Molecular weight and heating rate dependence of the cloud points of polystyrene/poly(2-chlorostyrene) blends

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Cloud points of polystyrene/poly(2-chlorostyrene) blends of narrow molecular weight distribution were measured with changing heating rate and molecular weight of polystyrene. Cloud points were also measured for blends containing various amounts of the plasticizer di-n-butyl phthalate. A large heating rate dependence of cloud points is observed at very small heating rates when no or a small amount of the plasticizer is contained. Cloud points extrapolated to zero plasticizer content are very different from directly observed cloud points of the binary blends, especially for large molecular weight samples. This is explained by the very slow phase separation kinetics of this system. The Flory–Huggins interaction parameter χ was calculated from the extrapolated cloud points using the spinodal condition. The χ parameter is positive and has a very weak temperature dependence.

(Keywords: polymer blend; polystyrene; poly(2-chlorostyrene); cloud point; molecular weight dependence; heating rate dependence; plasticizer)

INTRODUCTION

Compatibility of two different polymers is rare since a very small contribution of combinatorial entropy is accompanied by mixing. Because of their industrial importance, extensive efforts have been made to find compatible polymers[1,2]. The main concern of these studies lies in confirmation of compatibility, and either phase boundary or sample characterization is not clearly given in many cases. However, phase boundary, or the more readily measurable cloud point curve, is of fundamental importance, and it is indispensable for the study of thermodynamics of polymer blends to measure the phase boundary and its molecular weight dependence by using samples of narrow molecular weight distribution. Furthermore, polymer blends have attracted considerable attention as suitable systems for investigation of phase separation kinetics in recent years because of their low mobility and mean-field type behaviour[3,4]. Determination of the phase boundary is also a starting point for these kinetic studies. In spite of their importance, there are few detailed studies on the phase behaviour of polymer blends[5-8].

Alexandrovich *et al.*[9] found that polystyrene (PS) and poly(2-chlorostyrene) (P2ClS) are compatible and that the system exhibits phase separation at elevated temperatures. In addition to this immiscible region at higher temperatures, it has been predicted that another immiscible region exists at lower temperatures[10], but this has not been confirmed experimentally. Only one measurement has been known so far for the cloud point curve of the PS/P2ClS system. Takahashi *et al.*[11] measured the cloud point curve at a fixed heating rate of 0.06°C min^{-1} in their study on phase separation kinetics of the blend. They observed that phase separation proceeded even when a sample was kept at a temperature 2.4°C below the predetermined cloud point. Thus, the heating rate dependence of the cloud point curves is quite large in this system, and it is necessary to measure the cloud point with even lower heating rates.

In the present work, we measured the cloud points of PS/P2ClS systems using samples of narrow molecular weight distribution. Four molecular weights of PS were used to investigate the molecular weight dependence of the cloud points. It is well known that the cloud point is a kinetic rather than a thermodynamic property[12,13], so we studied cloud points with special attention to the kinetic contribution by changing heating rates and adding a plasticizer to increase the mobility of the system.

EXPERIMENTAL

Materials

P2ClS was radically polymerized in toluene at 60°C for 90 h with 0.2 mol% 2,2′-azobis(isobutyronitrile) as initiator, and was fractionated by the precipitation method at 35°C using toluene and methanol. Weight average molecular weight M_w and polydispersity index M_w/M_n were determined by gel permeation chromatography (g.p.c.) with a low angle light scattering detector (Tosoh, Model HLC-803D; LS-8) to be 1.39×10^5 and 1.14 respectively. PSs with narrow molecular weight distribution were purchased from the companies listed in *Table 1* and used without fractionation. Their nominal M_w and M_w/M_n are also listed in *Table 1*. Di-n-butyl phthalate (DBP, > 99%) was obtained from Tokyo Kasei Kogyo Co. and used without further purification.

