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Kinetic effects on phase heterogeneity in bisphenol-A polycarbonate/poly(methyl methacrylate) blends

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Optical microscopy and d.s.c. were performed on PC/PMMA blends cast with THF at 50°C to demonstrate that the domain sizes were dependent on the film thickness, which should help provide yet stronger evidence that the blends were not of a single-phase nature with thermodynamic molecular mixing, but that the phase behaviour was governed by the kinetics of solvent evaporation rate. While thin blends were totally amorphous and possessed ultra micro heterogeneity, thicker-film blends possessed much greater scales of heterogeneity and developed solvent-induced PC crystallinity, which could suppress the T_g of the PC phase. This study further proved that the equilibrium phase behaviour of PC/PMMA was thermodynamically immiscible, and that the common thermodynamic factors such as solvent types and temperature could only affect the scales of heterogeneity in such systems. Cases influenced by solvent type and temperature were discussed to illustrate the dependence of heterogeneity on such factors. Also, given the same thermodynamic factors, kinetic factors can influence the scales of phase heterogeneity. Copyright © 1996 Elsevier Science Ltd.

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INTRODUCTION

Our previous studies[1,2] have provided experimental data supporting that the equilibrium phase behaviour in solvent-cast binary blends of bisphenol-A polycarbonate (PC) with poly(methyl methacrylate) (PMMA) is actually immiscibility, with micro heterogeneity beyond detection by a differential scanning calorimeter (d.s.c.) and transparent to unaided eyes. When processed with tetrahydrofuran (THF) and cast at 50°C to thin films (less than 15 μm), the PC/PMMA blends may appear transparent and possess one single T_g, but still exhibit ultra micro phase domains detectable using scanning electron microscopy (SEM). When otherwise processed, the blends are unambiguously of a two-phase structure. It is usually agreed that phase separation is observed in melt-processed blends[3] or in blends cast with solvents other than THF[4].

There have been extensive investigations by many interested polymer researchers, but the equilibrium phase behaviour has long been controversial. In the past, miscibility of these blends has been extensively debated[5–9]. Some investigators classified these as miscible with LCST and/or UCST behaviour, which have later been found to be questionable. Until we further established SEM data to reveal the true morphology of the transparent PC/PMMA blends and pointed out that the miscibility might have been incorrectly labelled, the issue has been quite unsettled[1,2]. Thus, the miscibility and the so-called 'lower critical solution temperature' (LCST) transition discussed widely in the literature for the PC/PMMA blends are now questionable since the blends below those 'LCST' temperatures are not thermodynamically miscible.

Ample reports in the literature have shown that solvent types can induce changes from phase separation to miscibility or *vice versa* due to preferential affinity toward one of the two polymer components. In addition, kinetic factors that might influence the scales of heterogeneity in various blend systems have been intensively investigated[10–12]. Although some pointed out that the type of solvents in casting blends could result in alteration from miscibilty to phase separation or *vice versa*, our recent studies on the PC/PMMA blend system[2] have clearly demonstrated that the scales of heterogeneity can be changed significantly by various kinetic factors and that the equilibrium morphology of the PC/PMMA blends is not of miscibility but phase separation.

The main objective of this report was to prove that the heterogeneity in the PC/PMMA blends could vary from an ultra micro scale to a macro scale (visible to the eyes) depending on various kinetic factors, such as cast temperature, film thickness, etc. that may not have been addressed in previous studies. Complicating factors, such as PC crystallinity in suppressing T_g, should be considered in analysing the results. These interpretations provide yet deeper insights into the true nature of the phase behaviour of the PC/PMMA blends.

EXPERIMENTAL

Materials and sample preparation

Poly(methyl methacrylate) (a-PMMA) with $M_n = 50\,000\,\mathrm{g\,mol^{-1}}$ and $M_w = 90\,000\,\mathrm{g\,mol^{-1}}$ was obtained from a commercial source (Chi-Mei Inc., Taiwan), and

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bisphenol-A polycarbonate (PC) was GE Lexan HF1130, which has $M_w = 23\,000\,g\,mol^{-1}$. The blend film samples were prepared by solvent casting at two temperatures (25 and 50°C). Also, two solvents were used: tetrahydrofuran (THF) and methylene chloride. PMMA and PC were first weighed respectively and dissolved with continuous stirring in one of the two solvents. Subsequently, the resulting polymer solution was then poured into an aluminium mould kept at one of the two chosen temperatures (25 or 50°C). The solvent in the cast samples was vaporized in a circulation oven with an exhaust fan at room temperature, followed by residual solvent removal in a vacuum oven for 24–48 h at 50–60°C. After this, most blend films were completely dry. However, some might still contain trace amounts of solvent, and subsequent degassing at 110°C was performed on these hard-to-dry samples.

