New miscibility phenomena in blends of polycarbonate with poly(styrene-co-methacrylic acid)

Saburo Akiyama, Koji Ishikawa and Hiroshi Fujiishi

Laboratory of Chemistry, Faculty of General Education, Tokyo University of Agriculture and Technology, 3-5-8 Saiwai-cho, Fuchu, Tokyo 183, Japan

The miscibility between bisphenol A polycarbonate (PC) and poly(styrene-co-methacrylic acid) (P(S-MAA)) has been studied via theoretical calculation and glass transition (T_g) behaviour. This blend had an upper critical solution temperature type of phase diagram. Also, at a fixed blend ratio of PC/P(S-MAA), a new 'miscibility valley' phenomenon was found from both experiments and calculation, in contrast to the previous 'miscibility window'. Miscibility of the blends was judged from the cloud points by means of photometry and also from the customary criterion of the T_g behaviour obtained by differential scanning calorimetry.

INTRODUCTION

Studies of polymer blends have been summarized in the literature[1-3], and have included work on polymer–polymer miscibility. Recently, reports on miscible binary blends have increased noticeably in homopolymer/random copolymer systems[4-6]. Random copolymers thus play an effective role in obtaining miscible blends. Most miscible polymers tend to phase-separate at elevated temperatures. This lower critical solution temperature (*LCST*) behaviour is typical for miscible polymer blends. Some miscible polymers, however, exhibit upper critical solution temperature (*UCST*) type phase separation, even though both components have high molecular weight[7-9].

In this paper, the miscibility of bisphenol A polycarbonate (PC) and a random copolymer, poly(styrene-co-methacrylic acid) (P(S-MAA))[10-13], was investigated via theoretical calculation and glass transition behaviour. The miscibility between PC and P(S-MAA) can be interpreted by the recent idea of 'repulsion' in random copolymers in relation to a 'miscibility window'[6,14-16]. At the same time, a new phenomenon[5,10,13] named 'miscibility valley' caused by the *UCST* phase behaviour is found in this blend. The calculated and some experimental results are shown in relation to this 'miscibility valley'.

EXPERIMENTAL

Materials

The PC sample used in this study was 'Novalex 7025A' (Mitsubishi Kasel Co. Ltd), while P(S-MAA) was supplied by Dainippon Ink and Chemicals Inc. The molecular weight of PC is $M_v = 2.35 \times 10^4$, which was obtained by viscosity measurement with $[\eta] = 1.23 \times 10^{-4} M_v^{0.83}$. The molecular weights of P(S-MAA) were measured by gel permeation chromatography (g.p.c.) using a Showdex A-80M column with tetrahydrofuran (THF) at 40°C. These values are shown in *Table 1*.

Preparation of polymer blends

Polymer blends were prepared by solution mixing. PC and P(S-MAA) were dissolved in THF at about 5 wt% polymer concentration and stirred overnight. After precipitation in methanol, the polymer mixture flake was dried for 3 days at 0.1 mmHg and 90°C and then at a temperature higher than the glass transition temperatures of the blends for 1 h.

Density

Densities of samples were measured by the use of a density gradient column composed of water and glycerine. All measurements were carried out at 25°C. The average of four measurements for each sample was taken as the experimental value.

Differential scanning calorimetry

A Du Pont 910-DSC was used to obtain the glass transition temperature (T_g) with a heating rate of 10°C min^{-1}. For the phase diagram, blend samples were annealed for 1 h at desired temperatures and then quenched in liquid N_2 before measurement.

Photometry

A home-made thermophotometer[17,18] was used to determine cloud points in the phase diagrams. The heating rates were set at 2°C min^{-1}.

EXPERIMENTAL RESULTS

Density

The densities of the polymers used are tabulated in

Table 1 Physical properties of PC and P(S-MAA) polymers

| Sample | MAA (wt%) | T_g (°C) | Molecular weight ($\times 10^{-4}$) | | | Density (g cm^{-3}) |
			M_w	M_n	M_v	
PC		154			2.35	1.19
M-4	4	119	28.0	11.0		1.052
M-6	6	124	29.5	11.6		1.057
M-10	10	132	30.2	11.7		1.062
M-15	15	143	30.8	12.1		1.067
M-23	23	157	20.8	8.8		1.082
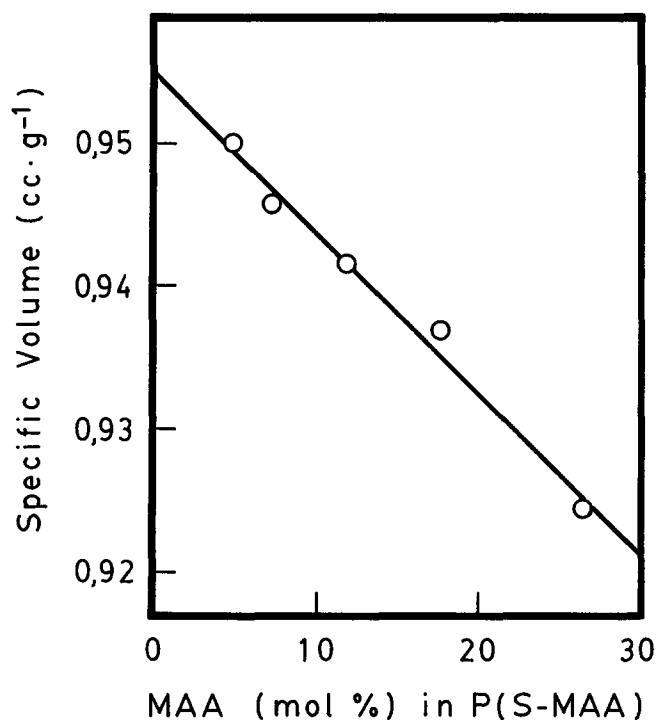
Figure 1 Specific volumes of P(S-MAA) plotted against mole per cent of MAA

Figure 2 Specific volumes of PC blends with P(S-MAA): (△) M-4; (□) M-6; (●) M-10; (▲) M-15; (■) M-23

Table 1, which were measured in this study. *Figure 1* shows specific volumes of P(S-MAA) plotted against mole per cent of methacrylic acid (MAA). It is clear that the specific volume of copolymer is a linear function of mole per cent of the copolymer[19]. By extrapolation of the straight line to 0 and 100 mol%, the specific volume of comonomer can be estimated to be 0.955 and 0.843 cm^3 g^{-1} for styrene (S) and MAA, respectively.

