

Studies on miscibility in polycarbonate/poly(styrene-*co*-acrylonitrile) blends by ellipsometry

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Abstract

The interfacial thickness between immiscible polymers, bisphenol A polycarbonate (PC) and styrene–acrylonitrile random copolymers (SAN), was measured by ellipsometry as a function of temperature and acrylonitrile content in SAN, in order to study the miscibility between PC and SAN. Both the temperature and copolymer composition (AN content) dependence of the interfacial thickness in the equilibrium state indicated a maximum. Using the values of the interfacial thickness, it is possible to calculate the polymer–polymer interaction parameter χ_{AB} between PC and SAN. The χ_{AB} exhibited the lowest positive value at about 200°C for each copolymer composition due to the maximum of the interfacial thickness, i.e. at low temperature range, χ_{AB} decreased with increasing temperature, then χ_{AB} increased at high temperature range. This behaviour implies the possibility of the coexistent behaviour of upper and lower critical solution temperature (UCST and LCST) in the phase diagram of the mixture consisting of polymers with suitable molecular weight. This coexistent behaviour of UCST and LCST was confirmed by measuring cloud point curves of the mixtures having lower molecular weight PC. On the other hand, the copolymer composition dependence of χ_{AB} also has a minimum in a certain copolymer composition, which leads to the miscibility window behaviour. From these results, it was shown that there appeared to be a loop-type miscibility window ('miscibility egg') in the miscibility diagram of copolymer composition versus temperature of PC/SAN. From the calculation based on these results, it has also been shown that all three segmental interaction parameters χ_{ij} of PC/SAN, i.e. $\chi_{S/C}$, $\chi_{AN/C}$ and $\chi_{S/AN}$, decreased with increasing temperature monotonically. It was predicted that the LCST behaviour in PC/SAN mixtures could occur due to the remarkable decrease of interaction $\chi_{S/AN}$ between comonomers in SAN at high temperature, without the free volume contribution. © 1998 Elsevier Science Ltd. All rights reserved.

Keywords: Polycarbonate; Poly(styrene-*co*-acrylonitrile); Ellipsometry

1. Introduction

Ellipsometry is a powerful tool for measuring the interfacial thickness between two polymers. This measurement can be carried out for immiscible polymer blends as well as miscible blends. For miscible blends, the investigation of changes of the interfacial thickness with time at a fixed temperature makes it possible to calculate mutual diffusion coefficients [1]. For immiscible blends, on the other hand, the Flory–Huggins interaction parameter χ can be deduced from measurements of the interfacial thickness in an equilibrium state, by use of the theory of Helfand and co-workers [2,3]. Thus, it provides one of the rare opportunities to study the positive χ parameter for immiscible blends. One of the advantages of ellipsometry is that it is an easy method to handle, especially in comparison with the neutron reflectivity measurements, which has an excellent depth resolution

of about 0.2 nm, but requires deuterated samples and large scale apparatus. The main limitations of ellipsometry are that the refractive index difference between polymers should be larger than 0.02, and the flat surface. The error of the method becomes tremendous when the system has a small refractive index difference and a thin interface, which is equivalent to a large positive χ .

For the last decade, the study of the miscibility window for blends containing random copolymer(s) has been carried out extensively. A homopolymer forms a miscible blend with random copolymer in a certain copolymer composition and temperature range, when there is a strong unfavourable interaction between comonomer units of copolymer, though all segmental interactions are positive. Therefore, the ellipsometric studies are very suitable for evaluating the miscibility of copolymer blends showing miscibility window behaviour, which show a broader interface than homopolymer pairs. The miscibility window behaviour has been reported for some blends, e.g. poly(methyl methacrylate)

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Table 1
Molecular weight data of polymers

Polymer	Source	M_w	M_w/M_n
PC	Mitsubishi Gas Chem.	37 500	1.4
	Mitsubishi Gas Chem.	6000	1.3
PS	Denka (Styrol GP-1)	180 000	2.0
	Aldrich Chem. Co.	2700	< 1.10
SAN-11.3 ^a	Mitsubishi Monsanto	269 000	2.1
SAN-25 ^a	Mitsubishi Monsanto	128 000	2.1
SAN-40 ^a	Mitsubishi Monsanto	75 800	1.9
SAN-50 ^a	Mitsubishi Monsanto	63 600	1.8
SAN-59.3 ^a	Mitsubishi Monsanto	49 500	1.8

^aNumber means wt% acrylonitrile in SAN.