Thin films (10 μm or less) cast with THF at 50°C were visually transparent and seemingly homogeneous. In addition, to further prove that THF casting of blends at 50°C does not ensure apparent homogeneity due to thickness-controlled evaporation rates, blend film samples of various thicknesses were cast on glass slides and characterized using optical microscopy. Samples for d.s.c. were obtained by scratching the cast films from the glass slides. By comparison, those cast at 25°C with THF were not cloudy regardless of film thickness.

Differential scanning calorimetry

The glass transition temperatures and PC crystallinity of the blends were measured with a d.s.c. (Perkin-Elmer DSC-7, power-compensated type) equipped with an intracooler and a computer for data acquisition/analysis. All T_g and/or crystallinity measurements were made at a scan rate of $10°C\,min^{-1}$ within the range of 25–250°C. The T_g values were taken as the onset of the transition (the change of the specific heat) in the d.s.c. thermograms, and the PC crystallinity was measured by integrating the areas of the melting peaks between 200–250°C.

Optical microscopy

A polarized-light optical microscope (Nikon Optiphot-2, POL) with UFX-DX automatic exposure was used. Samples for microscopy were solution-cast onto a glass slide, dried properly, and thermally treated in a temperature-controlled oven before they were placed on the observation stage of the microscope for examination and photograph recording.

RESULTS AND DISCUSSION

Domain sizes for blends cast under various conditions

Figure 1 shows the optical micrographs (A–E) of the methylene chloride-cast blend samples of five different compositions, all cast at 50°C. The blend films all had the same average thickness. Phase separation is apparent in all compositions, and the phase domain sizes are dependent on the composition. At or near the extreme compositions, the blends exhibit a simple dispersed phase morphology (binodal type). However, at compositions near 50/50, the morphology is quite different in that the domains in the blends are much larger and become inter-connected (spinodal type). An interesting phase-in-phase feature characterizes such an inter-connected morphology.

Figure 2 shows the optical micrographs (A–E) of the methylene chloride-cast blend samples of five different compositions, all cast at 25°C. Phase separation is more severe and apparent in all compositions than those cast at 50°C. Again, the phase domain sizes are dependent on the composition. At or near the extreme compositions, the blends exhibit a dispersed-phase morphology; however, the dispersed domains are much larger and the phase structure is more complex than those in *Figure 1* of the same compositions. Within each of the relatively large dispersed domains (about 40–80 μm), there are smaller particulate domains (less than 1 μm) existing in it. Again, at compositions near 50/50, the morphology become inter-connected, where a similar phase-in-phase feature characterizes these domains.

Optical microscopy revealed no phase separation in the blend samples THF-cast (15 μm or less in film thickness) at 50°C. The light microscopy photographs are not presented or discussed here due to the same plain features. However, the SEM results from our previous study[2] have demonstrated that ultra small (sub-micron) heterogeneity indeed exists in the PC/PMMA blends so cast. That is, these as-cast transparent blends with a single T_g actually were phase-separated, only with micro phase domains that are beyond detection limits of optical light techniques or thermal analysis.

On the other hand, THF-cast blend films at 25°C were visibly opaque, indicating phase separation and/or solvent-induced PC crystallinity. The PC crystals might be partially responsible for the opaqueness in the 25°C THF-cast blends. Preliminary d.s.c. analysis indicated that PC/PMMA blends cast with THF at 25°C did reveal PC crystals upon d.s.c. scanning. Thus, crystallinity might also contribute to the observed opaqueness. But primarily it was due to phase separation, which was apparent from the optical microscopy results. The micrographs for the blend films cast with THF at 25°C are similar to those in *Figure 2* (methylene chloride-cast at 50°C), and thus are not presented and discussed again here for brevity.

Table 1 shows the direct comparison of the numerical values of domain sizes of the PC/PMMA blends cast under various conditions. Interestingly, the domain sizes are not only dependent on the type of solvents and temperature, but also the blend composition. The irregular shapes of the domains for 50/50 compositions made it difficult to estimate the sizes; however, an averaging method was used to obtain a fair estimate.

Figure 3 shows the average domain sizes of the blends cast under various conditions, as a function of blend composition. Regardless of the vast difference in the scales of heterogeneity for the series of blends prepared under the various conditions, a maximum average size at the compositions near 50/50 is universally observed.