Figure 2 shows the specific volumes of the PC/P(S-MAA) blends with various MAA contents plotted against volume per cent of PC. The observed values are in excellent agreement with calculated ones based on the rule of volume additivity (full lines)). It can be concluded from measurements that the excess volume of mixing is very small.

Phase diagram

The cloud-point temperatures of PC/P(S-MAA) are shown in *Figure 3*. *UCST* behaviours are recognized for various MAA contents of copolymer used. The cloud-point temperatures of blends consisting of copolymer M-15 are lower than the corresponding values for M-4 and M-23. The *UCST* decreases as MAA content increases to 15 wt% but the trend is reversed for M-23
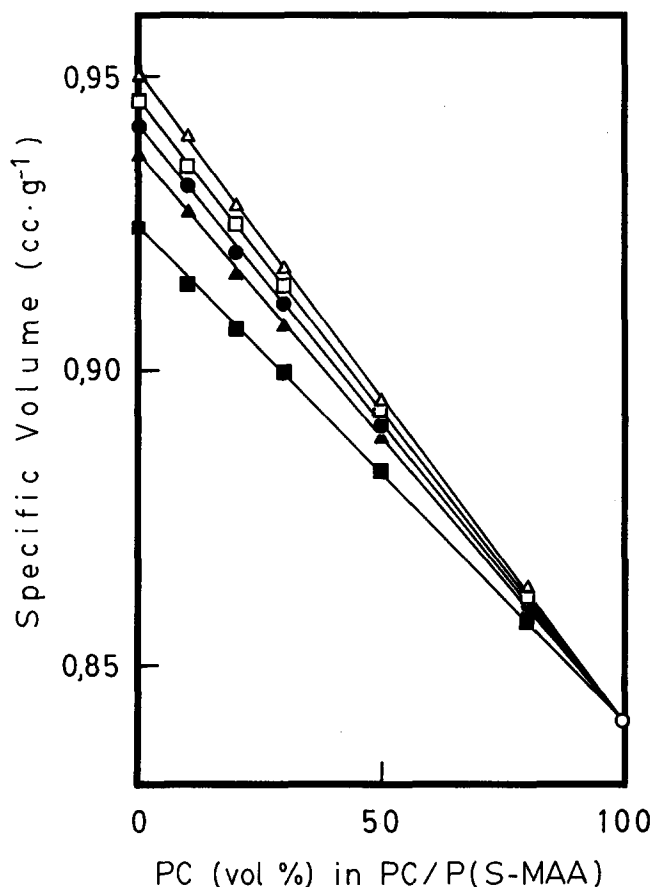
copolymer. An alternative representation of the phase diagrams depicted in *Figure 3* consists of plots of the cloud-point temperature as a function of copolymer composition[6,20] at different blend ratios, as shown in *Figure 4*. These phenomena are in contrast with the previous 'miscibility window'[6,14-16], which is obtained from *LCST* type behaviour. However, it is still partial and is not a perfect 'valley' due to the difficulty of making random copolymers containing more than 30 wt% of MAA.

