Miscibility of poly(2-chlorostyrene) and poly(vinyl methyl ether) blends

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In this work, the miscibility of poly(2-chlorostyrene) (P2CS) and poly(vinyl methyl ether) (PVME) mixtures was characterized and compared to polystyrene (PS)/PVME blends. It was found, by light scattering, that P2CS/PVME blends exhibit a lower critical solution temperature. Fourier transform infra-red spectra of these two blends indicate that the presence of the chlorine atom strengthens the attraction between the phenyl rings of P2CS and the electron lone pairs of the oxygen atoms on the PVME chains. This specific interaction is the main reason for the improvement of the miscibility of this particular blend in comparison to PS/PVME. These experimental results are in accord with the magnitudes of the binary interaction parameters, χ, of P2CS/PVME and PS/PVME blends estimated from the cloud point data based on the mean-field theory. The experimental results obtained in this work provide a molecular basis for the interpretation of polymer–polymer miscibility.

(Keywords: blends; miscibility; light scattering)

INTRODUCTION

Prediction of polymer–polymer miscibility is important not only for application-oriented studies in polymer materials science, but also for basic research in the field of critical phenomena. Though not perfect, the miscibility of a polymer mixture can be widely expressed by the Flory–Huggins mean-field theory[1]. In general, the miscibility of a polymer pair is dictated by the change in Gibbs free energy of mixing, ΔG_{mix}. Since the change in entropy of mixing, ΔS_{mix}, is usually small for polymers, miscibility of a polymer pair will be improved if the change in enthalpy of mixing, ΔH_{mix}, is negative. For this reason, a number of studies have been focused on polymer mixtures with specific interactions, such as hydrogen bonding[2–5] or charge-transfer complex formation[6].

The typical and well-known polymer mixture exhibiting a lower critical solution temperature (*LCST*) is polystyrene (PS)/poly(vinyl methyl ether) (PVME) blend[7]. It is known that the miscibility at low temperature of this particular polymer pair originates from the specific interactions between the π-electrons of the phenyl ring of PS and the electron lone pairs of PVME. These attractive interactions have been observed through the changes in i.r. absorption peaks of both PS and PVME upon mixing and increasing the temperature[8,9]. From the viewpoint of controlling miscibility of polymer blends, as well as understanding the contribution to miscibility of the specific interactions between two polymer components at the molecular level, it is of great interest to observe the effects of substitution on the phenyl rings of PS on its miscibility with PVME. It is also known that PS/PVME blends do not have sufficient contrast in electron density to scatter X-rays, and as a consequence it was not possible to characterize the phase behaviour of this blend by using small-angle X-ray scattering (SAXS)[10]. Therefore, mixtures of halogen-substituted PS and PVME can provide a model blend system for studies of critical phenomena of polymer mixtures with *LCST* by SAXS.

In the previous report, we showed that poly(2-chlorostyrene) (P2CS), a chlorine-substituted derivative of PS, can form a miscible blend with PVME, and their phase behaviour obeys the mean-field prediction as observed by SAXS[11]. In this work, details of the miscibility between P2CS and PVME are examined and compared to PS/PVME blends. First, the molecular weight dependence of the phase diagrams of P2CS/PVME blends is studied by light scattering. Then the specific interaction parameter, χ, between 2-chlorostyrene and vinyl methyl ether repeating units is estimated from the cloud point data based on the mean-field theory. Furthermore, the specific interactions between the two components of these blends are examined experimentally, by using Fourier-transform infra-red (*FT*i.r.) spectroscopy, together with the composition dependence of the glass transition temperatures (T_gs) of these blends. Finally, the relation between the molecular interactions and the corresponding miscibility is discussed.

