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Miscibility and phase behaviour of methyl methacrylate copolymer and polycarbonate blends

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Transparent blends were obtained by melt mixing with a copolymer of methyl methacrylate, 2,4,6-tribromophenyl methacrylate, and cyclohexyl methacrylate (MBC1) and polycarbonate (PC). Differential scanning calorimetry and dynamic mechanical measurements suggested that the blends are thermodynamically miscible. To investigate the miscibility quantitatively, we measured the cloud point curve, from which LCST phase behaviour of the MBC1/PC blend was confirmed below the thermal degradation temperature. Phase demixing process of the MBC1/PC (20/80) blend was measured by light scattering to estimate the spinodal temperature. By analysis with the linearized theory on spinodal decomposition and the mean field theory on free energy, the spinodal temperature was elevated to be 266.4°C. This result was in good agreement with that of the cloud point measurement. From the point of view of polymer–polymer miscibility, the contribution of comonomer unit in MBC1 was discussed. © 1997 Elsevier Science Ltd. All rights reserved.

(Keywords: methyl methacrylate copolymer; polycarbonate; cloud point curve)

INTRODUCTION

Poly(methyl methacrylate) (PMMA), having the highest transparency among the familiar commercial plastics, provided various industrial applications such as optical fibre, films, disks and grating. However, PMMA possesses some disadvantages for practical uses, e.g. brittleness and high water absorption. To improve these properties, many efforts for modification of PMMA have been made by copolymerization and polymer blend. Toughness of PMMA is conventionally developed by inclusion of rubbery phase, added as the core-shell type impact modifier[1], which is designed to have small particle size and isorefractive index to PMMA, in order to maintain high transparency. On the other hand, a homogeneous polymer mixture is also considered to contribute to the improvement of PMMA without a decrease in transparency. Among a number of miscibility studies on PMMA blends[2–8], the mixture of PMMA and bisphenol-A polycarbonate (PC) is one of the most deeply studied polymer pairs[9–16]. This may be attributed to the excellent properties of PC, including outstanding ductility, low water absorption and high glass transition temperature T_g. However, according to the recent report, the two-phase region prevails in PMMA/PC blends[9], and therefore one cannot obtain homogeneous PMMA/PC blend by melt mixing, which is easily used for industrial production. To promote miscibility of PMMA/PC blend by controlling the interaction energies in the blend, one can employ MMA copolymer instead of PMMA. It has been known that phenyl methacrylate (PMA) is an effective monomer unit to promote the miscibility of MMA copolymer with PC, and poly(PMA-*co*-MMA)/PC blends exhibit lower critical solution temperature (LCST) higher than 250°C[17], which is high enough to prepare a homogeneous mixture by melt mixing. However, this copolymer has been shown to possess poor thermal stability at the melt mixing or processing temperatures because of high PMA content (≈ 40 wt%).

In this study, we show that a copolymer of MMA, 2,4,6-tribromophenyl methacrylate (TBPM) and cyclohexyl methacrylate (CHMA), MBC1, is miscible with PC, providing thermally stable blends at the melt mixing temperature. The miscibility and the thermal stability of MBC1/PC blends are measured by differential scanning calorimetry (d.s.c.) dynamic mechanical measurement (DMA) and thermogravimetric analysis (t.g.a.). In order to investigate the miscibility quantitatively, a cloud point curve is measured. Furthermore, phase demixing processes from the single phase state are measured by time-resolved light scattering to determine the spinodal temperature. We discuss which monomer unit promotes better the miscibility of PMMA/PC blends. Finally, the miscibility of poly(TBPM-*co*-MMA) and PC is compared with that of poly(PMA-*co*-MMA) and PC.

EXPERIMENTAL

Specimens

The MMA copolymer, MBC1 was produced by Kuraray Co., Ltd. MBC1 is comprised of 70 wt% methyl methacrylate, 20 wt% 2,4,6-tribromophenyl methacrylate, and 10 wt% cyclohexyl methacrylate. The number-average molecular weight, $\overline{M}_n$ and the polydipersity index, $\overline{M}_w/\overline{M}_n$ are 4.5×10^4 and 2.0,

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respectively. A commercially available PC, L1250, whose $\overline{M}_n$ and $\overline{M}_w/\overline{M}_n$ measured by gel permeation chromatography (g.p.c.) in our laboratory were 2.3×10^4 and 2.0 respectively, was supplied by Teijin Chemical Co., Ltd. MBC1/PC blends were prepared by melt mixing at 230°C using a Mini-Max Injection Moulder (model CS-183, Custom Scientific Instruments, Inc.), and then pressed to be an appropriate shape at 230°C for the measurements.