The miscibility behaviours were also detected by T_g of annealed blend samples using d.s.c. Examples of the T_g behaviours for PC/P(S-MAA) are shown in *Figures 5* and *6* in which MAA contents and blend ratio are 10 wt%, 7/3 and 15 wt%, 8/2, respectively. The miscibility can be detected by single T_g or double T_g values on these d.s.c. curves. Every sample was annealed for 1 h at the respective temperatures. The resulting 'miscibility
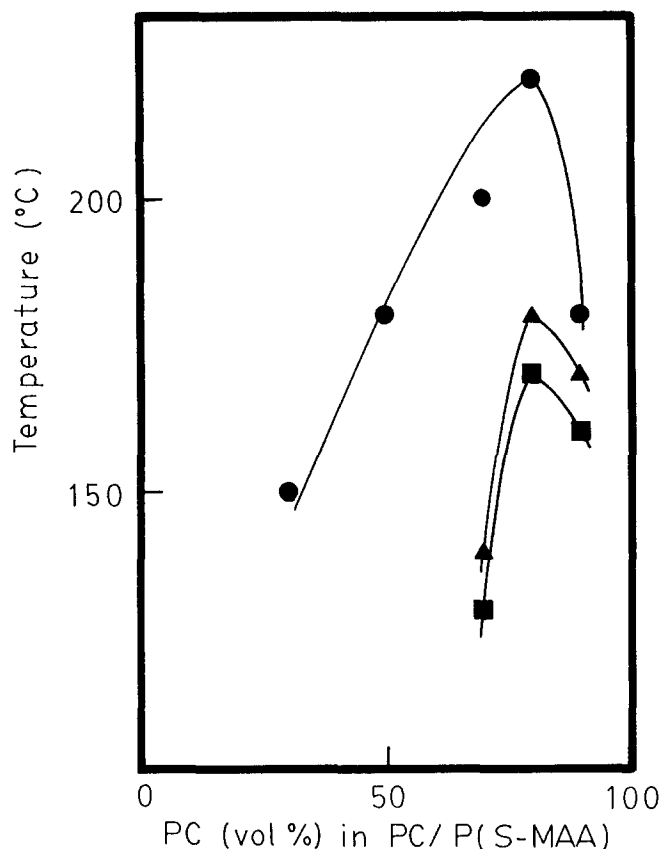
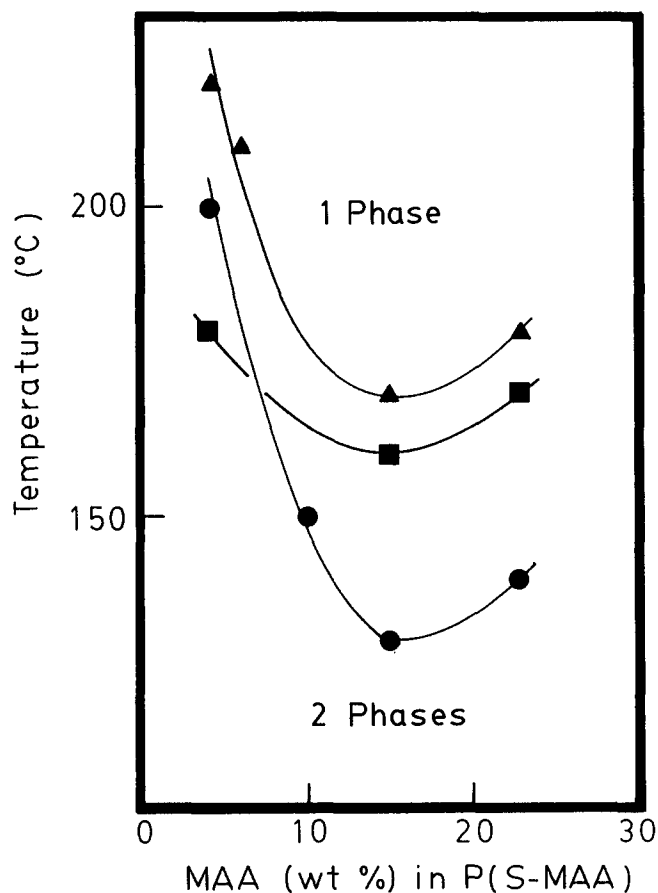**Figure 3** Phase diagrams of PC blends with P(S-MAA): (●) M-4; (■) M-15; (▲) M-23
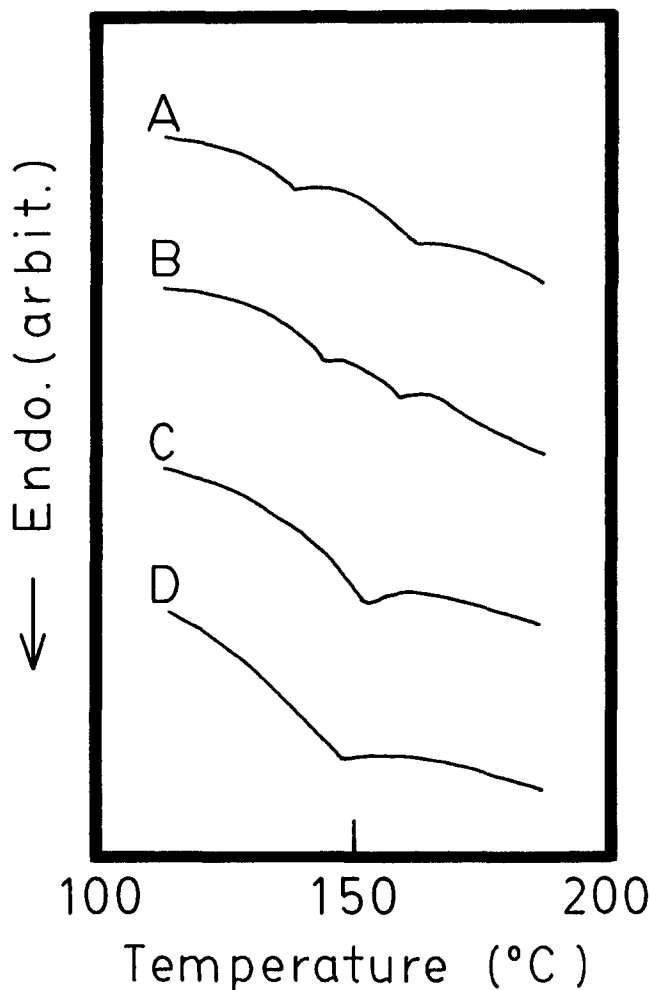

Figure 5 D.s.c. thermograms of PC/M-10 (7/3) blends annealed at (A) 140°C, (B) 180°C, (C) 200°C and (D) 220°C

valley' obtained from the T_g behaviour is also shown in *Figures 7* and *8*.

Using all cloud-point data, a three-dimensional stereo phase diagram can be drawn for the blend. From the above results, the three-dimensional phase diagram for PC/P(S-MAA) blend is shown in *Figure 9*, in which the upper side of curves represents a miscible stage. We name this new phenomenon a 'miscibility saddle'[10,12].

THEORETICAL DISCUSSIONS

For a binary mixture of two polymers, the free energy of mixing ΔG can be written[21]:

$$\Delta G/RT = (\phi_1/N_1)\ln\phi_1 + (\phi_2/N_2)\ln\phi_2 + \chi_{12}\phi_1\phi_2 \tag{1}$$

where R is the gas constant, T is temperature, ϕ_1 and ϕ_2 are the volume fractions of blend components in the blend. N_1 and N_2 are the degrees of polymerization of each polymer in terms of reference volume V_r, and χ_{12} is the net segmental interaction parameter between the two polymers.

The miscibility problem in general is simply an argument on the sign of χ_{12}, because of the very small combinatorial entropy contribution for a mixture of dissimilar polymers with high molecular weights. The following equation is more general with respect to the definition of miscibility[6,22]:

$$f = \chi_{12} - \chi_{12}^{crit} \tag{2}$$

Figure 4 Miscibility valley for PC/P(S-MAA) blends. Volume per cent of PC in the blends: (■) 90%; (▲) 80%; (●) 70%
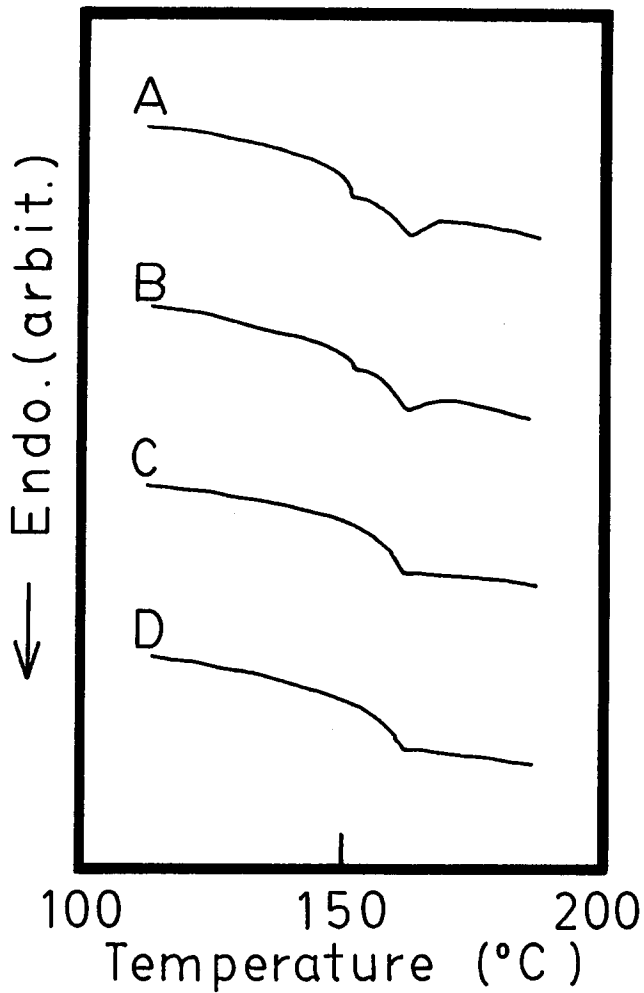
Figure 6 D.s.c. thermograms of PC/M-15 (8/2) blends annealed at (A) 150°C, (B) 180°C, (C) 200°C and (D) 220°C
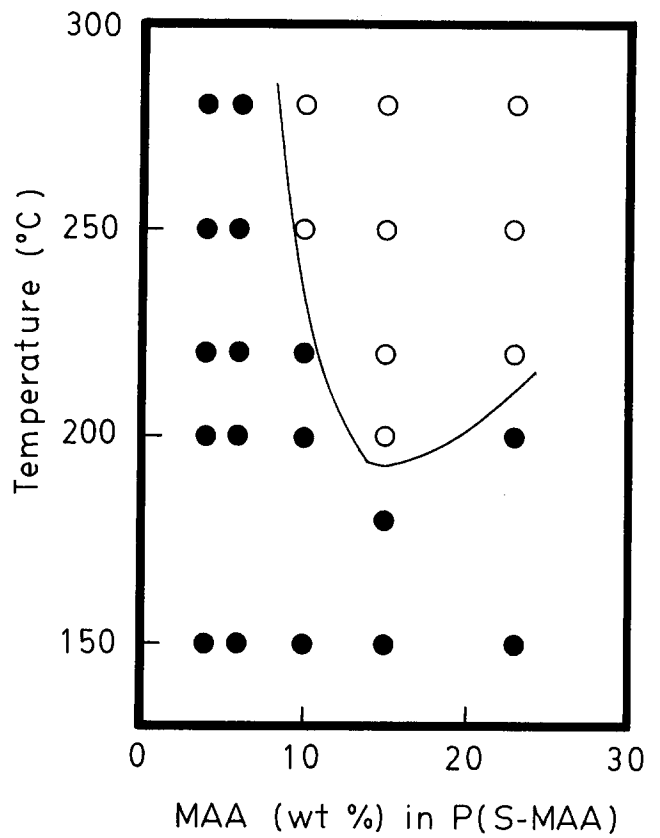

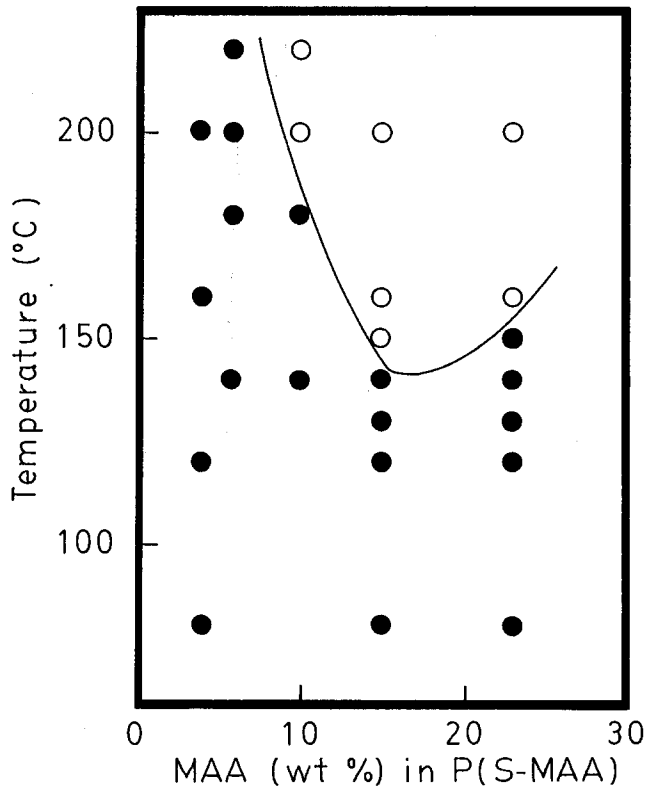**Figure 8** Miscibility valley for PC/P(S-MAA) blends (blend ratio 8/2):: (●) double T_g; (○) single T_g

Figure 7 Miscibility valley for PC/P(S-MAA) blends (blend ratio 7/3): (●) double T_g; (○) single T_g
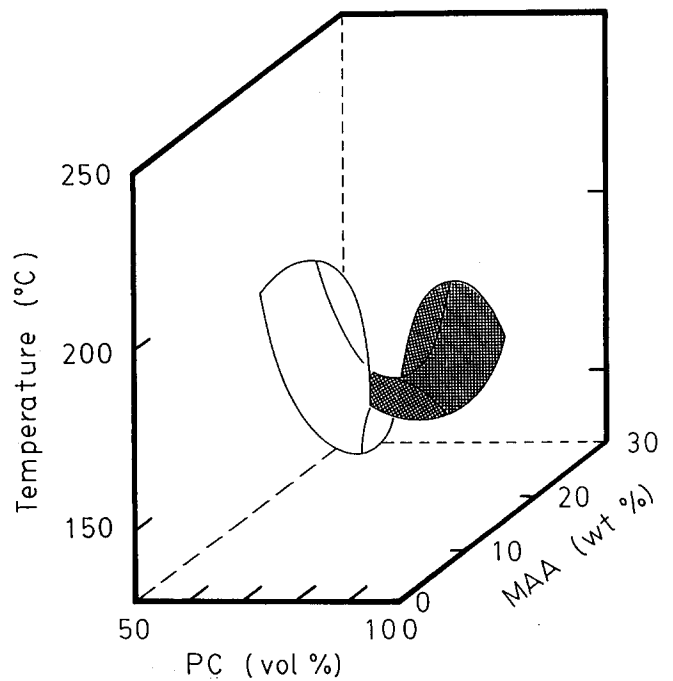
Figure 9 Miscibility saddle for PC/P(S-MAA) blends as a function of temperature, blend composition and copolymer composition. The upper side of the saddle is the miscibility region

where χ_{12}^{crit} is the critical value of χ_{12}, which is derived from the condition of a critical point. The value of χ_{12}^{crit} is obtained from equation (1) by applying the criterion[1-3]:

$$\partial^2 \Delta G / \partial \phi_2^2 = \partial^3 \Delta G / \partial \phi_2^3 = 0 \qquad (3)$$

which yields:

$$\chi_{12}^{\text{crit}} = \tfrac{1}{2}(1/N_1^{1/2} + 1/N_2^{1/2})^2 \qquad (4)$$

and

$$\phi_2^{\text{crit}} = 1/[1 + (N_2/N_1)^{1/2}] \qquad (5)$$

In equation (2), the regions of miscibility and immiscibility are defined by $f < 0$ and $f > 0$, respectively.

