Effects of chemical labelling on the phase behaviour of poly(2-chlorostyrene)/ poly(vinyl methyl ether) blends

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The phase behaviour of poly(2-chlorostyrene)/poly(vinyl methyl ether) blends (P2CS/PVME) was investigated by means of light scattering and small-angle X-ray scattering (SAXS) using synchrotron radiation. It was found that P2CS/PVME blends possess a lower critical solution temperature. Chemically labelling P2CS with photoreactive anthracene not only decreases the miscibility of the blends but also shifts the critical point of the phase diagram towards a composition higher in P2CS – a typical effect of such systems with polydispersity induced by the labelling reaction. Within the temperature range of the experiments, the critical behaviour of both unlabelled and labelled blends can be accurately expressed by the mean-field theory with the critical exponents $\nu = 1/2$ and $\gamma = 1$. These experimental results suggest that the effects of chemical labelling of polymer chains via polymer reactions may play an important role in the phase decomposition kinetics and morphological studies of polymer blends.

(Keywords: chemical labelling; phase behaviour; P2CS/PVME blends)

INTRODUCTION

Labelling polymer chains with some specific chemical groups is a popular procedure which has been widely used to investigate the physical properties of polymers, such as local chain dynamics in solutions and in bulk[1] or the compatibility of multicomponent polymers[2,3]. In particular, for polymer blends excimer fluorescence[4,5], non-radiative energy transfer[6], and electron spin resonance (e.s.r.)[7] have been efficiently employed to examine the compatibility of polymer blends in the range beyond or comparable to a single chain dimension. Recently, besides the scattering technique, fluorescence quenching has also been demonstrated as a tool to monitor the phase separation kinetics of binary polymer blends[8]. In these studies, polymer chains are labelled with a very small amount of molecular probe and the information on the local environment, described by a certain characteristic length scale which is determined by the lifetimes of the corresponding excited states, can be obtained from the appropriate measurements. For polymer blends, it is possible that the probe might alter the phase behaviour of the unlabelled mixtures, particularly when the polymer chains have a high concentration of these labels. The extreme example for such an alteration of phase behaviour can be seen in the enhancement of polymer compatibility by chemical modification. Copolymerization of polystyrene with a small amount of an α-methylstyrene derivative containing a hydroxy group which forms a hydrogen bond with poly(butyl methacrylate) leads to a blend exhibiting a lower critical solution temperature (*LCST*)[9]. Electrostatic attraction[10] and ion–dipole interactions[11] between the specific groups chemically incorporated into the polymer chains of incompatible polymer pairs and charge transfer complex formation[12] have also been used to enhance compatibility.

Recently, in an attempt to design multiphase polymers with controllable, ordered structures in the micrometre range, we have used photo-crosslink reactions to freeze the concentration fluctuations developing during the spinodal decomposition processes of polystyrene/poly(2-chlorostyrene)[13,14] and polystyrene/poly(vinyl methyl ether)[15] blends. In these studies, the crosslinking between polystyrene chains was accomplished by photodimerization of anthracene groups attached to the polystyrene chains. From the viewpoint of phase decomposition kinetics, it is necessary to understand the effects of labelling with anthracene on the phase behaviour of these photosensitive blends. This information is not only important in understanding the effects of chemical labelling or chemical modification on the phase behaviour of polymer mixtures, but can also provide information for quantifying experimental conditions for the photo-crosslink experiments[13–15], such as choosing the temperature-jump depths, determining the critical composition, etc.

The objective of this work was first to characterize the phase behaviour of a new blend, i.e. poly(2-chlorostyrene)/ poly(vinyl methyl ether) (P2CS/PVME), by light scattering and small-angle X-ray scattering (SAXS) using synchrotron radiation. In order to induce the interchain photo-crosslink reaction, P2CS chains were labelled with anthracene. The effect of labelling on

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the critical behaviour of the blends was investigated. This paper will end with a discussion of the phase behaviour of chemically labelled blends on the basis of mean-field theory[16].

