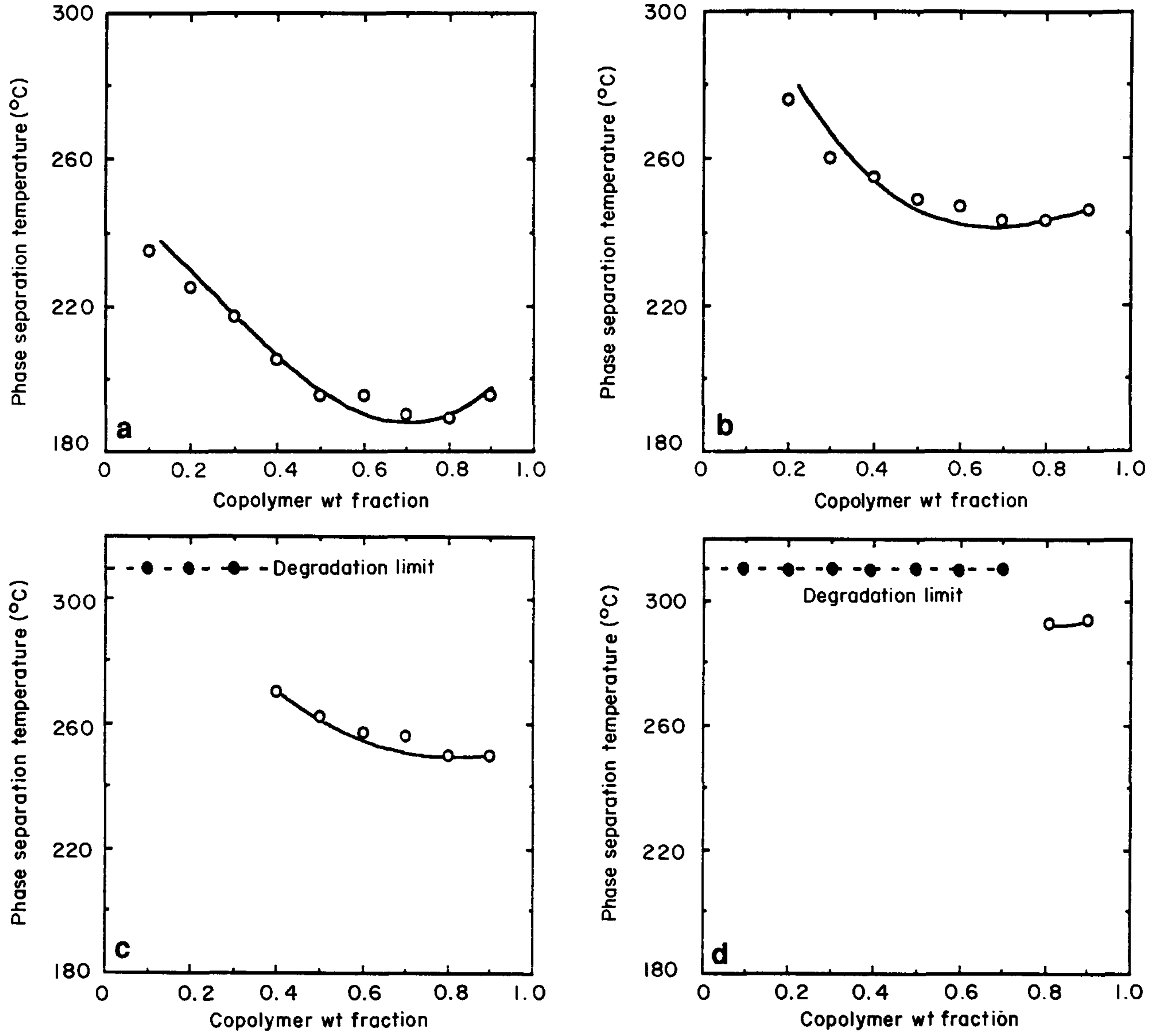


Figure 6 Phase boundaries of blends of PC–HFPC copolycarbonates with PMMA obtained by annealing. Solid symbols indicate that decomposition occurs on heating at ~310°C prior to phase separation: (a) PC–HFPC 6.5/PMMA; (b) PC–HFPC 8/PMMA; (c) PC–HFPC 10/PMMA; (d) PC–HFPC 15/PMMA