(PMMA) and styrene–acrylonitrile random copolymer (SAN) [4]. Higashida et al. [5] reported the temperature dependence of all three segmental interaction parameters, $\chi_{S/MMA}(T)$, $\chi_{MMA/AN}(T)$ and $\chi_{S/AN}(T)$, by ellipsometry [6]. It was indicated that the phase behaviour of PMMA/SAN blends could be explained by a simple mean field model considering the difference of the temperature dependence in $\chi_{ij}(T)$ [7]. Shimomai et al. [8] also showed that this phase behaviour could be explained by the equation of state theory applied for the mixture of homopolymer and random copolymer.

A shortcoming of ellipsometry is that concentration profiles usually can not be obtained, i.e. correction factors are necessary to convert the step interface into a real one. Therefore, the confirmation of the ellipsometric data by independent and direct methods is highly recommended. For this purpose, Kressler et al. [9] carried out the transmission electron microscope (TEM) measurements for PS/PMMA and PMMA/SAN-38.7 mixtures. These concentration profiles were obtained by densitometric measurements of TEM images across the interface using the image processing system. They showed that the interfacial thickness obtained from this TEM measurement was in fairly good agreement with a value measured by ellipsometry. Also, they investigated the concentration profile of the interface by the heavy ion elastic recoil detection (ERD) for the same mixtures [10]. The value of the interfacial thickness obtained by using the nitrogen profile which exists in SAN was in fairly good agreement with the values of TEM and ellipsometric data. Thus, after having confirmed the reliability of the ellipsometric data, it is possible to deduce thermodynamic data from the temperature dependence of the interfacial thickness.

In this paper, the miscibility in the immiscible blends of bisphenol A polycarbonate (PC) and SAN is investigated by the interaction parameter χ_{AB} calculated using the values of the interfacial thickness obtained from the ellipsometric measurements. The blends of PC/ABS (acrylonitrile–butadiene–styrene) have been widely used as commercial products for many years. One of the reasons why the useful properties appear in the blends is good compatibility between PC and SAN, which is the matrix of ABS. A lot

of the work focused on the relationship of the optimum mechanical properties and AN content of the copolymer [11–15]. Callaghan et al. [16] showed not only a good review of research on PC/SAN blends, but also their investigation of the miscibility of PC/SAN blends by measuring phase diagrams. They showed that low molecular weight mixtures of PC/SAN-25 (25 wt% AN) were miscible. They also calculated the interfacial thickness using the theory of Helfand and Tagami [2], and predicted that it had a maximum in PC/SAN-25. This seems to relate to the fact that PC/SAN blends often indicate the optimum physical properties at around 25 wt% AN content. We will evaluate the copolymer composition and temperature dependence of χ_{AB} and discuss the phase behaviour of PC/SAN blends from the viewpoint of thermodynamics.

2. Experimental

2.1. Materials

The source and molecular weight of polymers used in this study are listed in Table 1.

2.2. Ellipsometry

The bilayer specimens were prepared by mounting a thin film of SAN ($\sim 0.5 \mu\text{m}$) on the surface of a thick PC substrate ($\sim 0.5 \text{mm}$) which has $M_w = 37\,500$, by the following procedure. The PC was melt-pressed between two silicon wafers in order to obtain an optical flat surface. PS, SAN-11.3 and SAN-25 were dissolved in monochlorobenzene, and SAN-40 and SAN-50 in cyclohexanone, and SAN-59.3 in dimethyl formamide. The code SAN-x means the weight percentage of acrylonitrile in SAN. The 5 wt% solutions of polystyrene or SANs were filtered through a $0.2 \mu\text{m}$ Millipore membrane to remove dust particles. Films with a uniform thickness were prepared by spin-coating of the solution on a silicon wafer. Then, the film was floated onto the water surface and picked up with the PC substrate. Finally, the bilayer specimens were dried in a vacuum oven at 60°C for 24 h. Ellipsometric measurements were carried

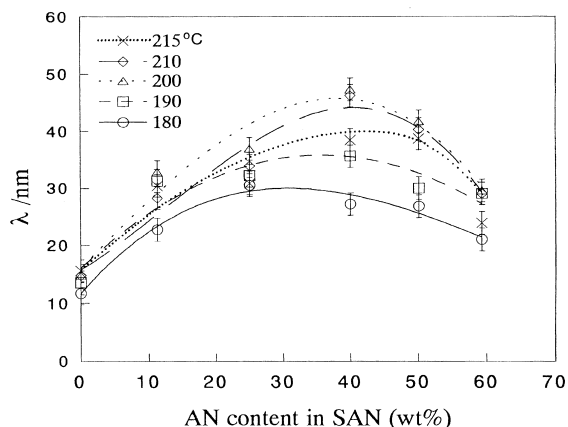


Fig. 1. Dependence of the interfacial thickness on AN content in SAN. The bars represent the confidence limit of ± 2 nm in the ellipsometric measurements.