Visual inspection showed that those blends cast using solvents other than THF at any temperatures were found to be visually cloudy. Methylene chloride casting of the blend films at either 25°C or 50°C yielded opaque, non-homogeneous films, and optical microscopy examination of these blend films also revealed large grossly separated domains. Predictably, d.s.c. could reveal two T_g's in the blend systems showing heterogeneity larger than 1 μm. The T_g results are shown in *Figure 4*, where *Figure 4A* shows the T_g's of the PC/PMMA blends cast

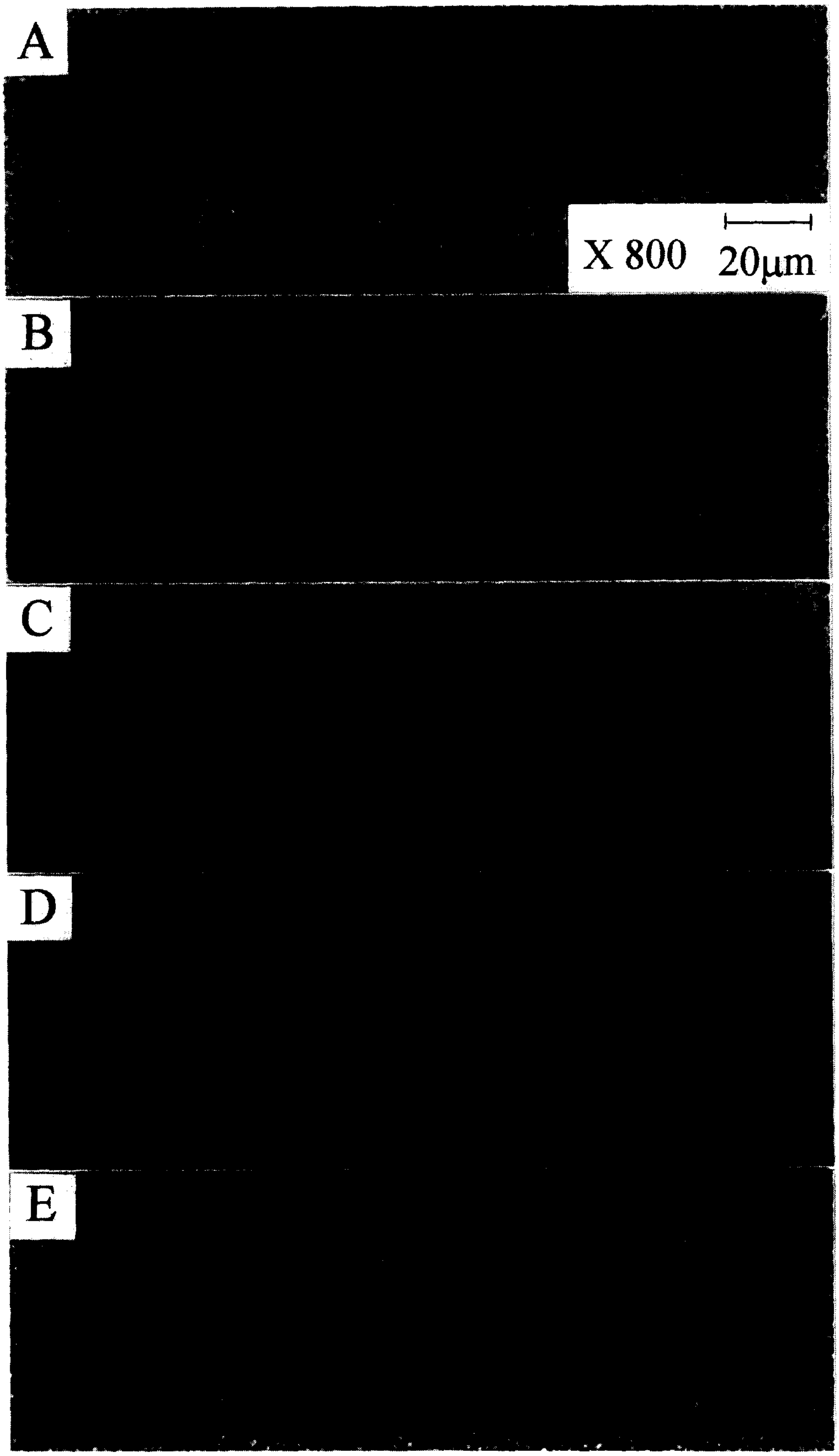

Figure 1 Optical micrographs of the methylene chloride-cast PC/PMMA blend samples of five different compositions, all cast at 50°C. (A) 10/90, (B) 30/70, (C) 50/50, (D) 70/30, and (E) 90/10

from methylene chloride at 25°C and *Figure 4B* shows the T_g's of the PC/PMMA blends cast from methlyene chloride at 50°C. Differences in these two diagrams are mainly in that T_g of the PC phase in the 50°C-cast (methylene chloride) blends is slightly depressed while the T_g of the PC phase in the 25°C-cast blends is negative. The optical morphology revealed that phase domain sizes in the 50°C-cast blends possessed a smaller scale of heterogeneity. This may be the reason for the depression in the T_g of the PC phase.

