Role of slow phase separation in assessing the equilibrium phase behaviour of PC–PMMA blends

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It is shown that the extent of miscibility of blends of polycarbonate (PC) and poly(methyl methacrylate) (PMMA) described in recent papers has been over estimated. The solvent preparation methods used cause the two polymers to become kinetically trapped in a homogeneous, but non-equilibrium, mixture below the glass transition. The phase separation that occurs on heating above the glass transition is not a result of a lower critical solution temperature (LCST) just above T_g but stems from an extremely slow rate of phase separation from the trapped non-equilibrium state. Based on this work, we believe that none of the LCST boundary may lie above the T_g line when the components have molecular weights in the commercially useful range. There is some uncertainty at the extremes of the composition scale because of the excessively long times required to reach equilibrium. The effects of polycarbonate molecular weight in this situation are considered. Even though the PC–PMMA interaction is not as favourable as originally thought, it is clear that this interaction is only weakly unfavourable for mixing.

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

INTRODUCTION

A number of recent papers[1–9] have described methods for preparing homogeneous blends of polycarbonate (PC) and poly(methyl methacrylate) (PMMA); however, these mixtures were found to phase separate on heating at relatively low temperatures. These observations suggested that the PC–PMMA system is thermodynamically miscible but that there is a lower critical solution temperature (LCST). Cloud point estimates further suggested that the temperature span between the LCST and T_g was too small to obtain homogeneous blends by melt processing. This is unfortunate because of the obvious commercial implications for a blend system that would offer continuously variable property/cost relationships between the limits of pure PC and PMMA while maintaining optical clarity. A thermodynamic LCST can be elevated by making the polymer–polymer interaction more favourable[10], and we have been investigating possibilities for accomplishing this through copolymerization[11,12].

During the course of this work, we have found that the cloud point estimates in the literature, including our own, provide poor estimates of the extent of miscibility that exists in PC–PMMA blends. We present here evidence that the solution preparation procedures used trap the blends in a homogeneous but non-equilibrium state and that the cloud points observed are not indicative of a thermodynamic phase boundary but an artifact of a very slow phase separation process. Nevertheless, we show in a subsequent paper[11] that a thermodynamically miscible PC–methacrylate system, having an LCST high enough that melt processibility may be feasible, can be achieved through copolymerization.

BACKGROUND

It is well documented that the phase structure of PC–PMMA blends depends critically on the method of preparation. Gardlund[13] and Chiou *et al.*[1] showed that melt processed blends have two distinct phases. A variety of solvent preparation methods[1,14,15] also lead to phase separated mixtures. However, several laboratories[1–9] have recently reported solvent preparation procedures that give single phase PC–PMMA blends.The reported procedures use tetrahydrofuran, THF, as the solvent. The polymers may be removed from solution by hot (47–60°C) evaporation of the THF[2–9] or by precipitation into an appropriate non-solvent[1]. Each method involves rapid removal of the polymers from a homogeneous solution. The blends prepared in this way have a single glass transition temperature. However, upon heating they phase separate. *Figure 1* compares the cloud point curves obtained on heating by three different laboratories[1–3,9] using different methods. The results by Chiou *et al.*[1] and Kambour *et al.*[2] are rather similar and show that phase separation occurs just above the T_g of these blends. In contrast, the cloud points given by Kyu *et al.*[3,9], at two different heating rates, are substantially higher. From these observations it seemed reasonable to conclude the following. The interaction between PC and PMMA is weak but perhaps slightly favourable. A thermodynamic lower critical solution temperature, LCST, exists just above the glass transition temperature which explains why melt processed blends are not homogeneous[13]. For

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some weakly interacting pairs, a combination of thermodynamic and kinetic factors has been known to lead to heterogeneous blends when, in fact, homogeneity is the equilibrium state[16]. This would perhaps explain why some solution preparation methods did not give homogeneous PC–PMMA blends. In general, there are a variety of reasons why various blending protocols may not give a homogeneous mixture even though this is the equilibrium state.

The opposite situation of a blending protocol that gives a homogeneous mixture when this is not the equilibrium state is also possible but has not been so frequently reported. The most known examples of this involve freeze-drying homogeneous solutions of two immiscible polymers[17–19]. Blends prepared in this way may show a single glass transition. However, in the original reports on this method, the mixtures rapidly separated into two phases on heating to only a few degrees above the glass transition temperature[19]. The rate of phase separation depends on a thermodynamic factor related to how far the system is from equilibrium and the mobility (viscosity) of the mixture[20]. Considering the wide variation possible, especially in mobility, phase separation may not always be as fast as in these earlier reports. Indeed, the very recent literature[20–23] describes several examples of quite slow phase separation of blends.