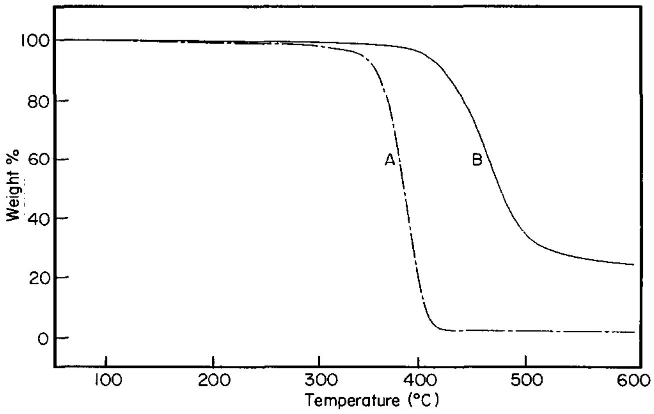


Figure 7 T.g.a. traces of (A) PMMA and (B) PC–HFPC 8 using a heating rate of 5°C min^{-1}

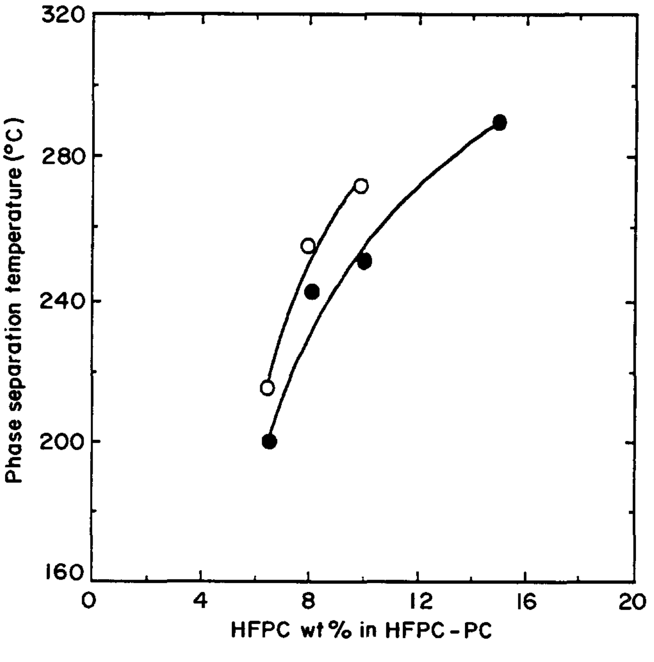


Figure 8 Phase separation temperatures of blends of PMMA with a series of PC–HFPC copolycarbonates: (○) 40 wt% copolycarbonate; (●) 80 wt% copolycarbonate

Since the lattice fluid equation of state only provides an accurate fitting function over a moderate pressure range, the characteristic parameters listed in *Table 4* were obtained over the range 0–50 MPa[67,68]. In addition, since characteristic parameters obtained from fitting the experimental *PVT* data to the lattice fluid equation of state depend on temperature, the same range (220–280°C) at which phase separation occurs was used for all polymers[69]. Characteristic parameters for PMMA have been reported in a previous paper[34].

