Miscibility of polycarbonate with methyl methacrylate-based copolymers

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Poly(methyl methacrylate) and bisphenol-A polycarbonate having high molecular weights do not form homogeneous mixtures above the glass transition temperature at equilibrium. This paper outlines a strategy for developing melt-processible, homogeneous blends of polycarbonate with an acrylic polymer through copolymerization. Nine different comonomers were copolymerized with methyl methacrylate and these polymers were blended with polycarbonate. Copolymers based on cyclohexyl methacrylate and phenyl methacrylate gave homogeneous mixtures with polycarbonate having cloud points (lower critical solution temperature behaviour) near or above the temperature range needed for melt processing. The thermal stability of the acrylic polymers was examined and in some cases a third monomer was used to obtain improvements.

(Keywords: polycarbonate; methyl methacrylate copolymers; blends; miscibility; lower critical solution temperature; phase separation)

INTRODUCTION

The phase behaviour of polymer blends is a function of component molecular weights (primarily through the combinatorial entropy), free-volume or equation-of-state effects, and especially the polymer–polymer interactions involved[1–6]. When the latter is strongly favourable, miscibility exists at all molecular weights in spite of potentially unfavourable equation-of-state contributions; whereas, strongly unfavourable interactions lead to immiscibility even at low molecular weights. When the interaction is weak or nearly zero, the phase diagram (lower or upper critical solution temperature) (*LCST* or *UCST*) behaviour) becomes very sensitive to molecular weight and slight modifications in component molecular structure. Homopolymer pairs with weak interactions are, consequently, of considerable interest because there are avenues to make their blends usefully miscible. For structural materials, reduction of molecular weight to achieve miscibility is generally of limited value because of minimum requirements on molecular-weight-sensitive properties. However, incorporation of a comonomer into one of the polymers can be an attractive possibility for making an immiscible pair into a miscible one or to alter the phase diagram enough to allow formation of homogeneous mixtures by melt processing[7–11].

Through recent observations[12–25] we have identified the system poly(methyl methacrylate) (PMMA) and polycarbonate (PC) as an interesting example for application of the copolymer approach. These homopolymers form separate phases when melt-blended[21], and several recent reports[12,13] suggest that the cause is an *LCST*-type phase boundary intermediate between T_g and minimum melt processing conditions (~260°C). Our most recent observations[22] show that these cloud points are a kinetic artifact and that the *LCST* boundary is probably below T_g for all commercially useful molecular weights. The slow kinetics of phase separation has to some extent also compromised conclusions in earlier attempts to improve the phase diagram by copolymerization[10]. While this means the PMMA–PC interaction is less favourable than previous reports suggest[12–20], there is still ample reason to believe that it is small enough that the phase diagram can be modified by copolymerization to give a melt-processible system. In what follows we examine the changes in miscibility and *LCST* boundaries caused by copolymerizing various monomers with methyl methacrylate with the goal of achieving an acrylic/PC blend whose *LCST* is above the processing temperatures required. Very special efforts have been made to ensure that the phase boundaries observed do reflect thermodynamic rather than kinetic issues.

BACKGROUND

The potential effects of copolymerization on blend phase behaviour can be easily visualized by aid of a simple binary interaction model for describing how the net interaction energy, B, depends on copolymer composition[3,23,24]:

$$B = B_{13}\varphi_1' + B_{23}\varphi_2' - B_{12}\varphi_1'\varphi_2'$$

Here we assume that 1 and 3 are the weakly interacting homopolymers and 2 is the new monomer that is to be copolymerized with 1. The φ_2' are the volume fractions of these units in the copolymer. Of course, miscibility is more likely the smaller is B, and negative values are preferred[5,23,25]. Thus, in the present case B_{13} is near zero but might be slightly positive (immiscible except at low molecular weights) or negative (low *LCST* relative to T_g or T_m).

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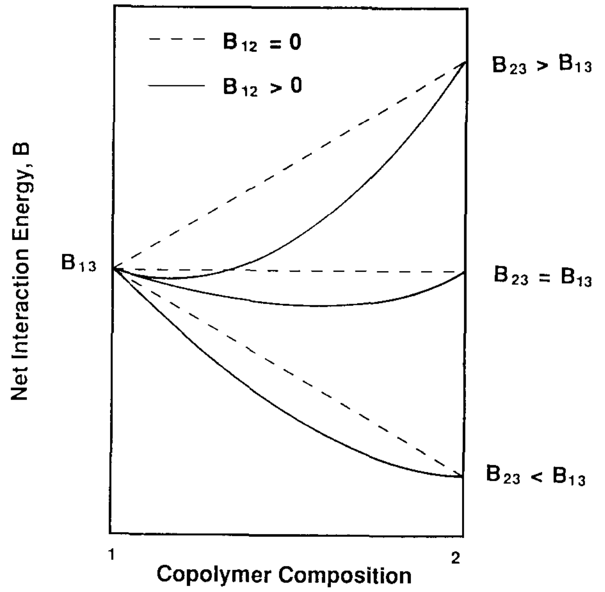

Figure 1 Schematic net interaction energy, *B*, for blends of a homopolymer (monomer 3) with a copolymer (monomers 1 + 2) as a function of copolymer composition

Figure 1 shows three sets of possibilities depending on the magnitude of the B_{23} interaction energy density relative to B_{13}. The broken lines show the simple case when the copolymer intramolecular interaction is negligible, i.e. $B_{12} = 0$, while the full curves show the more useful possibility when this interaction is repulsive, i.e. $B_{12} > 0$. It is clear that we can force B to become more favourable by selecting a second monomer, 2, that interacts unfavourably enough with 1 or more favourably with 3 than does 1. The most effective choice of 2 is one where both effects operate simultaneously, i.e. $B_{12} > 0$ and $B_{23} < B_{13}$; however, in general it may be difficult to identify such cases. A more likely one is where $B_{12} > 0$ and $B_{23} > B_{13}$. The latter can lead to success but depends on a delicate balance of all three interaction terms.