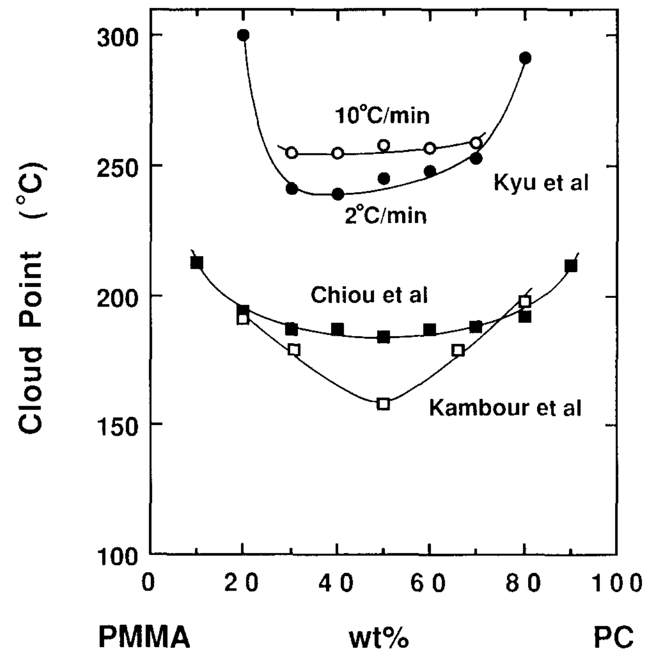

Figure 1 Published cloud point data for PC/PMMA blends. Data from Kyu and Saldanha[9] (○), 10°C min^{-1}; (●) 2°C min^{-1}; data from Chiou, Barlow and Paul[1] (■); data from Kambour *et al.*[2] (□)

Low mobility systems that phase separate slowly are exactly the kind that might be easily trapped into a non-equilibrium, homogeneous state by solvent preparation procedures other than freeze-drying. As shown here for PC–PMMA, such systems may be heated well beyond the T_g before phase separation becomes rapid enough to be detectable at even very slow heating rates. We show here that the cloud point curves in *Figure 1* are simply artifacts of a very slow rate of phase separation.

EXPERIMENTAL

Table 1 summarizes the information that is available for the bisphenol-A polycarbonate and poly(methyl methacrylate) materials used here and, for comparison, in the previous studies mentioned earlier. Only weight average molecular weights are shown because this is the most important factor for the entropy effect and it simplifies the presentation. Three polycarbonates were used here. One is a typical commercial moulding grade polymer while the other two are experimental low molecular weight materials. We used a single PMMA material from a commercial source. Typically, commercial PMMA products contain a small amount of a second monomer for improved thermal stability. Kyu *et al.*[3,4,6,9] used the same commercial grade of PMMA; however, the $\bar{M}_w$ they report is considerably lower than that provided by the supplier and expected for such materials.

The blends used in this work were prepared in the form of film by casting a 5% solution of the polymers in tetrahydrofuran onto a glass plate heated to 50–60°C. After slow drying at ambient conditions, the blends were dried in a vacuum oven at 120–140°C for four days.

Thermal analysis observations were made using a Perkin-Elmer DSC-7 system. Glass transitions were normally taken from a second scan to assure reproducible thermograms free of prior history effects. However, in some cases, the maximum temperature reached in the first scan may affect the second scan. In this work the T_g has been defined by the intersection of the straight lines through the glassy state baseline and through the transition zone, i.e., the onset method. Annealing of various blends was carried out by bringing the sample to a desired temperature for a specified time period. The sample was cooled and another d.s.c. scan was made immediately to ascertain changes in transition behaviour caused by the annealing.

Table 1 Molecular weight data of PC and PMMA used in miscibility studies

Polycarbonate		PMMA		
$\bar{M}_w$	Description	$\bar{M}_w$	Description	Reference
34 200	Lexan 131-111[a]	130 000	Plexiglass V-811[b]	This work
17 300	Dow, experimental	130 000	Plexiglass V-811[b]	This work
9 900	Dow, experimental	130 000	Plexiglass V-811[b]	This work
17 600	GE, experimental	75 000	unspecified	2
48 600	Lexan 141[a]	85 200	Plexiglass V-811[b]	4
65 000	Scientific Polymer Products	33 000	Aldrich Chem.	5
58 000	Lexan 141[a]	84 000	Plexiglass V-811[b]	3
58 000	Lexan 141[a]	84 000	Plexiglass V-811[b]	9
58 000	Lexan 141[a]	85 000	Plexiglass V-811[b]	6

[a] A commercial product of General Electric Co.
[b] A commercial product of Rohm and Haas Co.