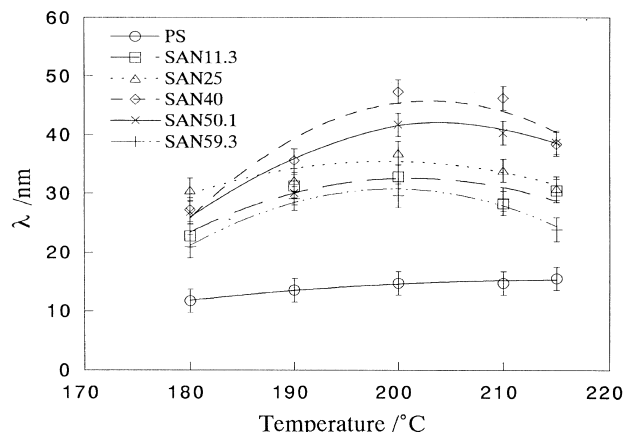


Fig. 2. Temperature dependence of the interfacial thickness. The bars represent the confidence limit of ± 2 nm in the ellipsometric measurements.

out using an autoellipsometer EL-8, Optec Co. The wavelength of the laser was 632.8 nm, and the incident light beam has an angle of 70° to the bilayer specimen. The bilayer specimen was brought into a heating cell under nitrogen and the temperature during isothermal runs was kept at $\pm 0.1^\circ\text{C}$. The measurements were limited between 180 and 215°C . Below 180°C , it should take a very long time to reach the equilibrium state, caused by the glass transition effect of PC ($T_g = 148^\circ\text{C}$). Above 220°C , the accurate measurements are difficult because the optical flat surface is not kept due to the fluidity of specimens at high temperature. Most of the systems reached the equilibrium state within 15 min and did not show any further growth. The measurements were continued for 1 h to ensure the interface reached equilibrium state. The calculations of interfacial thickness were based on a four-layer model, air(1)-SAN(2)-interface(3)-PC(4) [17]. The temperature dependence of refractive indices of neat SAN (n_2) and PC films (n_4) were previously measured by the ellipsometer. This model implies that the refractive index at the interface is approximated to being uniform and equals $n_3 = (n_2 + n_4)/2$. Though this stepwise approximation does not precisely show the real interface which has the concentration gradient, the values of interfacial thickness obtained were thus compared with those obtained by other methods, and good agreement was obtained, as mentioned in the Introduction [9,10]. The principle and experimental method of the ellipsometer were described in detail elsewhere [17,18].

2.3. Cloud point measurements

The 5 wt% solutions were prepared by using common solvent, tetrahydrofuran (THF) for PC/PS, PC/SAN-11.3 and PC/SAN-25, and chloroform for PC/SAN-40. The molecular weight of PC used in this measurement was 6000 gmol^{-1} , because one phase region was not observed for PC/SAN mixtures using a PC of $M_w = 37\,500$ and glass transition temperature (T_g) of PC, 6000 gmol^{-1} , is not as

high (110°C). The solution was cast on a cover glass and the solvent evaporated quickly at 40 or 50°C in order to prepare the transparent specimen. Then the specimen was dried in a vacuum oven at 50°C for 24 h. Thus, obtained specimens were isothermally annealed for 48 h under nitrogen flowing at different temperatures from 120 to 230°C . The phase behaviour was checked by an optical microscope and light scattering. Reversibility was found for almost all specimens, but could not be detected for the phase-separated specimen at lower temperatures because it is near to T_g of both polymers.

3. Results and discussion

Figs 1 and 2 show the equilibrium interfacial thickness λ as a function of AN content in SAN and temperature, respectively. It can be seen that the interfacial thickness of PC/SAN was thicker than that of PC/PS at all the measured temperatures. The interfacial thickness of PC/PS was about 12–16 nm, while the thickest interface of PC/SAN was about 45 nm. This value is very large in comparison with that predicted by Paul and co-workers [16,19]. Their value was calculated for an infinite molecular weight blend, and this may cause the difference. Therefore, we confirmed the interfacial thickness of some PC/SAN bilayer films by TEM or energy-filtering TEM measurements, as well as using the method of Kressler et al. [9], which was mentioned in the Introduction, and good agreement was obtained.