A rational design of copolymers based on this approach would be possible if there existed an adequate database of interaction energies for homopolymer pairs, i.e. values for B_{ij}. While the literature contains a growing amount of information about interaction energy values, the situation has not progressed enough to be of much help in the PMMA–PC case. As a result, what follows represents a more trial-and-error approach that has been guided by intuition gained from *Figure 1* and the limited data available. This case serves as a good example of how a reliable compendium of B_{ij} values, including those that are strongly positive, would be of value to this field.

EXPERIMENTAL

Commercially available PC, Lexan 131-111, from General Electric Co. ($\bar{M}_w = 34\,200$), and PMMA, Plexiglas V-811, from Rohm and Haas ($\bar{M}_w = 130\,000$), were used in this work. Various MMA-based copolymers were synthesized, and they are listed in *Table 1*. Polymerization of MMA with comonomers was carried out by using ethylbenzene as a solvent and azobisisobutyronitrile (AIBN) as the initiator at 75°C. Polymerization was stopped at an early stage, usually below 10% conversion, to minimize composition drift. The resulting solution was poured into a large excess of methanol to precipitate the polymer. The product was recovered by filtration followed by washing and then drying in a vacuum oven at 150°C for 2–3 days. Copolymer and terpolymer compositions were determined by ^{1}H n.m.r. spectra and elemental analysis. For relative comparisons of molecular weight the viscosity of a 10% solution in methyl ethyl ketone (MEK) was determined at 25°C.

Polymer blends were typically prepared by casting solutions containing 5% total polymer in tetrahydrofuran (THF) onto glass plates at room temperature or at 50–60°C. After slow drying at ambient temperature, the blends were finally dried in a vacuum oven at 120–140°C for four days. Melt blending was carried out in a Mini-Max moulder at 250°C.

Glass transition temperatures and other thermal characteristics of the blends were determined using a Perkin–Elmer DSC-7 system. In most cases a heating rate of 20°C min^{-1} was used. Reported T_g data were obtained on a second scan. The first scan was run to 170°C, followed by fast cooling. The first run was necessary to assure well defined and reproducible transitions. The T_g was determined by the onset method defined by the intersection of the heat capacity baseline in the glassy state and a line drawn through the transition region. Thermal stability of a number of copolymers was determined using a Perkin–Elmer TGA-7 unit. Samples were heated at 10°C min^{-1} in nitrogen up to 300°C.

Cloud-point temperatures caused by *LCST* behaviour were determined in a manner designed to minimize artifacts caused by slow phase separation kinetics that have been found for this system[22] at temperatures near T_g. Blends were maintained at various constant temperatures near the cloud point for up to 15 min followed by a visual observation or by use of d.s.c. scan to monitor glass transition behaviour. At the temperature reported here, 15 min is an adequate isothermal period to ascertain equilibrium stability even though determinations made at slow heating rates may lead to some error.

THERMAL STABILITY OF METHACRYLATE POLYMERS

It is well known that methacrylate polymers are prone to depolymerization by an unzipping mechanism caused by a low ceiling temperature[26]. To achieve melt processibility, commercial products like PMMA materials generally contain a small amount of a non-methacrylate comonomer that can interrupt the thermal unzipping process. Thus, the non-methacrylate comonomers listed in *Table 1* also serve the additional purpose of improving thermal stability relative to PMMA homopolymer. On the other hand, the methacrylate comonomers in *Table 1* do not stabilize the acrylic polymer against thermal depolymerization. In these cases, a small amount of a termonomer was added for this purpose. Either methyl acrylate (MA) or styrene (S) was used for this purpose. The content of this third monomer listed in *Table 1* was not determined by analysis but was estimated from the feed composition. *Figure 2* illustrates the beneficial effects of small amounts of MA on the stability of compositions containing approximately one part by weight of cyclohexyl methacrylate (CHMA) and four parts MMA.

Polymers containing phenyl methacrylate (PhMA) showed particularly serious degradation problems. These were presumably related to depolymerization although the complex shape of the t.g.a. curve in *Figure 3* suggests

Table 1 Characterization of MMA-based polymers used here and their blends with PC

	Comonomer				Blends with PC		
Sample no.	Type	Amount (wt%)	Termonomer[b]	Solution viscosity (cP)[c]	Film clarity[d]	Cloud point (°C)	Blend precipitated from solution
1	Styrene	4.1	none		cloudy	<150	showed one T_g
2		7.0	none		cloudy	<150	showed one T_g
3	α-Methylstyrene	5.2	none	1.5	clear	<150	
4		13.0	none	1.2	cloudy	–	
5		19.1	none	1.1	cloudy	–	
6		27.2	none		cloudy	–	
7	t-Butylstyrene	9.9	none	8.9	cloudy	–	
8		14.2	none	5.7	cloudy	–	
9	Acrylonitrile	3.4	none	8.6	cloudy	–	
10		4.5	none	13.0	cloudy	–	
11		12.3	none	3.4	cloudy	–	showed two T_g
12		26.4	none	6.2	cloudy	–	showed two T_g
13	Butyl acrylate	2.8	none	5.3	cloudy	–	
14		7.7	none	2.6	cloudy	–	
15	t-Butyl methacrylate	10.6	none	16.8	cloudy	–	
16		21.9	none	31.2	cloudy	–	
17		33.8	none	28.7	cloudy	–	
18		45.0	none	16.9	cloudy	–	
19	Methacrylic acid	4.0[e]	none		cloudy	–	
20		5.0	none		cloudy	–	
21		8.0[e]	none		cloudy	–	
22	Cyclohexyl methacrylate	11.6	none		clear	[f]	
23		22.5	none	4.9	clear	[f]	
24		33.5	none	3.3	clear	[f]	
25		41.8	none	2.3	clear	[f]	
26		6.1	MA	10.3	clear	<180	
27		11.2	MA	7.5	clear	<180	
28		14.7	MA	5.3	clear	180–210	
29		21.1	MA	4.0	clear	180–210	
30		28.5	MA	3.8	clear	180–210	
31		34.4	MA	3.0	clear	180–210	
32		43.8	MA	3.7	clear	<180	
33		56.7	MA	3.2	cloudy	–	
34		5.5	S	6.6	clear	<150	
35		10.1	S	6.5	clear	<150	
36		14.3	S	4.2	clear	<180	
37		19.0	S	2.8	clear	<180	
38	Phenyl methacrylate	16.0	MA	5.0	clear	210–240	
39		28.3	MA	3.4	clear	210–240	
40		39.2	MA	2.7	clear[g]	>240	
41		51.1	MA	2.2	clear	>240	
42		63.0	MA		clear	>240	
43		81.0	MA		cloudy	–	showed one T_g
44		100.0	MA		cloudy	–	showed one T_g

