Some observations on the behaviour of the thermodynamic interaction parameter in dilute polymer solutions

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The value of the interaction parameter χ in dilute polymer solutions is usually higher than would be expected on the basis of simple theory. This is caused by a large entropic contribution, for which there is, as yet, no theoretical explanation. In this paper the results are presented of a study of the behaviour of the energetic and entropic contributions to χ. It is shown that the two contributions are closely correlated and exhibit qualitatively similar molecular-weight dependences. These observations may guide future theoretical efforts towards the understanding of the thermodynamic phase behaviour of polymer solutions.

INTRODUCTION

The phase behaviour of polymer solutions is still far from being quantitatively predictable. Since the formulation of the Flory–Huggins (FH) theory[1], progress towards *a priori* predictability has been rather marginal. The most eminent success of the Flory–Huggins theory is the correct prediction of the fact that phase diagrams of polymer solutions are highly skewed towards the solvent side. The most evident shortcomings are the large underestimation of the critical miscibility temperature and the failure to describe lower critical solution behaviour. For example, for polystyrene in cyclohexane, a theta temperature of the order of 40 K is predicted (using solubility parameters), whereas experimentally one finds a value of 303 K[1].

In FH theory, the interaction parameter χ plays a key role. Originally, χ was taken to be purely enthalpic. However, it was soon realized that, in order to describe the thermodynamic behaviour quantitatively, χ should be considered a free-energy parameter. This implies that it can have an arbitrary temperature dependence. In yet other modifications χ was also made a function of composition.

In general, one should make a clear distinction between the interaction parameters of a polymer blend and those of a polymer solution. Experimentally, much higher χ values are found in solutions than in (miscible) blends. This fact has hitherto not been understood and is one of the key issues to be addressed in this paper.

The focus is on the thermodynamic behaviour of dilute polymer solutions. The composition dependence of χ is thus ignored. In fact, the limit of zero-concentration behaviour of the interaction parameter is discussed. Special attention is paid to the temperature dependence of χ. From the temperature dependence, χ can be split into entropic and enthalpic contributions. This provides more insight into the physical origins of the interaction parameter.

In this paper, a large number of experimental interaction parameters of polymer solutions are collected and analysed in terms of temperature and molecular-weight dependences. It will be shown that all polymer solutions show qualitatively similar behaviour.

THEORY

The phase behaviour of a polymer solution is determined[1] by the Gibbs free energy of mixing, $\Delta G_M(\Phi_p, T)$, where Φ_p denotes the polymer volume fraction and T denotes the temperature of the mixture. Since all quoted experiments were performed at atmospheric pressure, the pressure dependence of ΔG_M is ignored. ΔG_M contains entropic (ΔS_M) and enthalpic (ΔH_M) contributions:

$$\Delta G_M = \Delta H_M - T \Delta S_M \qquad (1)$$

The following fundamental thermodynamic relations allow ΔH_M and ΔS_M to be calculated from an arbitrary temperature depencence of ΔG_M (ref. 2):

$$\Delta S_M = -(\partial \Delta G_M / \partial T) \qquad (2)$$

$$\Delta H_M = \Delta G_M + T \Delta S_M \qquad (3)$$

The most widely employed expression for ΔG_M is given by:

$$\frac{\Delta G_M(\Phi_p, T)}{NRT} = \frac{\Phi_p}{r_p} \ln(\Phi_p) + \Phi_s \ln(\Phi_s) + \chi \Phi_p \Phi_s \qquad (4)$$

where N is the total number of segments, or basic volume elements, in the mixture, r_p is the polymer chain length, i.e. the number of segments occupied by one polymer molecule, and R is the gas constant. With:

$$\chi = \chi_h / T \qquad (5)$$

equation (4) is the original Flory–Huggins expression

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for the Gibbs free energy of mixing. Using solubility parameters, χ_h can be expressed as[1,2]:

$$\chi_h = (V_L/R)(\delta_p - \delta_s)^2 \qquad (6)$$

where δ_p and δ_s are the solubility parameters of, respectively, the polymer and the solvent, and V_L is the molar volume of the above-mentioned basic segment, in principle the molar volume of the solvent molecules.