It is noticeable that equation (2) is available only at the critical point. For the overall blend ratio, a binodal and/or a spinodal curve is more appropriate for the judgement of miscibility. Thus, the condition of the binodal is used to judge miscibility in the following calculation.

Condition of the binodal curves

In order to calculate a binodal phase diagram we need to derive a chemical potential $\Delta\mu$. When the free energy of mixing ΔG is expressed as equation (1), the chemical potentials are given by[1-3]:

$$\Delta\mu_1 = RT[\ln \phi_1 + (1 - N_1/N_2)\phi_2 + \chi_{12}N_1\phi_2^2]$$
$$\Delta\mu_2 = RT[\ln \phi_2 + (1 - N_2/N_1)\phi_1 + \chi_{12}N_2\phi_1^2] \qquad (6)$$

For the system to consist of two phases, denoted by prime and double prime, in equilibrium—the condition described by the binodal—the chemical potential of a component must be the same in both phases:

$$\Delta\mu_1' = \Delta\mu_1''$$
$$\Delta\mu_2' = \Delta\mu_2'' \qquad (7)$$

A binodal curve is shown[3] schematically in *Figure 10*. A horizontal tie line connects the phase ' and ", which are in equilibrium at the temperature denoted by the tie line.

Applying the superscripts to the set of equations comprising equation (7) yields the set below[1-3]:

$$\ln \phi_1' + (1 - N_1/N_2)\phi_2' + \chi_{12}N_1\phi_2'^2$$
$$= \ln \phi_1'' + (1 - N_1/N_2)\phi_2'' + \chi_{12}N_1\phi_2''^2 \qquad (8)$$
$$\ln \phi_2' + (1 - N_2/N_1)\phi_1' + \chi_{12}N_2\phi_1'^2$$
$$= \ln \phi_2'' + (1 - N_2/N_1)\phi_1'' + \chi_{12}N_2\phi_1''^2$$
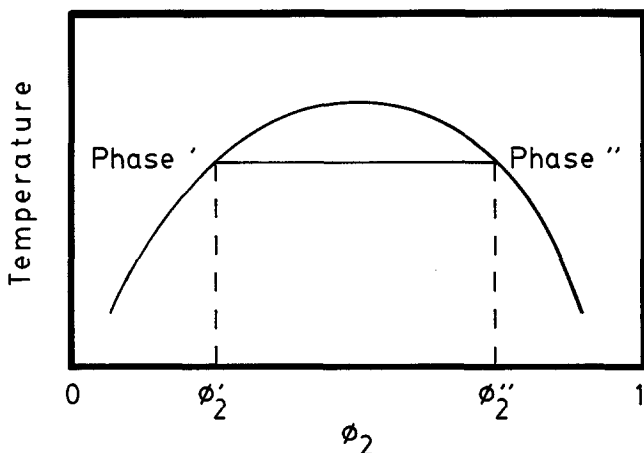

Figure 10 Schematic phase diagram. At a given temperature, phases ' and ", containing both polymers 1 and 2, are in equilibrium with each other

where

$$\phi_1' + \phi_2' = 1$$
$$\phi_1'' + \phi_2'' = 1 \qquad (9)$$

The above equations (8) and (9) have two unknowns ϕ_2' and ϕ_2''. A relation between ϕ_2' and ϕ_2'' is obtained from the following section. A parameter on the binodal curve is derived from equation (8), as follows:

$$\chi_{12}^{\text{bn}} = \frac{1}{2(\phi_2' - \phi_2'')}\left[\frac{1}{N_1}\ln\left(\frac{1 - \phi_2''}{1 - \phi_2'}\right) - \frac{1}{N_2}\ln\left(\frac{\phi_2''}{\phi_2'}\right)\right] \qquad (10)$$

where ϕ_2'' is a solution of[2,23]:

$$2(1/N_1 - 1/N_2)(\phi_2' - \phi_2'') + \frac{2 - (\phi_2' + \phi_2'')}{N_1}\ln\left(\frac{1 - \phi_2'}{1 - \phi_2''}\right)$$
$$+ \frac{\phi_2' + \phi_2''}{N_2}\ln\left(\frac{\phi_2'}{\phi_2''}\right) = 0 \qquad (11)$$

Interaction parameter of blends with random copolymer

For blends of homopolymer $(A)_{N_1}$ and random copolymer $(B_{1-x}C_x)_{N_2}$, according to ref. 6, χ_{12} is given by:

$$\chi_{12} = (1 - x)\chi_{\text{AB}} + x\chi_{\text{AC}} - x(1 - x)\chi_{\text{BC}} \qquad (12)$$

where x is the copolymer composition in volume fraction, and χ_{ij} is the interaction parameter of repeat units i and j.

Corresponding to the conditions expressed by equation (12), a number of different cases will be considered. They are grouped overall according to the signs of individual χ_{ij}: (a) all $\chi_{ij} > 0$; (b) two $\chi_{ij} > 0$; (c) one $\chi_{ij} > 0$; and (d) all $\chi_{ij} < 0$. Even if all $\chi_{ij} > 0$, χ_{12} can be negative in a limited range of x. This happens when χ_{BC} is very large. Thus, the apparent attractive interaction between homopolymer and random copolymer comes from the large repulsive interaction between comonomers B and C.