[a] Composition of terpolymers is on a termonomer-free basis

[b] Small amounts of either MA (2–4% by weight estimated from feed composition) or S (5–7% by weight determined by ^{1}H n.m.r. spectrum) incorporated to improve thermal stability

[c] Viscosity (centipoise) of 10 wt% solution in MEK at 25°C

[d] Films prepared by hot casting of THF solution

[e] Values shown are feed composition, since polymer composition could not be determined

[f] Could not be determined because of degradation

[g] A sample melt blended at 250°C was also clear

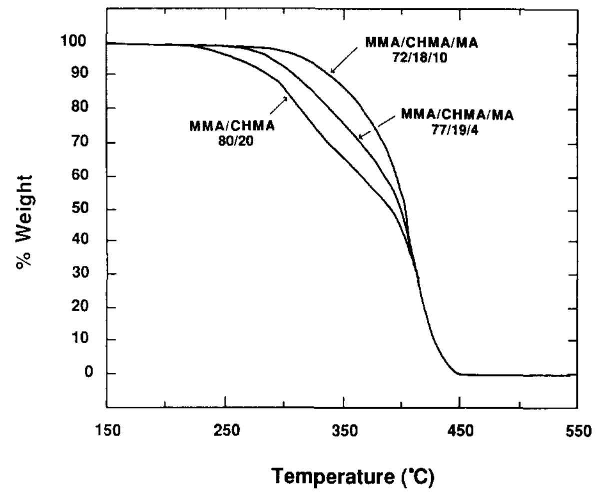

Figure 2 T.g.a. traces showing the improved thermal stability due to the presence of MA in MMA/CHMA copolymers

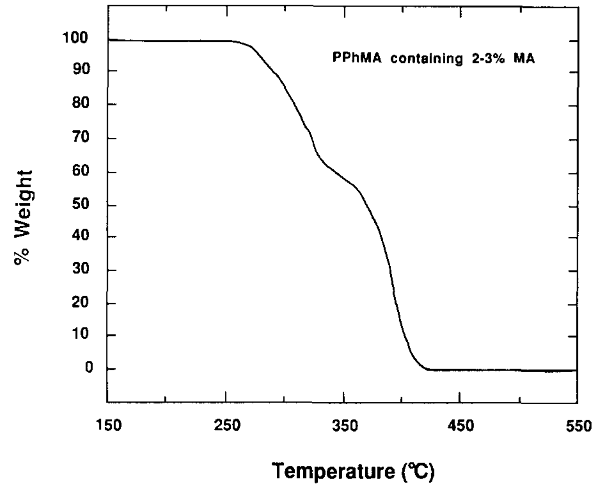

Figure 3 T.g.a. trace of PPhMA containing 2–3% MA

additional mechanisms. In spite of the presence of 2–3% MA, this material shows the beginning of detectable weight loss at about 250°C when the heating rate is 10°C min^{-1}. However, the boiling point of PhMA monomer is above this temperature, so there may be significant depolymerization prior to 250°C that is undetected because the monomer does not readily desorb until high enough temperatures are reached. Evidence for this is seen in the d.s.c. thermograms shown in *Figure 4*. In this experiment, the control is the first heat of an as-prepared material free of residual monomer or solvent. Thermograms are also shown for a PhMA homopolymer and a composition containing 2–3% MA after heating to 240°C in the d.s.c. at 20°C min^{-1} and then quenching. The T_g of the homopolymer after heating is more than 50°C lower than that of the control because of depolymerization products (presumably monomer) remaining in the polymer. Use of MA significantly limits the reduction in T_g observed but does not totally eliminate the effect.

No effort was devoted to optimizing the thermal stability of these materials. The steps taken here were made to gain a better picture of the blend phase behaviour with minimal obscuration caused by thermal stability problems. Certainly, to some degree, more stable materials than those described here are possible through optimization.

BLEND PHASE BEHAVIOUR

Investigations of the phase behaviour of blends involving experimental polymers usually require a solvent-based preparation method because of the limited amount of sample available. Many studies[6,7,22,27–29] have shown that for some systems considerable care must be exercised to ensure that the state of mixing achieved is the equilibrium one. On one extreme, solution casting can lead to phase-separated mixtures, even though the pair is thermodynamically miscible, because of the so-called 'solvent' or $\Delta\chi$ effect[6,30–32]. Recent results have shown another extreme in which rapid solvent removal, by evaporation or by precipitation, can trap two immiscible materials into a homogeneous, non-equilibrium state[22] especially for low-mobility polymers where the kinetics of phase separation is slow[33–36]. The systems of interest here seem especially prone to such behaviour and due care has been exercised to avoid being misled by such artifacts.

In this programme, nine comonomers were examined for their potential to yield an MMA-based material that would be miscible with PC when both components have molecular weights in the range needed for commercially useful materials. The first subsection below presents results from the initial screening, while two subsequent subsections describe more detailed results for the most promising of the nine.

Comonomer selection and screening

Table 1 shows the nine comonomers, the various co- and terpolymers formed from them, and some preliminary results on blending with the PC described in the 'Experimental' section. The blends prepared by hot casting from THF were checked for clarity and the temperature for phase separation, when appropriate, with the results summarized in *Table 1*. The most promising are compositions containing cyclohexyl methacrylate (CHMA) and phenyl methacrylate (PhMA). Specific comments about why certain monomers were included in this study and the results obtained from this preliminary screening are given below.