Note that, in accordance with common practice, the left-hand side of equation (4) gives the free energy divided by temperature. The first two terms on the right-hand side of equation (4) represent the combinatorial entropy of mixing. This Flory–Huggins entropy-of-mixing term is present in almost all theories on polymer thermodynamics. It can be derived in many ways. Essentially, it describes the excluded-volume effect in the combination of two types of molecules of unequal size.

An important experimental parameter is the osmotic second virial coefficient A_2. For the Gibbs free energy of mixing in equation (4), the relation between χ and A_2 is given by[3]:

$$A_2 = (1/2 - \chi)/(\rho_p^2 V_m) \qquad (7)$$

where ρ_p is the density of the polymer and V_m is the molar volume of the solvent. Experimental interaction parameters are often derived from measured virial coefficients using equation (7).

Equations (4) and (5) turn out to be highly inappropriate for a quantitative description of the thermodynamics of polymer solutions. It was soon realized that the interaction parameter should be considered as a free-energy parameter instead of an enthalpy parameter. This means that χ can have an arbitrary temperature dependence. The entropic (χ_s) and enthalpic (χ_h) contributions to χ can be calculated using equations (2) and (3). It is common practice to write:

$$\chi = \chi_s + \chi_h/T \qquad (8)$$

Unfortunately, this is rather confusing, since the sign of χ_s is opposite to the sign of ΔS_M, while the signs of χ_h and ΔH_M match. In the following we shall stick to this common usage. The reader should bear in mind that a positive value of χ_s implies an entropy decrease on mixing. From an arbitrary temperature dependence of χ, the entropic and enthalpic contributions can be calculated according to:

$$\chi_s = \partial(T\chi)/\partial T \qquad (9)$$

$$\chi_h = -T^2 \partial\chi/\partial T \qquad (10)$$

The experimental data that will be discussed here cover a temperature range that is too small to allow fitting to more complicated expressions than equation (8). So equation (8) will play a central role in the following discussions, where a large number of polymer solutions will be characterized by their experimental χ_s and χ_h values.

If the interaction parameter χ is allowed to be both temperature- and composition-dependent, then equation (4) is fully general. Most experimental measurements of the interaction parameter were done with dilute or semidilute polymer solutions, i.e. $\Phi_p \to 0$ or $\Phi_p\Phi_s \to \Phi_p$. The experiments yield χ_{exp}, given by:

$$\chi_{exp} = \lim_{\Phi_p \to 0} \chi(\Phi_p) \qquad (11)$$

which corresponds to the first-order term in the composition-dependent interaction term in equation (4).

EXPERIMENTAL OBSERVATIONS

Introduction

In this section, a large collection of experimental interaction parameters is analysed. This collection is not exhaustive, but it is sufficiently large to make our points. Only experiments in which interaction parameters were measured at different temperatures have been considered. A simple, straightforward linear least-squares fit of χ versus $1/T$ is used to calculate χ_s and χ_h via equation (8). In those cases where second virial coefficients A_2 are given, we first calculated the corresponding interaction parameters by means of equation (7), which can be written as:

$$\chi = 1/2 - \rho_p^2 V_m A_2 \qquad (12)$$

where ρ_p is the density of the polymer and V_m is the molar volume of the solvent. In all cases, the polymer density was assumed to be constant, and a small correction for the molar volume due to the thermal expansion of the solvent was applied. Volumetric data were taken from ref. 4. The results are summarized in *Table 1*.