EXPERIMENTAL

Sample synthesis and characterization

Poly(2-chlorostyrene) (P2CS) was prepared by radical polymerization of 2-chlorostyrene (Tokyo Kasei Co., Japan) in benzene with α,α'-azobisisobutyronitrile as initiator. After the polymerization, P2CS was purified by using benzene/methanol mixtures and was subsequently chloromethylated according to the conventional procedure using chloromethyl methyl ether[17]. It is worth noting that P2CS can only be chloromethylated in neat chloromethyl methyl ether. Chloromethylation of P2CS did not proceed when mixtures of dichloromethane and chloromethyl methyl ether were used as solvent[18]. Anthracene-labelled poly(2-chlorostyrene) (P2CS-A) was obtained by reacting chloromethylated P2CS with the potassium salt of 9-anthracenecarboxylic acid (Aldrich, recrystallized twice from ethanol) in anhydrous dimethylfomamide over 8 h at 65°C. The weight-average molecular weight M_w of the labelled polymer was 2.1×10^5 and the corresponding molecular weight distribution M_w/M_n was 1.8. The former was determined from intrinsic viscosity data[19] and the latter by gel permeation chromatography (g.p.c.). The average label content of P2CS-A chains was estimated as ca. 16 per chain from the u.v. absorbance of the anthracene moieties. Poly(vinyl methyl ether) (PVME, Scientific Polymer Products Inc., $M_w = 6.8 \times 10^4$, $M_w/M_n = 2.5$) was purified using methanol/n-heptane mixtures. The weight-average molecular weight was obtained from the intrinsic viscosity in toluene[20]. P2CS/PVME and P2CS-A/PVME blends were prepared by casting from benzene solutions and were dried at 80°C under vacuum for several nights prior to the scattering experiments. Blends with a thickness of ca. 100 μm and 1 mm, respectively, were used for the cloud point measurements by light scattering and for the determination of the spinodal temperatures (T_{sp}) by small-angle X-ray scattering (SAXS).

Instruments

The cloud points of the unlabelled and labelled blends with various compositions were measured using a light-scattering photometer at a fixed angle (20°)[13,14]. Since the glass transition temperatures of these blends depend strongly on the composition, the cloud points were obtained by extrapolating the data to a zero heating rate in order to avoid errors in the cloud point determination due to the kinetic effects[21] which become significant as the compositions increase in P2CS and P2CS-A. The heating rates used in these experiments were 0.1, 0.2, 0.5 and 1°C min^{-1}. SAXS experiments were performed using the synchrotron radiation facilities at the National Laboratory for High Energy Physics, Tsukuba, Japan (Photon Factory, BL-1OC). The details of the SAXS instrument have been described elsewhere[22]. Briefly, the incident X-ray with a wavelength of 1.488 Å selected from a 2.5 GeV storage ring was point focused by using a double-flat monochromator combined with a bent cylindrical mirror. The scattering intensity from the sample was detected by a one-dimensional, position-sensitive proportional counter (PSPC, 512 channels). The distance between the sample and the detector was 1.9 m. The sample of 1 mm thickness was mounted on a sample holder and kept in a brass heating block which was thermostated with a precision of ±0.5°C. The blend was sandwiched between two Mylar (PET) thin films each with a thickness of 5 μm. Scattering due to the two Mylar windows was subtracted from the total scattering intensity. The absorption of the sample was also corrected to give the excess scattering as a function of the scattering angle.

Data analysis

The SAXS scattering profiles of the blends observed at a given temperature were fitted to the Ornstein–Zernike (O–Z) equation[23] by using a linear, least-squares method

$$S(q)/S(0) = 1/(1 + \xi^2 q^2) \tag{1}$$

where $q = (4\pi/\lambda)\sin(\theta/2)$ is the magnitude of the scattering vector $\mathbf{q}$ at the angle θ and λ is the wavelength of the incident X-ray; $S(q)$ is the scattering intensity observed at the scattering vector $\mathbf{q}$; $S(0)$ is the scattering intensity at zero angle; and ξ is the correlation length physically corresponding to the wavelength of the fluctuations.