EXPERIMENTAL

Samples

P2CS was obtained by radical polymerization of 2-chlorostyrene (Tokyo Kasei, Japan) in benzene at 60°C over 3 days with α,α'-azobis(isobutyronitrile) (AIBN) as initiator. The polymer was fractionated at 30°C by using benzene/methanol mixtures to obtain five fractions with molecular weights ranging from 10^5 to 10^6. The charac-

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teristics of the P2CS used in this work are summarized in *Table 1*. PVME ($M_w = 1.05 \times 10^5$, $M_w/M_n = 2.2$, Scientific Polymer Products Inc.) was purified before use by precipitating with methanol as good solvent and n-heptane as non-solvent. P2CS/PVME blends of given compositions, with a thickness of about 100 μm, were obtained by casting benzene solutions of P2CS/PVME mixtures at room temperature. Subsequently, these thin films were dried at 80°C over 2 nights to remove solvent prior to the experiments.

Instruments

Cloud points of P2CS/PVME blends were measured by using a light scattering photometer at a fixed angle[12]. The T_gs of these polymer mixtures were obtained by using a thermal analyser system (Mac Science 3100) with a heating rate of 5°C min^{-1}. To determine the cloud point of a given blend composition, the scattering data were first taken at three heating rates, 0.1, 0.2 and 0.5°C min^{-1}. These apparent cloud points were then extrapolated to zero heating rate. This procedure was employed in order to avoid the kinetic effects accompanying the large change in the T_gs with the blend composition. As an example, the extrapolation procedure to determine the cloud point of a P2CS/PVME (20/80) blend is shown in *Figure 1*. All the cloud points fall on a straight line, justifying the determination of the cloud points by this extrapolation procedure. I.r. absorption spectra of these blends were measured by using an *FT*i.r. spectrometer (Firis Model 100, Fuji Electric Co.) with a resolution of 2 cm^{-1}.

Table 1 Characteristics of fractionated P2CS

M_w	M_w/M_n
61 000	1.84[a]
182 000	1.26
331 000	1.20
660 000	1.43
1 470 000	1.26

[a] Unfractionated sample

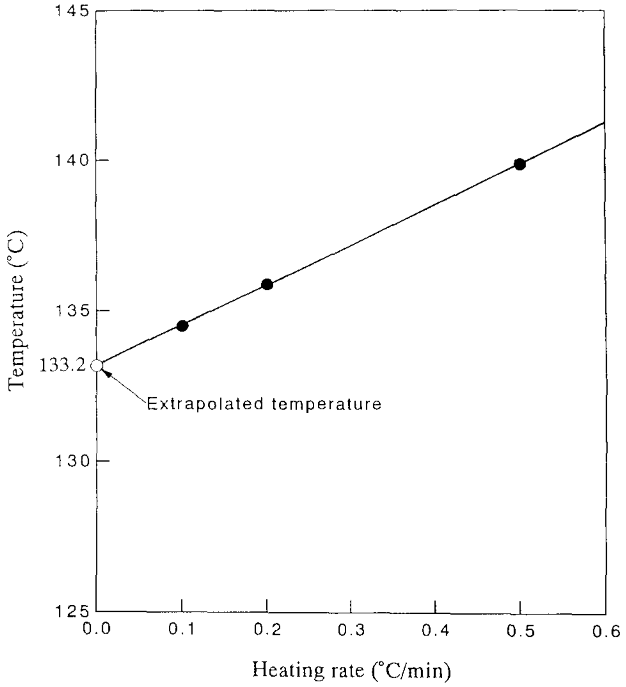

Figure 1 Determination of the cloud point of a P2CS/PVME (20/80) blend by extrapolation to zero heating rate (M_w of P2CS = 331 000)

RESULTS AND DISCUSSION

The composition dependence of the cloud point curves of P2CS/PVME blends obtained by light scattering is shown in *Figure 2*. Obviously, P2CS/PVME blends exhibit an *LCST*, resembling that of PS/PVME blends.