Figure 9 shows ΔP^* values calculated from the experimental phase separation temperatures for PMMA blends with a low molecular weight PC ($\bar{M}_w = 9900$) determined by Nishimoto *et al.*[19]. The values of ΔP^* are nearly zero at high PC content near the critical composition ($\sim 80\%$ PC) but tend to become positive at low PC content in the blend. *Figure 10b* shows ΔP^* values calculated from the experimental phase separation temperatures for BCPC/PMMA blends (see points in *Figure 10a*). The values of ΔP^* obtained are negative and tend to show composition dependence at the ends of the composition spectrum. The solid line in *Figure 10a* is the calculated spinodal using a fixed value of $\Delta P^* = -0.077\ \mathrm{cal\ cm^{-3}}$, which corresponds to the value obtained around the critical point. Values of ΔP^* calculated from data in *Figure 6* for selected HFPC–PC/PMMA systems are shown in *Figure 11*. The ΔP^* values are negative and also show some composition dependence at the ends of the composition range. In contrast to similar estimates for ΔP^* for blends of tetramethyl polycarbonate with styrenic-based polymers[34,35], all of the calculated values shown in *Figures 9–11* tend to show a similar upturn at both ends of the composition spectrum. The latter results from the fact that the spinodal curve for a constant ΔP^* is narrower than the experimental phase boundary[65] (cf. points and line in *Figure 10a*). This may reflect nothing other than the possible breakdown of the assumption that the spinodal curve approximates the experimentally observed phase separation temperature at compositions away from the critical point. To some extent the shape of the phase boundary is affected by molecular weight distribution[70,71]. Another possibility is found in the work of Sanchez and Balaz[65] who showed that adding a strong specific interaction character to the lattice fluid model broadens the spinodal region. As mentioned in connection with *Figure 1*, the possibility of stronger specific interactions does exist for these systems. However, with the present techniques, we cannot ascertain which of the possibilities is the most likely.

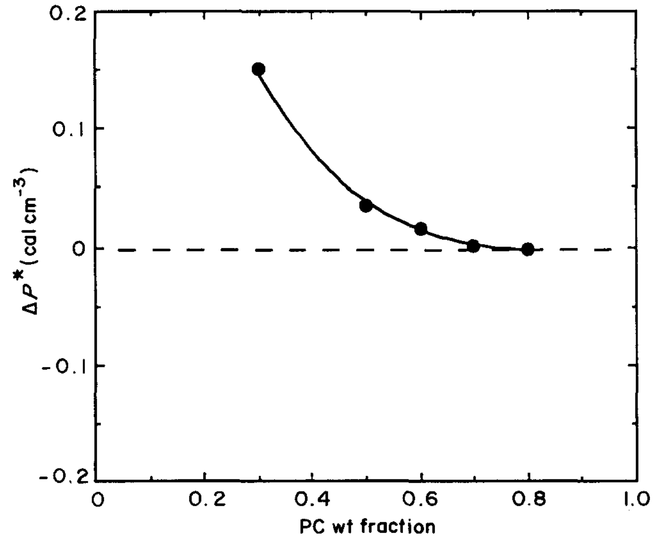


Figure 9 Bare interaction energies for blends of PMMA with low molecular weight PC ($\bar{M}_w = 9900$) computed from data reported by Nishimoto *et al.*[19]