All the scattering data were fitted to equation (1) within the region $q\xi < 1$. To obtain the correlation length ξ of a blend with a particular composition at a given temperature, the inverse scattering intensity $1/S(q)$ was plotted *versus* q^2. Subsequently, ξ was calculated from the ratio of the slope to the intercept, whereas $S(0)$ was obtained from the intercept of this plot.

RESULTS AND DISCUSSION

With increasing temperature, the scattering intensity from P2CS/PVME and P2CS-A/PVME blends gradually increases, particularly at low q. At a certain temperature, $S(q)$ increases steeply with $q \to 0$, exhibiting a typical critical scattering behaviour due to the formation of precipitated domains with dimensions larger than the

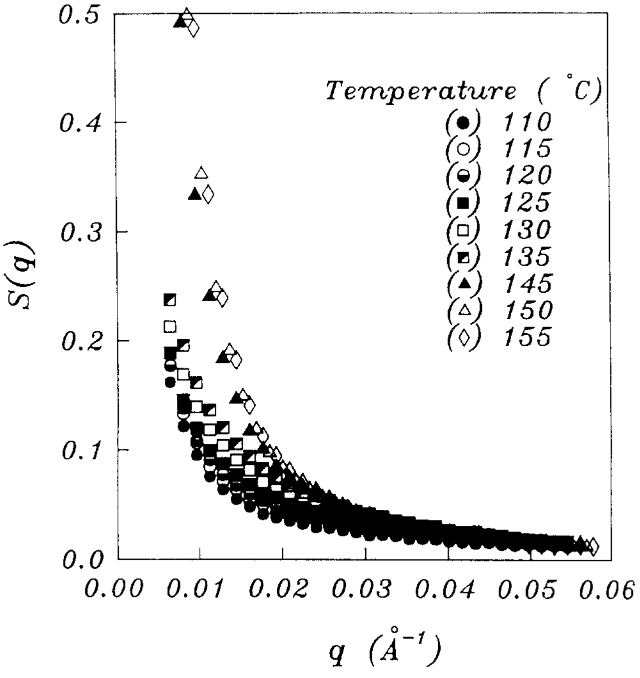

Figure 1 Temperature dependence of the scattering function $S(q)$ for a P2CS-A/PVME 70/30 blend

wavelength of the incident X-ray. As an example, the temperature dependence of the scattering function for a P2CS-A/PVME 70/30 blend is shown in *Figure 1*.

These experimental results indicate that the components of the P2CS/PVME and P2CS-A/PVME blends are miscible at low temperature and undergo phase separation at a high temperature. To estimate the correlation length, the scattering intensities obtained at different temperatures and compositions were fitted to the Ornstein–Zernike function. Typical inverse scattering intensities $1/S(q)$ for a P2CS-A/PVME 50/50 blend at 120°C and a P2CS/PVME 70/30 blend at 125°C are plotted against q^2 in *Figure 2*. The scattering function at low q can be fitted to the O–Z equation in the region $q\xi<1$. The correlation lengths ξ obtained from these plots increase with increasing temperature, suggesting the existence of a lower critical solution temperature (*LCST*) in these blends. As shown in *Figures 3a* and *3b*, the dependence of $1/\xi^2$ on the reciprocal absolute temperature is linear for all compositions of P2CS/PVME and P2CS-A/PVME blends. From the linear dependence between $1/\xi^2$ and $1/T$, the spinodal temperature corresponding to each composition of these blends is obtained by extrapolating these data to zero $1/\xi^2$, provided that the critical behaviour of P2CS/PVME and P2CS-A/PVME follows the prediction of the mean-field theory[24,25]. This assumption is also justified by the dependence of the correlation length on the order parameter $\varepsilon=|T-T_{sp}|/T_{sp}$ shown in *Figure 4* for the unlabelled and labelled blends. Within experimental error, the slopes of these straight lines are close to $-1/2$, as predicted by the mean-field theory ($\xi\approx\varepsilon^{-\nu}$, $\nu=1/2$). However, for the composition close to the edge of the phase diagram, i.e. P2CS/PVME 8/92, this slope is somewhat smaller. One possible reason is that the assumption of the mean-field theory[16] is not satisfied owing to a dilution effect. A similar behaviour is observed for the dependence of the zero-angle scattering intensity $S(0)$ on the order parameter ε, as depicted in *Figure 5*. The critical exponent γ for all the compositions is close to 1, as predicted by the mean-field theory ($S(0)\approx\varepsilon^{-\gamma}$,