Changes in light transmission through blend films were quantitatively measured using an FM 80 Mettler Thermosystem at wave lengths of 440 and 635 nm. The specimens were heated on a microscope hot stage (Mettler Hot Stage FP 82) at a constant rate (2–20°C min^{-1}) or held isothermally for observation.

RESULTS AND DISCUSSION

Films of PMMA/PC blends were quite transparent when prepared by the hot casting method described earlier. These blends exhibited a single, composition dependent glass transition as expected for homogeneous blends and as reported earlier for this system[1–9]. The LCST behaviour of miscible blends is normally quantified by measurement of cloud point temperatures while heating at finite rates. However, if the phase separation process is very slow, then this approach is not appropriate because even the slowest practical heating rate may seriously over estimate the true thermodynamic cloud point.

Recognizing this as a possibility for PC–PMMA, an alternative approach using isothermal annealing was adopted. *Figure 2* shows the annealing results obtained using the commercial PC ($\bar{M}_w = 34\,200$) and PMMA ($\bar{M}_w = 130\,000$). The solid line shown for reference represents the glass transition temperature found for as-cast blends. Blends that were originally transparent became opaque within 15 min at 180°C for all compositions. At 160°C, initially transparent blends became cloudy on annealing but this required up to 8 h for some compositions. At 140°C, the two extreme compositions remained transparent even after 80 h of annealing. At the lowest annealing temperature, 130°C, blends containing 30, 40 and 50% PC became opaque within 60 h. However, films containing 10, 20 and 60% PC remained clear even after 140 h of annealing. These observations, plus others to be shown subsequently, make it abundantly clear that the cloud points shown in *Figure 1* are substantially higher than the equilibrium phase boundary.

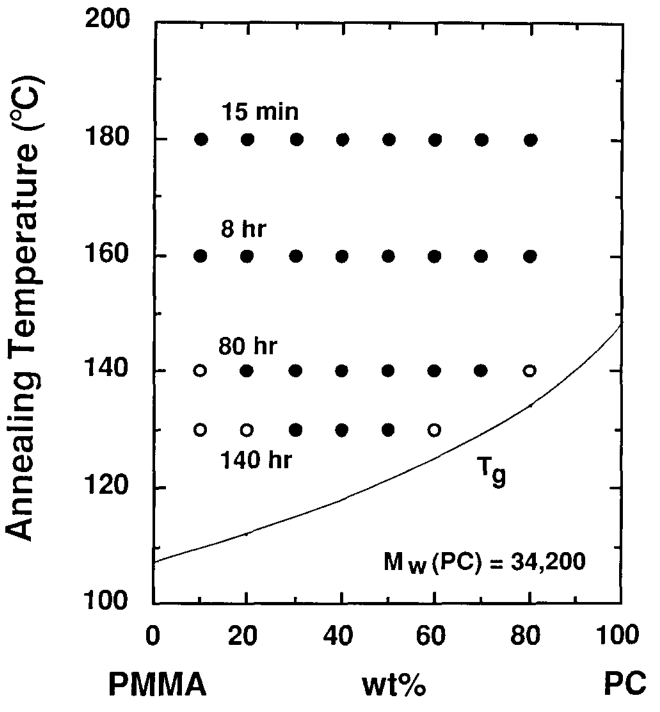

Figure 2 Phase structure of PC ($\bar{M}_w = 34\,200$)/PMMA blends after annealing at various temperatures; (○) clear; (●) opaque. T_g of homogeneous mixtures indicated by the solid line

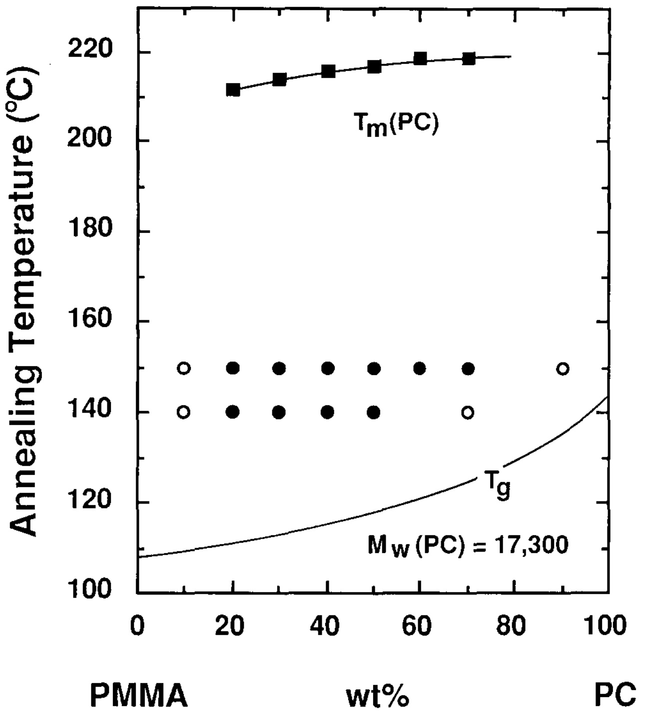

Figure 3 Phase structure of PC ($\bar{M}_w = 17\,300$)/PMMA blends after annealing for 80 h: clear (○); opaque (●). T_m of PC is shown after annealing blends at 150°C (■)