Sample preparation

Blend films were prepared by coprecipitation or solvent cast. Binary blends of PS/P2ClS were prepared

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Table 1 Characteristics of samples

Sample	M_w	M_w/M_n	Source
Polystyrenes			
PS30K	29 400	< 1.06	Scientific Polymer Products
PS37K	37 000	< 1.06	Pressure Chem.
PS44K	43 900	1.01	Tosoh
PS50K	50 000	< 1.06	Pressure Chem.
Poly(2-chlorostyrene)			
P2ClS	139 000	1.14	

by coprecipitation. PS and P2ClS of desired composition were dissolved in toluene to a total polymer concentration of 3 wt% and the solution was then added dropwise to a large excess of methanol with stirring. After the coprecipitate had been dried at room temperature overnight, it was dried further at 80°C under vacuum for at least 3 d. The dried powder was pressed at 100 kg cm^{-2} at room temperature and subsequently melted at 130°C in vacuum to make a transparent film. Ternary blends of PS/P2ClS/DBP were cast from ≈ 3 wt% benzene solution. The cast films were air-dried at 50°C overnight and then vacuum dried at 80°C for at least 3 d. Binary and ternary blend films were cut and placed between circular microscope slide glasses of 6 mm diameter with a 0.2 mm thick spacer and then annealed at 140°C for 12 h. Samples were stored in a desiccator until use.

Cloud point measurements

Two ways of changing temperature, heating at a constant rate and changing temperature stepwise, were adopted in the determination of cloud points. In the conventional constant-rate heating measurement, a sample was heated at a constant rate of 1.2 or 0.067°C min^{-1}, while the intensity of light scattered from the sample was measured at an apparent scattering angle of 20°. The cloud point was determined as the temperature at which an abrupt increase in scattered light intensity was observed. Since heating at a very slow constant rate was difficult to carry out, we changed temperature stepwise at regular long intervals instead. In the stepwise temperature change measurement, the sample was visually inspected after being kept at a constant temperature for 1 d. If the sample was clear and transparent its temperature was considered to be in the one phase region and the temperature was increased stepwise by 1°C. The cloud point was determined by repeating the procedure until the sample film became bluish or opaque.

Glass transition temperature measurement

The glass transition temperatures (T_g) of PS ($M_w = 5 \times 10^4$)/DBP mixtures and P2ClS(PS equivalent $M_w = 1.5 \times 10^5$ measured by g.p.c.)/DBP mixtures were measured by a Perkin–Elmer Model DSC-2 differential scanning calorimeter at a heating rate of 10°C min^{-1}. We neglected the molecular weight dependence of the glass transition temperature and used P2ClS of different molecular weight from that used in the cloud point measurement.

RESULTS AND DISCUSSION

Figure 1 shows the cloud point curves of PS/P2ClS blends with M_w of PS ranging from 29 400 to 50 000 measured at a heating rate of 0.067°C min^{-1}, along with the glass transition temperatures of the blends of PS ($M_w = 50\,000$)/P2ClS($M_w = 139\,000$)[11]. Lower critical solution temperature (LCST) behaviour is observed and miscibility decreases with increasing M_w of PS. When M_w of PS was reduced to 19 600, a cloud point (T_{cl}) was not observed in the temperature range investigated (< 235°C). T_{cl} of the blend with PS37K has very weak composition dependence and its cloud point curve is unusually flat compared with those of the other blends. It is also unusual that T_{cl}s of the three blends with PS37K, PS44K and PS50K appear likely to cross at a point around $w_{PS} = 30$ wt%.

Figure 2 shows the effect of heating rate on the cloud point curves of the PS37K/P2ClS blend. The cloud point curve measured at the higher heating rate, 1.2°C min^{-1} is convex downward in contrast to the unusually flat shape at 0.067°C min^{-1}, which indicates that the kinetic factor in determining T_{cl} depends on composition. More striking is that T_{cl} measured by the stepwise temperature change is much lower than T_{cl} measured at a heating rate of 0.067°C min^{-1}. This is more clearly shown in *Figure 3*, where the data at 50 wt% PS are plotted against heating rate R. The value 1°C d^{-1} is given as a virtual heating rate for the stepwise temperature change. As shown by open circles, the cloud points are not on a straight line and a strong heating rate dependence is observed in a small R range.