Poly(TBPM-*co*-MMA) and poly(PMA-*co*-MMA) were synthesized by free radical polymerization and purified in the ordinary way. Characteristics of the obtained copolymers are summarized in *Table 1*.

D.s.c., T.g.a. and DMA

D.s.c. and t.g.a. measurements were carried out on TC11 and TC10A, respectively (Mettler Inc.) under a nitrogen atmosphere at a heating rate of $10° \mathrm{min}^{-1}$. Thermal degradation temperature was defined as the temperature at which the sample weight loss started.

In DMA, temperature dependence of dynamic storage modulus, E' and tan δ were measured on a Rheospectler (Rheoroji Inc.) in a tensile mode at a heating rate of $3° \mathrm{min}^{-1}$ and a frequency of 11 Hz.

Cloud point and light scattering measurements

In cloud point measurement, transparent blend films cast from tetrahydrofuran solution containing 5 wt% total polymer at 20°C and then dried under a vacuum of 10^{-4} mmHg for 24 h were kept at an appropriate temperature for 15 min followed by a rapid quench into ice water. The elevated temperature was judged to be at the two-phase region if the obtained sample was seen to be cloudy by the naked eye.

Time-resolved light scattering was measured on the apparatus shown in *Figure 1*. A He–Ne laser was exposed to a sample film vertically and the angular dependence of the scattered light was measured by a photomultiplier at an appropriate time interval. The sample in the heating block was kept at a constant temperature within an error of 0.2° during the measurement. The measurements were carried out at 268, 270, 272, 274, and 275°C.

RESULTS AND DISCUSSION

Miscibility of MBC1/PC blends

In *Figure 2* are shown the d.s.c. thermograms of the MBC1/PC blends prepared by melt mixing at 230°C, indicating a single glass transition at all compositions. The T_g of the MBC1/PC blends, summarized in *Table 2* changed monotonically between the T_g of MBC1 and that of PC, with blend composition. *Figure 3* shows the temperature dependence of E' and tan δ on the blend composition, where the arrows in the figure indicate the peak positions of tan δ curve. E' began to drop around the T_g, which decreased with an increase in the MBC1 content of the blends, and a single peak of tan δ, which shifted to lower temperature with an increase in the MBC1 content, was observed. These results suggest that the MBC1/PC blends melt-mixed at 230°C are homogeneous and this temperature is at a single-phase region in the phase diagram.

Figure 4 shows the cloud point curve, T_g and thermal degradation temperature as a function of blend composition. The thermal degradation temperature is also listed in *Table 2*. In the figure, the crosses designate compositions at which the cast film become opaque after annealing for 15 min at the indicated temperature,