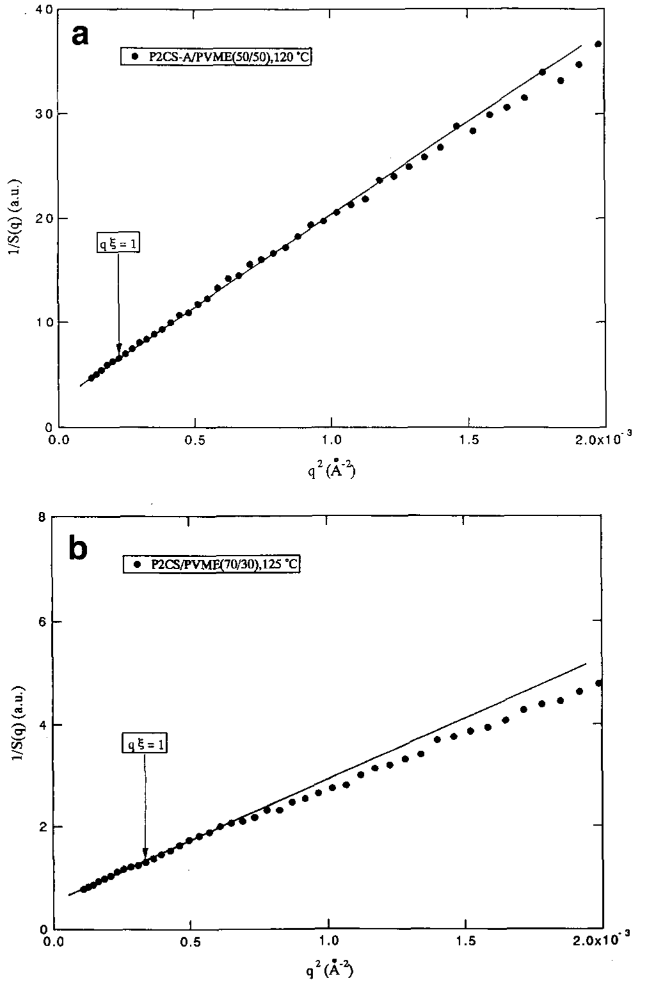

Figure 2 Ornstein–Zernike plots for (a) a P2CS-A/PVME 50/50 blend at 120°C ($\xi=70.4$ Å) and (b) a P2CS/PVME 70/30 blend at 125°C ($\xi=60.6$ Å)