To investigate further the unexpectedly large dependence of cloud points on heating rate in the small R range, we added DBP to the blends as a plasticizer and made the same measurements. Since the stepwise temperature change measurement is time-consuming, the cloud points of these ternary systems were measured only at a fixed polymer composition of PS/P2ClS = 50/50 wt%. *Figure 3* shows the heating rate dependence of the cloud point of PS37K/P2ClS blends containing

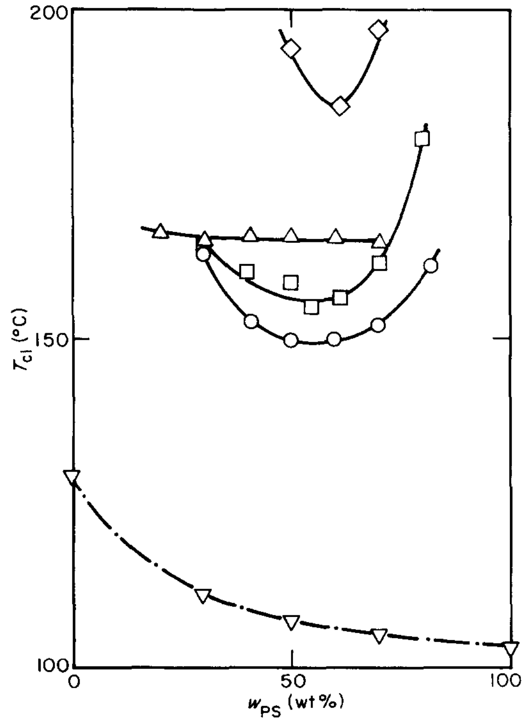

Figure 1 Cloud point curves of PS/P2ClS blends with M_w of PS of: ◇, 29 400; △, 37 000; □, 43 900; ○, 50 000, measured at a heating rate of 0.067°C min^{-1}, and glass transition temperatures (▽) of the PS50K/P2ClS blend[11]

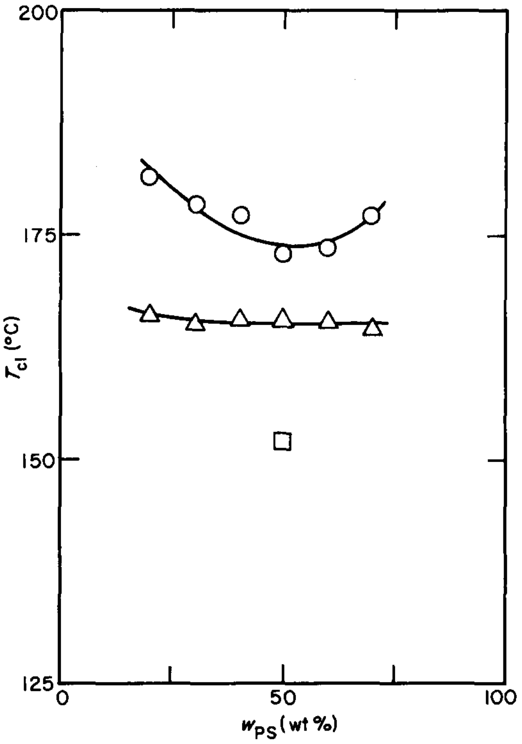

Figure 2 Cloud point curves of PS37K/P2ClS blend measured at various heating rates: ○, 1.2°C min^{-1}; △, 0.067°C min^{-1}; □, 1°C d^{-1} (stepwise change)