Styrene (S) was selected as a comonomer because some early observations offered encouraging results[10]. However, the two high-molecular-weight S copolymers given

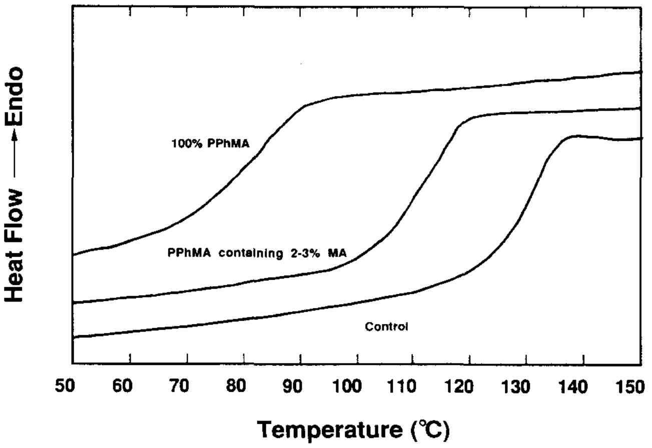

Figure 4 D.s.c. thermograms of PPhMA polymers. Control represents the first heat of PPhMA homopolymer. PPhMA (100%) and PPhMA (2–3% MA) indicate second heat results for homopolymer and copolymer after heating samples to 240°C in d.s.c. at 20°C min^{-1} and quenching

in *Table 1* failed to give clear blends when hot cast from THF. Single-T_g blends were obtained by precipitation from solution, but isothermal annealing suggested an *LCST* of less than 150°C in striking contrast to our earlier report[10]. These copolymers have very high molecular weights and the phase separation process is extremely slow. While a more in-depth study of these blends would be of interest, it is clear that S does not meet the requirements of the current objective. The reasons, in terms of *Figure 1*, are now clear in light of recent information. The S–MMA repulsion is very weak[37], $\sim$0.18 cal cm^{-3}, while the interaction between PS and PC seems to be even more unfavourable[38] than that for PMMA and PC. The MMA–acrylonitrile (AN) repulsion is much larger[37], $\sim$4.1 cal cm^{-3}, but evidently the interaction of PAN units with PC is also very unfavourable based on the results in *Table 1*.

From considerable experience we know that aliphatic units and ester groups have a strong repulsion[3,5,39–42]. Thus, we can aid the intramolecular repulsion part of the strategy illustrated in *Figure 1* by selecting comonomers containing aliphatic groups to interact with the ester part of MMA, and this formed part of the rationale for selecting α-methylstyrene (α-MS), t-butylstyrene, butyl acrylate, t-butyl methacrylate and cyclohexyl methacrylate (CHMA). Of course, the same effect may also make the interaction of the comonomer with PC more unfavourable. One copolymer with αMS showed some encouragement but not enough to pursue more fully here. This may be simply due to the less unfavourable interaction of PαMS with PC compared to that for PS with PC[38]. However, the alkyl repulsion reasoning evidently has merit for CHMA but not any of the others.

The choice of methacrylic acid was prompted by the possibility of some favourable interaction with the carbonate group in PC; however, any tendency for this could be offset by an intramolecular attraction to MMA[28,29] through its ester group. Whatever the reason, *Table 1* suggests this is not a promising choice.

Phenyl methacrylate (PhMA) was suggested as a comonomer in a recent patent[43]. This choice can be rationalized on the basis that an aromatic unit might give a more favourable interaction with PC than aliphatic units. Evidence for this is seen later.

Cyclohexyl methacrylate

MMA-based polymers containing CHMA and a small amount of MA for thermal stability were prepared for further study. As seen in *Figure 5*, hot cast blends of