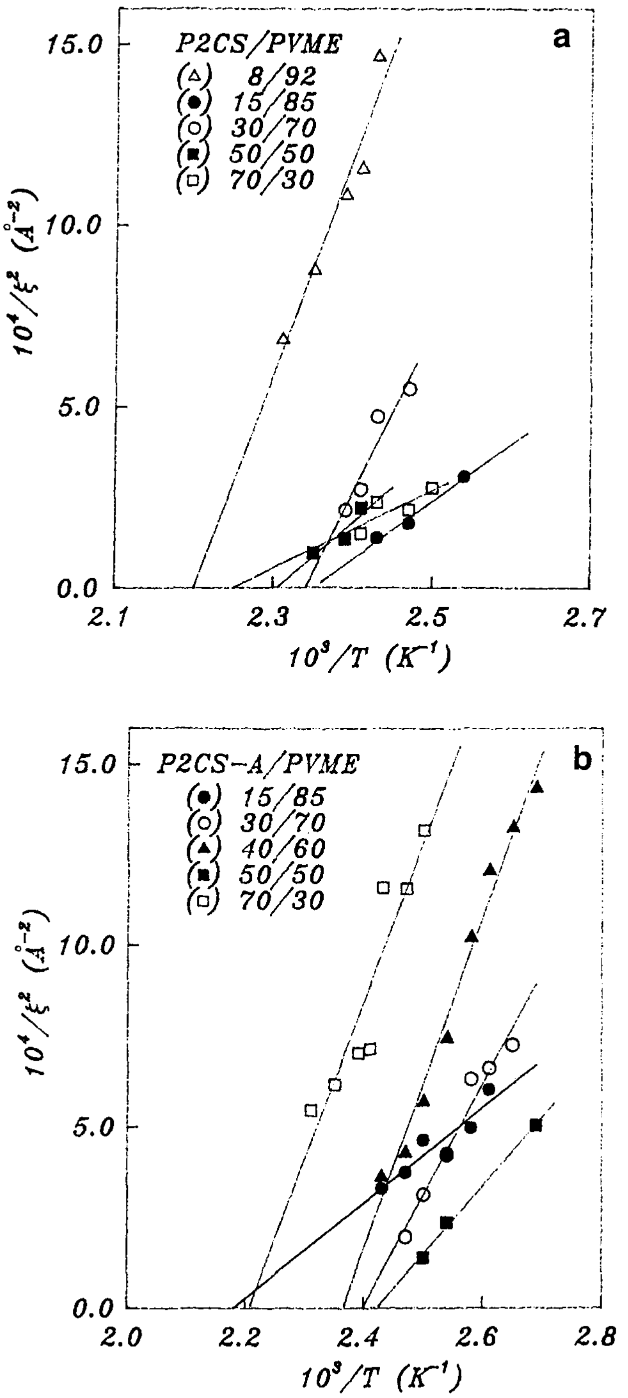

Figure 3 Plots of $1/\xi^2$ *versus* $1/T$ for (a) P2CS/PVME and (b) P2CS-A/PVME blends

$\gamma = 1$), except for the P2CS/PVME 8/92 composition. Recently, the mean-field Ising crossover phenomena observed by small-angle neutron scattering (SANS) were reported for a series of binary polymer blends[26–29]. This particular transition was not observed in the present work since the temperatures were not sufficiently close to the critical point for these blends. Therefore, we conclude that both P2CS/PVME and P2CS-A/PVME blends possess a lower critical solution temperature and their critical behaviour obeys the mean-field theory within the temperature range of our experiments.