Two possibilities exist for the latter. In one, the thermodynamic phase boundary lies below the T_g line only in the mid-composition region but above the T_g line at the composition extremes. In such a case, points like the open ones in *Figure 2* may lie below the phase boundary indicating that the homogeneous state would be thermodynamically stable. The second possibility is that there is no region of thermodynamic stability, for a homogeneous phase, at temperatures above T_g, i.e. the thermodynamic phase boundary lies entirely below T_g. In this case, the blends represented by the open points in *Figure 2* would phase separate at the indicated temperature given enough time. Annealing times considerably longer than the one week used here would be needed to distinguish between these two possibilities, and a completely unambiguous determination by this approach may not be feasible since the time scale for phase separation may become very protracted as T_g is approached.

Figure 3 gives the results for a similar set of experiments using the medium molecular weight PC ($\bar{M}_w = 17\,300$) in blends with PMMA. All compositions became opaque during annealing for 80 h at 170°C and 180°C. However, at 150°C and 140°C the extreme compositions remained transparent at 80 h. It was found that crystallization of the medium molecular weight PC occurred during annealing which makes it difficult to judge stability with respect to liquid–liquid phase separation. The evidence for the crystallization is illustrated in *Figure 4* by a d.s.c. scan of a 50% PC ($\bar{M}_w = 17\,300$) blend that had been annealed for 80 h at 150°C. Similar crystallization was not a factor in *Figure 2*. *Figure 5* shows a d.s.c. scan for a 50% PC ($\bar{M}_w = 34\,200$) blend after annealing for 80 h

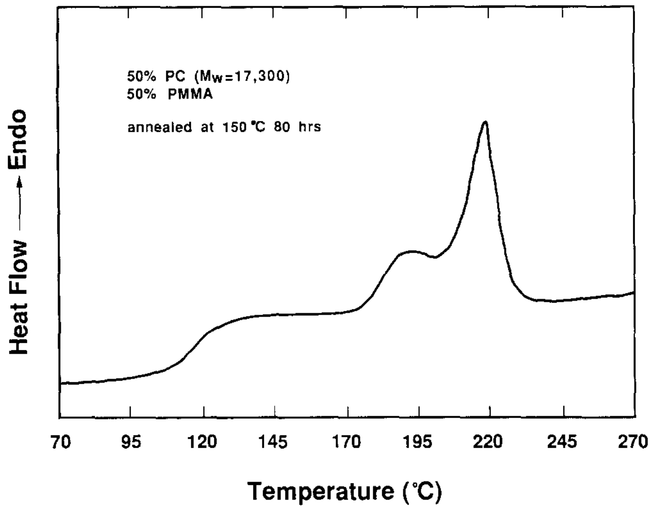

Figure 4 D.s.c. trace of a 50/50 PC ($\bar{M}_w = 17\,300$)/PMMA blend after annealing for 80 h at 150°C

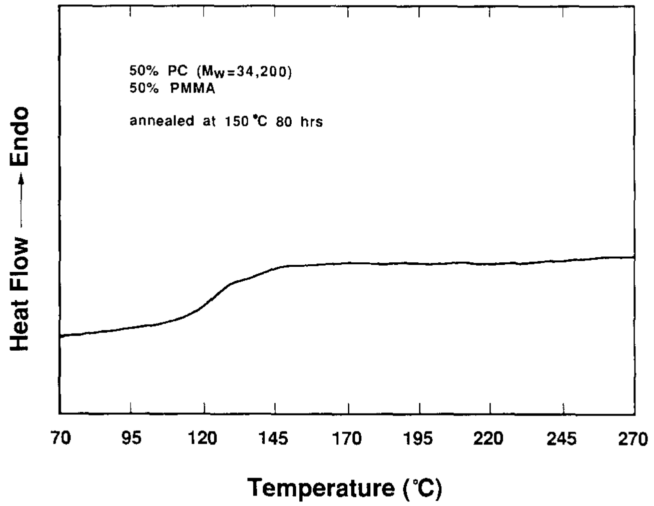

Figure 5 D.s.c. trace of a 50/50 PC ($\bar{M}_w = 34\,200$)/PMMA blend after annealing for 80 h at 150°C. Phase separated blend shows no indication of PC crystallinity

at 150°C. There is no PC melting peak because the low mobility of PC at this molecular weight kinetically precludes crystallization at these times and temperatures. *Figure 3* shows the PC melting points for samples annealed 80 h at 150°C. The crystallization precluded a complete mapping of the relationship between time and temperature for phase separation in this case. However, at 170°C, the phase separation was faster than crystallization. A sample annealed at 170°C for 30 min showed two T_g values by d.s.c. but no T_m. Thus, we can conclude that the cloud point curve does lie below 170°C for PC with $\bar{M}_w = 17\,300$. However, further conclusions cannot be made owing to the obscuration caused by PC crystallization.