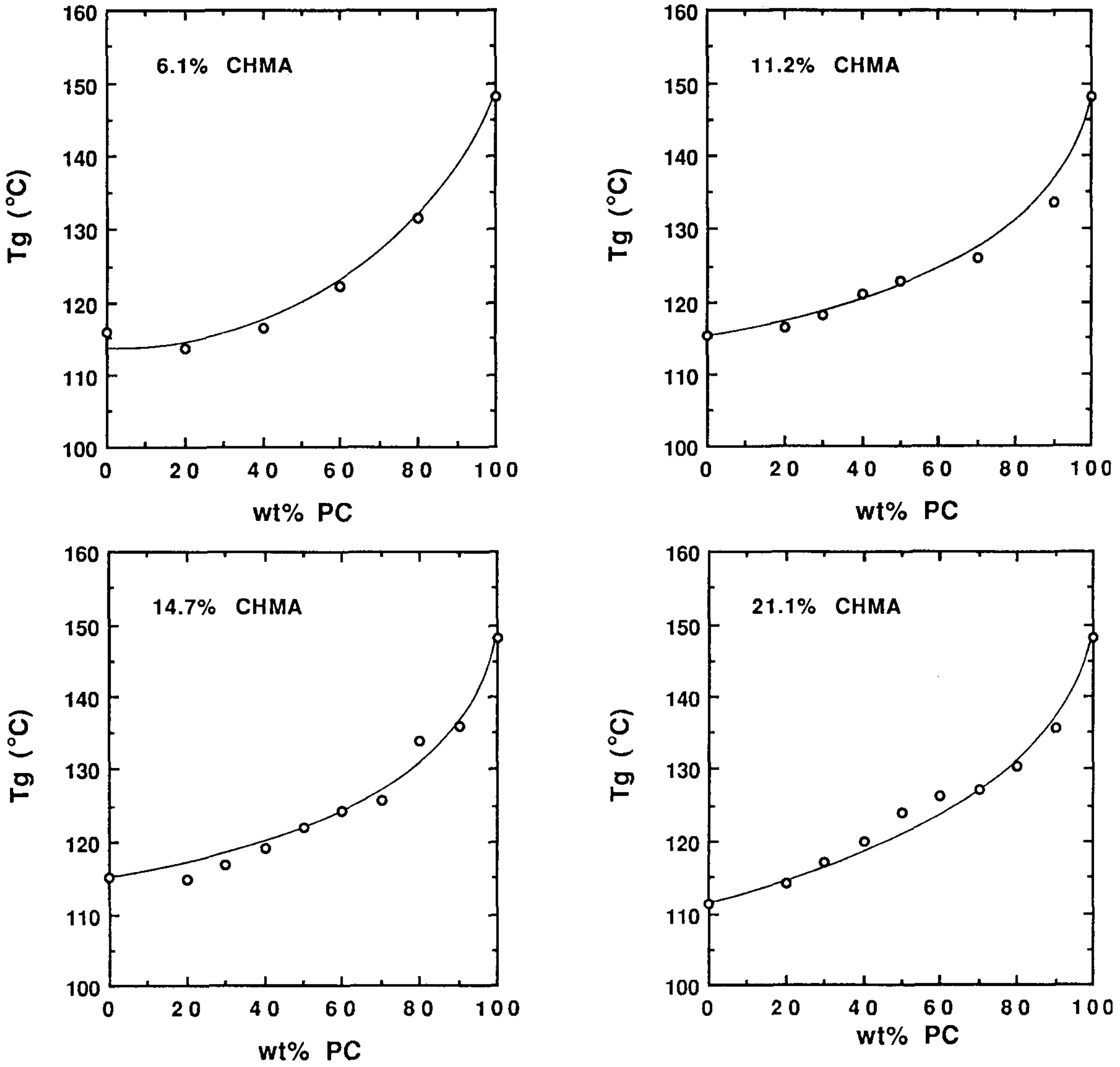

Figure 5 T_g blends of PC and MMA/CHMA copolymers. Wt% of CHMA in the copolymer is shown on each plot

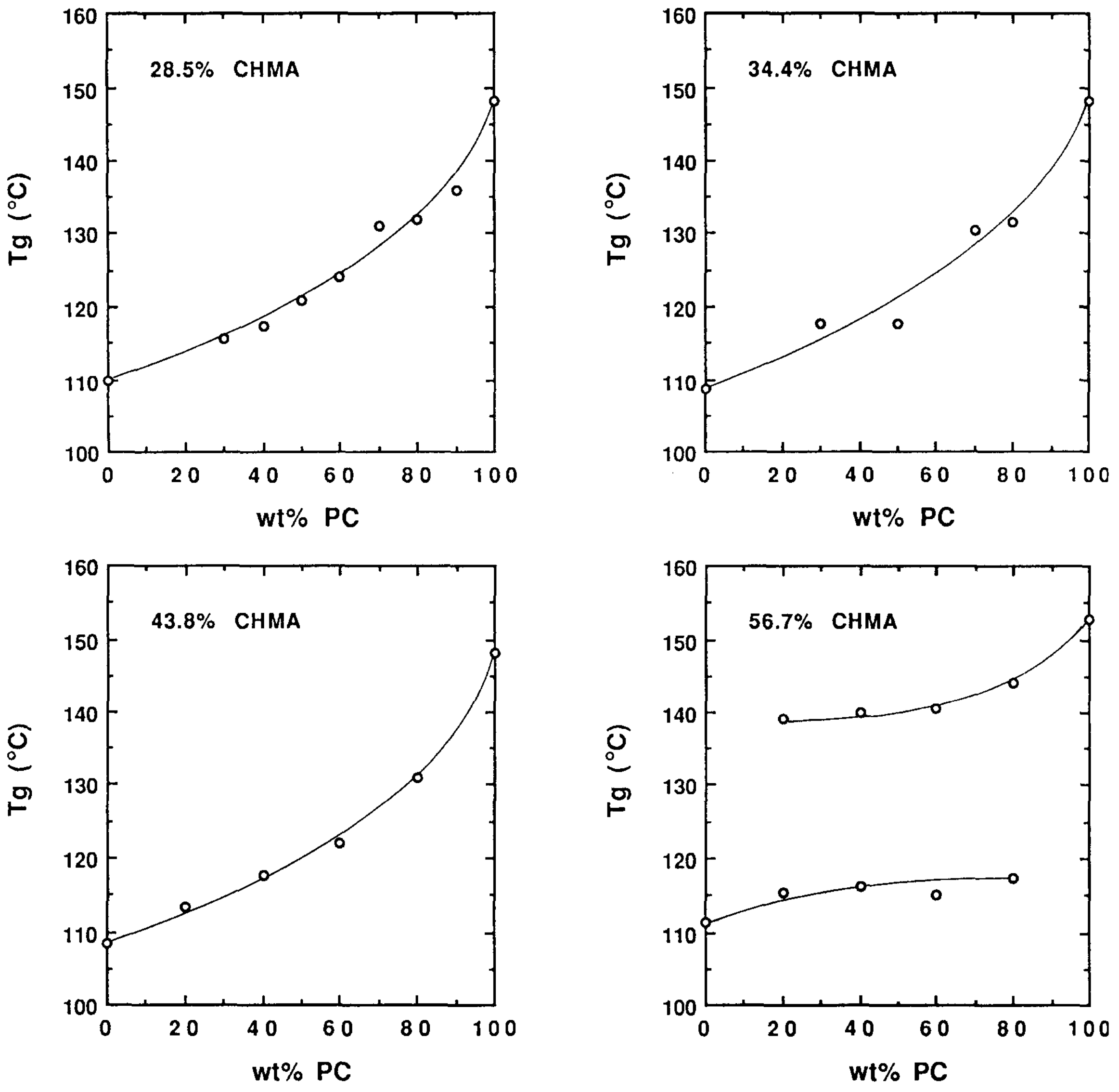

Figure 5 *cont.*

these copolymers with PC showed a single T_g except for the copolymer containing the highest amount, 56.7 wt% of CHMA. The glass transition regions for these blends were relatively narrow as illustrated in *Figure 6*. Another series of copolymers stabilized by styrene (S) was also prepared. These copolymers showed results consistent with the MA-stabilized series, but these materials were not examined extensively. The blends showing a single T_g in *Figure 5* were examined for phase separation on heating. Those with a cloud point less than 180°C (low and high CHMA levels) were eliminated for further study. *Figure 7* shows estimated cloud-point curves for blends with PC for four of these acrylic polymers having CHMA levels in the range 14.7 to 34.3%. These curves are all very similar with each showing a minimum at about 80% PC and 200°C. These results are replotted in *Figure 8 versus* weight per cent CHMA, for fixed PC contents in the blends, with curves drawn to reflect the fact that the cloud points must be very low at both higher and lower CHMA levels. Thus, there is a broad maximum centred at about 25 wt% CHMA.