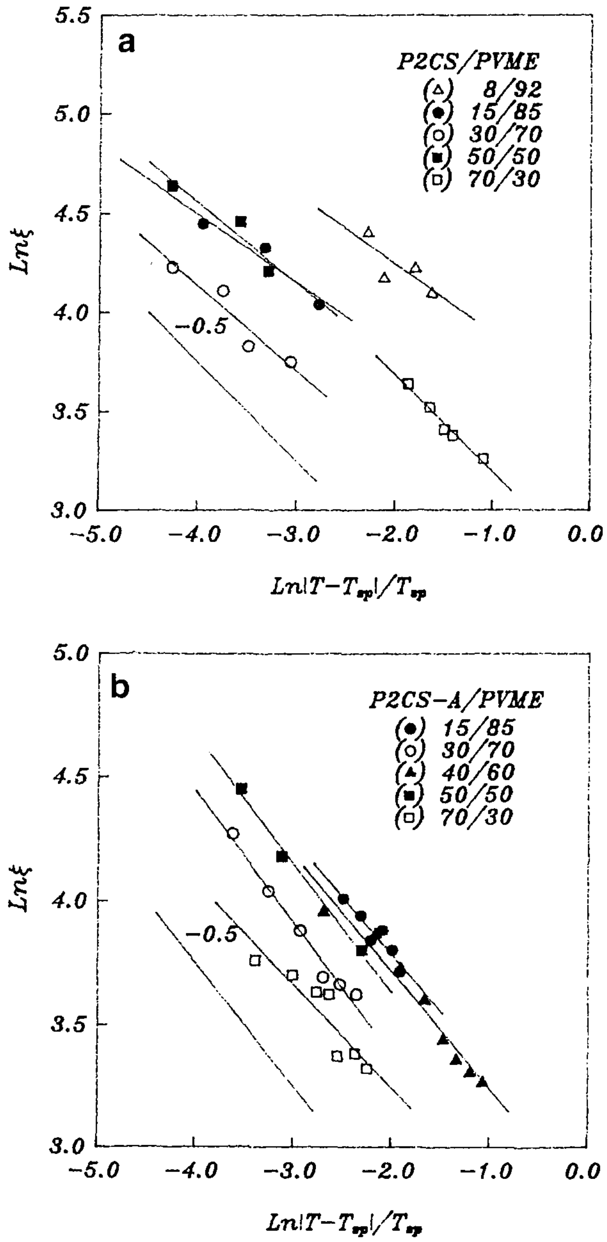

Figure 4 Dependence of the correlation length ξ on the order parameter ε for (a) P2CS/PVME and (b) P2CS-A/PVME blends

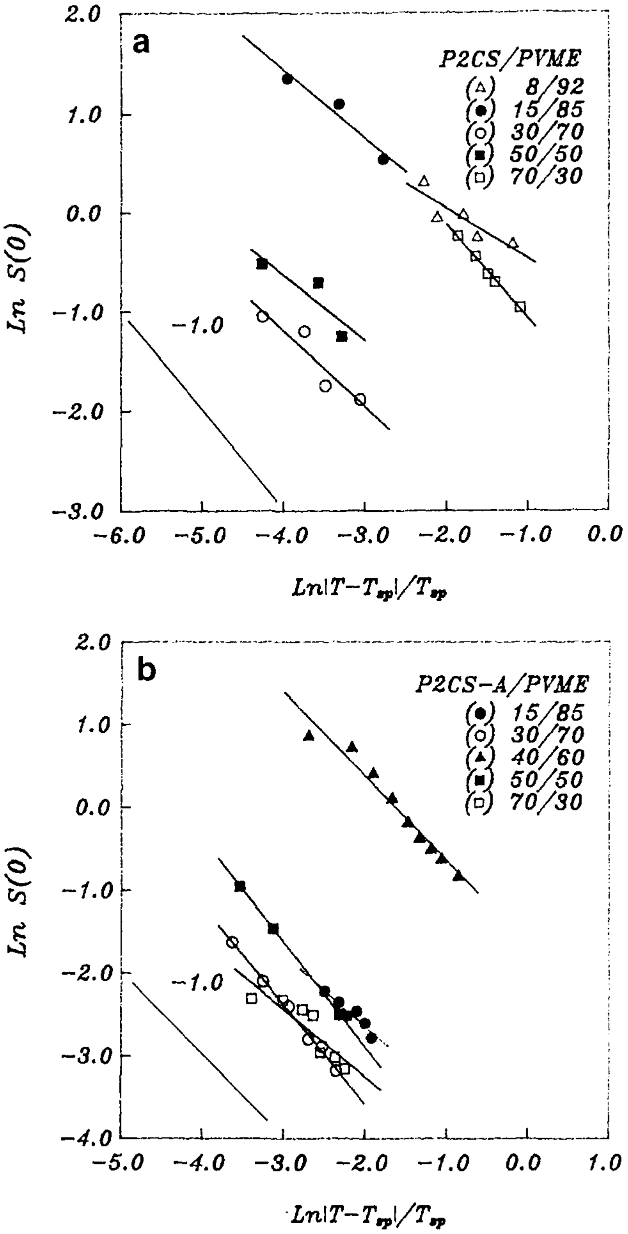

Figure 5 Dependence of the zero-angle scattering $S(0)$ on the order parameter ε for (a) P2CS/PVME and (b) P2CS-A/PVME blends