From Fig. 1, there is an AN content in which the maximum interfacial thickness appears at each temperature. The AN content having the thickest interface is 25 wt% at 180°C , but 40–50 wt% at higher temperature. This may be inconsistent with previous predictions, in which the interaction is optimum at about 25 wt% AN. However, this inconsistency may be caused by the fact that SAN with higher AN content used in this measurement has smaller molecular weight. This will be discussed later. In Fig. 2, it is shown that with increasing temperature the interface of PC/PS

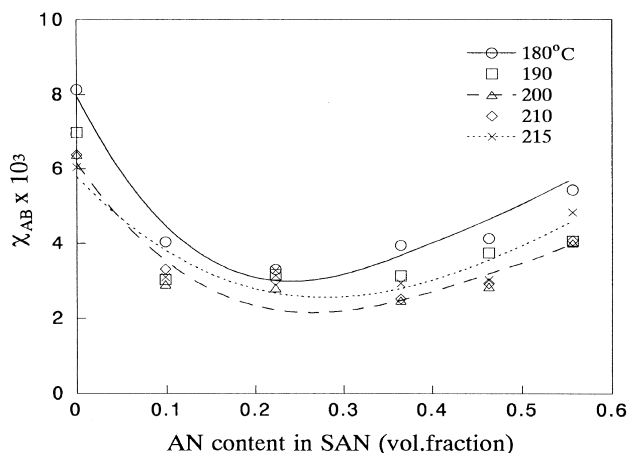


Fig. 3. Dependence of the χ_{AB} parameter on AN content in SAN.

increased slightly and monotonically. However, PC/SAN blends exhibited a maximum interfacial thickness at about 200°C.

According to recent theory, the equilibrium interfacial thickness λ is connected with the interaction parameter χ_{AB} between A and B polymers by [3]

$$\lambda = \frac{2b}{\sqrt{6\chi_{AB}}} \left[1 + \frac{\ln 2}{\chi_{AB}} \left(\frac{1}{r_A} + \frac{1}{r_B} \right) \right] \quad (1)$$

where r_i is the number of segments per polymer chain and b is the Kuhn segment length. The Kuhn segment length is an experimentally extremely difficult to handle quantity even if it is well defined within the concept of random walk statistics. The number of segments r_i was then calculated from the ratio of the overall length of a polymer chain to the segment length b . Therefore, one should use a plausible value of b in order to estimate the value of χ_{AB} . Also, since Eq. (1) contains only one segment length, an average of the two polymers must be used. Though in most cases r_i is calculated on the basis of monomer unit, the value of b does not correspond that of a monomer unit generally. Ballard et al. [20] found a value of 6.8 Å for PS, and Kressler et al. [6] used a value of 8 Å for the system PS/PMMA to calculate χ_{AB} from the interfacial thickness data. However, there are no plausible data for PC and PAN. As a trial, we use 7.66 Å, which is a diameter calculated from the van der Waals volume of a monomer unit of PC on the basis of Bondi's method by assuming spherical shape [21]. This is not very different from the value of PS mentioned above. If one sets the value of b , it is easy to calculate the interaction parameter χ_{AB} between two polymers from the interfacial thickness measured by ellipsometry.

Figs 3 and 4 show χ_{AB} calculated thus as a function of AN content in copolymer and temperature, respectively. From Fig. 3, all the values of χ_{AB} are positive and the AN content dependence of χ_{AB} shows a concave curve at each temperature. The interaction parameter between PC(A) and SAN(B)

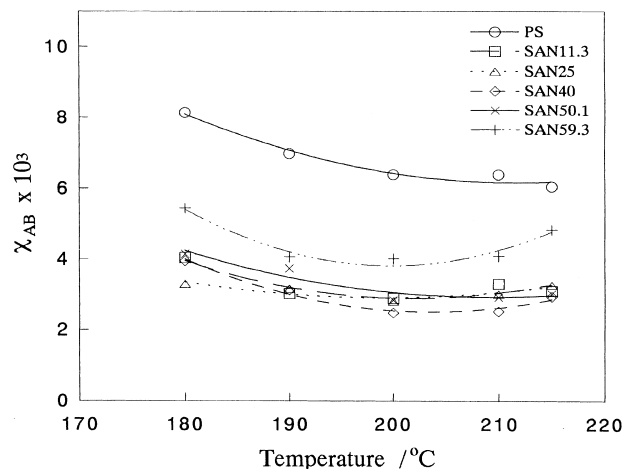


Fig. 4. Temperature dependence of the χ_{AB} parameter.