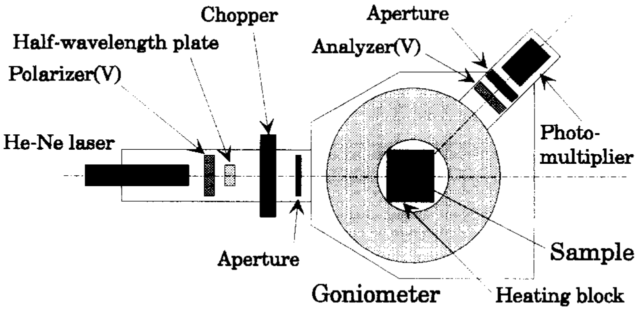

Figure 1 Light scattering apparatus used for this study

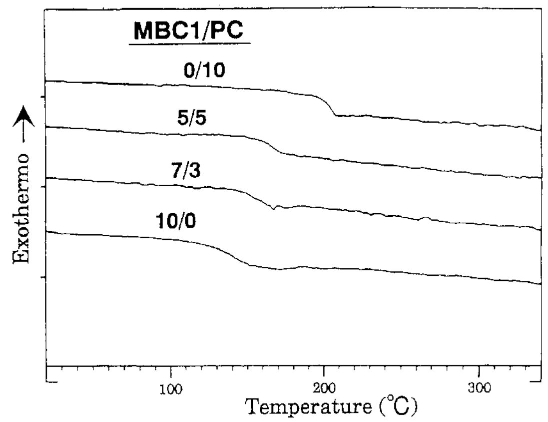

Figure 2 D.s.c. thermograms of MBC1/PC blends prepared by melt mixing at 230°C

Table 1 MMA copolymers used in this study

	TBPM or PMA[a]		$\overline{M}_n$[b]	
Code	(mol%)	(wt%)	($\times 10^{-5}$)	$\overline{M}_w/\overline{M}_n$[b]
BM-1[c]	2.7	10.0	4.20	2.7
BM-2[c]	6.8	22.5	3.41	2.1
BM-3[c]	12.9	37.1	2.94	2.0
BM-4[c]	18.6	47.7	2.11	2.6
PM-1[d]	6.5	10.0	3.12	2.1
PM-2[d]	12.8	19.2	3.43	2.2
PM-3[d]	19.4	28.1	4.22	2.0
PM-4[d]	32.1	43.3	4.04	2.3

[a] Measured by ^{1}H n.m.r. in $CDCl_3$
[b] Measured by g.p.c. with tetrahydrofuran
[c] Poly(methyl methacrylate-*co*-2,4,6-tribromophenyl methacrylate)
[d] Poly(methyl methacrylate-*co*-phenyl methacrylate)

Table 2 Thermal parameters of MBC1/PC blends

PC fraction	T_g(°C)[a]	T_d(°C)[b]
0.0	117	305
0.1	122	310
0.3	127	315
0.5	132	326
0.7	139	336
0.9	146	343
1.0	151	365

[a] Glass transition temperature
[b] Thermal degradation temperature

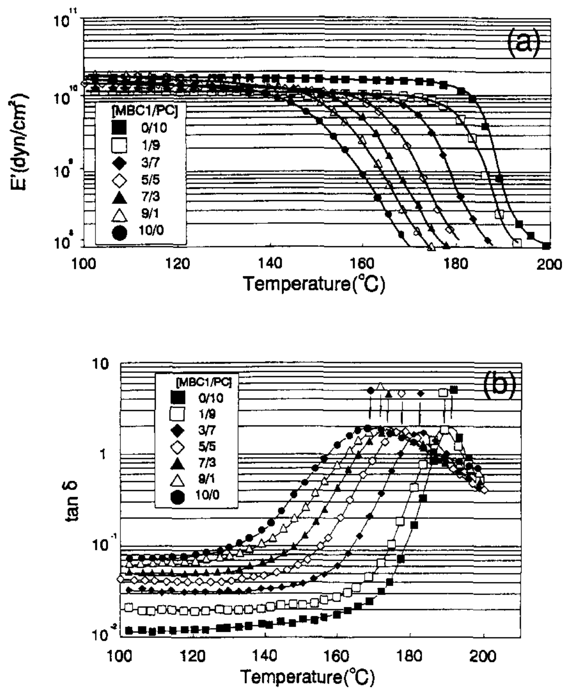

Figure 3 Temperature dependence of E' and tan δ of MBC1/PC blends prepared by melt mixing at 230°C

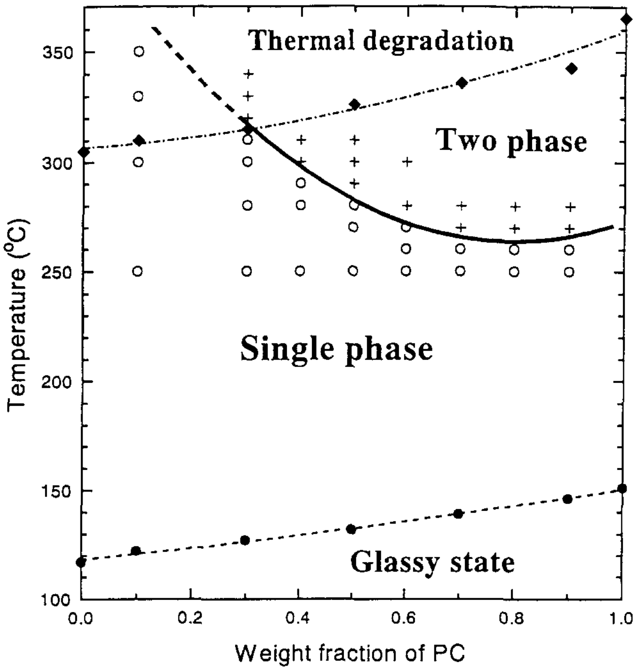

Figure 4 Phase behaviour of the MBC1/PC blend designated by cloud point curve, T_gs, and thermal degradation temperatures

while the open circles designate compositions at which the cast film remained transparent after annealing. The cloud point curve thus obtained indicated LCST phase behaviour for the MBC1/PC mixture.

