perpendicular to the chain axis. The solid circles in the figure represent the observed values by Sakurada et al.[2] The solid curve is our calculated result. The magnitudes of the observed and calculated results are in the same order, except for the direction of the maximal value of the calculated anisotropy for which the observed value is not known.

The Young's moduli in the direction perpendicular to the chain axis of the PVA crystal are appreciably larger and the linear compressibilities are smaller than those of the PE crystal as shown below, reflecting the strength of hydrogen bonding forces.

	Young's modulus, $\times 10^{10}$ dyn/cm^2	linear compressibility, $\times 10^{-12}$ cm^2/dyn
PVA	22.0–8.5	1.9–7.7
PE	9.2–6.9	6.8–9.7

On the other hand, the value of Young's modulus (287.4×10^{10} dyn/cm^2) in the chain direction of PVA is in the same order as that of PE (315.5×10^{10} dyn/cm^2), which is in the range characteristic to the planar-zigzag chain. This may suggest that the intermolecular interactions (even for appreciably strong hydrogen bonding) hardly affect the Young's modulus in the chain direction, which is mainly determined by the strong covalent bondings and conformation of the skeletal chain. In fact, the calculated value of Young's modulus along the chain direction without taking into account the intermolecular hydrogen bondings is 287.2×10^{10} dyn/cm^2, almost the same as the value considering the hydrogen bonds. These circumstances can be shown also for the cases of other polymers such as poly(vinylidene fluoride), whose mechanical properties are governed by the electrostatic interactions. The calculated results for crystallite moduli of poly(vinylidene fluoride) will be reported in a subsequent paper.[22]

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Use of a Gas Chromatographic Technique for the Study of the Variation of the Interaction Energy Parameter with Temperature

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ABSTRACT: The dependence of the interaction energy parameter is investigated by means of a gas-liquid chromatographic technique for the solutes tetrahydrofuran, methyl ethyl ketone, diethyl ketone, ethyl propyl ketone, and toluene in poly(vinyl chloride), polystyrene, and poly(methyl methacrylate) used as stationary phases. In all cases plots of the interaction energy parameter against temperature showed positive minima and curvature which remained positive throughout the range of temperature which was investigated in agreement with more recent theoretical predictions. The results obtained are discussed in terms of concepts of contact energy dissimilarity and free volume dissimilarity between the solute and polymer molecules.

The use of a polymeric stationary phase in gas-liquid chromatographic studies of polymer–solute interactions was first made in 1969 by Smidsrød and Guillet[1] who determined values for the activity coefficients of various solutes such as acetic acid, butyl alcohol, α-chloronaphthalene, naphthalene, and hexadecane at near infinite dilution (near zero solute concentration) in a poly(*N*-isopropylacrylamide) stationary phase. Since this initial application gas-liquid chromatography, GLC, has been used by a number of investigators[2–15] to obtain infinite dilution data on a number of polymeric systems, since under these experimental conditions one is effectively studying the properties of solvent molecules isolated in pure polymer. Both polar[1,8,14,15] and nonpolar[4–7,11,14,15] solutes have been used over a fairly wide range of temperature (25–100 °C).

In an earlier publication[16] we have established that values of χ_1, obtained from GLC measurements, are in close agreement with those determined using the vapor pressure method. In the present study the dependence of the interaction parameter, χ_1, on temperature is investigated for tetrahydrofuran, methyl ethyl ketone, diethyl ketone, ethyl propyl ketone, and toluene at infinite dilution in the stationary polymeric phases poly(vinyl chloride), polystyrene, and poly(methyl methacrylate). These results are considered to be of relevance in that they demonstrate the usefulness of GLC in providing information concerning polymer solute interactions and their variation with

Table I
Column Composition

	poly(vinyl chloride)	polystyrene	poly(methyl methacrylate)
column length, cm	120	180	180
wt of support, g	31.55	10.69	10.82
type of support	glass beads	Chromosorb W	Chromosorb W
wt of polymer, g	0.1200	0.5000	0.4997

temperature. In particular the contact energy dissimilarities and free volume dissimilarities between solute (liquid) molecules and polymer segments may be investigated.

Experimental Section

Materials. Polymers: The polymers, poly(vinyl chloride), polystyrene, and poly(methyl methacrylate), which were used are the same samples as described in a previous publication.[16]

Solutes: The solutes used in the present work were tetrahydrofuran (THF), methyl ethyl ketone (MEK), diethyl ketone, ethyl propyl ketone, and toluene. These were purified in the same manner as has been described earlier.[16] Since the equations of state for these solutes are known the evaluation of their physical behavior was easily affected.