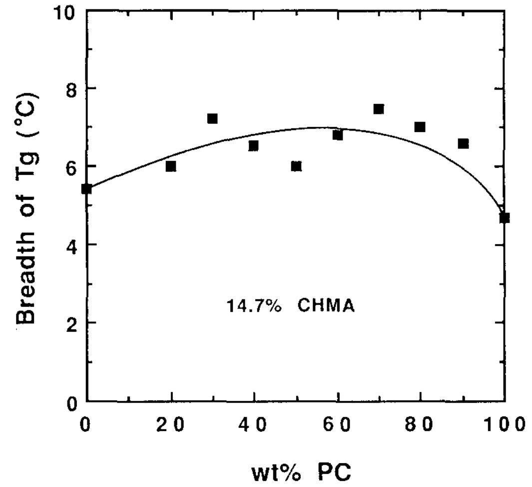

Figure 6 Breadth of the T_g region of PC blends with MMA/CHMA (85.3/14.7) copolymer. The measure shown was determined by subtracting the onset temperature from the mid-point temperature of the transition region

Recent observations in this laboratory[44] have shown that the interaction energy between MMA and CHMA is about 0.75 cal cm^{-3}. Thus, as a comonomer CHMA has considerably greater intramolecular repulsion to MMA than does S. However, the interaction energies for PC with PS and with PCHMA are not known, so the analysis suggested by *Figure 1* cannot be carried further.

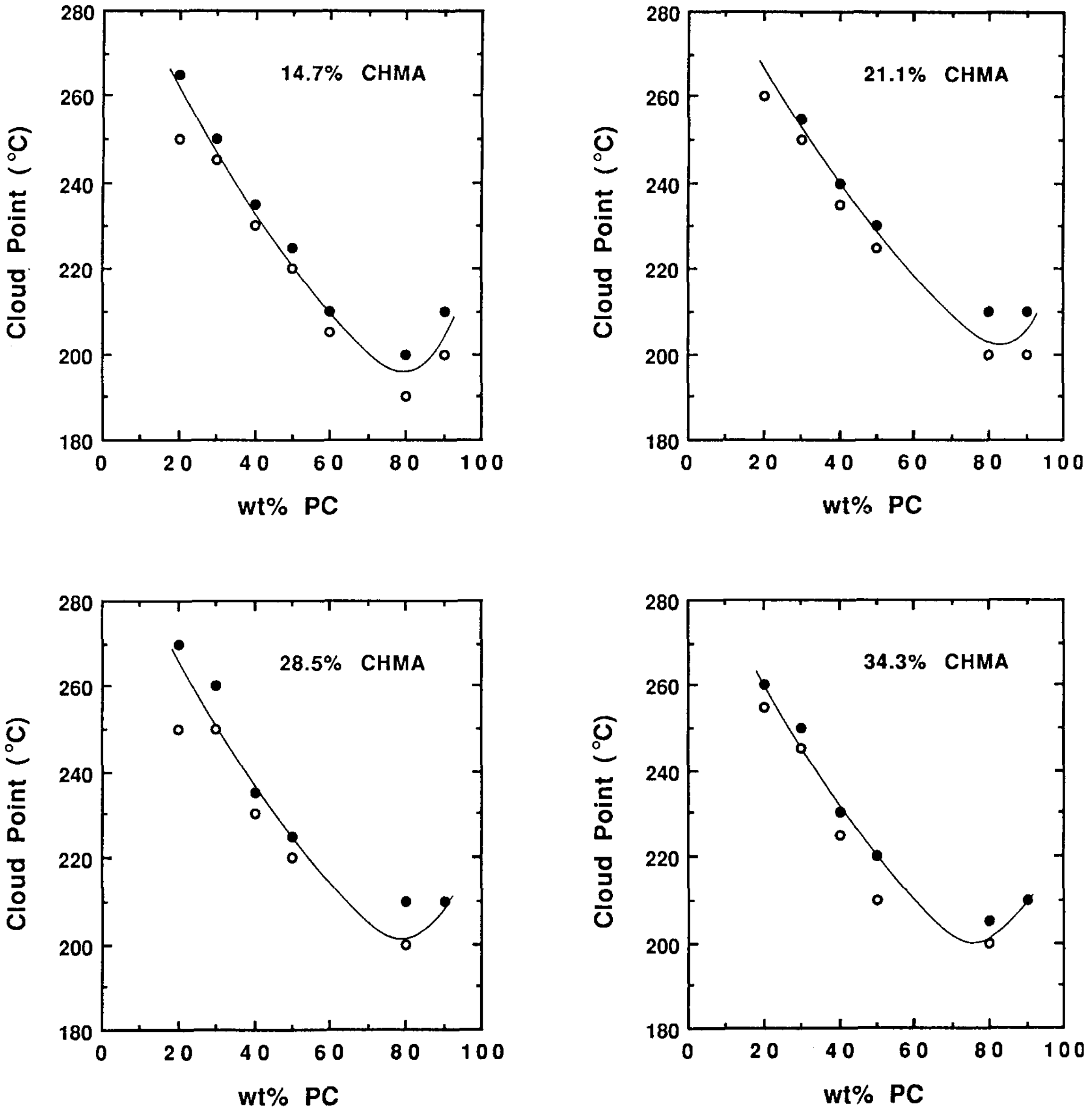

Figure 7 Cloud-point curves of PC blends with MMA/CHMA copolymers (○) clear, (●) cloudy. Wt% comonomer is indicated on each plot

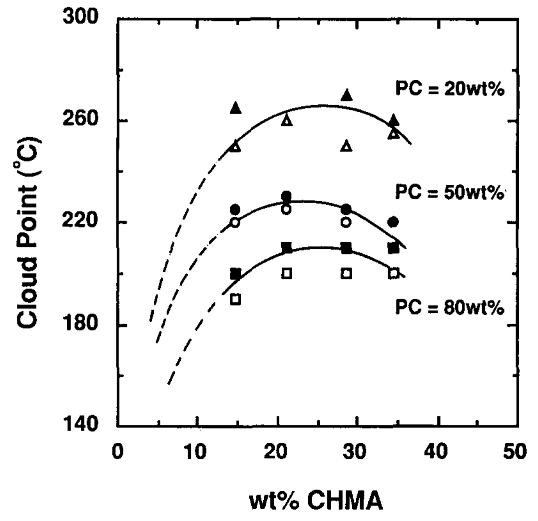

Figure 8 Cloud-point curves of PC blends with a series of MMA/CHMA copolymers containing 20, 50 and 80% PC. Open symbols indicate clear blends, while filled symbols represent opaque blends