is given by

$$\chi_{AB} = (1 - \beta)\chi_{S/C} + \beta\chi_{AN/C} - \beta(1 - \beta)\chi_{S/AN} \quad (2)$$

where β is the volume fraction of AN in SAN, and χ_{ij} is the segmental interaction parameter. It is understood that the concave curve in Fig. 3 is caused by repulsion between S and AN in SAN copolymer (large positive $\chi_{S/AN}$). This behaviour is similar to PMMA/SAN blends, though χ_{AB} of PC/SAN does not become negative. At 180°C, the minimum value of χ_{AB} is close to 25 wt% AN. Though the calculated values of χ_{AB} indicate a minimum at 40 wt% AN for other temperatures, the curves drawn by a polynomial regression show a minimum close to 25 wt% AN. This may be caused by an error, however, the tendency to which the interaction is optimum at about 25 wt% AN appears. In Fig. 1, the interfacial thickness shows a maximum at 40 or 50 wt% AN, except for data at 180°C. It is considered that this is mainly caused due to the molecular weight effect. From Fig. 4, χ_{AB} of PC/PS decreased with increasing temperature monotonically, but the temperature dependence of χ_{AB} in all the measured SAN shows a concave curve. The minima of χ_{AB} appears at about 200°C.

There are a few measurements of the interaction parameter for PC/SAN blends because of immiscible blends. Nishi et al. [22] showed that the χ_{AB} of PC/SAN-27.5 blend was negative and PC/SAN-27.5 was miscible even for a high molecular weight blend. On the other hand, Callaghan et al. [16] pointed out that the apparent miscibility reported by Nishi et al. [22] was an artifact of a non-equilibrium preparation. They also estimated the value of interaction energy B by measurements of phase diagram (Critical MW Analysis) and showed that B was a positive value. The value of B is related to χ_{AB} by

$$\chi_{AB} = BV_r/RT \quad (3)$$

where V_r and R are a molar volume of segment and gas constant, respectively. The value of B from Callaghan et al. is about 0.15 cal cm⁻³ at 50°C for PC/SAN-25. Kim and Paul [23] also estimated the value of B by analysis using a

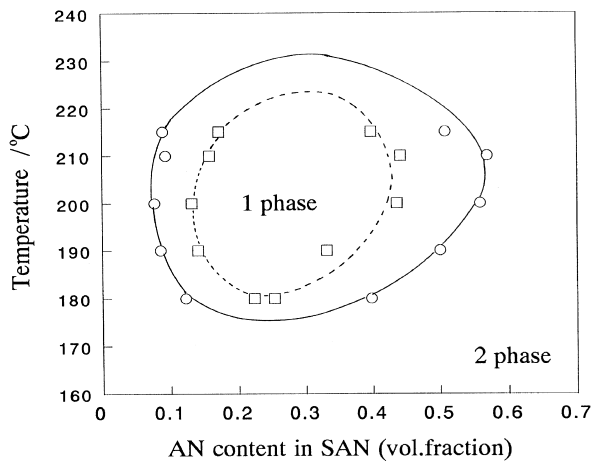


Fig. 5. Miscibility diagram of the PC/SAN system for two χ_{crit} values: (---) 0.003, (—) 0.004.

copolymer of PC with SAN and obtained $B = 0.04 \text{ cal cm}^{-3}$ at 140°C for PC/SAN-28. If we reduce our χ_{AB} to B by Eq. (3), $B = 0.014 \text{ cal cm}^{-3}$ (V_r is the monomer size of PC) and $0.034 \text{ cal cm}^{-3}$ (V_r is the monomer size of PS) at 180°C for PC/SAN-25. Though the compared temperatures are different, the value estimated here is similar to the value of Kim et al. [23] and somewhat lower than that of Callaghan et al. [16], who pointed out that the value of Kim et al. [23] was too low. If the value of the interaction parameter estimated by ellipsometry is also low, Eq. (1) may not give a precise value of χ_{AB} for relatively thick interfacial thickness.