Spinodal temperature

There are some reports on the phase behaviour of PMMA/PC blends including cloud point measurements. Nishimoto *et al.* pointed out that homogeneous PMMA/PC blends phase-separate so slowly that the cloud point is seriously affected by the annealing time[9]. We measured the phase demixing process of MBC1/PC blend in order to estimate spinodal temperature[18,19]. The measurement was carried out at the composition of MBC1/PC = 20/80. *Figure 5* shows the time variation of scattering intensity at 274°C. The film sample used here was prepared by melt mixing and hot press at 230°C. As seen in the figure, the scattering intensity first increased with time and a peak appeared after 765 s, and after that, the peak shifted to smaller angle and the peak intensity increased. This characteristic change of the light scattering profile seemed to be similar to that of spinodal decomposition (SD)[19]. The results were then analysed based on the linearized theory of SD of Cahn[20]. *Figure 6* illustrates the logarithmic plots of scattering intensities against time according to the following equation (1)

$$I = I(t = 0)\exp[2R(q)t] \qquad (1)$$

$$R(q) = -Mq^2\left(\frac{\partial^2 f}{\partial c^2} + 2\kappa q^2\right) \qquad (2)$$

where I, q, and t are scattering intensity, wave number, and time, respectively. The rate constant of growth in scattering intensity is expressed by equation (2), where f,

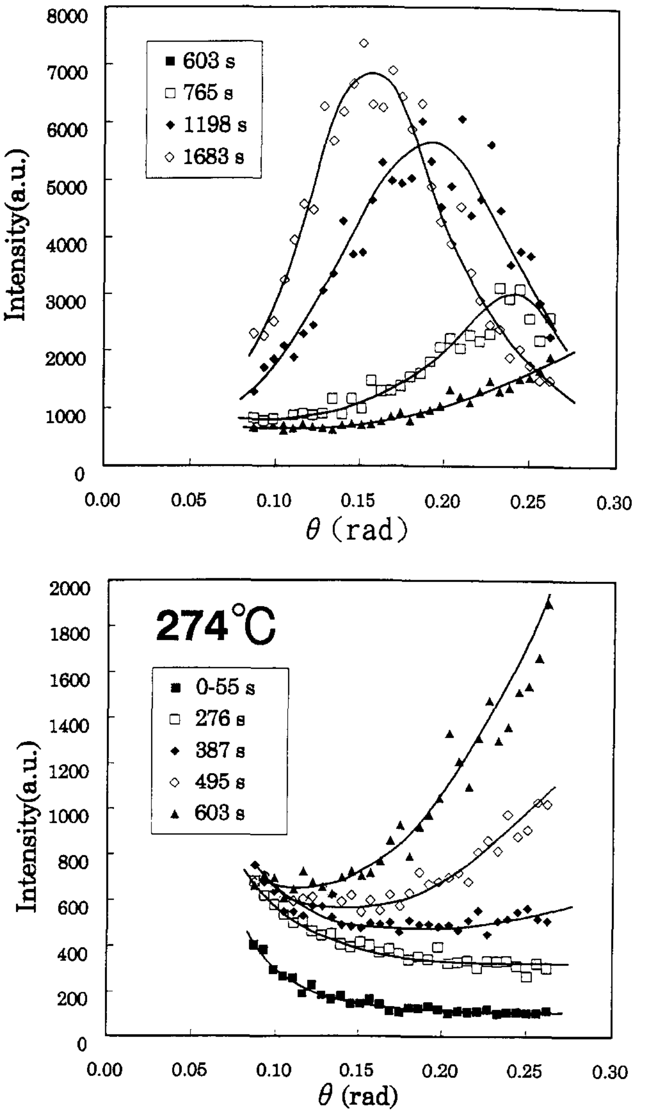

Figure 5 Time variation of light scattering profile of MBC1/PC (20/80) blend at 274°C

c, κ, and M are the free energy, the concentration, the energy gradient coefficient, and the diffusion mobility, respectively. As shown in *Figure 6*, a linear growth regime of scattering intensity was observed for every q, and a half of the line slope was plotted in *Figure 7*, according to equation (2). Except for the data at 275°C, $R(q)$ was well approximated by the straight line, and the kinetic parameters D_0 and q_m were evaluated in *Table 3*, where D_0 and q_m are the interdiffusion coefficient and the wave number with the largest growth rate of scattering intensity defined as follows

$$D_0 = M\left(\frac{\partial^2 f}{\partial c^2}\right) \tag{3}$$

$$q_m^2 = -\frac{1}{4\kappa}\left(\frac{\partial^2 f}{\partial c^2}\right) \tag{4}$$

The plot of $R(q)$ at 275°C exhibited curvature as shown in *Figure 7*. The phase demixing at this temperature seemed to be too fast to observe the early stage of SD to which the linearized theory can be applied.