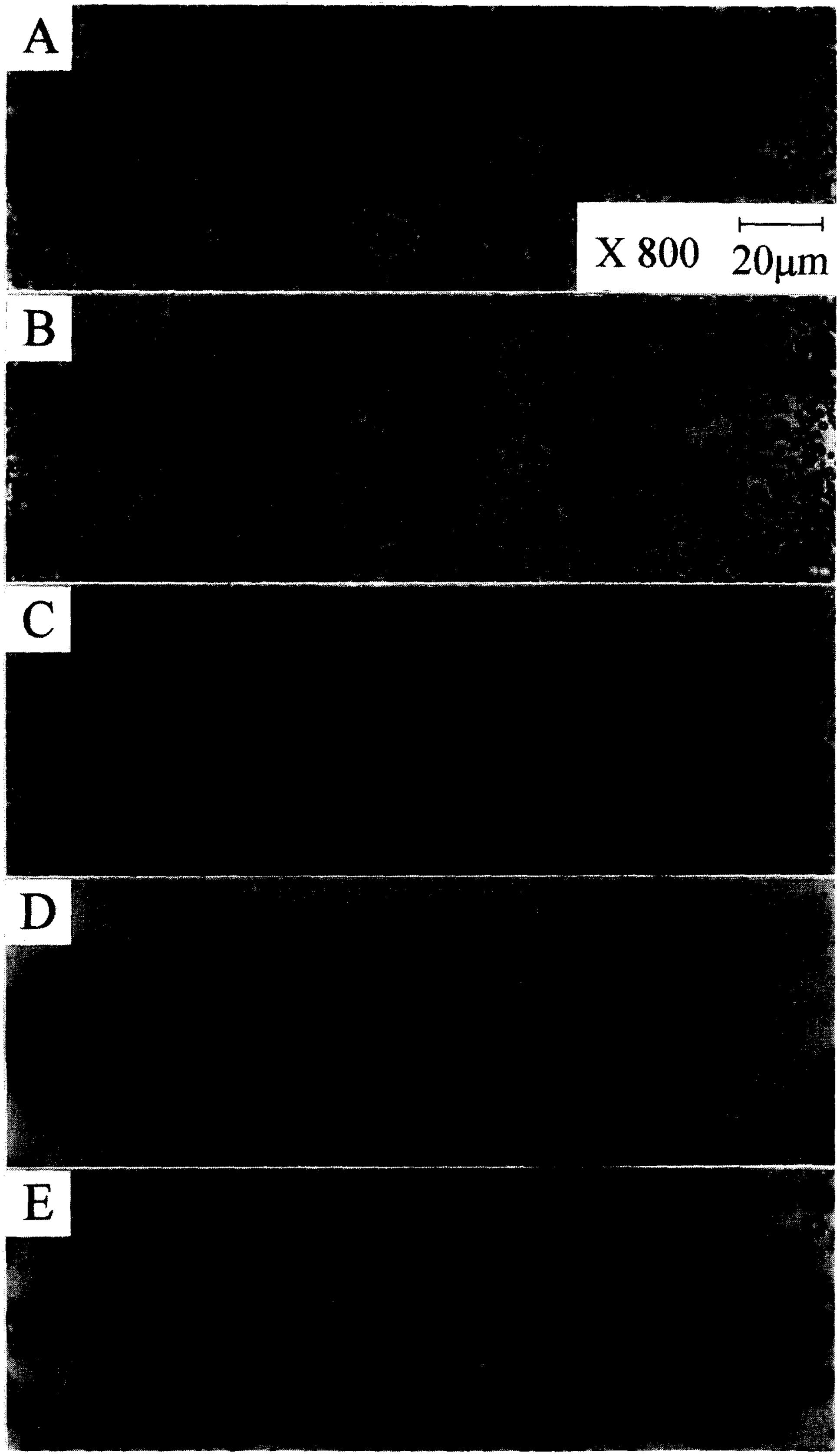

Figure 2 Optical micrographs of the methylene chloride-cast PC/PMMA blend samples of five different compositions, all cast at 25°C. (A) 10/90, (B) 30/70, (C) 50/50, (D) 70/30, and (E) 90/10

Effects of film thickness and casting temperature on domain sizes

Although casting with THF at 50°C yielded the most transparent blend films, the extent of heterogeneity in the cast blends was found to depend on the film thickness. It was suspected that the films cast with THF at 50°C were transparent and seemingly homogeneous only because they were extremely thin and thus solvent evaporation was relatively fast. Thicker films cast with THF at 50°C

Table 1 Domain sizes in PC/PMMA blends cast with two different solvents at two temperatures