From Fig. 3 (or Fig. 4), one can draw the miscibility diagram for PC/SAN by using the value of χ_{AB} at a critical point (χ_{crit}). From the Flory–Huggins theory, χ_{crit} is given by

$$\chi_{\text{crit}} = (r_A^{-1/2} + r_B^{-1/2})^2 / 2 \quad (4)$$

In the case of a smaller χ_{AB} than χ_{crit} , one phase is stable, but unstable in the opposite case. Fig. 5 shows the miscible–immiscible boundary estimated from the χ_{AB} –AN content curves in Fig. 3 for two values of χ_{crit} . The loop-type miscibility region (e.g. ‘miscibility egg’) appears in the PC/SAN system, instead of the usual miscibility window. This miscibility egg occurs because both the temperature and AN content dependence of χ_{AB} are U-shaped. As χ_{crit} decreases, i.e. the molecular weight of constituent polymers increases, the miscibility egg reduces. When χ_{crit} is always smaller than χ_{AB} for very high molecular weight blend, the miscibility egg disappears and one can not find the one phase region. This is consistent with the fact that high molecular weight blends of PC with any SAN are immiscible. However, for suitable low molecular weight specimens, one can observe the miscibility egg. In a PC/SAN-25 blend having suitable molecular weight specimens, e.g. the system undergoes a change of two phase–one phase–two phase with increasing temperature. This implies the coexistence of UCST and LCST behaviour in the PC/SAN-25 phase

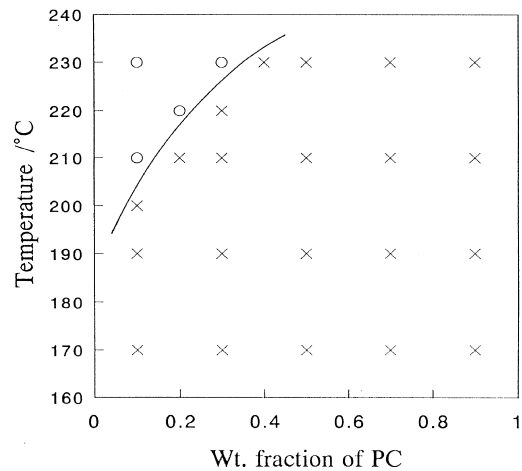


Fig. 6. Phase diagram of the PC ($M_w = 6000$)/PS ($M_w = 2700$) mixture measured by the cloud point method. (x) Cloud samples; (o) transparent samples.

diagram. This is also understood from the temperature dependence of χ_{AB} (Fig. 4) apparently. From Fig. 4, the PC/PS blend will exhibit UCST behaviour in the low molecular weight specimens.

To testify the phase behaviour of PC/SAN blends based on these results, the cloud point measurements were carried out by using low molecular weight PC ($M_w = 6000$). Fig. 6 shows the phase diagram of the blend of PC/PS ($M_w = 2700$). The UCST-type phase behaviour appears, as predicted. This is qualitatively consistent with the result of Callaghan and Paul [24].

Figs 7–9 are the phase diagrams of the blends of PC/SAN with different AN content obtained from the cloud point measurements. In the PC/SAN-11.3 blend (Fig. 7), an hour-glass-type phase behaviour appears, though one phase region can not be observed in PC-rich blends. In the PC/SAN-25 and PC/SAN-40 blends (Figs 8 and 9, respectively), both UCST and LCST behaviour appear. This is the

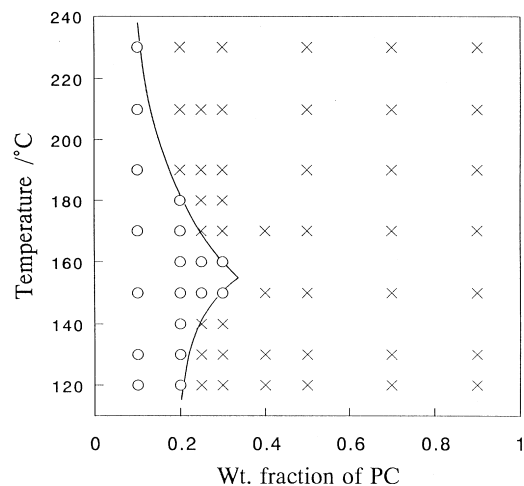


Fig. 7. Phase diagram of the PC ($M_w = 6000$)/SAN-11.3 mixture measured by the cloud point method. (x) Cloud samples; (o) transparent samples.