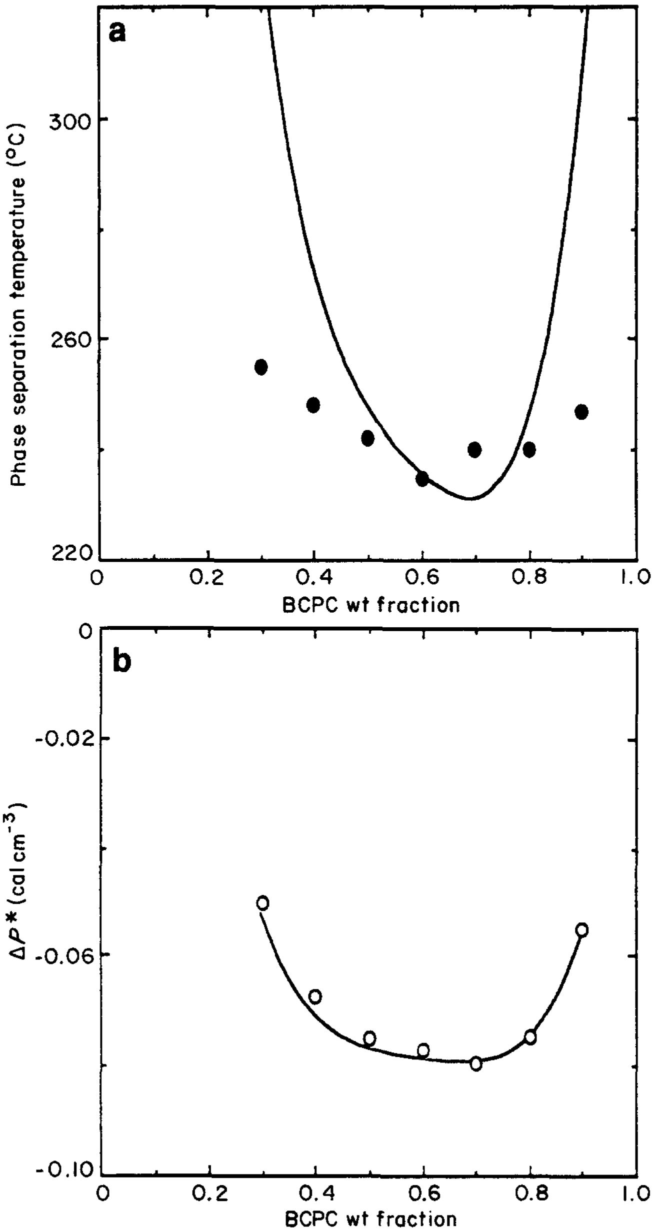


Figure 10 Phase separation temperatures and ΔP^* for BCPC/PMMA blends. The line in (a) is the predicted phase separation temperature assuming $\Delta P^* = -0.077\ \mathrm{cal\ cm^{-3}}$ at all compositions while the solid symbols are the experimentally determined phase separation temperatures. The open symbols in (b) indicate ΔP^* calculated from the experimentally determined phase separation temperatures

Our main purpose here is not the accurate simulation of phase diagrams but rather to extract estimates of interaction energies that may be useful in the design of copolymer systems. For this purpose we choose to use the nearly constant values of ΔP^* found in the mid composition range. This minimizes errors stemming from the assumption that the observed phase boundary is approximated by the spinodal curve. Values of ΔP^* at 50% PMMA are plotted in *Figure 12 versus* the HFPC

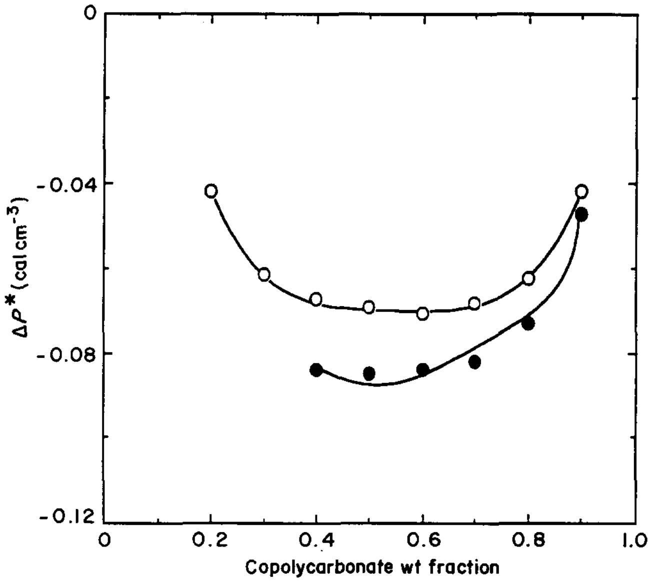


Figure 11 Composition dependence of the calculated bare interaction parameters (ΔP^*) for blends of PMMA with two copolycarbonates: (○) PC–HFPC 6.5; (●) PC–HFPC 10