From the spinodal temperatures obtained by SAXS and the cloud points measured by light scattering, the phase diagrams of the unlabelled P2CS/PVME and anthracene-labelled P2CS-A/PVME blends were constructed. These results are shown in *Figure 6*. For the unlabelled blends, the minimum of the spinodal line coincides with that of the cloud point curve. This phase behaviour with the critical point located at ca. 20% P2CS is similar to that observed through small-angle neutron scattering in polystyrene/poly(vinyl methyl ether) blends[24]. However, labelling the P2CS chains with one anthracene per 95 repeat units of P2CS not only lowers the miscibility of the components in the blend but also shifts the critical point towards a composition higher in P2CS-A on the phase diagram. There are two possibilities for this peculiar behaviour of P2CS/PVME blends. One is that the molecular weight of P2CS and its distribution may have been appreciably modified by the labelling reaction. The other originates from the specific interaction between the labelled P2CS and PVME. Gel permeation chromatograms of the unlabelled P2CS and the anthracene-labelled P2CS-A are shown in *Figure 7*. Compared to P2CS, the weight-average molecular weight of P2CS-A has increased by a small amount $\Delta M = 30\,000$, whereas the molecular weight distribution is almost unchanged ($M_w/M_n = 1.9$ for P2CS-A and $M_w/M_n = 1.8$ for P2CS). These values were estimated using standard polystyrenes as reference samples. These results imply that the hydrodynamic volumes of the unlabelled P2CS chains were slightly modified by the presence of anthracene in THF (the elution solvent) in the g.p.c. experiments. Therefore the large shift of the spinodal line of P2CS-A/PVME blends shown in *Figure 6* cannot be explained by this small increase in molecular weight. We think that this shift is probably due to the thermodynamic interactions between the anthracene label and PVME. Though the label content of P2CS-A is constant (16 anthracene groups per chain), the total number of anthracene molecules present in the blend increases with increasing P2CS-A content. Consequently, it is highly possible that the dependence of the effective χ parameter (χ_{eff}) between P2CS-A and PVME on the concentration of the anthracene label is responsible for the large shift in the critical composition of P2CS-A/PVME. There also exists an inhomogeneous distribution of the label on the P2CS-A chains owing to the nature of the labelling reaction. A large shift in the critical composition can be expected if χ_{eff} strongly depends on the label content. This problem can be elucidated by performing more elaborate experiments such as measuring the dependence of χ_{eff} on the label content. Detailed experiments are currently under consideration.

It is worth noting that the results obtained in this work are not generally applicable to all polymer blends chemically labelled with photosensitive probes. Firstly, compared with end-labelled polymers, the label content of the polymer used in this work is fairly high (ca. 1 mol%) owing to the requirement for crosslink efficiency. The general answer to the question of whether the phase behaviour of polymer mixtures will be modified by chemical labelling depends on both the label concentration and the interaction parameter between the label molecules and the two polymer components. Nevertheless, the large deviation in the critical point of the P2CS/PVME blend caused by the anthracene labelling plays an important role in the phase separation kinetics and is also critical for the morphological studies using photo-crosslinks since the so-called transnodal region has been found recently[30,31]. On the other hand, compared to polystyrene with a similar molecular weight and label content[15], P2CS-A seems to be more miscible with PVME. The presence of the chlorine atom may play a key role in the difference in miscibility between these two blends since the lone pairs of the PVME oxygens interact more strongly with the π electrons of the benzene rings on P2CS. These intermolecular interactions can be quantitatively elucidated by using *FT*i.r. spectroscopy[32].