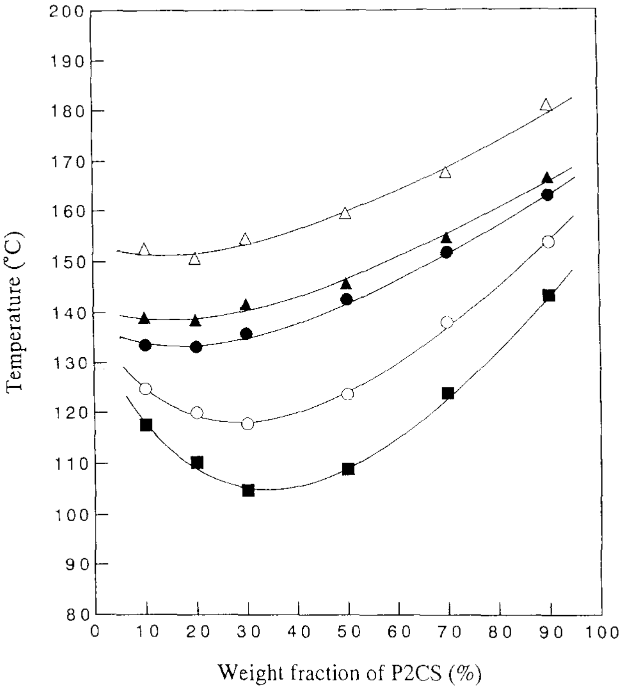

Figure 2 Molecular weight dependence of the cloud point curves of P2CS/PVME blends obtained after extrapolation. M_w of P2CS: △, 61 000; ▲, 182 000; ●, 331 000; ○, 660 000; ■, 1 470 000

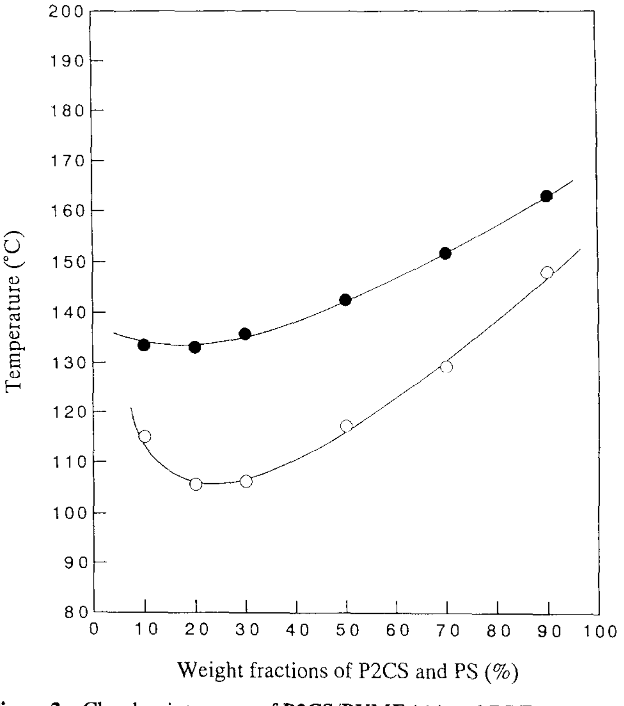

Figure 3 Cloud point curves of P2CS/PVME (●) and PS/PVME (○) blends. M_w(P2CS) = 331 000; M_w(PS) = 300 000; M_w(PVME) = 105 000

These data were obtained by extrapolating the cloud points to zero heating rate after measurements under several different conditions, as shown in *Figure 1*. In order to compare the miscibility of P2CS and PS with PVME, the cloud points of PS/PVME blends with PS of molecular weight $M_w = 3.0 \times 10^5$ were measured. This particular molecular weight was chosen to match the degree of polymerization of PS to that of P2CS ($M_w = 3.3 \times 10^5$). The cloud point curves of the two blends, P2CS/PVME and PS/PVME, are shown in *Figure 3*. Under this particular condition, P2CS/PVME blends are apparently more miscible than PS/PVME blends. To examine the miscibility of P2CS/PVME and PS/PVME blends in more detail, the binary interaction parameters, χ, of these two blends were calculated using the extrapolated cloud point data. The calculation was based on the following assumptions.