Results with the PC having $\bar{M}_w = 9900$ were more definitive because the LCST is elevated above the T_m of PC. *Figure 6* summarizes the results. PC also crystallized from blends with PMMA at temperatures between T_g and T_m. The crystallization rate was much faster for this material than for the one with $\bar{M}_w = 17\,300$. Blends were transparent as prepared, however, by heating at about 1°C min^{-1} such blends became cloudy at around 200°C (crystallization) and then became clear again at around 230°C (melting) but eventually became cloudy again at a high temperature (LCST behaviour). Of course, phase separation is quite rapid at these high temperatures and for such a low molecular weight PC.

Figure 6 shows the PC melting point for samples annealed at 200°C for 30 min. Samples annealed at 180°C showed a lower T_m. The points above T_m give information about the cloud point curve (LCST). The open points designate compositions which remained transparent after annealing for 15 min at the indicated temperature while the closed points represent blends that became cloudy after annealing for 15 min at the indicated temperatures. The latter became clear again when cooled by 10°C which is evidence that these results adequately reflect an equilibrium cloud point curve.

The rate of phase separation or homogenization for blends with PC having $\bar{M}_w = 9900$ is much faster than those with PC having $\bar{M}_w = 34\,200$ for two reasons. First, there is the obvious effect of lower viscosity or higher mobility associated with the lower molecular weight. However, because of the lower molecular weight the equilibrium cloud points are shifted to higher temperatures, apparently well above T_g, where mobility is much higher. The second is probably the more significant effect. The asymmetric shape of the cloud point curve in *Figure 6* is similar to that found for blends of PC with various methyl methacrylate copolymers[11]. The LCST appears to be in the range of 230 to 240°C. This indicates that, even at such a low molecular weight for the PC component, the cloud point curve is only marginally high enough for melt processing to give homogeneous PC/PMMA blends.

The observations noted above can be more graphically illustrated using quantitative measurements of the extent that light is transmitted through the various blend films. *Figure 7* shows the fraction of light transmitted through

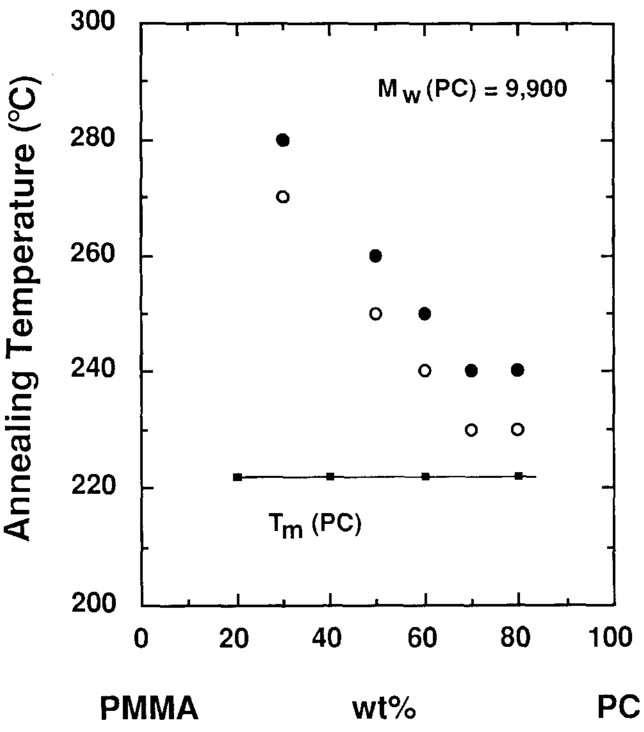

Figure 6 Phase structure of PC ($\bar{M}_w = 9900$)/PMMA blends after annealing at various temperatures for 15 min: clear (○); cloudy (●). T_m of PC is shown for blends annealed for 30 min at 200°C (■)