Table 1 Experimentally observed values of χ_h and χ_s in various polymer solutions

Molecular weight (kg mol^{-1})	χ_h (K)	χ_s	Ref.
Polystyrene (PS)–cyclohexane			
50.5	97	0.184	6
51	89	0.207	5
68.7	128	0.087	6
125	83	0.230	6
163	67	0.281	5
359	72	0.264	6
406	93	0.199	6
520	47	0.346	5
566	66	0.283	6
1610	43	0.359	7
4000	55	0.320	6
PS–toluene			
51	48	0.258	5
163	47	0.278	5
520	12	0.402	5
770	−0.3	0.465	8
1610	−14	0.509	7
PS–*trans*-decalin			
180	93	0.184	9
12000	30	0.397	9
PS–methyl ethyl ketone (MEK)			
69	−7	0.50	10
520	0.36	0.491	7
1640	−1.98	0.497	7
1770	−0.27	0.488	7
Poly(methyl methacrylate) (PMMA)–butyl chloride			
30	64	0.292	11
210	52	0.330	11
1100	43	0.360	11
4000	38	0.376	11
Polyisobutylene (PIB)–benzene			
90	89	0.193	13
101	91	0.193	12
191	84	0.218	12
206	78	0.240	12
710	76	0.250	12

Polystyrene solutions

Cyclohexane. One of the most widely studied polymer solutions is polystyrene in cyclohexane. It has a theta temperature of 35°C. Several authors have measured temperature-dependent interaction parameters. An elaborate light-scattering study has been published by Scholte[5], in which interaction parameters were measured at three different temperatures (35, 45 and 65°C) and as a function of concentration. After extrapolation to zero concentration, the data were fitted to equation (8). From the tabulated results of Scholte, three χ_h, χ_s pairs for three different molecular weights were extracted.

From the second virial coefficients (from osmometry) listed by Wedgeworth and Glover[6], another series of χ_h, χ_s pairs with molecular weights ranging from 50 to 4000 kg mol^{-1} could be calculated. Finally, light-scattering measurements of A_2 from Outer *et al.*[7] for a molecular weight $M_w = 1.660$ kg mol^{-1} were analysed.

The data in *Table 1* show a rather large scatter, but there appears to be a tendency for χ_h to decrease and χ_s to increase with molecular weight.

Toluene. Toluene is a good solvent for polystyrene. No upper critical solution temperature has been reported, which means that polystyrene will dissolve in toluene at all practical temperatures (i.e. above the melting point and below the boiling point of toluene). Scholte[5] reports extensive light-scattering measurements of the interaction parameter in toluene of the same samples as used above in cyclohexane. Again, three pairs of χ_h, χ_s values are extracted. From the second virial coefficients at two different temperatures (22 and 67°C) reported in ref. 7, another pair is obtained. Finally, a pair of data from our own light-scattering experiments have been included[8].

From the data on polystyrene–toluene solutions in *Table 1*, two observations can be made:

(1) The χ_h decreases and χ_s increases with molecular weight.

(2) At high molecular weights ($M > 800$ kg mol^{-1}), a negative χ_h value, meaning exothermic mixing, is found.

trans-Decalin. Nose and Chu report A_2 values for polystyrene in *trans*-decalin at three different temperatures and two molecular weights from static light-scattering experiments[9]. From the data, extracted from a table and a graph in their paper, a strong molecular-weight dependence of χ_s and χ_h is observed (see *Table 1*). The theta temperature of this system is 30°C.

Methyl ethyl ketone. A paper by Outer *et al.*[7] yields three χ_h, χ_s pairs from A_2 light-scattering data at $T = 22$ and 67°C. Also from light scattering in the range 7.5–45°C, one data point has been obtained from Cantow[10]. The results are shown in *Table 1*. The data show hardly any molecular-weight dependence and small χ_h values. MEK is a good solvent for polystyrene.

Poly(methyl methacrylate) solutions

Butyl chloride. Kirste and Schulz[11] have published a large number of temperature-dependent second virial coefficient measurements by means of light scattering of PMMA solutions in various solvents. Butyl chloride solutions were most extensively investigated. *Table 1* shows extracted values of χ_h and χ_s for four different

molecular weights. One observes a clear molecular-weight dependence of χ_h and χ_s that is qualitatively similar to that of polystyrene solutions. The theta temperature of this system is 32°C.