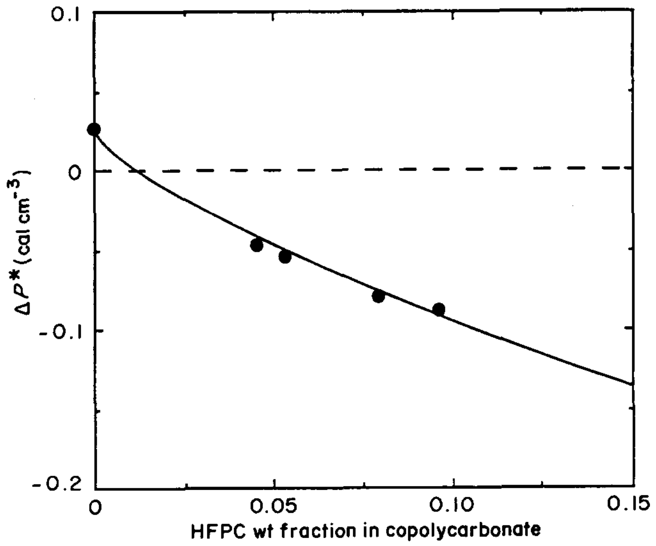


Figure 12 Effect of HFPC content of copolycarbonate on ΔP^* for their blends containing 50% PMMA

fraction in the copolycarbonates for each mixture for which an equilibrium phase separation temperature could be determined. As expected, the interactions become more favourable as the HFPC content increases. Setting $\Delta P^*_{\text{PC-PMMA}} = 0.03\,\text{cal cm}^{-3}$, quadratic curve fitting of equation (5) to these data gives $\Delta P^*_{\text{HFPC-PMMA}} = -0.6\,\text{cal cm}^{-3}$ and $\Delta P^*_{\text{PC-HFPC}} = 0.67\,\text{cal cm}^{-3}$. Note that simple linear extrapolation of these data to 100% HFPC gives $\Delta P^*_{\text{HFPC-PMMA}} = -1.1\,\text{cal cm}^{-3}$. However, it should be noted that small errors in the copolymer composition or in the value of $\Delta P^*_{\text{PC-PMMA}}$ amplify the errors in the estimates of $\Delta P^*_{\text{PC-HFPC}}$ and $\Delta P^*_{\text{HFPC-PMMA}}$.

Accurate estimates of even two ΔP^*_{ij} values by fitting equation (5) to the data in *Figure 12* is hampered by the fact that ΔP^* values are only available for blends with copolymers containing 0–10% HFPC. As an alternative procedure, we attempt to estimate the positive PC–HFPC interaction from δ values so that only the negative PMMA–HFPC interaction must be extracted from the data in *Figure 12*. From the notions of Scatchard[72] and of Hildebrand and Scott[73], the binary interaction parameters are given by[2]:

$$B_{ij} = (\delta_i - \delta_j)^2 \tag{9}$$

Similarly, ΔP^*_{ij} is given by[4]:

$$\Delta P^*_{ij} = (\sqrt{P^*_i} - \sqrt{P^*_j})^2 \tag{10}$$

The $\Delta P^*_{\text{PC-HFPC}}$ obtained from equation (10) is 0.49 cal cm^{-3} (see *Table 3*). Using this estimate for $\Delta P^*_{\text{PC-HFPC}}$ and $\Delta P^*_{\text{PC-PMMA}} = 0.03\,\text{cal cm}^{-3}$, we obtain $\Delta P^*_{\text{PMMA-HFPC}} = -0.82\,\text{cal cm}^{-3}$ by fitting equation (5) to data in *Figure 12*.