	THF		CH_2Cl_2	
PC/PMMA blends composition	25°C (OM)[c] (μm)	50°C (SEM) (μm)	25°C (OM)[c] (μm)	50°C (OM) (μm)
10/90	2.3	0.3[a]	2.3	2.3
30/70	7.0	0.5[a]	71	8.5
50/50	Spinodal decomposition (~122)[b]	0.5[a]	Spinodal decomposition (~245)[b]	Spinodal decomposition (~120)[b]
70/30	54	0.4[a]	56	8.0
90/10	2.0	0.2[a]	16	2.2

[a] For film thickness of 5–8 μm only
[b] Hard to estimate due to complex phase-in-phase structure
[c] OM: optical microscopy

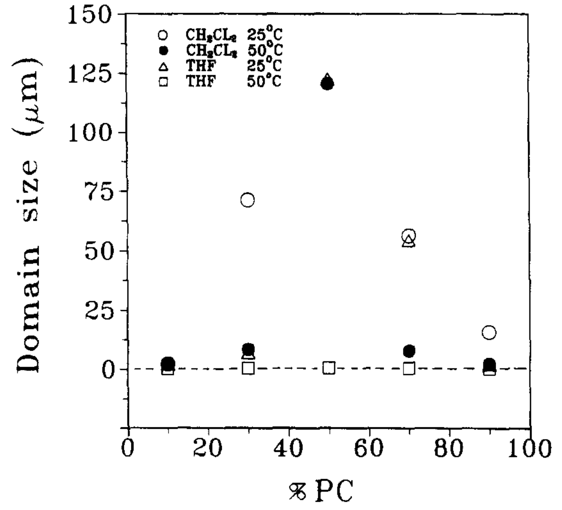

Figure 3 Average domain sizes (viewed perpendicular to sample film) of the blends cast under various conditions as a function of blend composition

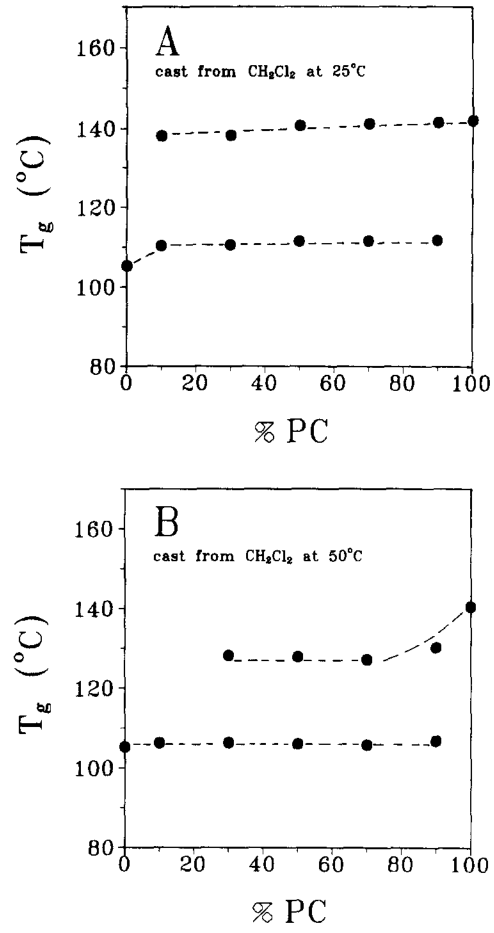

Figure 4 (A) T_gs of the PC/PMMA blends cast from methylene chloride at 25°C; (B) T_gs of the PC/PMMA blends cast from methylene chloride at 50°C

might still be phase-separated since the apparent homogeneity observed in the thin blend films is not the true thermodynamic state but is influenced by kinetic factors. Our other concurrent studies[1,2] have provided direct evidence for an earlier postulation by Nishimoto *et al.*[9], who stated that the THF solution-cast PC/PMMA blends might be in a state of polymer chains being temporarily trapped into a non-equilibrium homogeneous state by solvent preparation procedures. The phase domain sizes may be simply beyond the detection or resolution limits of the optical methods or thermal analysis including d.s.c. or dilatometry. The domain sizes were difficult to estimate from the SEM micrographs of the fracture blend samples. Experimentally, it was relatively more difficult to fracture a thin sample for SEM characterization. Optical microscopy was thus performed on the 50°C-THF cast blends of various cast thicknesses.