Polyisobutylene solutions

Benzene. Krigbaum and Flory[12] have reported temperature-dependent osmotic-pressure measurements for benzene solutions of four fractionated polyisobutylene samples with different molecular weights. From Flory and Daoust[13], one may also derive a set of χ_h, χ_s parameters for a fifth value of the molecular weight. *Table 1* shows the calculated interaction parameters. The same molecular-weight dependence as found above can be seen in this system. Benzene is a theta solvent for polyisobutylene at 24.4°C.

RESULTS AND DISCUSSION

In the previous section, a large number of interaction parameter data for polymer solutions have been analysed. The experimental χ parameters covered a range of 0.43 to 0.52 but usually varied much less within one type of polymer solution. By fitting the temperature dependence of χ to equation (8), much more outstanding differences between systems become evident. This is illustrated in *Figure 1*, where the temperature dependences of three different polymer solutions (with approximately equal molecular weights) are shown. From these linear fits, each solution is characterized by one set of χ_h, χ_s values. One thus obtains χ_h values ranging from -14 to 128 K and χ_s values ranging from 0.09 to 0.51, as shown in *Table 1*.

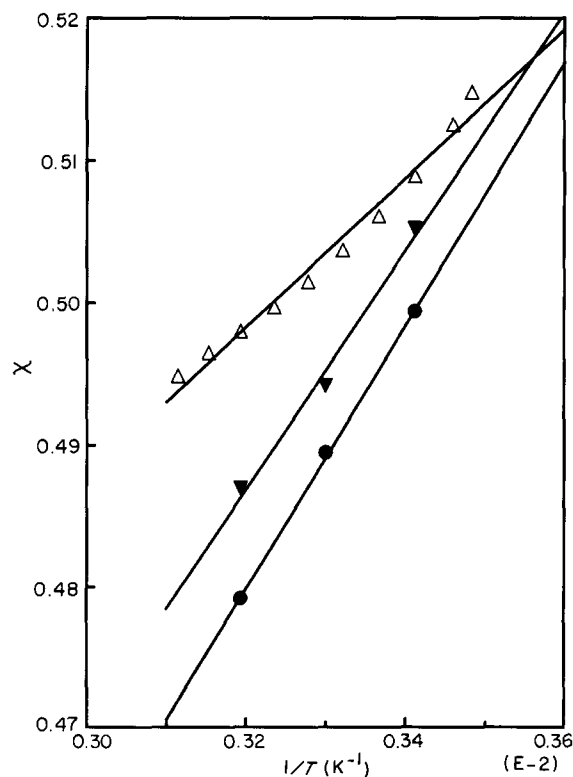From the experimental data one observes a strong correlation between the χ_h and χ_s values. *Figure 2* is a

Figure 1 Temperature dependence of the interaction parameter in three different polymer solutions: △, PMMA–butyl chloride; ●, PS–*trans*-decalin; ▼, PIB–benzene
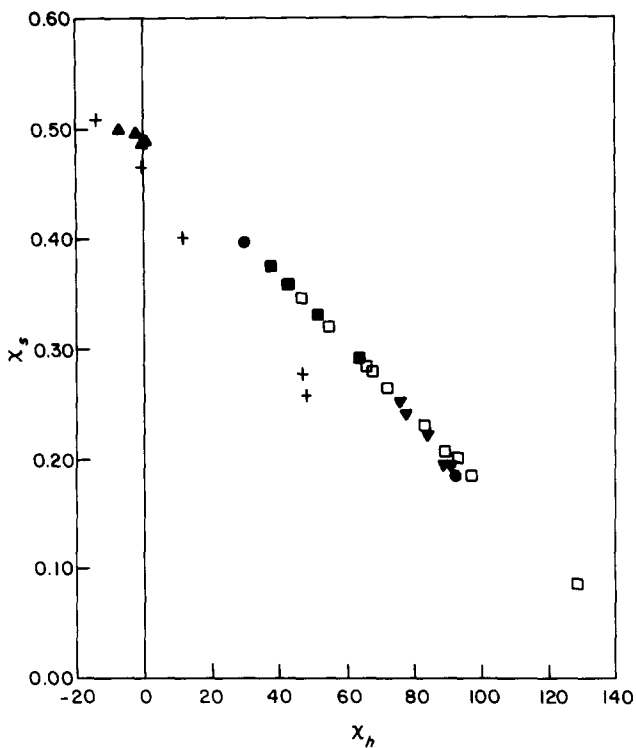
Figure 2 Entropic parameter χ_s *versus* enthalpic parameter χ_h of all experimental systems studied in this paper: $\square$, PS–cyclo hexane; $+$, PS–toluene; $\bullet$, PS–*trans*-decalin; $\blacktriangle$, PS–MEK; $\blacksquare$, PMMA–butyl chloride; $\blacktriangledown$, PIB–benzene