Gas-Chromatographic System and Procedure. When using polar solutes difficulties in obtaining symmetrical peaks can arise[17] due to isotherm curvature, surface adsorption, and nonequilibrium conditions resulting from slow diffusion into the stationary phase. These possible problems were overcome by using the following equipment and procedure.

A dual-column GLC apparatus was used which incorporated a Perkin-Elmer hot-wire thermal conductivity detector. The column temperature was controlled to within ±0.2 °C over the temperature range 25 to 160 °C. Helium was used as the carrier gas and great care was taken to ensure that the retention volumes were completely independent of flow rates. The steady flow of gas was monitored using a flow meter and the steadiness of the base line carefully checked. The inlet pressure was controlled by precision regulators and measured by means of a mercury manometer. This pressure was kept to a minimum. The outlet pressure was always atmospheric.

Solutes were injected into the carrier gas stream using a 1-μL syringe. Since infinite dilution conditions are required only about 0.2 μL of solvent was employed. The infinite dilution conditions were confirmed by the uniformly symmetrical elution peaks which were obtained when using this injection procedure.[18] These symmetrical peaks also indicate the establishment of equilibrium interaction conditions between the solutes and the polymeric stationary phase. No dependence of retention time on the size of the sample could be observed when the latter was increased by small amounts, indicating the absence of complications due to adsorption.

Column Preparation. The same method of preparation was used as has been reported earlier,[16] but three further columns were prepared for the present work. The coated supports were packed into 0.25 in. (o.d.) copper tubing. The exact weights inside the columns were determined by a combustion and ashing method. Details of column composition are given in Table I.

Results and Discussion

The specific retention volumes, V_g^0, were averaged from six runs each and were calculated from the familiar expression of Littlewood et al.[19] Values of the interaction energy parameter, χ_1, were calculated by means of the equation[3]

$$\chi_1 = \ln\left[\frac{273.2KR\tilde{v}_2}{V_g^0 V_1 P_1^0}\right] - \left[1 - \frac{V_1}{M_2\tilde{v}_2}\right] - \frac{P_1^0}{RT}(B_{11} - V_1) \tag{1}$$

Table II
Values of χ_1 for Various Solvents at Differing Temperatures[a]

solvent	21.5	55.5	74.5	94.5	118.0	155.5
	temperature, °C					
tetrahydrofuran	0.830	0.545	0.301	0.131	0.253	0.843
methyl ethyl ketone	1.661	0.811	0.686	0.435	0.465	0.912
diethyl ketone	1.639	0.729	0.552	0.402	0.417	0.984
ethyl propyl ketone	1.896	1.058	0.769	0.510	0.500	0.750
toluene	1.531	0.813	0.571	0.300	0.350	0.612

[a] Stationary phase poly(vinyl chloride).

Table III
Values of χ_1 for Various Solvents at Differing Temperatures[a]

solvent	25.0	50.5	72.4	90.5	110.5	155.5
	temperature, °C					
tetrahydrofuran	0.847	0.569	0.584	0.337	0.460	0.658
methyl ethyl ketone	0.966	0.520	0.566	0.328	0.432	0.932
diethyl ketone	1.210	0.869	0.769	0.597	0.558	0.589
ethyl propyl ketone	1.556	1.101	0.982	0.759	0.719	0.860
toluene	0.947	0.612	0.495	0.423	0.454	0.830

[a] Stationary phase poly(methyl methacrylate).

Table IV
Values of χ_1 for Various Solvents at Differing Temperatures[a]

solvent	25.2	50.5	72.4	90.5	110.5	145.5
	temperature, °C					
tetrahydrofuran	0.697	0.339	0.339	0.223	0.352	0.709
methyl ethyl ketone	0.901	0.628	0.465	0.418	0.409	0.582
diethyl ketone	1.271	0.507	0.375	0.339	0.281	1.154
ethyl propyl ketone	1.757	0.753	0.518	0.432	0.424	1.250
toluene	0.868	0.420	0.327	0.277	0.311	0.723

[a] Stationary phase polystyrene.

where V_1 is the molar volume of pure (liquid) solute, P_1^0 is its vapor pressure at the thermodynamic temperature T, $\tilde{v}_2$ is the specific volume of polymer solvent, and B_{11} is the gas state second virial coefficient of the solute. Appropriate values of χ_1 are listed in Tables II–IV.