Figure 5 shows the optical micrographs of the 50°C-THF cast blend film samples of 50/50 composition with various thickness of 8, 18, 23, 28 and 36 μm, respectively. The optical microscopy revealed no separated domains in the thinnest blend films (less than 10 μm). Nevertheless, it must be noted that the SEM study did reveal phase-separated domains of about 0.3–0.4 μm in such blend films[2]. For other thicker blend films, the scales of heterogeneity apparently increase with the thickness. This is interesting since all the thermodynamic factors, such as composition, temperature, and solvent type, which might affect the phase behaviour, were kept the same in preparing the blend films. The fact of thickness-dependent domain sizes suggests that the phase behaviour might be governed by the kinetics of solvent evaporation rate, and that the blends are not of a single-phase nature with thermodynamic molecular mixing. Faster rates of evaporation in thin blend films resulted in higher extents of temporarily trapped PC/PMMA chain entanglement, which thus induced smaller scales of heterogeneity. Note that other than the heterogeneity, there might be some micro voids in the samples, especially those of greater thickness, which was probably caused by evaporation of the residual trapped THF solvent in thicker blends.

Figure 6 shows the estimated domain sizes of the 50°C-THF cast blend sample (50/50 composition) as a function of film thickness. Overall, the extent of heterogeneity in the blend samples initially increases only very gently, but quite rapidly if the film thickness is greater than 30 μm. It must be pointed out here that solvent-induced PC crystallinity in the blends might develop in the thicker blend films due to relatively slower evaporation of THF. Thus, the solvent-induced PC crystalline domains might also contribute to change the overall scales of heterogeneity in the blends. This may be the case. However, the PC crystals could be easily identified as tiny white crystalline dust-like particles

