higher. Such a result has also been obtained for conventional poly(alkyl α-chloroacrylates) and the corresponding poly(alkyl methacrylates). This is probably due to the strong intermolecular forces introduced by the presence of the polar chloride groups.

An assumption inherent in the theoretical treatment is the applicability of the Simha–Boyer relationship[9] to the polymers, regardless of tacticity

$$T_g\Delta\alpha = 0.113 \qquad (4)$$

where $\Delta\alpha$ is the difference in the volume expansion coefficient above and below T_g. Values of $\Delta\alpha$ derived from eq 4 are given in Table II for the stereoregular poly(ethyl α-chloroacrylates) and the stereoregular poly(ethyl methacrylates). These values have not been experimentally verified and work is in progress to accomplish this.

Conclusions

The predictions of the simple model proposed earlier regarding the effect of stereoregularity on the glass transitions of disubstituted vinylidene polymers appear to have been confirmed in a test case. The reasonably satisfactory quantitative agreement lends some support to the basic assumptions of the theory.

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The Prediction of Surface Tensions of Liquid Polymers

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ABSTRACT: Values of the surface tension of polymers as a function of temperature and molecular weight have been predicted and compared with experimental values from the literature. The following methods of prediction were used: a corresponding states correlation, a modified solubility parameter approach, a relation of Schonhorn,[7] and the parachor. The corresponding states correlation and the parachor are more successful than the other two approaches. They give similar, and good results predicting the LeGrand–Gaines $M^{-2/3}$ dependence of γ. The parachor is preferred on grounds of simplicity.

Recent work has yielded a considerable amount of data on the surface tension of liquid polymers, and its variation with temperature[1,2] and the molecular weight of the polymer.[2,3] The decrease of γ with T is less rapid than for a low molecular weight substance, implying a lower surface entropy, while LeGrand and Gaines[3] have shown that a linear dependence of γ on $M^{-2/3}$ holds with remarkable generality

$$\gamma = \gamma_\infty - kM^{-2/3} \qquad (1)$$

We propose using these data to test three approaches which allow polymer surface tensions to be predicted from the bulk properties, as follows.

(1) Correlation with Solubility Parameters. Hildebrand and Scott[4a] found a correlation of γ with the solubility parameter (δ) of a low molecular weight substance. Their relation can be expressed[4b] as

$$\gamma = 0.039\delta^{2.30}V^{1/3} \qquad (2)$$

where V is the molar volume in cm^3 of the molecules which are assumed to be spherical, and the units of γ and δ are ergs cm^{-2} and cal$^{1/2}$ cm$^{-3/2}$, respectively. The solubility parameter is related to the cohesive energy density (CED), energy of vaporization (ΔE^V) and internal pressure (P_i) through

$$\delta^2 = (\text{CED}) = \Delta E^V/V \simeq P_i/1.1 \qquad (3)$$

The factor 1.1 is generally applicable for nonpolar liquids.[5] Hildebrand and Scott point out[4a] that a linear relation between γ and the CED would yield almost as good a correlation of the data as eq 2. A least mean squares analysis of the data[4a] shows the relation to be

$$\gamma = 0.075\delta^2V^{1/3} \qquad (4)$$

$$\gamma = 0.075\Delta E^V/V^{2/3} \qquad (5)$$

It is clear that the rationale of the form of this expression lies in $\Delta E^V/V^{2/3}$ being a contact energy between molecules expressed per unit area of the molecule, which is necessarily spherical. However, Lee[6] has calculated γ for many polymers using eq 2 with V replaced by the volume per mole of a chain element which is taken to be the polymer repeat unit. Theoretical work by Schonhorn[7] gives a result similar to eq 4 but with a different numerical factor and a slightly different choice of chain element

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$$\gamma = 0.168\delta^2(V/n)^{1/3} \tag{6}$$

This is eq 17 of ref 7 with the constant 0.310 × 1.1 changed to give the same units as above to γ and δ; V is again the volume per mole of repeat units, and n is the number of identical groups in the repeat unit. Thus, in polyethylene, Lee takes $(CH_2)_2$ to be the chain element while Schonhorn takes CH_2.