plot of χ_s *versus* χ_h of all the systems discussed in the previous section and tabulated in *Table 1*. Higher χ_s values correspond to lower χ_h values in a seemingly linear manner. In fact, all data, except those for PS in toluene, fall on the same line.

The strong correlation in the solutions can partly be explained by the fact that all solutions have a theta temperature around room temperature. This is not a coincidence; in fact, it is in most cases the reason for these systems being investigated in the first place. If we take equation (8) and require that χ be equal to $1/2$ at the theta temperature $T = \Theta$, we obtain:

$$\chi_s = 1/2 - \chi_h/\Theta \qquad (13)$$

which represents, for fixed Θ, a linear correlation of the form of the data in *Figure 2*. In order to illustrate this in more detail, consider three systems with almost identical theta temperatures: PMMA–butyl chloride ($\Theta \approx 305$ K), PS–*trans*-decalin ($\Theta \approx 303$ K) and PIB–benzene ($\Theta \approx 297$ K). *Figure 1* has already shown the temperature dependence of the interaction parameter of these systems. In all three cases the polymer molecular weight was about 200 kg mol^{-1}. While the values of χ differ by only 3%, the χ_s, χ_h parameters show a much more explicit difference between the systems, as can be seen from *Figure 3*. A linear least-squares fit of χ_h and χ_s to equation (13) yields $\Theta = 297$ K, which is in good agreement with the experimental theta temperatures. The question 'Why do these totally different systems have almost identical theta temperatures?' is thus equivalent to 'Why are the χ_s, χ_h parameters of these totally different systems linearly related as in equation (13)?' The latter question puts the problem in thermodynamic terms, thus facilitating a theoretical approach.

Another interesting observation can be made on the molecular-weight dependence of χ_s and χ_h of a given polymer solution. *Figure 4* shows the molecular-weight dependence of χ_s of three different polymer solutions. All solutions show qualitatively the same behaviour: a steep increase with molecular weight at low values and a
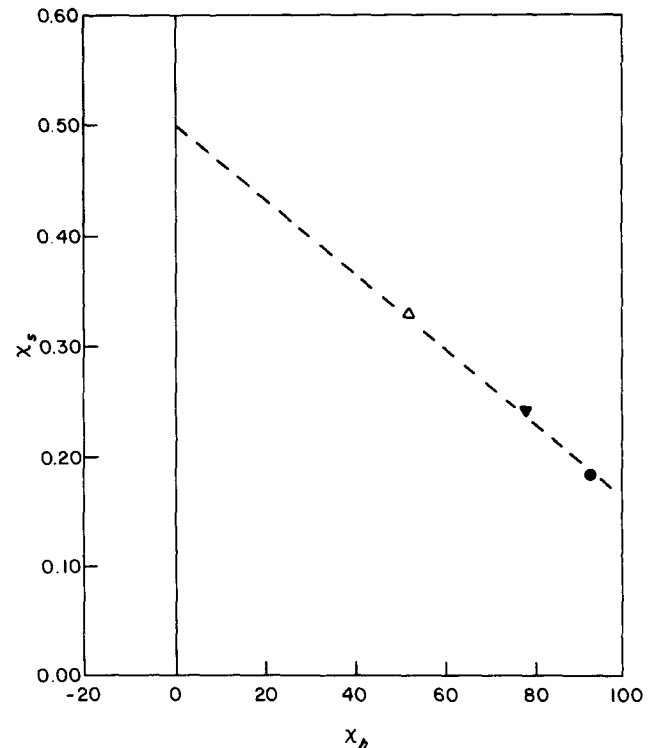