Variation of the Interaction Energy Parameter with Temperature. Plots of χ_1 against temperature for poly(vinyl chloride), polystyrene, and poly(methyl methacrylate) with the solvents THF, diethyl ketone, MEK, ethyl propyl ketone, and toluene are shown in Figures 1–3. It is evident that all these systems exhibit the same general behavior. In particular all plots show a positive minimum and a curvature which remains positive throughout the range of temperature which was investigated.

Over the years a number of different expressions have been derived to predict the relationship between χ_1 and temperature. According to the earlier Flory[20] treatment χ_1 and temperature were related by the expression

$$\chi_1 = Z\Delta w_{1,2}/kT \tag{2}$$

where Z was the lattice coordination number, $\Delta w_{1,2}$ is the change in energy due to the formation of unlike contact pairs, k is the Boltzmann constant, and T is the absolute temperature. Expression 2 is solely associated with the heat of mixing of polymer and solvent and neglects entropy changes. According to this expression a plot of χ_1 against

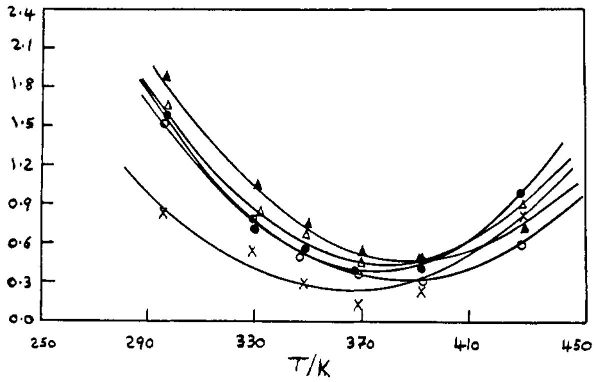

Figure 1. Plot of the values of the interaction energy parameter χ_1 against temperature: polymer, poly(vinyl chloride); ×, tetrahydrofuran; ○, toluene; ●, diethyl ketone; △, methyl ethyl ketone; ▲, ethyl propyl ketone.

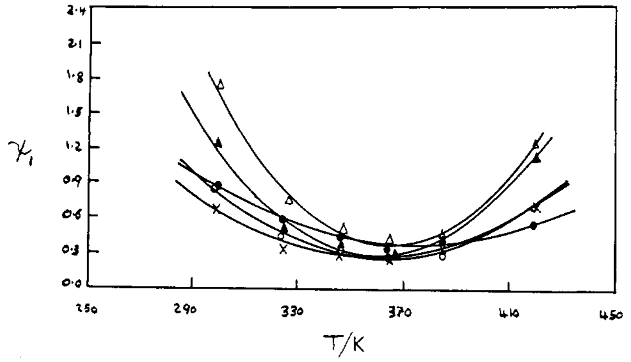

Figure 2. Plot of the values of the interaction energy parameter χ_1 against temperature: polymer, polystyrene; ×, tetrahydrofuran; ○, toluene; ●, methyl ethyl ketone; ▲, diethyl ketone; △, ethyl propyl ketone.

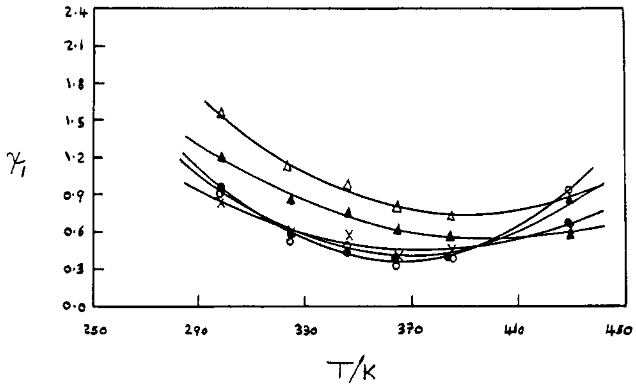

Figure 3. Plot of the values of the interaction energy parameter χ_1 against temperature: polymer, poly(methyl methacrylate); × tetrahydrofuran; ○, toluene; ●, methyl ethyl ketone; ▲, diethyl ketone; △, ethyl propyl ketone.

$1/T$ should give a straight line with slope equal to $Z\Delta w_{1,2}/k$.