1. The critical behaviour of both P2CS/PVME and PS/PVME follows the prediction of the mean-field theory. The critical behaviour of P2CS/PVME was recently confirmed by SAXS experiments where the critical exponents, ν and γ, for the correlation lengths, ξ, and the zero-angle scattering intensity, $S(0)$, were found to be 1/2 and 1, respectively[11]. On the other hand, the critical behaviour of PS/PVME blends is known to obey the mean-field theory by a series of small-angle neutron scattering (SANS) experiments[14].
2. For a given blend, the minimum of the cloud point curve obtained after extrapolating to zero heating rate coincides with the corresponding critical point of the blend. This assumption is supported by the existing SAXS[11] and SANS[13,14] data.
3. The binary interaction parameter χ does not depend on the blend composition.

From these assumptions, the χ parameters at the critical composition, χ_{cal}, of P2CS/PVME and PS/PVME blends with different molecular weights were calculated using the following equations:

$$\chi_s = \frac{v_0}{2}\left[\frac{1}{v_A N_A \phi_A} + \frac{1}{v_B N_B \phi_B}\right] \tag{1}$$

$$\frac{1}{v_0} = \frac{\phi_A}{v_A} + \frac{\phi_B}{v_B} \tag{2}$$

where χ_s is the value of χ at the spinodal temperature, v_0 is the molar volume of the reference cell, and v_i, N_i and ϕ_i are the molar volume of segment, degree of polymerization and volume fraction, respectively, of the ith polymer component.

First, the critical compositions and temperatures of P2CS/PVME and PS/PVME blends with different molecular weights were estimated from the cloud point curves shown in *Figures 2* and *3*. Then the molar volumes of the reference cell, v_0, corresponding to these critical compositions were calculated using equation (2). The values of χ at the critical compositions, i.e. χ_{cal}, were finally obtained from equation (1) by using the corresponding molecular weights. Note that a similar procedure to estimate the χ parameters of PS/P2CS blends containing plasticizer has been carried out previously by Kwak *et al.*[15]. In *Figure 4*, the χ_{cal} values obtained in this way are plotted against the corresponding critical temperatures for P2CS/PVME blends. For comparison, the χ parameters of hydrogenated polystyrene (PSH)/PVME blends calculated by the same procedure are shown in the same figure. Note that the value at the lowest temperature is obtained from the data shown in *Figure 3* and the other two are calculated by using the cloud point data obtained by light scattering in ref. 16. Over the range of molecular weights used in these experiments, $\chi_{\text{P2CS/PVME}}$ is slightly smaller than $\chi_{\text{PS/PVME}}$. These results indicate that P2CS seems to be more miscible than PS with PVME.

In order to elucidate the role played by intermolecular interactions in the miscibility of these blends, i.r. absorption of the individual polymer components, PVME, P2CS and PS, was measured in the bulk state and compared to that in the mixtures. For this purpose, P2CS/PVME (43/57) and PS/PVME (39/61) blends were chosen in order to adjust the ratio of the total repeating units of two polymers in these blends close to unity. As shown in *Figure 5*, the two characteristic absorption bands of PVME at 1088 and 1107 cm^{-1} (C–O stretching mode) in PS/PVME (39/61), and at 1084 and 1107 cm^{-1} in P2CS/PVME (43/57) blends, exhibit significantly different behaviour: the intensity of the absorption band at 1084 cm^{-1} of P2CS/PVME blends is almost the same as that at the higher wavenumber, 1107 cm^{-1}, whereas the latter absorption band is more intense than the former in