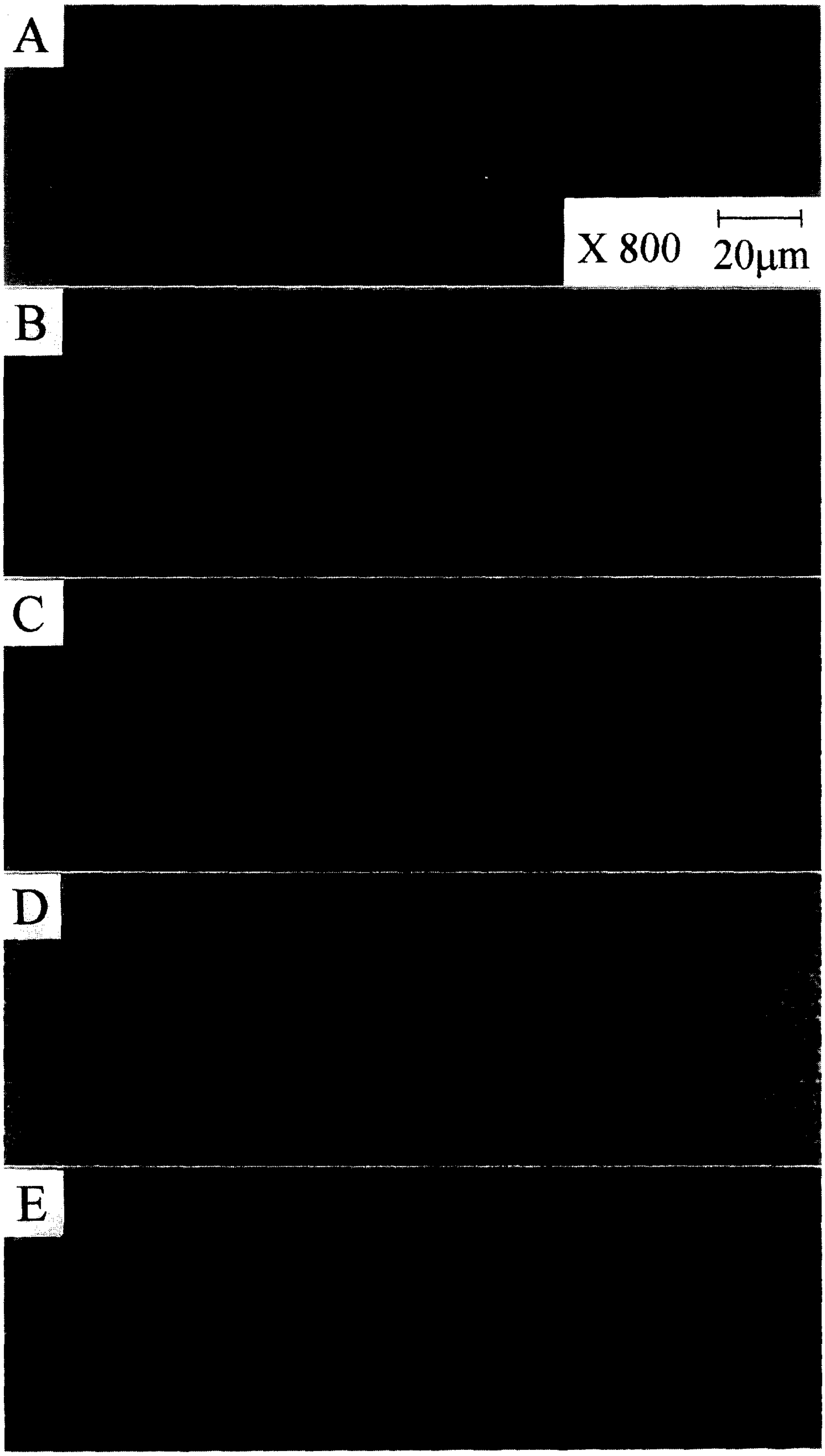

Figure 5 Optical micrographs of 50°C–THF cast PC/PMMA blend film samples of 50/50 composition with thickness: (A) 8, (B) 18, (C) 23, (D) 28, and (E) 36 μm, respectively

located within the segregated PC phase domain. Thus, PC crystals could be easily distinguished from the relatively larger scales of phase separation-induced heterogeneity. If magnifications were great enough, the 'white dust-like particles' within the PC-rich phase were actually shown to be tiny spherulites with Maltese cross. In this study, we also performed separate experiments on PC/PMMA films (large thickness, THF cast 50°C) that

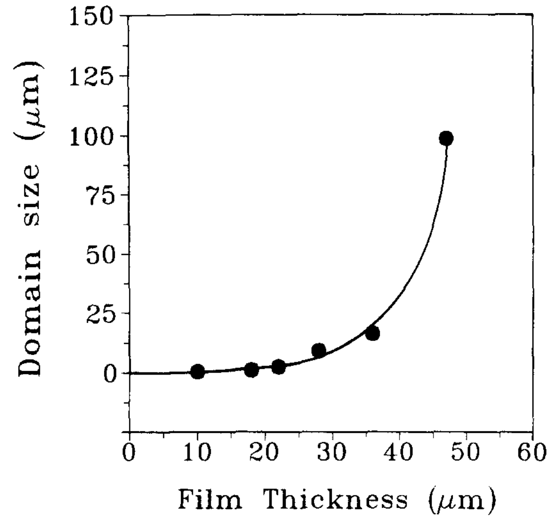

Figure 6 Estimated domain sizes (viewed perpendicular to sample film) of the 50°C-THF cast blend sample (50/50 composition) as a function of film thickness

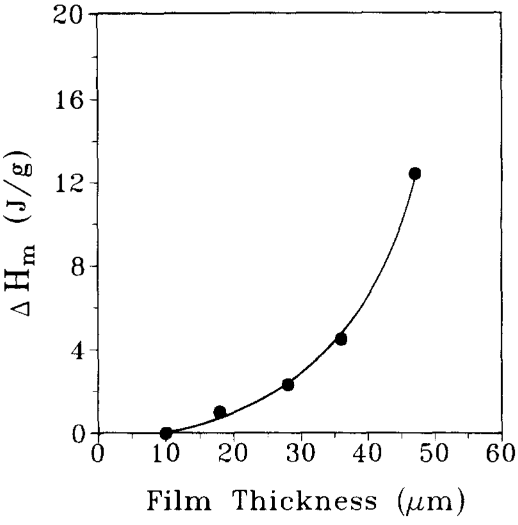

Figure 8 PC crystallinity, as measured indirectly by the endothermic melting peak in d.s.c. thermograms (based on unit weight of total blend), for PC/PMMA blend (50/50 composition) of various thickness

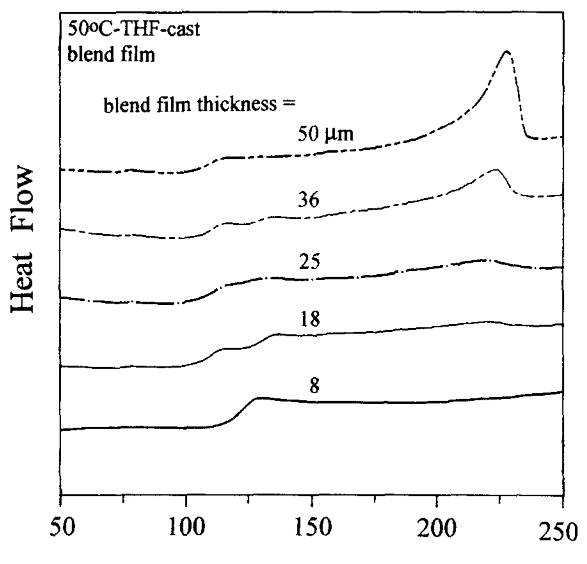

Figure 7 D.s.c. thermograms of the 50°C-THF cast PC/PMMA blends (50/50 composition) of various thicknesses, as indicated on the graph

were expected to develop PC crystallinity. After extended annealing at high temperatures (160°C or so), these 'tiny white particles' grew larger and spherulites with easily identified Maltese cross were identified.