Figure 3 Entropic parameter χ_s *versus* enthalpic parameter χ_h of three polymer solutions with almost identical molecular weights and theta temperatures. Symbols as in *Figure 1*
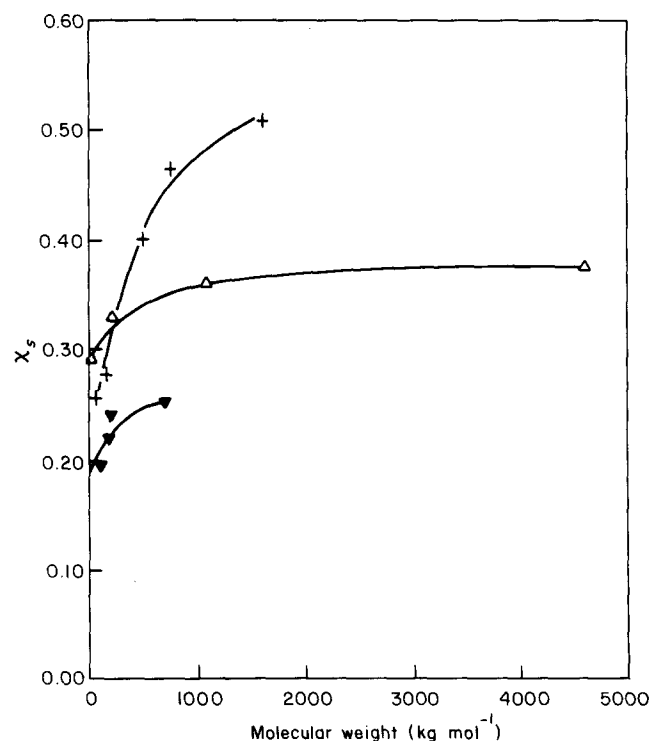

Figure 4 Molecular-weight dependence of the entropic parameter χ_s of three different polymer solutions. Curves serve as a guide to the eye: $+$, PS–toluene; $\triangle$, PMMA–butyl chloride; $\blacktriangledown$, PIB–benzene
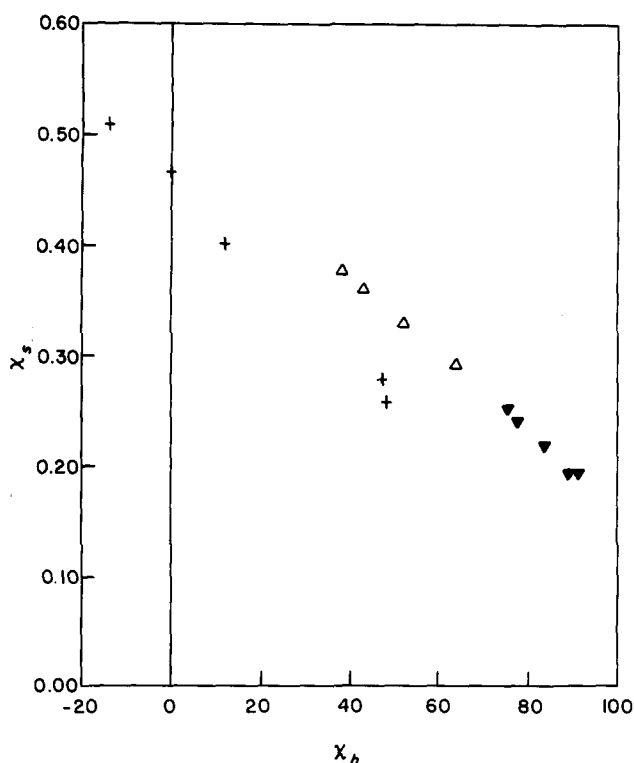
Figure 5 Entropic parameter χ_s *versus* enthalpic parameter χ_h of the polymer solutions represented in *Figure 4*. Symbols as in *Figure 4*