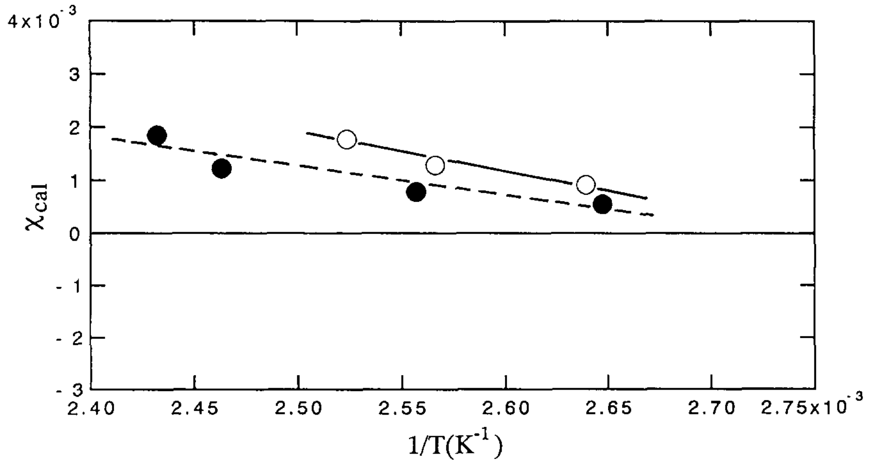

Figure 4 Temperature dependence of the χ parameters estimated by using equations (1) and (2). ●, P2CS/PVME blends: M_w (P2CS) (from left to right) = 182000, 331000, 660000, 1470000; M_w (PVME) = 105000 (this work). ○, PS/PVME blends: from left to right, M_w (PS) = 100000, 233000, M_w (PVME) = 99000 (ref. 16), and M_w (PS) = 300000, M_w (PVME) = 105000 (this work)

PS/PVME blends. These bands were obtained after subtracting the contribution of homo-PS and homo-P2CS components from the spectra of the corresponding blends by using the absorption band at 1036 cm^{-1} as an internal standard. The assignment of these characteristic bands has been discussed previously and it is also known that the relative intensities of these two specific bands are sensitive to the miscibility[8,9]. According to these works, the absorption band at higher wavenumber (1107 cm^{-1}) of PVME increases with the inhomogeneity in the blends induced by heating. Since the relative intensity of the particular band at higher wavenumber reflects the population of the rotational isomers of the ether groups, the absorption spectra shown in *Figure 5* imply that the rotation of the methyl groups of PVME chains in the P2CS/PVME blend might be more restricted by the stronger attraction between the oxygen atoms of the ether units of PVME chains and the phenyl rings of P2CS chains. On the other hand, as shown in *Figure 6*, the C–H out-of-plane bending vibrations of the phenyl rings on PS and P2CS chains in bulk, appearing respectively at 698 and 750 cm^{-1}, shift towards the side of high wavenumber upon blending with PVME. The shift in wavenumber of this particular vibrational mode for P2CS/PVME, i.e. 4 cm^{-1}, is larger than in PS/PVME (2 cm^{-1}). These *FT*i.r. results also indicate that this particular vibrational mode of the phenyl ring on the P2CS chains requires more energy than the phenyl ring of PS in the blends with PVME, and are in accord with the results of C–O stretching modes of PVME shown in *Figure 5*. The experimental results obtained so far by both light scattering and *FT*i.r., together with the estimated χ parameters depicted in *Figure 4*, obviously prove that the higher miscibility of P2CS with PVME is due to the strong attraction between the chlorine-substituted phenyl ring and the electron lone pair of PVME.