According to the mean field theory on polymer blends[19], D_0 is expressed by the following equation

$$D_0 \approx M \mid T_s - T \mid \tag{5}$$

where T_s is the spinodal temperature. Therefore a plot of D_0 vs T should yield a straight line when the temperature dependence of M is negligible. In *Figure 8* is shown the plot of D_0 against temperature giving a fairly straight line, from which T_s was extrapolated to be 266.4°C. Mean field theory on polymer blends predicts the linear dependence of q_m^2 on T, and T_s can also be obtained from the plot of q_m^2 vs T. However, the temperature dependence of the obtained q_m^2 seemed too complicated to estimate T_s by extrapolation. This may be due to the experimental error in q_m.

The spinodal temperature of MBC1/PC (80/20) blend was thus deduced to be 266.4°C. Also, the miscibility gap of the same blend was shown to exist between 260 and 270°C from the cloud point measurement. These results seem to be in good agreement with each other, and therefore the cloud point curve in *Figure 4* is considered to be reliable enough to describe the phase behaviour of MBC1/PC blends. Homogeneous mixtures of MBC1 and PC are expected to be obtained by melt mixing at the temperature below the curves of cloud point and thermal degradation if the effect of shear flow on phase behaviour is negligible[21].

Contribution of comonomers to miscibility

MBC1 contains two kinds of monomer other than MMA, i.e. TBPM and CHMA. The next question is which monomer unit promotes better miscibility of MMA copolymer/PC mixtures. According to the literature, poly(CHMA-*co*-MMA) and PC mixture exhibits

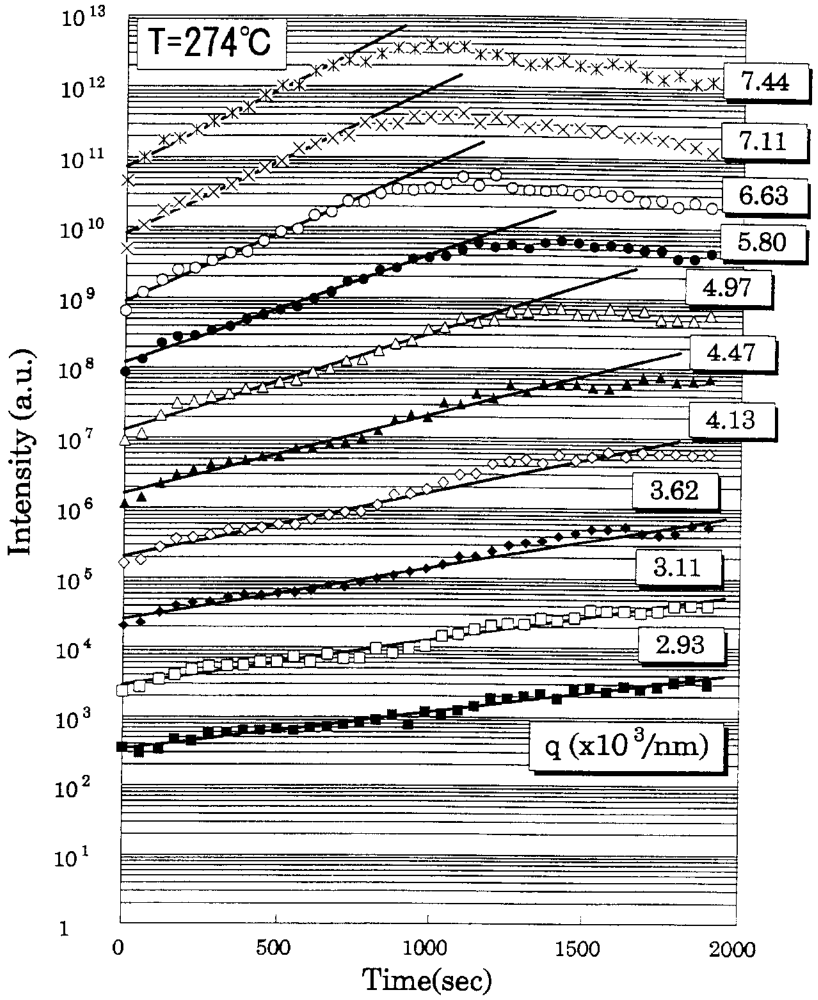

Figure 6 Logarithmic plots of the scattering intensity in *Figure 5* against time according to equation (1)