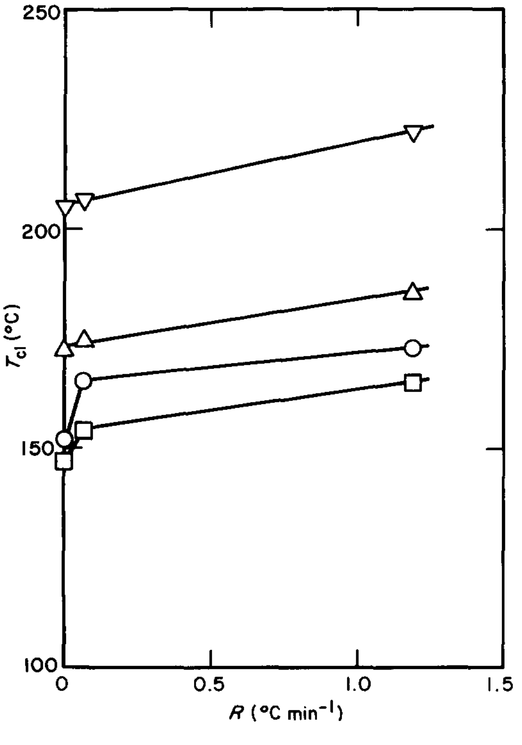

Figure 3 Heating rate (R) dependence of cloud points of ternary blends containing equal weights of PS37K and P2ClS and varying amounts of DBP (wt%): ○, 0; □, 3.5; △, 5.8; ▽, 9.3

from 3.5 to 9.3 wt% DBP plasticizer, together with that of the original binary blend. For higher DBP contents, i.e. 5.8 and 9.3 wt%, the heating rate dependence is given by a straight line over the whole heating rate range investigated. If the DBP content is decreased to 3.5 wt%, an abrupt decrease in T_{cl} is observed in a small R range, similarly to the case of the binary blend, but the decrease is smaller than that for the binary blend. Miscibility of the blend is increased when more than 5.8 wt% DBP is added. However, the apparent miscibility is decreased by the addition of a small amount of DBP, as seen in the data for the 3.5 wt% sample.

Figure 4 shows the same data as in *Figure 3*, but with DBP content on the abscissa. T_{cl}s of the ternary blends decrease linearly with decreasing DBP content at all heating rates, but T_{cl}s of the binary blends are not on these straight lines. The difference in T_{cl} at the two lower heating rates, 0.067°C min^{-1} and 1°C d^{-1}, increases with decreasing DBP content, which is consistent with the large kinetic contribution in the binary system. The observed linear relationship between T_{cl} of the ternary blend and DBP content and the above-mentioned observation that T_{cl} varies linearly with R over the whole investigated R range at the higher DBP contents allow us to make a double extrapolation to zero heating rate and zero DBP content. The difference between $T_{cl}(R = 1°C\,d^{-1})$ and T_{cl} extrapolated to $R = 0$ is negligible compared with experimental accuracy. By extrapolating three data points at a heating rate of 1°C d^{-1} for the ternary blends to zero DBP content, we obtain $T_{cl} = 113$°C. T_{cl} extrapolated to zero DBP content is as much as 40°C lower than T_{cl} of the binary blend obtained directly at a heating rate of 1°C d^{-1}.

Cloud points of blends other than PS37K/P2ClS were also measured at fixed polymer composition PS/P2ClS = 50/50 wt% with varying heating rate and DBP content. *Figure 5* shows the results obtained at a heating rate of 1°C d^{-1}, except for two data points at higher DBP contents of PS30K series which are substituted by the data at $R = 0.067$°C min^{-1} since no difference was observed between the two heating rates 0.067°C min^{-1}

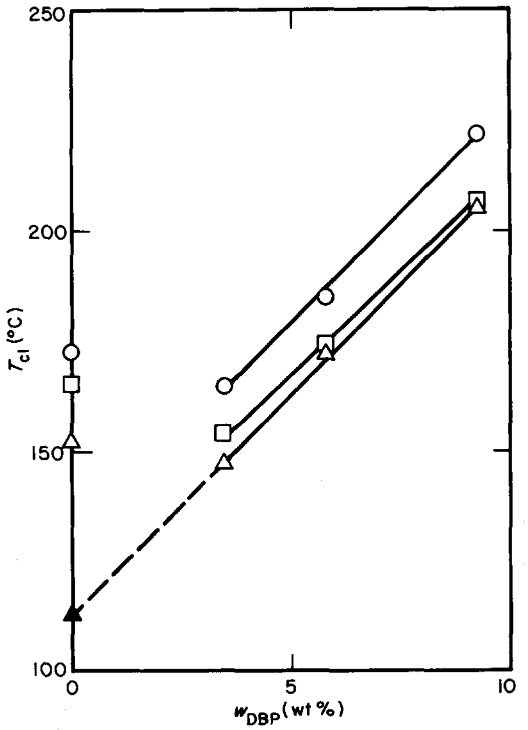

Figure 4 Dependence on DBP content, w_{DBP}, of cloud points of blends containing equal weights of PS37K and P2ClS at various heating rates: ○, 1.2°C min^{-1}; □, 0.067°C min^{-1}; △, 1°C d^{-1}. ▲, Obtained by extrapolation to zero DBP content