To explore whether the interaction energy for HFPC with PC obtained from the δ value approach is reasonable or not, some additional experiments involving HFPC blends with PC and HFPC–PC copolymers are considered. From equation (2), the interaction energy between PC and an HFPC–PC copolymer is given by

$$B = B_{12}(\phi'_1)^2 \tag{11}$$

where 1 = HFPC and 2 = PC. For finite molecular weights, there is a contribution to the free energy from the combinatorial entropy, so some finite mismatch in composition can be tolerated before phase separation occurs when $B_{12} > 0$. The critical interaction energy for miscibility is:

$$B_{\text{critical}} = \frac{RT}{2}\left(\frac{1}{\sqrt{\tilde{V}_1}} + \frac{1}{\sqrt{\tilde{V}_2}}\right)^2 \tag{12}$$

where $\tilde{V}_i$ is the molar volume of component i. Combining equations (11) and (12) gives:

$$B_{12}(\phi'_1)^2 = \frac{RT}{2}\left(\frac{1}{\sqrt{\tilde{V}_1}} + \frac{1}{\sqrt{\tilde{V}_2}}\right)^2 \tag{13}$$

The HFPC homopolymer described in *Table 1* was found to be immiscible with PC (Lexan 131-111) as mentioned previously. HFPC was also found to be immiscible with the low molecular weight PC ($\bar{M}_w = 9900$) used by Nishimoto *et al.*[19]. From equation (13) with $\phi'_1 = 1$, the latter result indicates that the PC–HFPC interaction energy of B_{12} must be $> 0.09\,\text{cal cm}^{-3}$. As a further attempt to obtain more information about the PC–HFPC interaction, PC (Lexan 131-111) and the copolymer containing 15% HFPC were blended and judged to be miscible. Since the glass transitions of these materials are too similar to resolve by d.s.c., it was necessary to rely on visual observations of blend clarity. Crystallinity develops when these polycarbonates are cast from tetrahydrofuran which can obscure this visual assessment; however, this problem was avoided by using methylene chloride. The refractive index difference between these components ($\Delta n = 0.008$) should be sufficient to detect significant phase separation since immiscible blends of PS and SAN 5.7 ($\Delta n = 0.004$) lead to detectably cloudy film. Based on this observation, B_{12} must be $< 2.5\,\text{cal cm}^{-3}$. In fact, if $B_{12} \approx \Delta P^*_{12} = 0.49\,\text{cal cm}^{-3}$ as estimated above, miscibility of these copolycarbonates with PC would extend to about 32 wt% HFPC in the copolymer. Compositions with HFPC levels of $> 15\%$ were not available to further refine this estimate for B_{12} in this way. In summary, $\Delta P^*_{\text{HFPC-PC}} = 0.49\,\text{cal cm}^{-3}$ is consistent with all the available experimental evidence, and so a value of $\Delta P^*_{\text{HFPC-PC}} = -0.82\,\text{cal cm}^{-3}$ is our best estimate at this time.

SUMMARY

The interaction between PMMA and PC is not sufficiently favourable to produce single-phase blends at equilibrium above the T_g for molecular weights that are commercially useful. However, PMMA was found here to be miscible with HFPC, and these mixtures do not phase separate on heating prior to decomposition. Copolycarbonates of bisphenol-A containing relatively small amounts of hexafluorobisphenol-A were also found to be miscible with PMMA. The *LCST* of the copolymer blends with PMMA increases rapidly with HFPC content and exceeds 280°C at $\sim 15\%$ HFPC. Thus, blends of PMMA with these copolymers can be melt processed to give homogeneous mixtures.

PMMA is also miscible with BCPC; however, these mixtures do show *LCST* behaviour. Halogenation of the bisphenol connector group seems to be a useful route for achieving miscibility of polycarbonates with PMMA. The main factor affecting the interaction with PMMA appears to be the electronegativity of these polar connector groups themselves; although, the electronic charge distribution within the phenyl rings is somewhat rearranged.

Interaction energies were calculated for blends displaying phase separation on heating using the Sanchez–Lacombe lattice fluid theory as described previously[34,35]. For these systems, the bare interaction energy for each blend, ΔP^*, was found to be relatively constant over the mid composition range but increases at both extremes of composition. This may reflect the fact that the calculated spinodal curve does not represent the experimental phase separation temperatures except near the critical point or the possibility of specific interactions[58]. The effect of copolymer composition on the interaction energy is discussed in terms of the binary interaction model for copolymers.

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