Guggenheim[21] reinterpreted $\Delta w_{1,2}$ to be a free-energy term with both enthalpic and entropic contributions. Thus

$$\chi_1 = \chi_H + \chi_S = \frac{Z\Delta w_H}{kT} - \frac{Z\Delta w_S}{k} \qquad (3)$$

From this equation it is evident that a plot of χ_1 against $1/T$ should give a straight line but in this instance one of finite intercept.

However, such refinements are still insufficient to explain many experimental observations associated with the variation of χ_1 with temperature. Clearly neither of these equations is applicable to the results shown in Figures 1 to 3, indicating that division of χ into enthalpic and enthropic contributions is not a meaningful procedure for the present study.

In more recent years, however, the corresponding states theory (CST) of Prigogine[22] has attracted attention and has led Flory[23-25] and Patterson[26] to derive more sophisticated expressions for the variation of χ_1 with temperature. Although it is realized that the corresponding states theory was derived for nonpolar systems it is considered of interest, in the absence of any satisfactory treatment of polar systems, to apply the resulting equations for χ_1 to the present study which involves both nonpolar and polar materials. A similar application has already been carried out by Kuwahara et al. for the systems polystyrene in benzene, methyl ethyl ketone, and cyclopentane[27] and polystyrene in various acetates.[28] Their results however were based on cloud-point determinations.

Since somewhat similar expressions for the dependence of χ_1 with temperature are obtained it is considered sufficient for the purposes of the present study to discuss the experimental results only in terms of that derived by Patterson[26] which has the form

$$\chi_1 = -(U_1/RT)\nu^2 + (C_p/2R)\tau^2 \qquad (4)$$

where $-U_1$ is the energy of vaporization of the solvent, C_p is the configurational heat capacity, and R is the gas constant. The parameter ν^2 is related to the difference of cohesive energy and size between the solvent molecule and polymer segments. The τ parameter reflects the free volume change which occurs on mixing the dense polymer with solvent and is defined by

$$\tau = 1 - (T_1^*/T_2^*) \qquad (5)$$

where T_1^* and T_2^* are the characteristic temperature reduction parameters of the solvent and polymer, respectively.

Before eq 4 may be used in the present discussion it is necessary to know how the coefficients of the two terms vary with temperature. This has been discussed by Patterson[26,29,30] and Kuwahara et al.[28] who conclude that the first term, which represents the contact energy dissimilarity and is positive, should decrease with an increase in temperature, while the second term, reflecting the free volume dissimilarity, should increase without limit and eventually bring about phase separation at the LCST. This situation would clearly allow a plot of χ_1 vs. T to show a minimum.

Plots of χ_1 vs. T were constructed and are shown in Figures 1 to 3. It is to be noted that all the solutes, irrespective of their polarity, behave in the same manner and the plots all exhibit distinct minima in qualitative agreement with the newer theories. A closely similar behavior has been described by Kuwahara et al.[28] for polystyrene in various acetates. It is significant that such a qualitative agreement has been obtained since two very different techniques were used. This may be regarded as good evidence for the separation of χ_1 into two terms of the kind described above. Alternatively the present results may be regarded as a good demonstration of the applicability of the GLC technique to problems of this kind. Although the temperatue range which has been investigated encompasses the T_g values of the polymeric stationary phases employed in the present research there is no indication that this has given rise to any serious complications for the comparative study which has been carried out using these systems. Obviously the method could not be applied for the present purposes to a temperature range which included T_m.

Effect of the Contact Energy Dissimilarity and the Free Volume Dissimilarity on the Behavior of the

Polymer–Solute Systems. Although in principle the temperature dependence of the two terms which make up χ_1 could be investigated by drawing limiting tangents to the various plots, it is not considered that the present study has been carried out over a sufficiently wide range of temperature to permit this to be accomplished with any reasonable degree of accuracy. Also it must be realized that even in the low and high temperature regions the values of χ_1 will still to some extent be dependent on both the contact energy and free volume dissimilarity terms. For these reasons only a qualitative discussion of these results is possible.

Each of the Figures 1 to 3 may nevertheless be studied at low temperatures where the first term of eq 4 is predominant, and at higher temperatures where the second term is predominant.