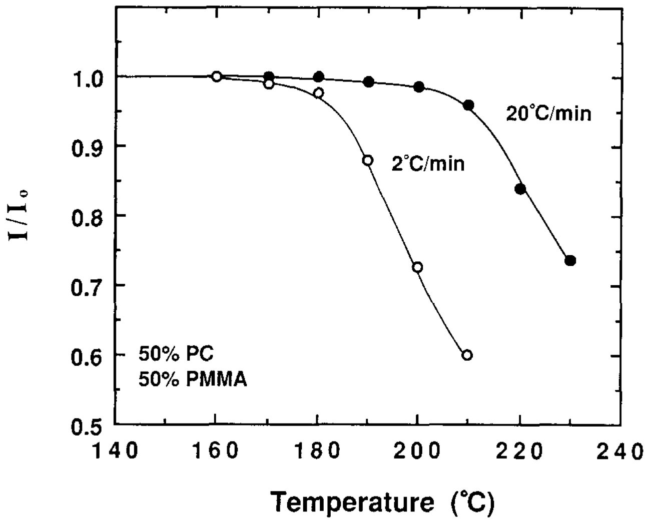

Figure 7 Change of light transmittance ratio of 50/50 PC ($\bar{M}_w = 34\,200$)/PMMA blend at $\lambda = 640$ nm and at two heating rates: (○) 2°C/min; (●) 20°C/min

initially homogeneous blends of PC ($\bar{M}_w = 34\,200$)/PMMA at constant heating rates. The large effect of the rate of heating is quite evident. In the absence of any other information, one might conclude, based on the 2°C min^{-1} scan, that there is a thermodynamic cloud point in the vicinity of 180°C. However, it is obvious from the long term annealing experiments described earlier that any specific event at 180°C is just an artifact of the slow rate of the phase separation process for this system. Isothermal changes in the fraction of light transmitted makes this apparent.

Figure 8 shows the effect of the choice of film thickness. Thick films scatter significantly more of the incident light than do thin ones when the film begins to phase separate. Therefore, for comparison purposes, it is useful to normalize by the film thickness in the manner suggested by Beer's law and as shown in *Figure 9*. The wavelength of the incident light is also important as seen in *Figure 9*. For a given stage of phase separation there is more light scattered (therefore, less transmitted) for the lower wavelengths as expected from light scattering theory. *Figures 8* and *9* clearly show the extreme effect of temperature on the kinetics of phase separation. Only a few minutes are required for these films to become totally opaque at 180°C, whereas this state was achieved at 150°C only after several hours. For a system showing an LCST, the thermodynamic driving force for phase separation lessens as temperature approaches the LCST, but the mobility becomes greatly diminished as the glass transition is approached. The latter is believed to be the more significant factor in the present case.

Likewise, the molecular weight of either component plays an important role in the kinetic process as seen in the isothermal comparison shown in *Figure 10*. Again, there are two effects. As the molecular weight of one of the components is reduced, the LCST is raised so the net driving force is reduced for a fixed temperature of phase separation. However, the mobility is greatly increased and as seen in *Figure 10*, this must be the dominant factor in the present case. It should be noted again that under the conditions shown in *Figure 10*, crystallization is much slower so the changes shown are entirely due to liquid–liquid phase separation.

Another way to examine the consequences of iso-

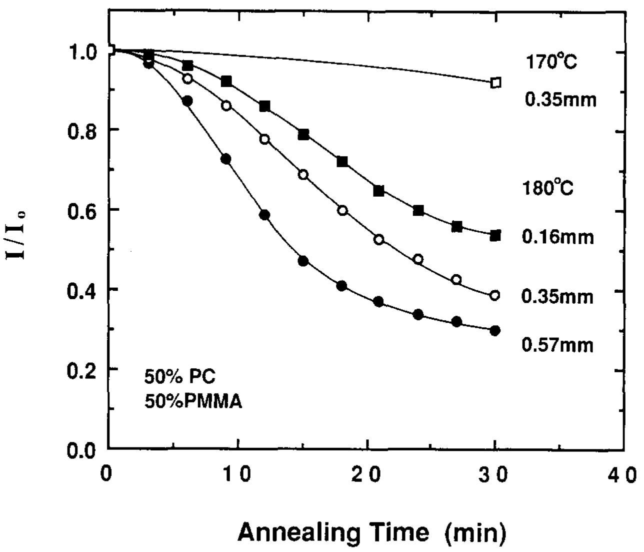

Figure 8 Change of light transmittance ratio of a 50/50 PC ($\bar{M}_w = 34\,200$)/PMMA blend as a function of time and film thickness at $\lambda = 640$ nm: (□) 0.35 mm at 170°C; (■) 0.16 mm at 180°C; (○) 0.35 mm at 180°C; (●) 0.57 mm at 180°C