Phenyl methacrylate

A series of copolymers of PhMA including the homopolymer (a small amount of MA was included in each for stability) were prepared (see *Table 1*) for detailed blending studies with PC. Blends hot cast from THF were clear and showed a single, narrow T_g (see *Figure 9*) except for those with the copolymers containing 81.0 and 100.0% PhMA. Blends of the latter with PC were cloudy as cast and showed two separate glass transitions. However, when THF solutions of these polymers with PC were precipitated into heptane, clear blends with a single T_g could be obtained. These mixtures became somewhat cloudy after annealing for 30 min at 180°C. A more detailed investigation was not made partly because of the poor thermal stability of PhMA-rich polymers; however, these observations suggest that PPhMA may be miscible with PC but certainly only at relatively low temperatures.

Figure 10 shows estimated cloud-point curves for blends of PC with four PhMA-containing polymers. In all cases, there seems to be a minimum near 80% PC as

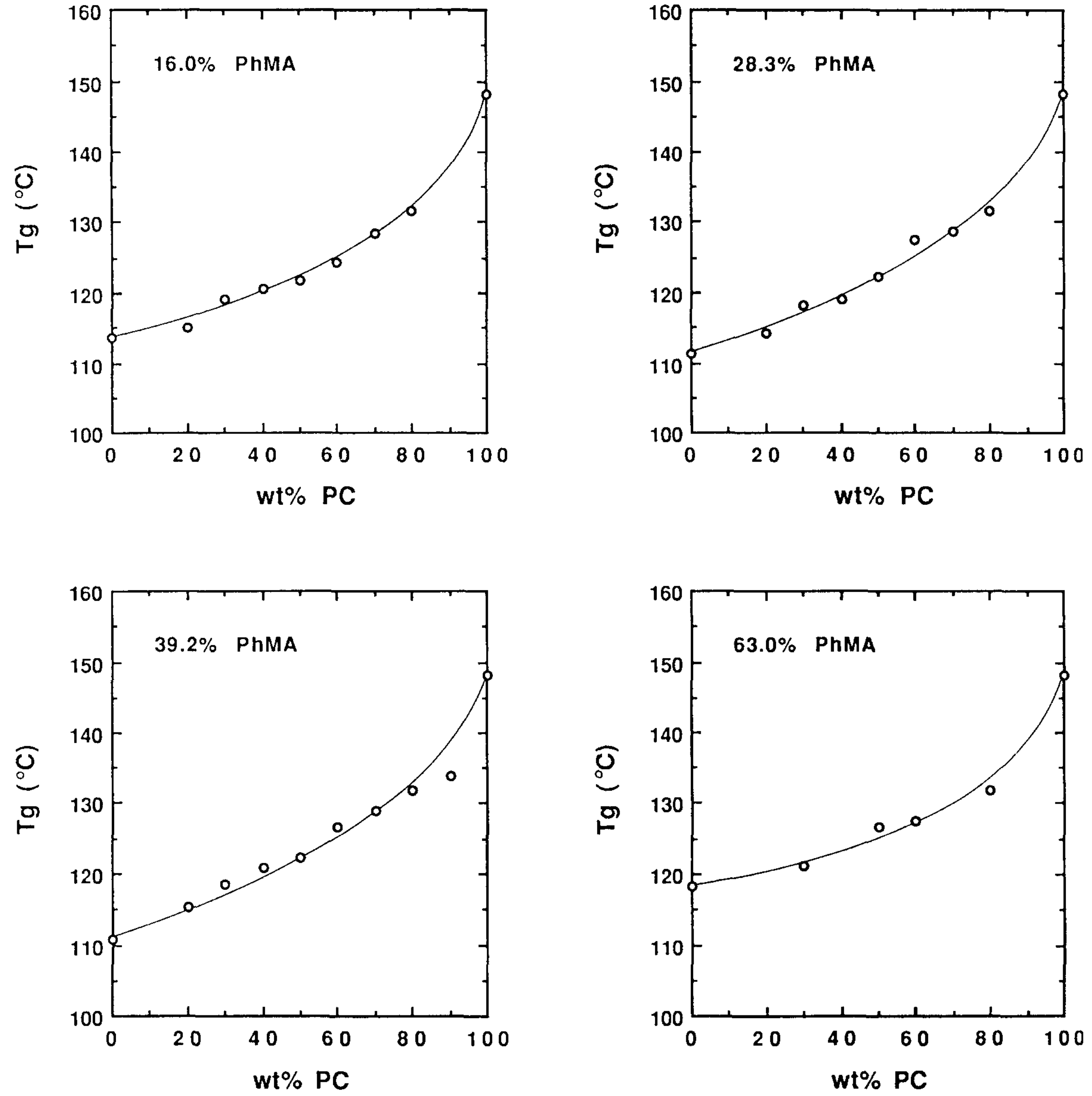

Figure 9 T_g of PC and MMA/PhMA copolymer blends. Wt% of PhMA in the copolymer is shown on each plot

found for blends of CHMA copolymers with this PC and for blends of a low-molecular-weight PC ($\bar{M}_w = 9800$) with PMMA. The cloud point at 80% PC is plotted in *Figure 11 versus* PhMA content in the acrylic copolymer up to the point where severe degradation precluded meaningful determinations. Based on these data and the observation for the PhMA homopolymer, it appears that the cloud point goes through a maximum at about 50–60% PhMA.

To demonstrate the possibility of melt processibility, a 50% PC blend with the copolymer containing 28.3% PhMA was mixed at 250°C in the mixing chamber of a Mini-Max moulder. The resulting blend was clear and had a single T_g.

The interaction energies for PhMA units with MMA units or with PC are not known. However, it is clear that the interaction of PhMA with PC is certainly more favourable than that of PC with CHMA or any of the other comonomers in *Table 1*, which probably explains its superiority for elevating the *LCST*.