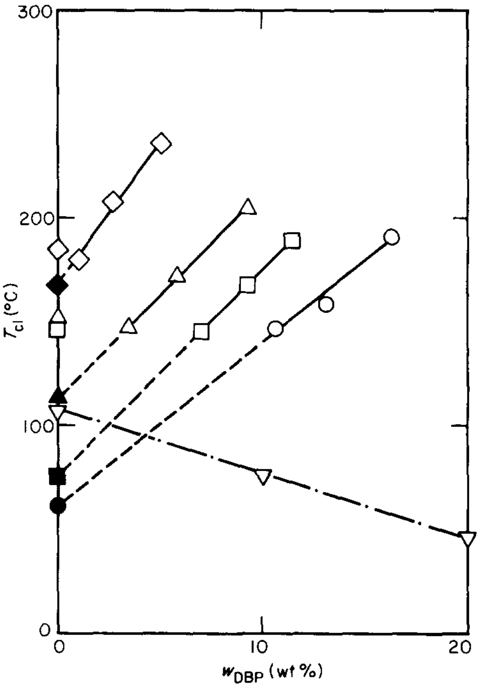

Figure 5 Cloud points of blends containing equal weights of PS and P2ClS and varying amounts of DBP measured at a heating rate of 1°C d^{-1}, along with glass transition temperatures (▽). M_ws of PS are: ◇, 29 400; △, 37 000; □, 43 900; ○, 50 000. Filled symbols denote cloud points of the binary blends estimated by extrapolation to zero DBP content

and 1°C d^{-1} even for lower DBP content (1.04 wt%) than these samples. The glass transition temperatures of blends containing equal weights of PS and P2ClS and varying amounts of DBP are also shown in *Figure 5*. They were calculated by assuming the additivity of experimentally determined T_gs of component polymers containing the same amount of DBP. Except for the points at zero DBP content, a linear relationship between $T_{cl}(R = 1°\mathrm{C\,d^{-1}})$ and DBP content is observed in all series of molecular weights of PS over a large range of DBP content. There seems to be a slight deviation from linearity in the data for the blends with PS50K, but it is within the experimental scatter. Similarly, for PS37K, we can estimate T_{cl}s of the binary blends by extrapolating to zero DBP content for all series of PSs. The difference between observed and extrapolated T_{cl}s of the binary blends is very large, especially for PSs of higher molecular weight. The difference decreases with increasing T_{cl}, but there still remains a difference between the two T_{cl}s even when the extrapolated T_{cl} is 60°C higher than T_g, as seen in the data for PS30K.

Two of the extrapolated T_{cl}s locate below T_g and one is very close to T_g. As the binary blend samples were annealed above T_g, they were exposed, in the sample preparation process, at higher temperatures ($\approx$ 140°C) than the extrapolated cloud point except for the blend PS30K/P2ClS. These samples were clear and transparent as judged by visual inspection. Angular dependence of the intensity of the light scattered from these samples did not have a peak or a shoulder typical of a system under phase separation. However, the scattered light intensity was slightly too large compared with data from blends containing the plasticizer. Therefore, some microscopic inhomogeneity seems to exist, caused by very slow phase separation in these samples*. It is considered that the unusual behaviour of the cloud point curves observed in *Figure 1* and the large difference between the observed and extrapolated T_{cl}s of the binary blends are attributable to this microscopic inhomogeneity and kinetic effects in determination of cloud points.