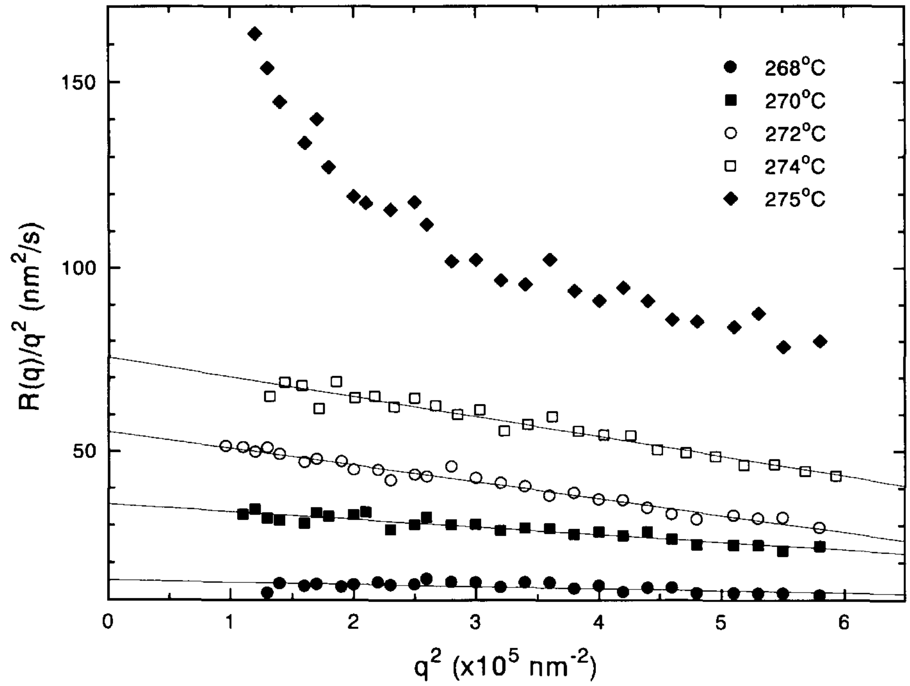

Figure 7 Plots of a half of the line slope in *Figure 6* according to equation (2)

Table 3 Kinetic parameters of MBC1/PC (20/80) blend obtained by LS

Temperature (°C)	$-D_0$ ($nm^2 s^{-1}$)	q_m ($\times 10^3 nm^{-1}$)	q_m^2 ($\times 10^5 nm^{-2}$)
268	15.3	11.8	13.9
270	35.7	9.36	8.76
272	55.3	7.81	6.10
274	75.6	8.38	7.02

LCST phase behaviour, and the LCST increases up to about 200°C, when the CHMA contents are between 20 and 30 wt%[17]. This seems to indicate that CHMA can promote somewhat the miscibility of MMA copolymer with PC. We then considered the TBPM unit to play an important role for the miscibility of MBC1/PC blend. The change in miscibility of poly(TBPM-*co*-MMA)/PC (50/50) with TBPM content is shown in *Figure 9a*, which is a so-called miscibility window. The open circles and