Table 2 Experimental and calculated interaction parameters of (extrapolated) infinite-molecular-weight polymer solutions

Solution	Experimental		Calculated
	χ_s	χ_h (K)	χ_h (K)
PS–toluene	0.51	−15	1
PMMA–butyl chloride	0.37	39	34
PS–cyclohexane	0.29	64	33
PIB–benzene	0.26	74	114

levelling off at higher values. The behaviour of the enthalpic part χ_h can best be illustrated by plotting χ_s *versus* χ_h once more. *Figure 5* again shows the clearly linear relation. We conclude that, with increasing molecular weight of the polymer in the solution, the entropic part of the interaction parameter increases and the enthalpic part decreases in such a way that both are linearly related.

It is interesting to consider the limiting case of $M \to \infty$. For infinite molecular weight the χ_h and χ_s parameters seem to converge to a limiting value. Unfortunately, no heats of mixing data on polymer solutions are available against which to check the χ_h values. However, χ_h can be estimated with group contribution schemes and solubility parameters (equation (6)). In *Table 2* are shown the extrapolated $M = \infty$ values (obtained by linear extrapolation to $1/M = 0$) of χ_h and χ_s of four systems where sufficient molecular-weight data were available and χ_h calculated from group contribution schemes. Considering the large uncertainties involved, the correlation between extrapolated and calculated values is reasonably satisfactory. Above all, the predicted χ_h values are clearly of the right order of magnitude.

From these observations we conclude that there is a universal type of behaviour of the interaction parameter in dilute polymer solutions. The value of the entropic contribution increases with molecular weight to a limiting value for infinite molecular weight that strongly depends on the particular polymer–solvent system. The enthalpic contribution to χ decreases with molecular weight to a limiting value at infinite molecular weight, which appears to correlate roughly with predicted values from solubility parameters. The two contributions are related in such a way that the theta point is independent of molecular weight ($\chi = 1/2$ at $T = \Theta$).

The physical origin of this behaviour is not certain. It

is interesting to note that the molecular-weight dependence of χ_s is qualitatively similar to the 'Huggins correction'[1], given by:

$$\chi_s = \frac{1}{z}\left(1 - \frac{1}{r}\right)^2 \qquad (14)$$

where z is the coordination number of the lattice, used to derive equation (14), and r is the degree of polymerization, i.e. the number of basic elements per polymer. Unfortunately, the relation between z and molecular structure is not clear. However, equation (14) also shows up as the first-order term in a systematic expansion of the Flory–Huggins model[14], so it may describe a fundamentally important effect. It originates in the dissimilar nature of the polymer and solvent. In a blend of polymers with equal molecular weights, it vanishes. This is in line with the experimental observation that interaction parameters in polymer blends are usually much smaller than in solutions because of the lack of the dominant entropic contribution χ_s.

If a polymer is dissolved in an ideal solvent (no energetic interactions), it swells because of the intermolecular steric interactions. In the pure polymer (or in a polymer blend!) these intermolecular steric interactions are essentially cancelled by intramolecular interactions. The ordering associated with the swelling in the solvent may be the basic physical origin of the large entropy penalty for dissolution. Unfortunately, these ideas do not have a firm theoretical basis. Hopefully, computer simulations, which are now becoming feasible, will enhance our understanding of these phenomena.

CONCLUSIONS

From a study of the behaviour of the thermodynamic interaction parameter χ in polymer solutions, the following observations can be made:

(1) Polymer solutions, in contrast to polymer blends, show a large and unfavourable entropic contribution to the interaction parameter.

(2) Polymer solutions show much larger differences in the entropic and enthalpic contributions to χ than in the total χ.

(3) The entropic contribution χ_s increases and the enthalpic contribution χ_h decreases with molecular weight.

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