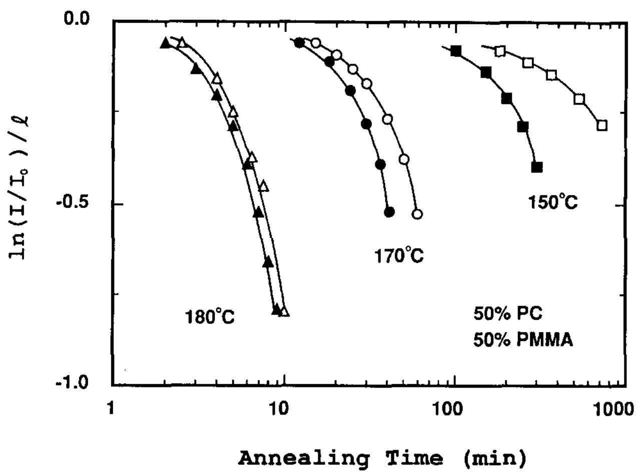

Figure 9 Change of ln light transmittance ratio per mm of film thickness of 50/50 PC ($\bar{M}_w = 34\,200$)/PMMA blends *versus* log annealing time in a Mettler Hot Stage: (△) 180°C, 635 nm; (▲) 180°C, 440 nm; (○) 170°C, 635 nm; (●) 170°C, 440 nm; (□) 150°C, 635 nm; (■) 150°C, 440 nm

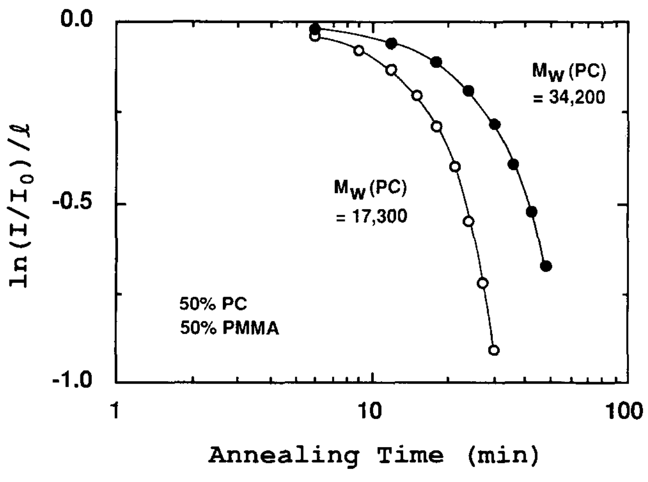

Figure 10 Change of logarithm of light transmittance ratio per mm of film thickness of 50/50 PC/PMMA blends *versus* log annealing time in a Mettler hot stage at $\lambda = 640$ nm and 170°C: (○) PC $\bar{M}_w = 17\,300$; (●) PC $\bar{M}_w = 34\,200$

thermal annealing is to monitor the glass transition temperature behaviour using d.s.c. As seen in *Figures 11–13*, as-cast blends have a single glass transition. Annealing at 170°C, results in the occurrence of two glass transitions as seen in *Figure 11*. Further annealing to 60 min produced no discernible enhancement of this situation. On the other hand annealing at 160°C for 15 min results in only a hint of two glass transitions as seen in *Figure 12*. The two glass transitions are fully evident after annealing for 60 min. After annealing for 15 or 60 min at 140°C the same blends did not show any evidence for two glass transitions, however, this becomes quite evident after 40 h. These results clearly demonstrate the extreme sensitivity of the kinetics of the phase separation process to temperature.

SUMMARY

This work reinforces a growing body of evidence that, in some cases, solvent casting procedures can trap blends of polymers into a homogeneous mixture when this is not the equilibrium state. The reverse phenomenon where certain solvent casting methods lead to phase separated samples of miscible polymer pairs is more widely known. The latter seems to be related to the choice of solvent and is believed to have a thermodynamic origin, e.g. a closed region of immiscibility in isothermal planes of the ternary phase diagram. To the contrary, the formation of a homogeneous mixture from a non-miscible pair must relate entirely to the rate processes associated with the removal of a solvent from an initially homogeneous solution. Fast solvent removal, by use of rapid evaporation (low boiling solvent or high casting temperature), or precipitation using a non-solvent, relative to the rate the polymers can diffuse favours entrapment of a more homogeneous mixture than would be expected from thermodynamic equilibrium. Flash evaporation and freeze-drying represent extremes of these two issues. Stiff polymer chains that lead to high viscosities may evidently lead to the same result at relatively moderate rates of solvent removal. In the present case, both polycarbonate and poly(methyl methacrylate) tend to have high viscosities and, as shown here, this pair can be formed into a homogeneous glassy mixture using several solvent removal methods.