SUMMARY

The results described here demonstrate that potentially useful blends can be designed by identifying homopolymer pairs that are on the edge of miscibility and then manipulating phase behaviour through copolymerization. The basic issues in comonomer selection have been outlined in terms of a simple interaction model. A more sophisticated model with temperature-dependent parameters is needed for actual prediction of phase diagrams. Unfortunately, for most cases, there is not enough information available about interaction energies to predict *a priori* the direction of changes in net interaction, let alone to predict phase diagrams. There is a clear need to improve on this situation.

In the present case, MMA-based copolymers have been identified whose blends with PC yield phase diagrams consistent with melt-processible materials. The onset of phase separation caused by an *LCST* can be elevated to even higher temperatures than shown here by using

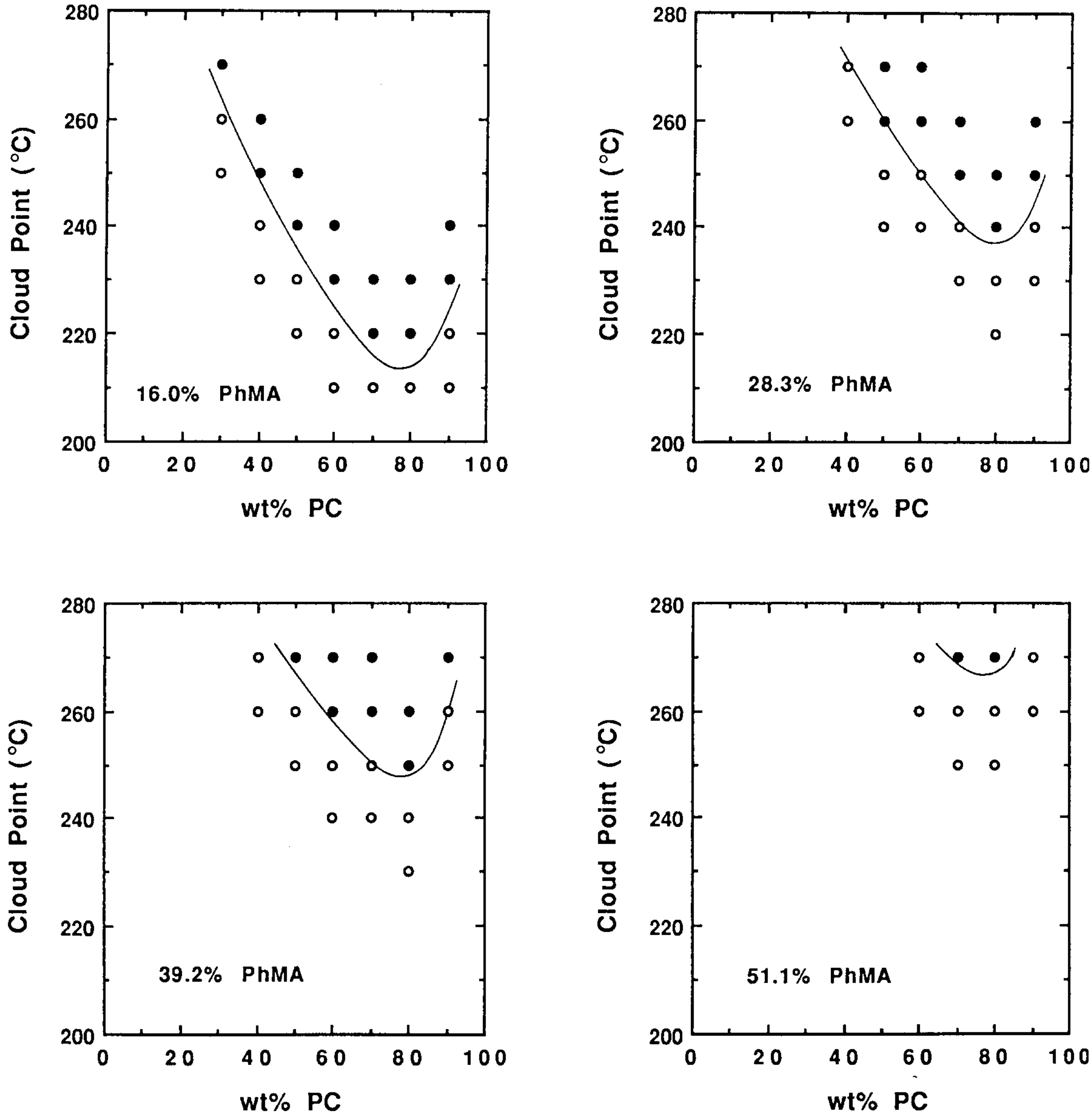

Figure 10 Cloud-point curves of PC blends with a series of MMA/PhMA copolymers: (○) clear, (●) cloudy. Wt% of PhMA in the copolymer is shown on each plot

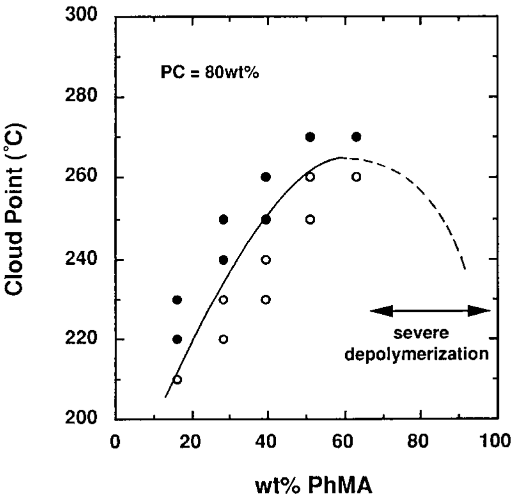

Figure 11 Cloud-point curves of PC and MMA/PhMA copolymer blends. All blends contain 80% PC and 20% of various copolymers

lower-molecular-weight grades of PC like those used for fabrication of optical data storage media. The latter application requires near-zero birefringence in injection moulded parts. Considering the complementary polarizabilities of acrylics and polycarbonate, their blends may provide this characteristic. However, to be useful in any practical way, the copolymers identified here need to be improved in terms of thermal stability.

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