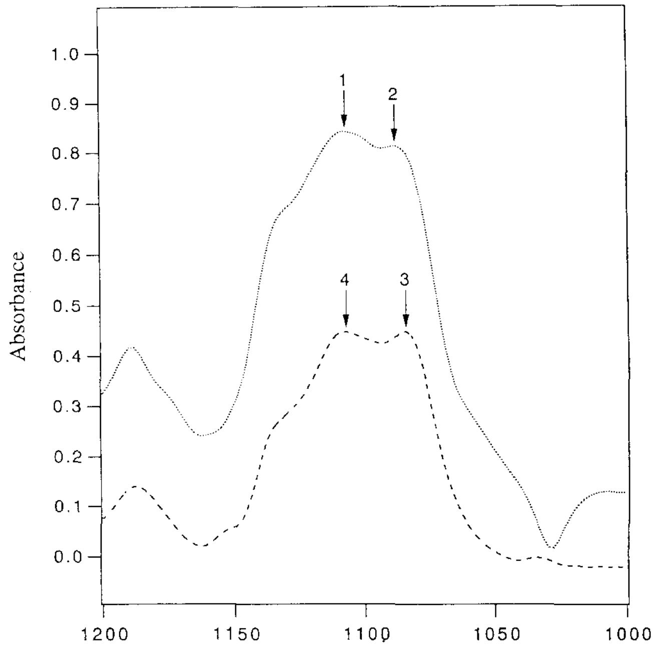

Figure 5 Characteristic absorption of C–O stretching vibration of PVME in P2CS/PVME (– – –) and PS/PVME (···) measured at room temperature. Absorption bands: 1, 1107 cm^{-1}, absorbance 0.843; 2, 1088 cm^{-1}, absorbance 0.814; 3, 1084 cm^{-1}, absorbance 0.448; 4, 1107 cm^{-1}, absorbance 0.448

The interactions of P2CS and PS with PVME can also be observed through the composition dependence of the T_gs of P2CS/PVME and PS/PVME blends. Some years ago, Kwei[17] proposed the following empirical formula for the composition dependence of T_gs of binary polymer blends including mixtures with strong specific interactions:

$$T_g = \frac{w_1 T_{g1} + k w_2 T_{g2}}{w_1 + k w_2} + q w_1 w_2 \qquad (3)$$

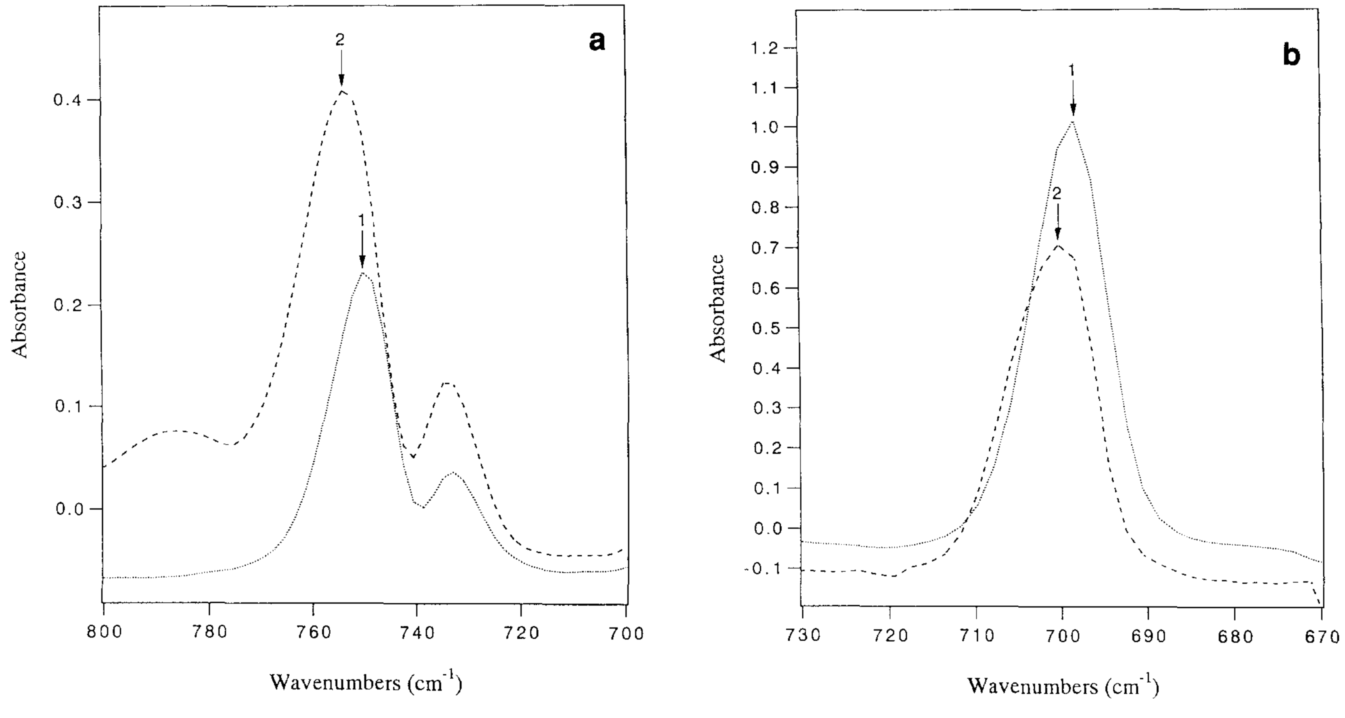

Figure 6 (a) C–H out-of-plane bending vibration of P2CS in bulk (···) and in P2CS/PVME (43/57) (– – –); (b) C–H out-of-plane vibration of PS in bulk (···) and in PS/PVME (39/61) (– – –). (a) 1, 750 cm^{-1}; 2, 754 cm^{-1}; 2 – 1, 4 cm^{-1}. (b) 1, 698 cm^{-1}; 2, 700 cm^{-1}; 2 – 1, 2 cm^{-1}

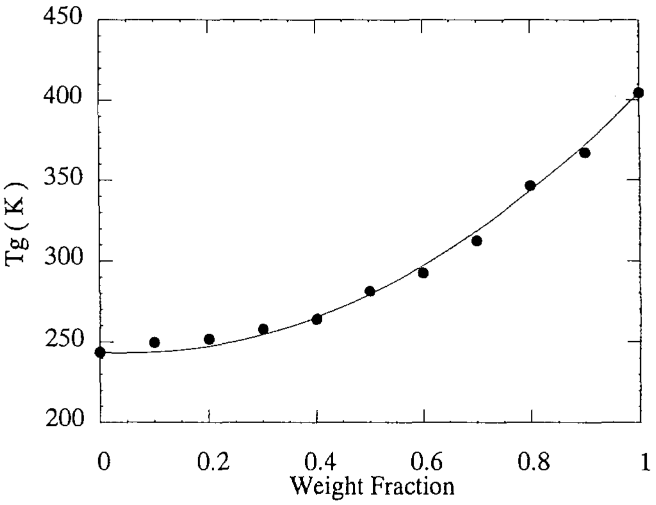

Figure 7 Composition dependence of the glass transition temperatures of P2CS/PVME blends. The solid line is obtained by curve-fitting using equation (3)

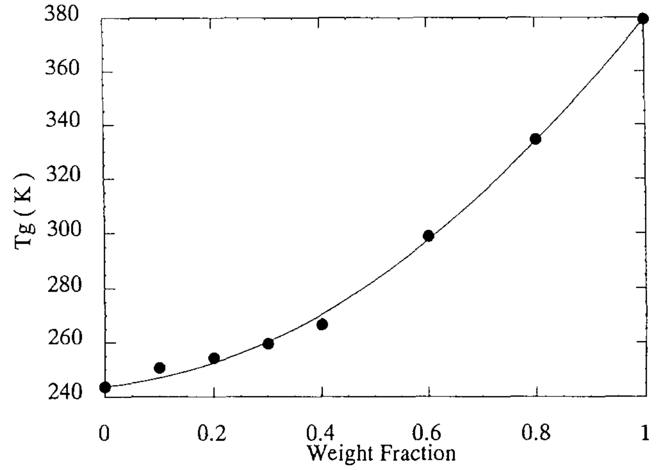

Figure 8 Composition dependence of the glass transition temperatures of PS/PVME blends. The solid line is obtained by curve fitting using equation (3)

where T_{gi} and w_i are, respectively, the glass transition temperature and the weight fraction of the ith polymer component. The constants k and q are fitting parameters.