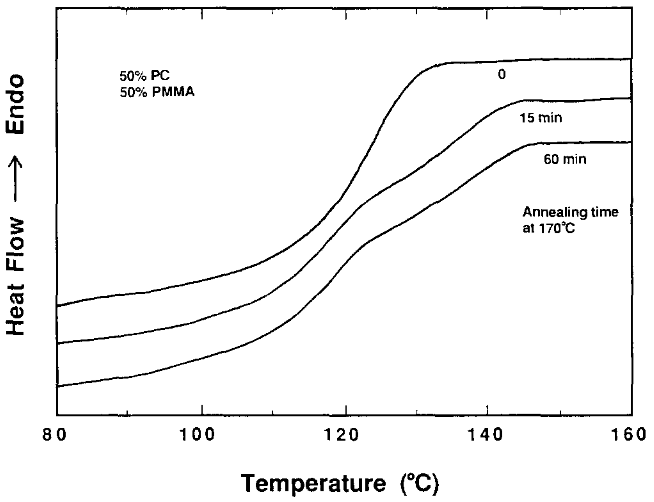

Figure 11 D.s.c. traces of 50/50 PC ($\bar{M}_w = 34200$)/PMMA blends after annealing at 170°C for 0, 15 and 60 min. Phase separation occurred after 15 and 60 min

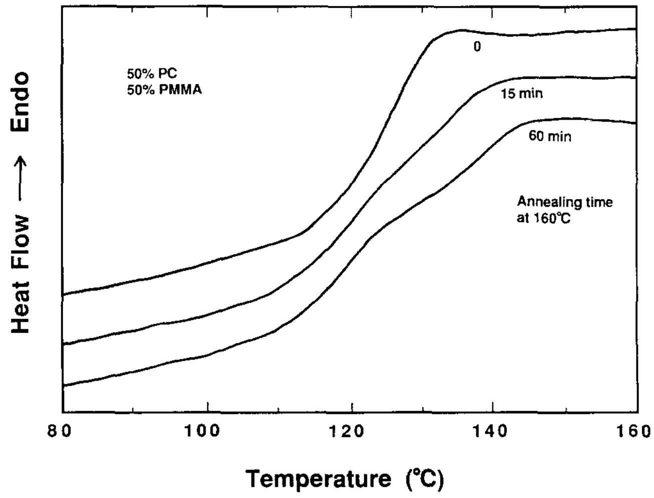

Figure 12 D.s.c. traces of 50/50 PC ($\bar{M}_w = 34200$)/PMMA blends after annealing at 160°C for 0, 15 and 60 min. Phase separation occurred after 15 and 60 min

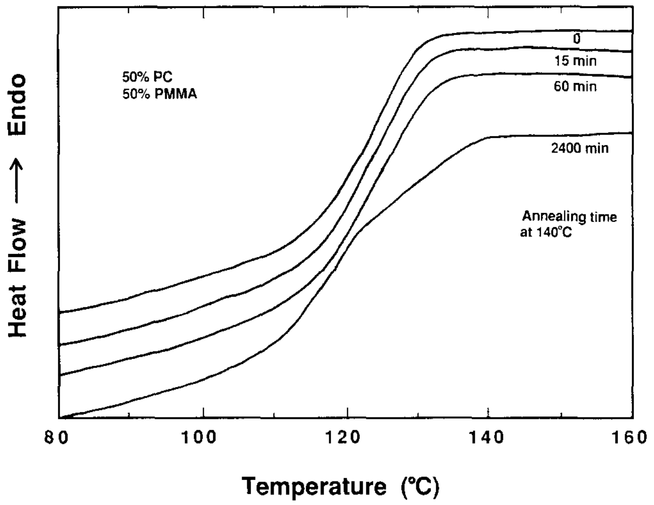

Figure 13 D.s.c. traces of 50/50 PC ($\bar{M}_w = 34200$)/PMMA blends after annealing at 140°C for 0, 15, 60 and 2400 min. Phase separation occurred after 40 h

Above the glass transition temperature, the rate at which these mixtures separate into two phases is extremely slow; similar slow phase separation has been noted in a few other systems[20–23]. Because of these issues, the cloud points for PC/PMMA blends found in previous reports[1–7,9] occur at temperatures far above any LCST type phase boundary. We have shown here that little, if any, of the equilibrium cloud point curve lies above the T_g line when both components have molecular weights typical of commercially useful materials. This means that the PC–PMMA interaction is less favourable than originally expected. Nevertheless, the PC–PMMA interaction is not strongly unfavourable because by lowering the PC molecular weight, the true equilibrium cloud point curve can be raised well above the glass transition temperature.

In fact, we believe that in general it is not likely that polymer pairs with strongly repulsive interactions could be so easily trapped into a homogeneous mixture. From a practical point of view, these findings mean that it will be somewhat more difficult than originally hoped to make a modified polycarbonate/polymethacrylate system that is melt processable but not impossible as we show later[11].

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