Assuming that the blend has no excess volume of mixing and there are no specific interactions such as hydrogen bonding and charge-transfer complex, without pure dispersive interactions, χ_{ij} may be represented by[24-28]:

$$\chi_{ij} = (V_r/RT)(\delta_i - \delta_j)^2 \qquad (13)$$

where δ_i and δ_j are the solubility parameters of the respective components.

From equations (12) and (13), χ_{12} is given by:

$$\chi_{12} = (V_r/RT)[(1 - x)(\delta_{\text{A}} - \delta_{\text{B}})^2 + x(\delta_{\text{A}} - \delta_{\text{C}})^2$$
$$- x(1 - x)(\delta_{\text{B}} - \delta_{\text{C}})^2] \qquad (14)$$

Equation (14) is rewritten as:

$$\chi_{12} = (V_r/RT)(\delta_1 - \delta_2)^2 \qquad (15)$$

where

$$\delta_1 = \delta_{\text{A}} \qquad \text{and} \qquad \delta_2 = (1 - x)\delta_{\text{B}} + x\delta_{\text{C}}$$

Furthermore, if one recalls that equation (13) comes from the assumption for the contact energies u_{ii} and u_{jj} $(u_{ij} \sim (u_{ii}u_{jj})^{0.5})$[28,29], equation (13) may be formulated more generally as:

$$\chi_{ij} = (V_r/RT)[(\delta_i - \delta_j)^2 + 2\kappa_{ij}\delta_i\delta_j] \qquad (16)$$

where κ_{ij} is a parameter describing the departure from the geometric mean rule[15,28]. In place of equation (2), we will take the following equation for the definition of miscibility:

$$f^{\text{bn}} = \chi_{12} - \chi_{12}^{\text{bn}} \qquad (17)$$

Then miscibility and immiscibility are represented by $f^{bn} < 0$ and $f^{bn} > 0$, respectively.

Calculation

In equation (11), ϕ_2'' is obtained by determining ϕ_2'. Equation (11) can be solved by using Newton's method[2]. Here we require a value of the reference volume V_r, the degrees of polymerization N_1 and N_2, and the solubility parameter δ. In PC/P(S-MAA) blends, subscripts (i.e. 1, 2, A, B and C) of these parameters (i.e. N, δ, ϕ and χ) mean the following: $1 = A = PC$, $2 = P(S-MAA)$, $B = S$ and $C = MAA$. The volume V_r has been taken as the geometric mean of the molar volumes of the involved polymer repeat units[19,25,26]. If we consider the copolymer as a 'homopolymer' with repeat unit $(B_{1-x}C_x)$, V_r is given by:

$$V_r = (\bar{V}_1 \bar{V}_2)^{1/2} \qquad (18)$$

where $\bar{V}_1$ and $\bar{V}_2$ are the molar volumes of PC and P(S-MAA) repeat units, respectively. As shown in *Figure 1*, $\bar{V}_2$ is given by:

$$\bar{V}_2 = [(1 - m_C)V_B + m_C V_C][(1 - m_C)\bar{M}_B + m_C \bar{M}_C] \qquad (19)$$

where m_C is the mole fraction of comonomer MAA, V_B and V_C are the specific volumes of comonomers S and MAA, and $\bar{M}_B$ and $\bar{M}_C$ are the molecular weights of comonomers S and MAA, respectively. The values of N_1 and N_2 are given by:

$$N_1 = M_1 V_1 / V_r \qquad \text{and} \qquad N_2 = M_2 V_2 / V_r \qquad (20)$$

where M_1 and M_2 are the molecular weights of PC and P(S-MAA), and V_1 and V_2 are the specific volumes of PC and P(S-MAA), respectively. Here we take them as $M_1 = 2.35 \times 10^4$ and $M_2 = 3.0 \times 10^5$.
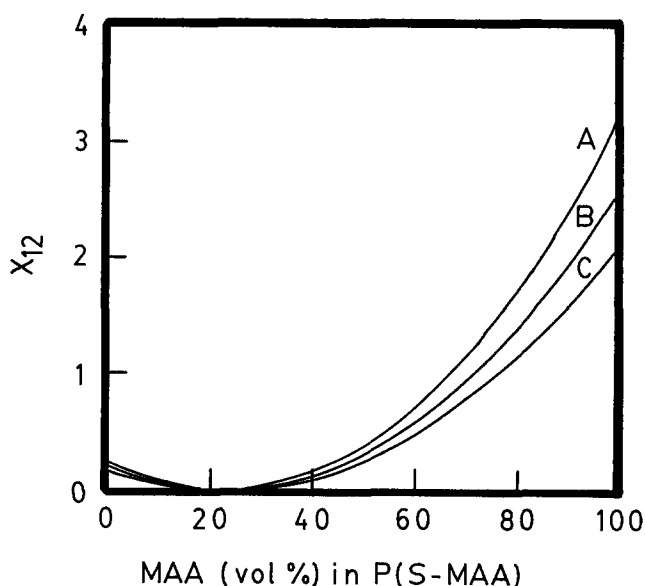
In *Tables 1* and *2*, the values used for the calculations are summarized. The solubility parameters of PC and S were obtained from group molar constants according to Hoy[30] and the molar volumes by density measurements in this study. The group molar constant of MAA was taken from ref. 31.

Phase diagram

From equation (15), the value of the interaction parameter χ_{12} varies as a function of MAA concentration in the copolymer. This in turn is determined by the change in solubility parameter δ_2 with MAA content of the P(S-MAA) copolymer and its value relative to the solubility parameter δ_1 of PC. *Figure 11* shows the calculated value of χ_{12} at various temperatures, which first decreases and then increases, as the amount of MAA in the copolymer increases. As is clearly seen, there is a point where theoretically the value of the solubility parameter of P(S-MAA) is equal to that of PC. It means that the value of χ_{12} is zero.

Figure 11 Variation of χ with P(S-MAA) copolymer composition in blends with PC at (A) 373 K, (B) 473 K and (C) 573 K

Figure 12, which was obtained by using equations (10), (11), (14) and (17), shows the calculated binodals for the hypothetical PC/P(S-MAA) blends. Between about 18 and 22 vol% MAA no binodal was obtained in this calculation, indicating that the blends with PC are miscible over a wide range of temperatures. Connecting the critical temperature in *Figure 12* with the copolymer composition, an indication of the 'miscibility valley' can be shown (see *Figure 13*). Thus, the existence of the 'miscibility valley' is predicted from the theoretical calculation.