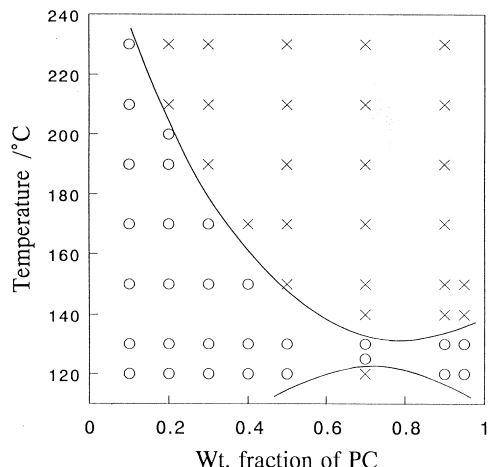


Fig. 8. Phase diagram of the PC ($M_w = 6000$)/SAN-25 mixture measured by the cloud point method. (x) Cloud samples; (o) transparent samples.

first time that the coexistent behaviour of UCST and LCST has been found in PC/SAN blends. We observed the phase diagram after 48 h annealing. Though its annealing time may not be enough to reach equilibrium state, the appearance of both UCST and LCST is clearly concluded from these figures. However, the temperature region in which the miscibility gap in the phase diagrams appears is different from that predicted from Fig. 5. From Fig. 4, the lowest χ_{AB} occurs at around 200°C. The reason for this inconsistency is not clear at present. Since the phase diagram of polymer blends is very sensitive for specimens, e.g. an end-group effect by using the low molecular weight PC may exist. Since Eq. (4) is derived from the assumption that χ_{AB} does not depend on composition, Eq. (4) may not be correct. At present, we do not discuss further details.

The relationship between the interaction parameter χ_{AB} in PC/SAN blends and the segmental interaction parameters χ_{ij} can be described by Eq. (2). Thus, by using at least three sets of χ_{AB} with different β in Fig. 4, all the χ_{ij} can be

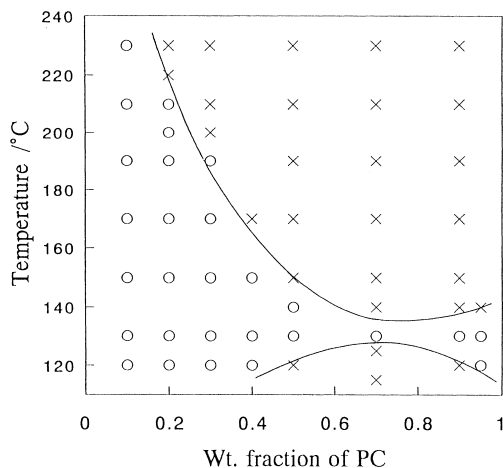


Fig. 9. Phase diagram of the PC ($M_w = 6000$)/SAN-40 mixture measured by the cloud point method. (x) Cloud samples; (o) transparent samples.

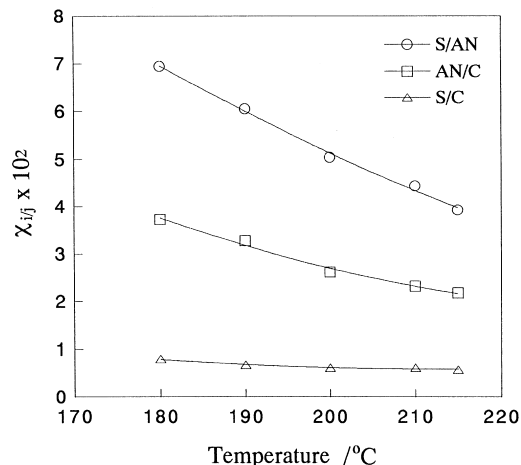


Fig. 10. Temperature dependence of the segmental interaction parameters χ_{ij} s in PC/SAN.

calculated at each temperature. Here, since we use χ_{AB} between PS and PC as the value of $\chi_{S/C}$, we can obtain the values of $\chi_{AN/C}$ and $\chi_{S/AN}$ from two sets of PC/SAN-x. However, the error becomes large because some combinations exist. Therefore, we estimated these values by a method of least squares for Eq. (2) using some values of χ_{AB} with different β . The temperature dependence of the segmental interaction parameters χ_{ij} included in the PC/SAN blends is shown in Fig. 10. Each χ_{ij} decreases monotonically with increasing temperature. Especially, the values of $\chi_{AN/C}$ and $\chi_{S/AN}$ decrease remarkably.