If one initially considers Figure 1, the two dissimilarities can be observed for poly(vinyl chloride) with THF, MEK, diethyl ketone, ethyl propyl ketone, and toluene. At low temperatures the contact energy dissimilarity of the polymer with each solute may be compared by means of the position and the magnitude of the gradients of each curve, the higher the gradient the higher will be the final value of the contact energy dissimilarity. Thus the contact energy dissimilarities of poly(vinyl chloride) with MEK, diethyl ketone, ethyl propyl ketone, and toluene may be seen from an examination of Figure 1 to be very similar to each other, but greater than that of poly(vinyl chloride) with THF. It is evident that increasing the size of the solute molecule by one CH_2 group has no significant effect on the contact energy dissimilarity.

A consideration of the right-hand side of Figure 1, i.e, at high temperatures, shows that besides the dissimilarity of free volume between poly(vinyl chloride) and each solute there is also a dissimilarity in thermal expansion among the solutes themselves. For example, while the THF curve is below the toluene curve on the left of Figure 1 it rises above the toluene curve (and also above that of ethyl propyl ketone as well) on the right. This indicates that the free volume dissimilarity between poly(vinyl chloride) and THF is greater than between poly(vinyl chloride) and toluene, i.e, a rise in the temperature of the system causes the molecules of THF to expand more rapidly than the molecules of toluene with respect to the poly(vinyl chloride) molecules. In the case of the poly(vinyl chloride)–THF system the free volume term is more significant than the contact energy term, as is shown by the sharp rise of the curve on the right relative to that on the left, indicating that the noncombinatorial entropy term is large.

Figure 2 shows the behavior of polystyrene with the same set of solvents. On the left of the figure the different gradients of the ketone series curves reflect the fact that here the chain length has a significant effect on the contact energy dissimilarity, the contact energy dissimilarity increasing with increase of chain length.

The behavior of poly(methyl methacrylate) is shown in Figure 3. With this polymer the contibution of the free volume dissimilarity is small for ethyl propyl ketone and diethyl ketone but larger for MEK. Thus it can be concluded that the thermal expansion of MEK is relatively larger than that of ethyl propyl ketone and diethyl ketone.

Prediction of Perturbation of Polymer Chains. These studies of the variation of χ_1 with temperature in the presence of various liquid solutes or solvents may be used to predict the change of the dimensions of the polymer molecules. Generally in a good solvent, classified as one which is highly compatible with the polymer, the solvent–polymer interactions expand the polymer coil from its unperturbed dimensions. This expansion is proportional to the extent of these interactions. In a poor solvent the interactions are weaker and coil expansion or perturbation is restricted. When the polymer–solvent interaction is a maximum the coil expansion is a maximum and consequently the value of χ_1 is a minimum. The minimum value of χ_1 usually appears at the bottom of the χ_1 vs. T curve. Figures 1 to 3 show this phenomena. Thus if Figure 1 is taken as an example the highest perturbation of the poly(vinyl chloride) molecules lies at the bottom of the PVC–THF plot. This curve also lies below the corresponding curves for toluene, methyl ethyl ketone, diethyl ketone, and ethyl propyl ketone. The minimum values of χ_1 for the solutes (liquid) used are listed in Table V. From this table it is immediately evident that the highest perturbation of the poly(vinyl chloride) molecules occurs at 95–115 °C with most of the solutes used. Beyond this temperature the value of χ_1 increases with an increase in temperature. Consequently the perturbation of the polymer chain decreases until it attains a minimum value in the neighborhood of the critical value of χ_1. At this value the lower critical solution temperature, LCST, occurs.

Table V
Minimum Values of the Interaction Energy Parameter

	$\chi_{1,c}$		
solvent	PVC (°C)	polystyrene (°C)	poly(methyl methacrylate) (°C)
tetrahydrofuran	0.20 (95)	0.27 (90)	0.45 (97)
methyl ethyl ketone	0.44 (108)	0.42 (92)	0.40 (97)
diethyl ketone	0.40 (104)	0.30 (88)	0.55 (132)
ethyl propyl ketone	0.48 (115)	0.43 (92)	0.74 (117)
toluene	0.30 (115)	0.27 (86)	0.38 (94)

It can be seen that the maximum coil expansion for poly(vinyl chloride) occurs with tetrahydrofuran, for polystyrene with toluene and tetrahydrofuran, and for poly(methyl methacrylate) with methyl ethyl ketone and toluene. Hence for any system the polymer–solvent compatibility may be deduced from the position of the appropriate plots. The solvent (or solute in the present case) which has lower values of χ_1 for a given polymer offers the higher compatibility, i.e., the solvent is more compatible with the polymer. Thus in Figure 1 poly(vinyl chloride) shows a higher compatibility with tetrahydrofuran than with the other solutes. Polystyrene and poly(methyl methacrylate) are more compatible with toluene and methyl ethyl ketone, respectively.