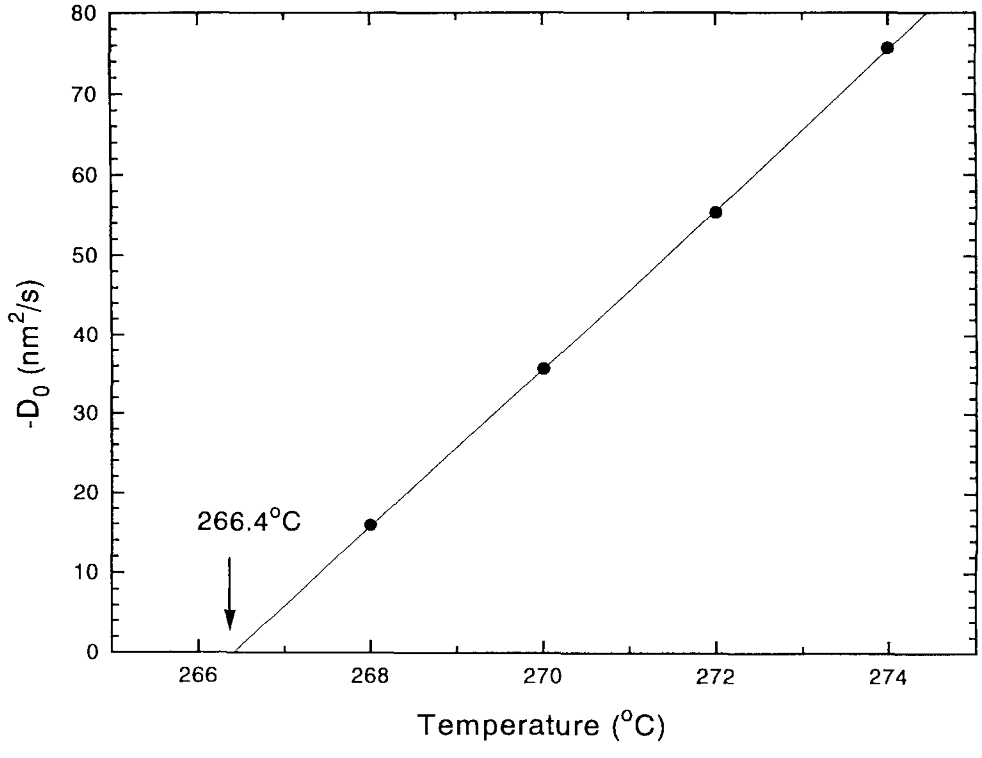

Figure 8 Evaluation of spinodal temperature of MBC1/PC (20/80) blend by the extrapolation with plot of D_0 and temperature based on the mean field theory

the crosses in *Figure 9* indicate transparent and cloudy blends after annealing for 15 min at the indicated temperature, respectively. The cloud point increased rapidly with an increase in TBPM content and reached 300°C at 15 wt% TBPM. Above this temperature, the curve in *Figure 9a* may not be reliable because of thermal degradation of the blends, but it suggests that TBPM unit promotes more effectively the miscibility of MMA copolymer/PC blend than CHMA.

The miscibility of the poly(TBPM-*co*-MMA)/PC blend was compared with that of the poly(PMA-*co*-MMA)/PC blend. *Figure 9b* shows the miscibility window of poly(PMA-*co*-MMA)/PC (50/50) blend measured in this study. The cloud point of poly(PMA-*co*-MMA)/PC increased gradually with PMA content, but did not reach 300°C at 40 wt% PMA. This result is in good agreement with that of the previous study[17], indicating that TBPM unit promotes the miscibility of MMA copolymer/PC blend more effectively than PMA.

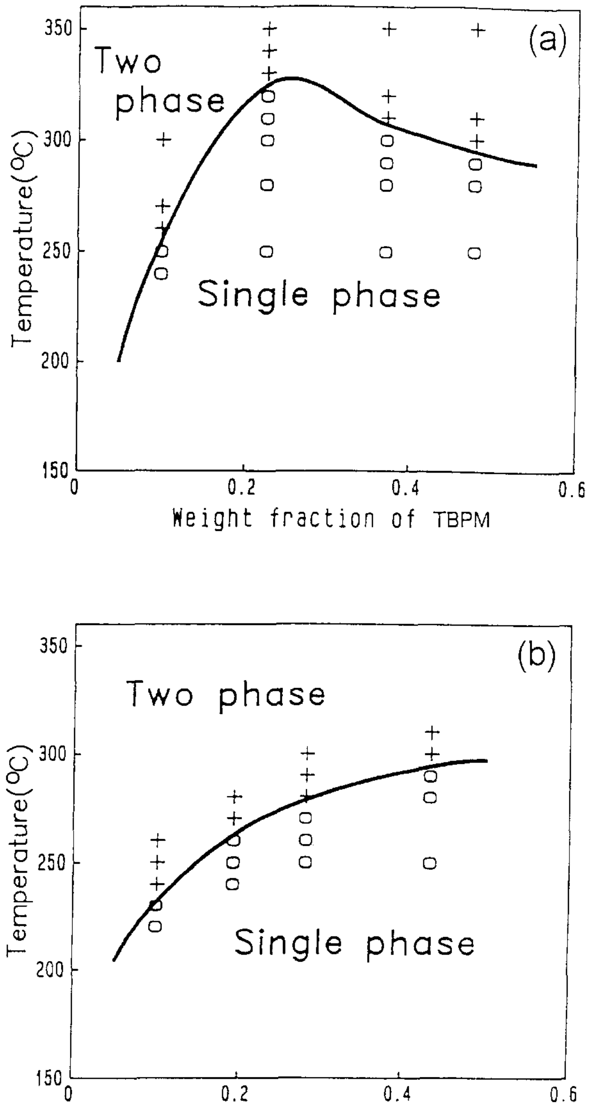

Figure 9 Changes in cloud point of MMA copolymer/PC (50/50) blends with comonomer content. Comonomer: (a) TBPM (b) PMA