The Flory–Huggins interaction parameter χ_{AB} can be separated into two contributions based on the equation of state theories for mixtures: an interactional term χ_{inter} and a free volume term χ_{free} . χ_{inter} corresponds to the van Laar-type exchange energy term, and χ_{free} reflects the difference of the free volumes or thermal expansions between components. The miscibility window behaviour of the mixtures including random copolymer(s) has been explained by both χ_{inter} and χ_{free} , i.e. the contribution of χ_{inter} is greatest for the miscibility window behaviour, but the two-phase behaviour at higher temperature (LCST behaviour) is driven by χ_{free} . χ_{free} always shows an unfavourable contribution for mixing, i.e. χ_{free} is always positive and increases with increasing temperature. Since all values of χ_{ij} decrease monotonically in Fig. 10, it is understood that the contribution of χ_{free} is remarkably small in each χ_{ij} . So there is the possibility that the LCST behaviour in PC/SAN blends is not driven by χ_{free} . Higashida et al. [5] also reported that some PMMA/SAN blends exhibited LCST behaviour, though all three χ_{ij} decreased with increasing temperature, as well as PC/SAN blends. They pointed out the possibility that the different temperature dependence of the segmental interaction parameters $\chi_{ij}(T)$ leads to LCST behaviour without any obvious influence of free volume contributions.

In Fig. 3, the curves of the AN content dependence of χ_{AB} at three temperatures are drawn. Though the χ_{AB} in the PC/PS system decreases with increasing temperature

monotonically, as is obviously shown in Fig. 4, the values of χ_{AB} in the PC/SAN systems decrease ($180 \rightarrow 200^\circ\text{C}$) and then increase ($200 \rightarrow 215^\circ\text{C}$). This behaviour causes the loop-type miscibility region ('miscibility egg'). This can be interpreted as the following. From Fig. 10, $\chi_{S/AN}$ and $\chi_{AN/C}$, especially $\chi_{S/AN}$, decrease remarkably in comparison with $\chi_{S/C}$. From Eq. (2), the concave curve of the AN content dependence of χ_{AB} is due to the large $\chi_{S/AN}$, i.e. the repulsive interaction between S and AN in the SAN copolymer. If $\chi_{S/AN}$ shows a large decrease with increasing temperature in comparison with a decrease of both $\chi_{S/C}$ and $\chi_{AN/C}$, the depression of the curves in Fig. 3 leads to a small decrease. Consequently, the value of χ_{AB} in a certain AN region increases, nevertheless, $\chi_{S/C}$ and $\chi_{AN/C}$ at the edge of Fig. 3 decrease with increasing temperature monotonically. This causes the coexistent behaviour of UCST and LCST in the phase diagram of some PC/SAN blends, e.g. Fig. 8, and the miscibility egg behaviour in the miscibility diagram of Fig. 5. This scenario can be considered as one of the plausible reasons for LCST behaviour in PC/SAN blends without the free volume contribution. This may also explain the LCST behaviour observed in other blends including SAN, e.g. PMMA/SAN and poly(ϵ -caprolactone)/SAN [25]. Moreover, this can be one of the reasons for the coexistent behaviour of UCST and LCST in a high molecular weight polymer blend of SAN/poly(acrylonitrile-*co*-butadiene) [NBR], which was first found by Ougizawa and Inoue [26].

4. Conclusions

The χ_{AB} parameter between PC and SAN was estimated from the interfacial thickness measured by ellipsometry as a function of temperature and AN content in SAN. The AN content dependence of χ_{AB} exhibited concave curves at measured temperatures due to the repulsive interaction of S and AN in SAN, i.e. large positive $\chi_{S/AN}$. The temperature dependence of χ_{AB} also has a minimum at about 200°C for each copolymer composition. This behaviour implies the coexistent behaviour of UCST and LCST for the mixture consisting of polymers with proper molecular weight. The coexistent behaviour of UCST and LCST was confirmed by measuring the cloud point curves of the mixtures having low molecular weight PC, though the location of the miscibility gap was not consistent with that predicted by the temperature dependence of χ_{AB} . It was also shown that the loop-type

miscibility window ('miscibility egg') appeared in the miscibility diagram of copolymer composition-temperature of PC/SAN. It has been shown that all three segmental interaction parameters χ_{ij} of PC/SAN, i.e. $\chi_{S/C}$, $\chi_{AN/C}$ and $\chi_{S/AN}$, decreased with increasing temperature monotonically. This implies that LCST behaviour in PC/SAN mixtures can occur due to the remarkable decrease of interaction $\chi_{S/AN}$ between comonomers in SAN at high temperature, without the free volume contribution. In order to make the contribution of free volume in these copolymer blends clear, further discussion using the equation of state theory may be necessary.

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