Fitting from the experimental results

Although *Figure 13* shows qualitatively the 'miscibility valley' phenomenon, the difference between the theoretical result and the experimental curve is still considerable. Here we attempt to fit the theoretical calculation to the experimental results. From equation (5), ϕ_2^{crit} is 0.2 ± 0.01. Therefore we assume that the blend ratio of PC/P(S-MAA) (8/2) is almost equal to ϕ_2^{crit}. This assumption is supported by the phase behaviour obtained by cloud-point measurement, which is shown in *Figure 3*. Thus the results shown in *Figure 8* were used to obtain the parameter κ_{ij}. Combining equations (10), (11), (14), (16) and (17), the calculated curve was fitted to the experimental result, as shown in *Figure 14*, where ϕ_2 is equal to ϕ_2^{crit}. The κ_{AB}, κ_{AC} and κ_{BC} values became about -6.44×10^{-3}, -6.24×10^{-2} and -1.11×10^{-1}, respectively. The details of this fitting process are described in the Appendix. As these absolute values become larger, the departures from the geometric rule become larger. As is clearly seen, the absolute value of κ_{AB} is smaller than that of κ_{AC} and κ_{BC}. This suggests that our evaluations with respect to the solubility parameters of each species (especially MAA) are still insufficient. This problem is discussed in a later paragraph.

Using these κ_{ij} parameters, the trend of the miscibility can be calculated under the various conditions. For example, *Figure 15* shows f^{bn} behaviours as a function of copolymer composition with various blend ratios at $T = 453$ K. In *Figure 15*, the region of miscibility is defined by $f^{bn} < 0$. As is clearly seen, the miscibility of

Table 2 Solubility parameters used for calculations

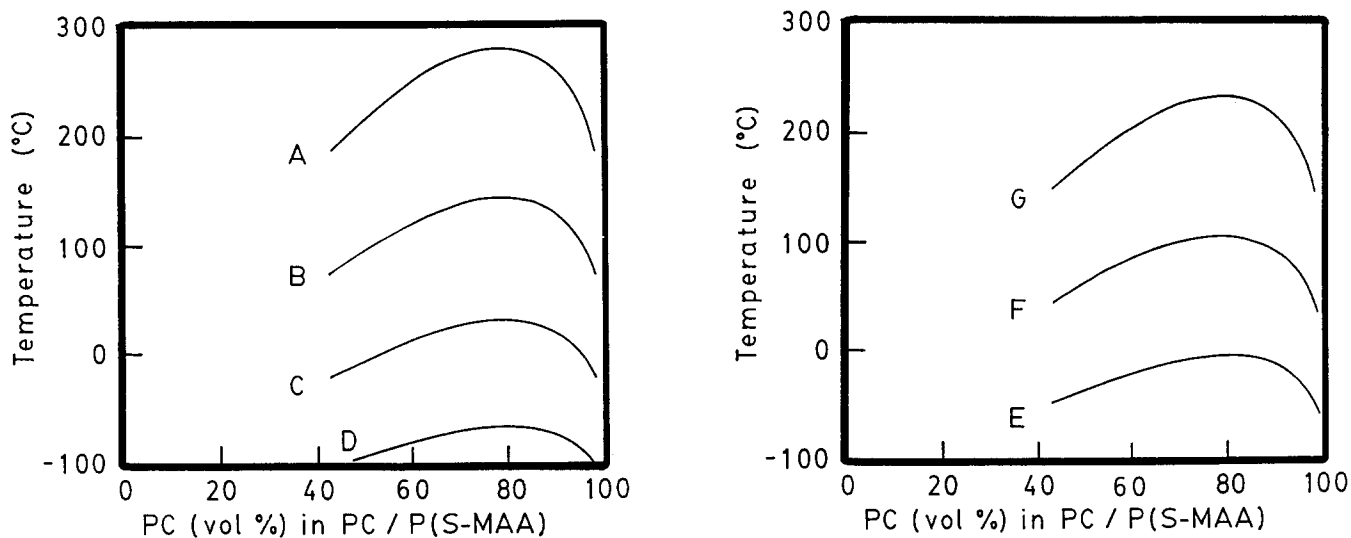|	Group molar constant $((\text{cal cm}^{-3})^{1/2} \text{mol}^{-1})$	Average molecular weight, M	δ $((\text{cal cm}^{-3})^{1/2})$
PC	2180	254	10.21
S	900	104	9.09
MAA	1058	86	14.599

Figure 12 Theoretical binodals of PC blends with P(S-MAA). Volume per cent MAA in copolymers: (A) 16.5%; (B) 17%; (C) 17.5%; (D) 18%; (E) 23%; (F) 23.5%; (G) 24%
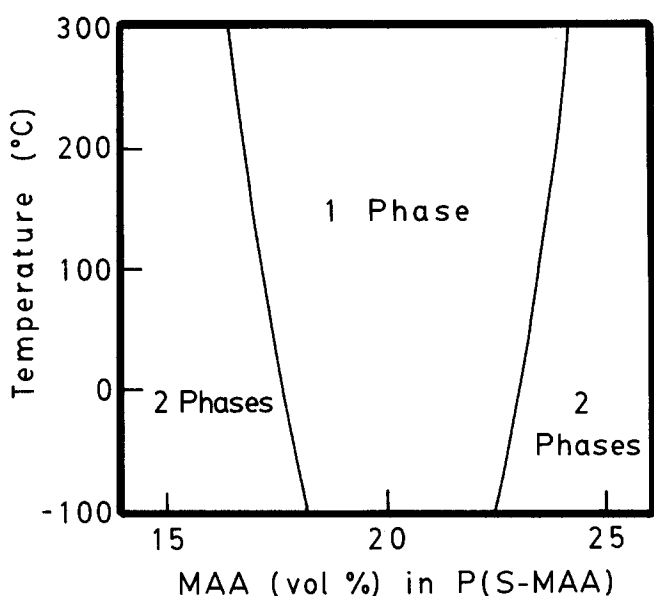