The choice of a polymer chain element to replace the spherical small molecule is crucial. Those made by Lee and Schonhorn are convenient, but there seems to be no reason why the repeat unit, of significance in the synthesis of the polymer, should also determine the physical properties. In fact, the rather poor comparison[6] between predicted and experimental γ values appears on inspection to be due in large part to the arbitrary choice of the polymer element. Wu[8] has obtained a good correlation between the dispersion-force contribution to δ and γ_c, the critical surface tension. The volume of the polymer element, however, is taken to be the average atomic volume of the polymer, which varies little from polymer to polymer in contrast to the repeat unit volume. It is probable that good results would be obtained by defining the polymer element as a length of the chain equal to the chain diameter, so that it might be considered approximately spherical. The surface tension would again correspond to a surface energy per unit molecular area of the polymer. Such a choice would have the disadvantage of requiring a molecular model from which to determine the chain diameter.

(2) The Parachor. Following its use with liquids of quasi-spherical molecules the parachor has been employed with polymers[6,9]

$$\gamma = ([\mathrm{P}]/V)^4 \tag{7}$$

Here [P] and V again refer to a mole of polymer repeat units. The value of γ is unchanged, however, by taking the element to be V/n with Schonhorn. Results have been good[9] with liquid polymers. The critical surface tensions, γ_c, found with solid polymers[6] seem to be close to the surface tension of the liquid. The poor agreement[6] of eq 7 with γ values obtained with these materials seems due to the use of the density of the solid in the equation instead of that of the liquid. The temperature dependence of γ from eq 7 is

$$\gamma^{-1}\mathrm{d}\gamma/\mathrm{d}T = -4\alpha \tag{8}$$

where α is the thermal expansion coefficient.

(3) Corresponding States Correlation with Bulk Properties. Values of the surface tension of liquids have been correlated[10,11] with bulk equation of state properties through the use of the Prigogine corresponding states principle.[12] This principle has been used extensively to deal with properties of liquids of both chain and quasi-spherical molecules. Although the definition of a chain element is not essential to the treatment of bulk properties, the Prigogine theory[12] divides the chain into quasi-spherical segments of a length equal to the chain diameter. This definition is thus the same as suggested above for the treatment of surface properties. On the other hand, Roe[10] has assumed that the polymer element is a length of chain having three external degrees of motion, in analogy with the three external degrees of a spherical molecule. The intuitive reasons for this choice of element are given by Roe. The volume of 1 mole of such elements may be found to be

$$\text{molar element volume} = RT^*/P^* \tag{9}$$

where P^* and T^* are the Prigogine reduction parameters for pressure and temperature. Since these parameters are obtainable from the bulk equation of state properties, eq 9 represents a convenient choice for the polymer element obviating any consideration of a molecular model. An empirical correlation[11] shows that the reduced surface tension

$$\tilde{\gamma} = \gamma/\gamma^* = \gamma/k^{1/3}P^{*\,2/3}T^{*\,1/3} \tag{10}$$

is a "universal" function of reduced volume, $\tilde{V}$, or reduced temperature, $\tilde{T}$. These are obtained from the molar volume and the temperature through

$$\begin{aligned}\tilde{V} &= V/V^* \\ \tilde{T} &= T/T^*\end{aligned} \tag{11}$$

At negligible pressure, $\tilde{V}$ and $\tilde{T}$ are related by an equation of state such as that recently proposed by Flory and collaborators[13]

$$\tilde{T} = (\tilde{V}^{1/3} - 1)/\tilde{V}^{4/3} \tag{12}$$

The empirical function, $\tilde{\gamma}(\tilde{T})$ is given quite well by a cell model,[14] also used for the calculation of the bulk thermodynamic properties, and may be expressed as[11]

$$\tilde{\gamma}\tilde{V}^{5/3} = M - (1 - \tilde{V}^{-1/3})\ln(\tilde{V}^{1/3} - 0.5)/(\tilde{V}^{1/3} - 1) \tag{13}$$

with $M = 0.29$.