The first term of equation (3) resembles the well-known Gordon–Taylor equation[18]. The second term was introduced to compensate the binary interaction between the segments of the two polymer components. The physical meaning of the parameter q, which is related to the change in energy associated with the formation of a contact pair between different segments in the mixture, has been discussed recently[19] and is given by the following equation:

$$q=\frac{2f}{3k_B}\left[E_{12}-\frac{1}{2}(E_{11}+E_{22})\right] \qquad (4)$$

where f is the dispersion factor related to the completeness of the intermixing process of the two polymers, k_B is the Boltzmann constant, and E_{11}, E_{22}, E_{12} represent the contact energy of the two segments belonging to polymers 1 and 2.

The composition dependence of the T_gs of P2CS/PVME and PS/PVME blends is shown in *Figures 7* and *8*. Since the negative deviation from the linear additivity is observed without any inflection points for these two blends, we fit these experimental data to equation (3), with $k=1$ and q as an adjustable parameter, by using the non-linear least square method. The experimental results are well expressed by equation (3), as indicated by the solid curves in *Figures 7* and *8*. The q values are found to be -179.7 and -114.4 for P2CS/PVME and PS/PVME blends, respectively. From the physical meaning of q given in equation (4), i.e. $q \propto \chi T$, the smaller value of q obtained for P2CS/PVME blends suggests that P2CS is more miscible with PVME. These results are also qualitatively consistent with the phase behaviour observed by light scattering, as shown in *Figure 3*, by *FT*i.r. absorption spectra, as depicted in *Figures 5* and *6*, as well as the calculated χ values indicated in *Figure 4*. In an attempt to estimate the binary interaction parameter, χ, of these blends from the composition dependence of the T_gs, we have fitted the T_g data to the model recently proposed by Lu and Weiss[20,21]. The curve fitting was very satisfactory. However, the χ values obtained for P2CS/PVME and PS/PVME blends are positive and contradict the light scattering data. From all the experimental results described above, we conclude that the increment of miscibility, as seen in *Figures 3* and *4*, is due to the electron withdrawing nature of the chlorine atom on the phenyl ring of P2CS. As a consequence, in comparison with PS, the electron density of the phenyl rings of P2CS chains decreases and results in an increase of the attractive force between the phenyl rings and the electron lone pair of the oxygen atom on PVME chains. This excess attraction caused by chlorine substitution is the main reason for the difference in the miscibility of P2CS/PVME and PS/PVME blends. With the consistency between the data of P2CS/PVME miscibility obtained by light scattering, *FT*i.r. spectroscopy and the χ parameters estimated by using the mean-field theory, the experimental results described in this work can provide a molecular basis for the interpretation, as well as the control, of the miscibility between polymers bearing aromatic rings and ether groups. Further experiments on the substitution effects of the phenyl rings are in progress to elucidate this problem.

SUMMARY

The miscibility of P2CS/PVME blends was examined and characterized by light scattering, differential scanning calorimetry and *FT*i.r. spectroscopy. The following results were obtained.

1. P2CS/PVME blends possess an *LCST*. Compared to PS, P2CS seems to be more miscible with PVME.
2. From *FT*i.r. spectroscopy it was found that the miscibility of P2CS/PVME originates from the enhancement of the attractive force between the phenyl moieties of P2CS and the electron lone pair of the oxygen atom on PVME chains. These results are supported by the magnitude of the binary interaction parameter estimated by using the mean-field theory.

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