Figure 13 Theoretical miscibility valley for PC/P(S-MAA)
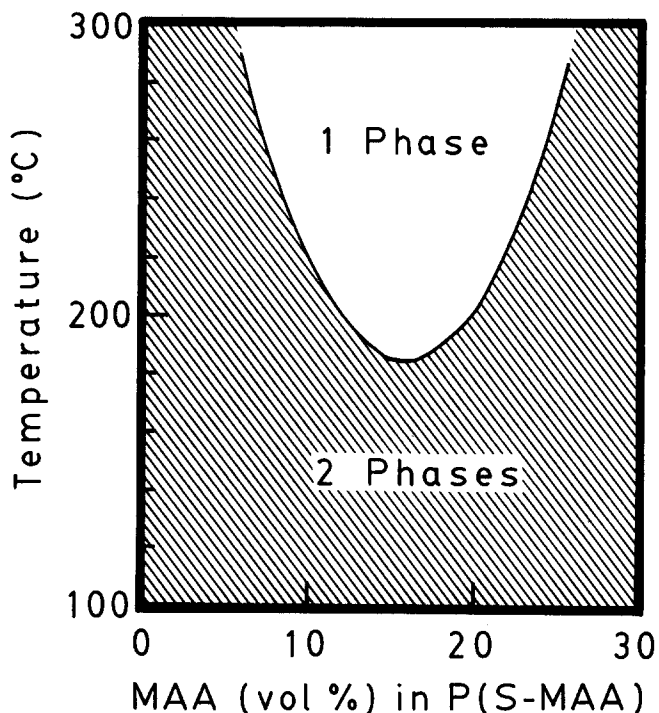

Figure 14 Theoretical miscibility valley for PC/P(S-MAA) with κ_{ij} parameters

the blends is strongly affected by the blend ratio and copolymer composition.

In our theory, we assume that there are no specific interactions between component polymers as mentioned above. However, MAA-containing polymers are, in general, strongly self-associated at ambient temperatures through the characteristic intermolecular hydrogen-bonded dimer. Coleman *et al.* investigated the self-association of MAA in the blend of poly(ethylene-*co*-methacrylic acid)/polyether and derived the equation for the free energy of mixing, which contains effects of the self-association[31,32]. In PC/P(S-MAA) blends, most MAA in copolymers seems to be free, because the excess volume of mixing is very small. As mentioned above, however, a very slight change in the value of the solubility parameter affects the miscibility of the blends, and the solubility parameter seems to be influenced by the self-association. Thus the theoretical calculation requires more detailed investigations. Further studies, such as infra-red spectrometry, are needed to pursue this problem.
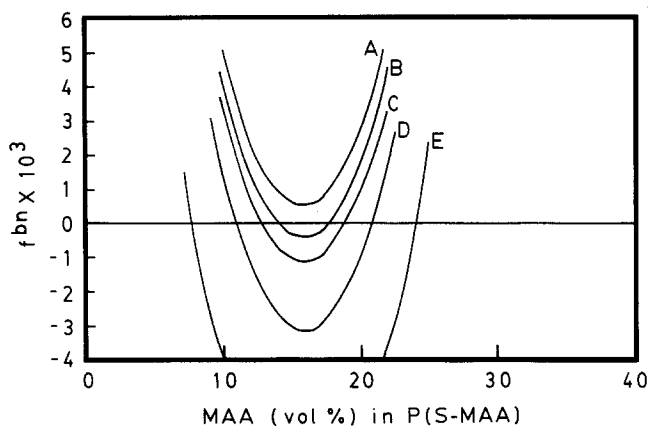

Figure 15 Variation of f^{bn} with P(S-MAA) copolymer composition. Volume percent PC in blends: (A) 80%; (B) 70%; (C) 90%; (D) 60%; (E) 50%

CONCLUSIONS

PC/P(S-MAA) blends with various MAA contents in the P(S-MAA) have upper critical solution temperatures.

PC/P(S-MAA) blends have no excess volume changes on mixing. The density of blends shows volume additivity with blend composition.

The calculated miscibility prediction can estimate the experimental result on miscibility of these PC/P(S-MAA) blends.

Both calculations and experimental results via T_g behaviour revealed the new 'miscibility valley' phenomenon against random copolymer compositions in P(S-MAA) in the blends.

A three-dimensional phase diagram named 'miscibility saddle' can be displayed in these PC/P(S-MAA) blends.

ACKNOWLEDGEMENT

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APPENDIX

Three fitting parameters are obtained as follows. Combining equations (14) and (16), χ_{12} is given by:

$$\chi_{12} = (V_r/RT)[(a_1 + 2a_2\kappa_{BC})x^2 + 2(b_1 + b_2)x + (c_1 + 2c_2\kappa_{AB})] \tag{A1}$$

where

$$
\begin{aligned}
a_1 &= (\delta_C - \delta_B)^2 \\
a_2 &= \delta_B\delta_C \\
b_1 &= \delta_A\delta_B + \delta_B\delta_C - \delta_A\delta_C - \delta_B^2 \\
b_2 &= \delta_A\delta_C\kappa_{AC} - \delta_A\delta_B\kappa_{AB} - \delta_B\delta_C\kappa_{BC} \\
c_1 &= (\delta_A - \delta_B)^2 \\
c_2 &= \delta_A\delta_B
\end{aligned}
\tag{A2}
$$

At the critical temperature, χ_{12} is equal to χ_{12}^{crit}. Thus the next equation is derived:

$$T = (V_r/RT)[(a_1 + 2a_2\kappa_{BC})x^2 + 2(b_1 + b_2)x + (c_1 + 2c_2\kappa_{AB})] \tag{A3}$$

Here, using the method of least squares, the experimental curve in *Figure 8* is expressed as follows:

$$T = Ax^2 + Bx + C \tag{A4}$$

where

$$
\begin{aligned}
A &= 1.05 \times 10^4 \\
B &= -3.33 \times 10^4 \\
C &= 7.21 \times 10^2
\end{aligned}
$$

At the fixed copolymer composition, κ_{ij} values are uniquely obtained from the following equations because χ_{12}^{crit} becomes a constant value:

$$
\begin{aligned}
\kappa_{BC} &= (A/K - a_1)/2a_2 \\
\kappa_{AB} &= (C/K - c_1)/2c_2 \\
\end{aligned}
\tag{A5}
$$

$$\kappa_{AC} = (-b_1 + \delta_A\delta_B\kappa_{AB} + \delta_B\delta_C\kappa_{BC} + B/2K)/\delta_A\delta_C$$

where

$$K = R/V_r\chi_{12}^{crit}$$