The cause of the drop in T_{cl} observed at very small heating rate in *Figure 3* is not clear. It may be considered that the drop in T_{cl} corresponds to a change in the mechanism of phase separation from spinodal decomposition to nucleation and growth, since there must be a heating rate below which phase separation from the metastable state can be observed in principle. However, this does not seem to be consistent with the results of the ternary blends. In the ternary blends, phase separation by nucleation and growth is expected to be observed at higher heating rates since mobility is increased by addition of plasticizer, but the amount of the drop in T_{cl} decreases with increasing DBP content. Furthermore, the spinodal temperature estimated from the kinetic study of phase separation has turned out to be close to the cloud point obtained at the slowest heating rate of 1°C d^{-1} (Reference 15). The initial stage of the spinodal decomposition is thought to be described by the Cahn theory[16,17]. According to the Cahn theory, the diffusion constant can be determined from the rate of increase of initial scattered intensity after the temperature jumps into the unstable region, and the spinodal temperature is determined as the temperature at which the diffusion constant becomes zero. The spinodal temperature of the blend PS37K/P2ClS/DBP (= 47.3/47.3/5.4 wt%) was estimated by this method to be 156°C, which is slightly lower than the T_{cl} at 1°C d^{-1} shown in *Figure 4*. Therefore, we do not believe that phase separation from the metastable state was observed at the slow heating rate.

A cloud point extrapolated to zero heating rate is generally considered to be located somewhere between the spinodal and binodal points. Since the phase separation from a metastable state is considered to be very slow in such a highly viscous polymer blend as the present system, the extrapolated cloud point is expected to be located very close to the spinodal point. This is supported by the results of kinetic study of phase separation as mentioned above. By assuming that the extrapolated T_{cl} corresponds to the spinodal point, we calculated the Flory–Huggins interaction parameter χ using the spinodal condition. The condition is given by the Flory–Huggins theory[18] as

$$\chi = \frac{1}{2}\left(\frac{1}{N_A\phi_A} + \frac{1}{N_B\phi_B}\right)$$

where N_i is the degree of polymerization and ϕ_i is the volume fraction of polymer i (i = A, B). We also calculated the χ parameter by using the critical condition to estimate how much χ depends on evaluation conditions. The results are shown in *Figure 6*. The difference between the results is not large. Both results give straight lines when plotted against $1/T$. The temperature dependence of χ calculated from the spinodal condition is given by fitting these data to be

$$\chi = 0.0078 - 1.63/T\,(\mathrm{K})$$

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* In Reference 14, Tsujita *et al.* measured the glass transition temperatures of PS(M_w = 236 900, M_w/M_n = 2.13)/P2ClS by dilatometry and observed a broad transition region in contrast to the sharp transition of both pure components, which they also attributed to microheterogeneous mixing of both polymers in the blend.

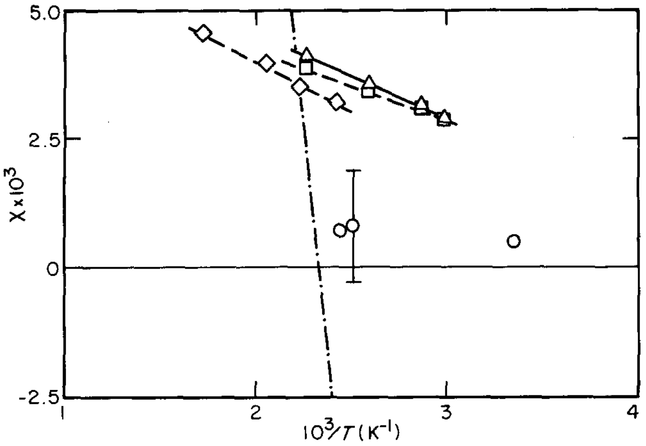

Figure 6 Reciprocal temperature dependence of the Flory–Huggins interaction parameters χ of the PS/P2ClS system calculated from T_{cl} of binary blends using (△) the spinodal and (□) the critical conditions, and from T_{cl} of PS/P2ClS/DBP blends containing 10 wt% DBP assuming the Scott equation for (◇) the spinodal condition, together with χ parameter (○) of the d-PS/P2ClS system[19] and (—·—) of the d-PS/PVME system[8]