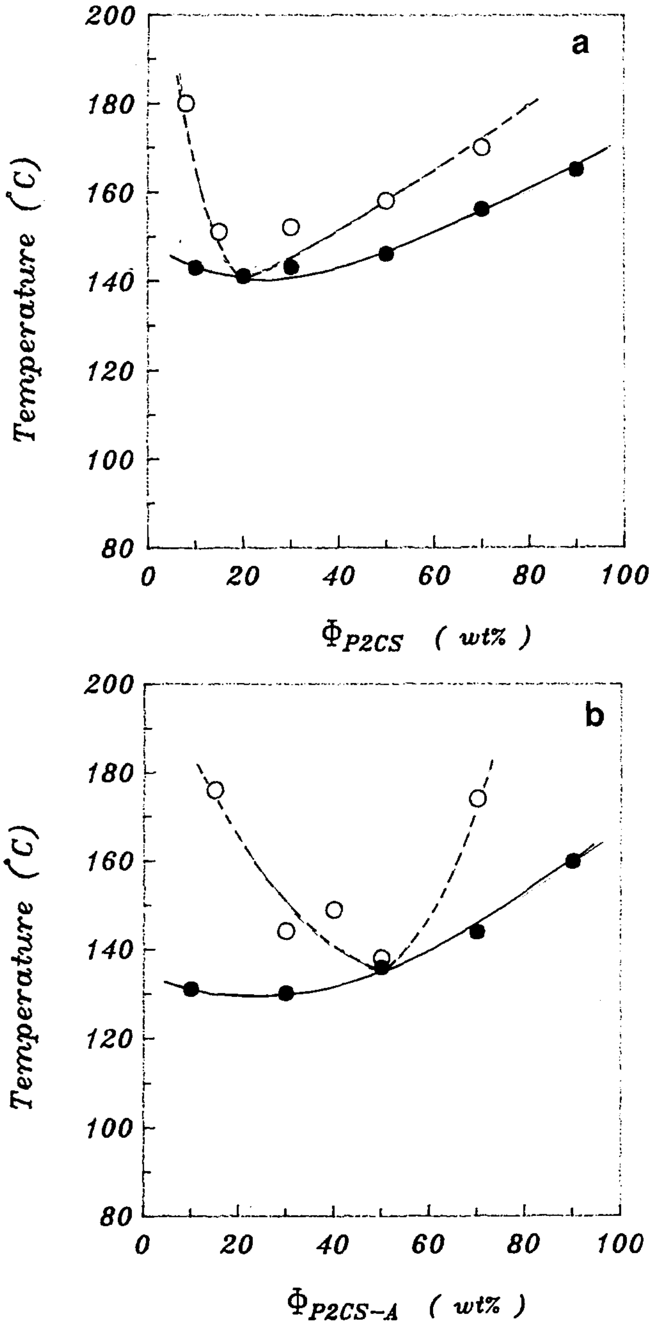

Figure 6 Phase diagrams of (a) P2CS/PVME and (b) P2CS-A/PVME blends

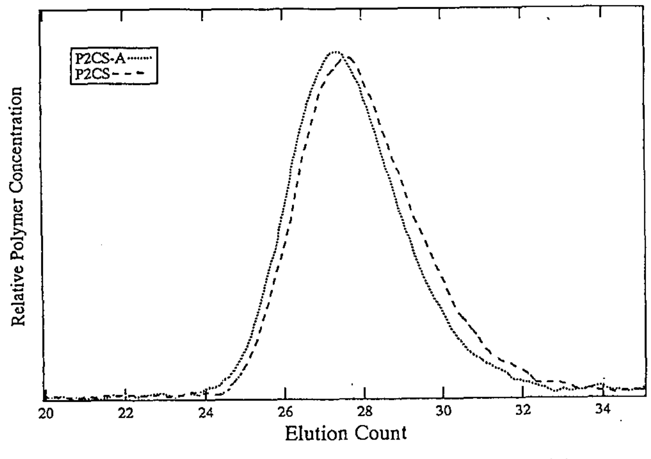

Figure 7 Chromatograms of P2CS and P2CS-A obtained by g.p.c. with THF as eluent

CONCLUSIONS

The phase behaviour of poly(2-chlorostyrene)/poly(vinyl methyl ether) blends (P2CS/PVME) was characterized using light scattering and small-angle X-ray scattering. The following results were obtained.

1. P2CS/PVME blends exhibit a lower critical solution temperature (*LCST*). The critical behaviour of this blend as well as the blend with anthracene-labelled P2CS is in good agreement with the prediction of the mean-field theory. The critical exponent ν is 1/2 for the correlation length and γ is 1 for the scattering intensity.
2. Labelling P2CS chains with ca. 1 mol% anthracene reduces the miscibility in the blends and also results

in a large shift of the critical composition. These results provide important information for morphological studies of photocurable polymer mixtures.

3. Since polystyrene/PVME blends do not have an electron density contrast sufficient for SAXS studies[33], P2CS/PVME blends with the characteristics described in the present investigation can provide a blend suitable for this purpose.

An advantage of the characteristics of these blends is that systematic studies on the morphology resulting from the photo-crosslinking of P2CS chains during the time evolution of the spinodal decomposition can be carried out in a more quantitative way. These experiments are currently in progress.

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