Region of Complete Miscibility and Lower Critical Solution Temperature. The determination of the region of complete miscibility of the polymer may be carried out by calculating the critical value of the interaction parameters, $\chi_{1,c}$. This calculation was performed using Flory's[20,28,29] approximation in the following form

$$\chi_{1,c} = \tfrac{1}{2}(1 + r^{-1/2})^2 \qquad (6)$$

where r is the ratio of the molar volumes of polymer and solvent (or liquid solute in the present case). The derivation[28] of this equation is solely dependent upon the combinatorial entropy while the noncombinatorial part is neglected. If the molecular weight of the polymer is very high the value of $\chi_{1,c}$ will be about 0.5. Patterson[29] has stated that the critical value of χ_1 corresponds to the lower critical solution temperature, LCST, of the solution. In the present work eq 6 was used to determine $\chi_{1,c}$ and the results are listed in Table VI.

Table VI
Critical Values of the Interaction Energy Parameter

solvent	$\chi_{1,c}$ PVC	poly-styrene	poly(methyl methacrylate)
tetrahydro-furan	0.503	0.508	0.502
methyl ethyl ketone	0.503	0.510	0.502
diethyl ketone	0.504	0.511	0.502
ethyl propyl ketone	0.505	0.513	0.502
toluene	0.504	0.511	0.502

Applying these critical values to Figures 1 to 3 the region of complete miscibility may be determined for each polymer–solute system. This can be performed by drawing a horizontal line through the critical value of χ_1. Since all the listed values of $\chi_{1,c}$ are very near to 0.5 only one critical line is required for the purpose of illustration. In any of the curves which are displayed the complete miscibility region may be regarded as the area bounded by the appropriate curve and the critical line, i.e., by the two points of intersection of the critical line with the curve. Thus in Figure 1 the area relating to the poly(vinyl chloride)–THF system is the largest and so the complete miscibility region of poly(vinyl chloride) is greatest with tetrahydrofuran relative to the other solutes. Consequently the regions decrease in the order THF > toluene > diethyl ketone > methyl ethyl ketone > ethyl propyl ketone.

In Figure 2 the LCST of the poly(vinyl chloride)–ethyl propyl ketone system appears in the neighborhood of the boiling point of the liquid solute. This suggests that the interaction between poly(vinyl chloride) and ethyl propyl ketone is related to secondary bonding which may be a type of dipole–dipole bonding.

The LCST phenomenon can be interpreted using the concept of free volume. As the temperature rises the solvent expands much more rapidly than the polymer which is restrained by the covalent bonding between its segments. With increase in temperature the volume between the solvent molecules increases and eventually phase separation occurs.

The thermodynamic conditions for the LCST are that ΔH_M and ΔS_M are both negative. The entropy of mixing, ΔS_M, is affected by two contributions, the combinatorial and the noncombinatorial terms. This latter contribution is always negative and becomes predominant at high temperatures. However, the negative enthalpy associated with the LCST arises from the effective condensation of the solvent in the polymer. This contributes to a negative value of ΔG_M and so the solubility of the polymer increases as the temperature rises. The overall solubility is nevertheless dominated by the negative value of ΔS_M (due to the noncombinatorial contribution) and the high temperature. This gives rise to a positive contribution to ΔG_M which in turn causes phase separation to occur in the neighborhood of the LCST.

The same type of analysis can be applied to polystyrene and poly(methyl methacrylate) in Figures 2 and 3, respectively. Polystyrene gives the largest region of complete miscibility with toluene and tetrahydrofuran while poly(methyl methacrylate) shows the largest region of complete miscibility with methyl ethyl ketone.

Conclusion

In conclusion these results are believed to demonstrate the usefulness of the GLC technique as a means of examining the variation of the interaction energy parameter, χ_1, with temperature, and to support the division of χ_1 into two terms, a contact interaction term which is a decreasing function of temperature, and a configurational heat capacity term which on the other hand is an increasing function of temperature. Also they reveal that there is still a need for additional experimental data determined over wider temperature ranges before the full potential of the corresponding states approach to polymer solutions can be utilized. When these data are available a sharper analysis will be possible. However, it is quite clear that the concepts of the corresponding states approach promise to be of considerable importance in understanding some of the fundamental aspects of polymer–solvent interaction.

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