Murray *et al.*[19] measured the χ parameter of a blend of P2ClS ($M_w = 65\,000$, $M_w/M_n = 1.15$) and deuterated (d-)PS ($M_w = 30\,500$, $M_w/M_n = 1.06$) by performing a small angle neutron scattering experiment. *Figure 6* shows their results for volume fraction $\phi_{d\text{-PS}} = 0.53$. They obtained values slightly smaller than our results and found no temperature dependence in a temperature range from 25 to 135°C. They estimated a relatively large error for their measurement. The temperature dependence obtained by us is compatible with their results when the error is taken into account. The observed difference can be ascribed in part to the isotopic difference. The χ parameter of the present system has very small temperature dependence. This is more clearly exhibited when it is compared with that of the most extensively investigated polymer blend, d-PS/poly(vinyl methyl ether) (PVME). The data of Han *et al.*[8] for a blend containing equal weights of d-PS ($M_w = 2.3 \times 10^5$, $M_w/M_n = 1.14$) and PVME ($M_w = 3.89 \times 10^5$, $M_w/M_n = 1.25$) can be approximately expressed by $\chi = 0.083 - 35.6/T$. As shown in *Figure 6*, χ for d-PS/PVME blend has a very large temperature dependence and changes its sign from negative to positive as temperature is increased, which is characteristic of a system where miscibility is caused by a specific interaction. Isotopic polymer blends are characterized by non-zero χ: the values of $d\chi/d(1/T)$ of isotopic blends known so far range from 0.1 to 0.4[20,21]. The temperature dependence of χ of the present system is intermediate between those of the isotopic blends and that of a blend having a specific interaction. The small temperature dependence of χ results in the large molecular weight dependence of the phase diagram. It is difficult to find a combination of molecular weights having a LCST in an experimentally accessible temperature range in such a system.

Zacharius *et al.*[10] have pointed out the possibility that the PS/P2ClS system has an upper critical solution temperature (UCST) as well as a LCST. The small value and small temperature dependence of χ obtained from the cloud point data support their speculation. In fact, an isotopic blend, which is characterized by a very weak positive interaction, exhibits UCST behaviour. However, we could not actually observe an UCST in the investigated temperature range, nor positive $d\chi/d(1/T)$ at lower temperatures. According to Zacharius *et al.*[10], Ryan postulated the critical double point, where UCST and LCST merge, to be 550 K, but our results suggest that the critical double point is located at a temperature lower than the glass transition temperature, if it exists.

According to Scott[22], the principal role of a solvent in a polymer–polymer–solvent system is a diluent of the interaction between polymer segments, and a symmetrical ternary system can be treated as a binary polymer blend if an effective interaction parameter $\chi' = \chi(1 - \phi_{\text{solvent}})$ is used. We attempted to calculate the χ parameters from T_{cl}s of blends containing 10 wt% DBP, although the applicability of the effective χ parameter to the present system is not clear. The χ parameters thus calculated do not connect smoothly with those calculated from the extrapolated T_{cl}, but both results show roughly the same temperature dependence and order of magnitude as shown in *Figure 6*.

The kinetics of phase separation depends on the mobility of components and the thermodynamic driving force. In the present system, mobility is considered to be very small since the cloud points are located below or relatively close to the glass transition temperature, and the driving force is also very small unless the temperature is much higher than the spinodal point because of the very small temperature dependence of χ. Thus the kinetic contribution is quite large in determination of cloud points. Such a large kinetic contribution can cause unusual phase behaviour in PS/P2ClS blends. For example, in the measurement of the molecular weight dependence of cloud points at various heating rates higher than 0.1°C min^{-1}, Imura and Tran-cong have observed that cloud points of samples of higher molecular weight appear at higher temperatures[23]. In addition, we are apt to fail to notice the microscopic inhomogeneity or phase separation generated in the sample preparation process since phase separation is too slow. Inconsistency among the data regarding the miscibility of the PS/P2ClS system is considered to be caused by the very slow phase separation kinetics of the system.

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