Figure 7 shows the d.s.c. thermograms of the 50°C-THF cast PC/PMMA blends of various thicknesses. The d.s.c. thermogram for the thinnest blend sample of 8 μm exhibits a clearly single T_g. It is this type of PC/PMMA samples that have been labelled by some investigators as 'miscible' in the literature. The so-called 'miscibility', however, has been questioned. It has been demonstrated by SEM that micro heterogeneity of a scale of 0.3–0.5 μm does exist in the transparent thin PC/PMMA blends (10 μm or less in film thickness) cast with THF at 50°C, which also exhibit one single T_g upon d.s.c. determination[2]. With an increase in the blend film thickness, however, the scales of heterogeneity increase rapidly, and the 50°C-THF cast blends turn to a gradually cloudy appearance. With the increase in film thickness, two T_g's are observed in blend films of thickness larger than 18 μm. With further increase in thickness, a PC melting peak associated with PC crystallinity stars to appear in the thermogram. For the blend sample of the highest thickness, the T_g of the PC phase in this blend sample is much suppressed by the crystallinity, and only the T_g of the PMMA phase is observed at about 105°C.

Figure 8 shows the PC crystallinity as measured by the melting peak area in the d.s.c. thermograms for the blends of various thickness. Apparently, the PC melting peak endotherm area increases with the increase in the film thickness. This is a clear proof that both the scales of phase separation (in *Figure 6*) and extents of solvent-induced PC crystallization increase with film thickness. The same kinetic factor of solvent evaporation rate governs the phase separation as well as solvent-induced PC crystallization. As the rate of evaporation is increased (as in thin films), chain entanglement is more rapidly trapped into a temporarily homogeneous state. In the meantime, PC chains do not have enough time to crystallize. Thus, when freshly cast from the THF solution into thin films at 50°C, an amorphous homogeneous blend was obtained.

By using an oligomeric epoxy as a co-solvent for PC and PMMA for lowering the T_g of the blend and enhancing the segmental mobility of polymer chains, our earlier published work[1] has demonstrated that at relatively low isothermal temperatures of 68°C, the epoxy-solubilized PC/PMMA blends can exhibit a distinct phase-separated morphology, which normally occurs only at T_g's above the constituting components (110 and 150°C, respectively for PMMA and PC). That study further supported that blend heterogeneity PMMA/PC is governed by the kinetic factors and that the equilibrium state of the blend is phase separation, whose scales of heterogeneity is kinetically dependent.

CONCLUSION

This study further furnished optical microscopy and d.s.c. results revealing the fact of film thickness-dependent domain sizes, which should help provide yet stronger evidence that the blends were not of a single-phase nature with thermodynamic molecular mixing, but that the phase behaviour was governed by the kinetics of solvent evaporation rate. Faster rates of evaporation in thin blend films (10 μm or less) resulted in higher extents of temporarily trapped PC/PMMA chain entanglement, which thus induced smaller scales of heterogeneity. Although these thin blends exhibited a single T_g and optically homogeneous, our earlier SEM study[2] has shown that the solvent-cast 'transparent' blends of PC/PMMA of thickness equal to 10 μm or less are actually not 'miscible', but display micro-heterogeneity of about 100–300 Å (0.1–0.3 μm) in domain sizes. It is only because the micro-heterogeneous domains are so small that the blends exhibit single T_g and optically appear transparent. On the other hand, the thicker blends cast from the same solvent of THF at the same temperature of 50°C exhibited two T_g's and possessed much greater scales of heterogeneity. Thicker-film blends also developed solvent induced PC crystallinity, which could suppress the T_g of the PC phase. This must be taken into consideration in interpreting the glass transition behaviour of PC/PMMA blends with crystallinity.

Other than the thin PC/PMMA blends cast with THF at 50°C, which had sub-micron heterogeneity and possessed one single T_g, the optical microscopy revealed that all otherwise cast blends exhibited heterogeneity of scales much above 1 μm. Also, for THF solvent-processed PC/PMMA blends, temperatures other than 50°C or near can also result in a phase-separated blend. Even for the thin-film PC/PMMA blends, suggestion of equilibrium phase separation behaviour has been proposed and tentatively verified in our previous studies[1,2]. However, by examining thicker PC/PMMA blend films all processed with THF at the same temperature of 50°C, this study has shown that given the same thermodynamic factors, such as composition, temperature, and solvent type, the scales of heterogeneity in the blends could be changed significantly. Then, if the phase behaviour of PC/PMMA is thermodynamically immiscible, all thermodynamic factors such as solvent types and temperature can only change the scales of heterogeneity. Also, given the same thermodynamic factors, kinetic factors can influence the scales of phase heterogeneity.

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