According to the miscibility consideration for copolymer containing blends[22], the segmental interaction energy B_M for A–B copolymer and C homopolymer is expressed as follows

$$B_M = \phi_A B_{C\text{-}A} + (1 - \phi_A) B_{B\text{-}C} - \phi_A (1 - \phi_A) B_{A\text{-}B} \quad (6)$$

where $B_{i\text{-}j}$ corresponds to the interaction energy between *i* and *j* monomer units, and ϕ_A is the volume fraction of A monomer unit in the copolymer. $B_{i\text{-}j}$ is related to the interaction parameter, $\chi_{i\text{-}j}$

$$\chi_{i\text{-}j} = \frac{B_{i\text{-}j} RT}{V} \quad (7)$$

where V is the reference volume. In this case A, B and C correspond to the comonomer unit in MMA copolymer (COM), MMA, and PC monomer unit, respectively. Since a relatively small value, $B_{MMA\text{-}PC} = 0.03\text{–}0.05\,\mathrm{cal\,cm^{-3}}$ has been reported[23,24], equation (6) may be reduced to the following equation

$$B_M = \phi_{COM} B_{COM\text{-}PC} - \phi_{COM}(1 - \phi_{COM}) B_{COM\text{-}MMA} \quad (8)$$

This equation predicts that the miscibility state appears when $B_M < 0$ in the case of infinite molecular weight polymers. Since $B_{COM\text{-}MMA}$ should be a positive value because of the miscibility windows in *Figure 9*, a relationship with the parameters on the right hand of equation (8) to satisfy $B_M < 0$ is shown to be $B_{COM\text{-}PC} < B_{COM\text{-}MMA}$. To our knowledge, the specific interactions of $B_{COM\text{-}PC}$ and $B_{COM\text{-}MMA}$ have not been known so far, and $B_{i\text{-}j}$ may be written as equation (9), where δ_i and δ_j are solubility parameters of *i* and *j* monomer units, respectively.

$$B_{i\text{-}j} = (\delta_i - \delta_j)^2 \quad (9)$$

Since δ_{MMA} and δ_{PC} have been reported to be $9.1\,\mathrm{cal^{1/2}\,cm^{-3/2}}$ and $10.6\,\mathrm{cal^{1/2}\,cm^{-3/2}}$ respectively[23], $B_{COM\text{-}PC} < B_{COM\text{-}MMA}$ is rewritten to be $\delta_{COM} < 9.85\,\mathrm{cal^{1/2}\,cm^{-3/2}}$. This means that MMA copolymer should be miscible with PC if the δ of comonomer is more than $9.85\,\mathrm{cal^{1/2}\,cm^{-3/2}}$, and the larger δ of the comonomer, the more miscible of the blend. Therefore, it is expected that the δ values of TBPM and PMA should be $\delta_{TBPM} > \delta_{PMA} > 9.85\,\mathrm{cal^{1/2}\,cm^{-3/2}}$.

CONCLUSIONS

The MMA copolymer, MBC1 was shown to be thermodynamically miscible with PC at 230°C irrespective of blend composition by d.s.c. and the dynamic mechanical measurements. The result of cloud point measurement suggested that MBC1/PC blend exhibits LCST phase behaviour. To estimate the spinodal temperature around the LCST, phase demixing process of 20/80 MBC1/PC was measured by light scattering. The spinodal temperature was evaluated to be 266.4°C and was in good accordance with the result of the cloud point measurement. This suggested that the obtained cloud point curve is reliable enough to describe the phase behaviour of the MBC1/PC blend. It was shown that TBPM plays an important role for the miscibility of the MBC1/PC blend, and the TBPM unit promotes more effectively the miscibility of MMA copolymer/PC than PMA. This result was discussed based on segmental interaction energies between monomer units and the solubility parameter theory. We are going to report the mechanical properties of homogeneous MBC1/PC blends, which are comprised of a brittle and a ductile polymers, in the following paper.

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