Finally, it should be mentioned that the significant structures theory has been applied to polymers,[15] giving reasonable results for polyethylene.

Comparison of the Correlations. The functional form of eq 13 was found[11] to be almost identical with $\tilde{\gamma} = 0.247/\tilde{V}^4$ so that the surface tension is given by

$$\gamma = 0.154P^{*\,2/3}T^{*\,1/3}/\tilde{V}^4 \tag{14}$$

where P^* is in cal/cm^3 and T^* in °K. Also, using eq 11, the parachor eq 7 may be rewritten as

$$\gamma = \{[\mathrm{P}]/V^*\}^4/\tilde{V}^4 \tag{15}$$

i.e., in the same form as eq 14.

A comparison between corresponding states and the solubility parameter correlations is afforded by replacing V in eq 4 by the volume of the polymer element, as given by Roe, *i.e.*, eq 9. Furthermore the ΔE^{V} taken

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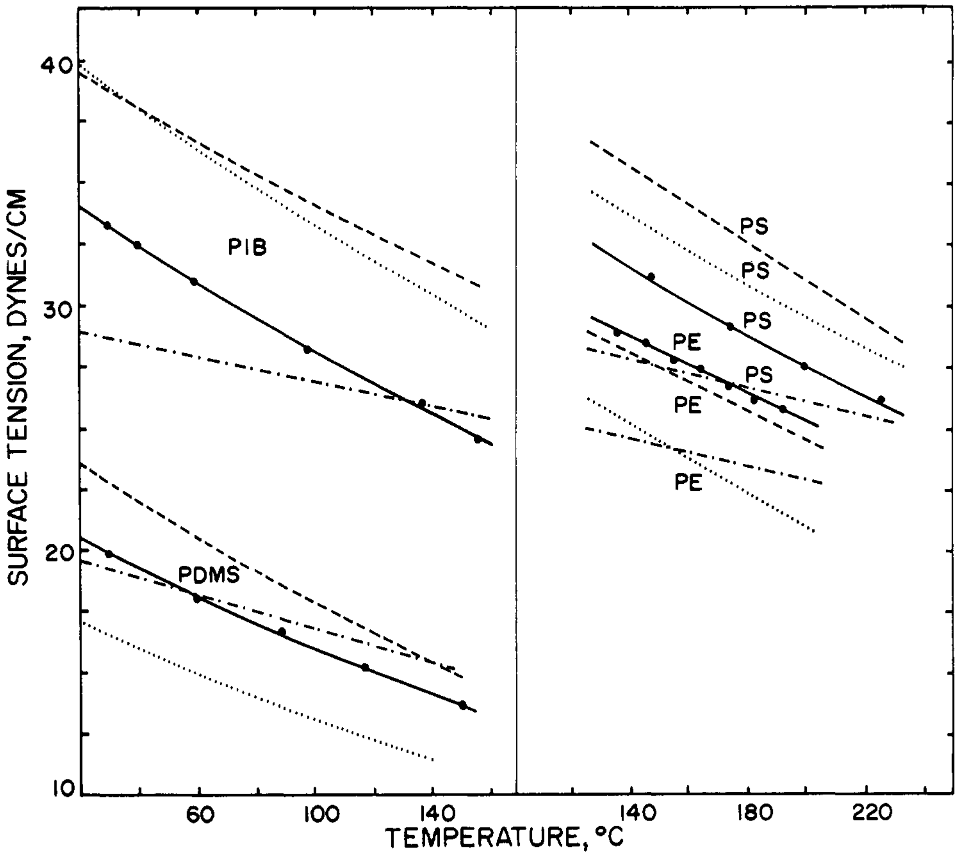

Figure 1. The surface tension of polymers as a function of temperature: ●, literature experimental values; dashed line, corresponding states theory (eq 10–13); dotted line, parachor (eq 7); dot–dash line, solubility parameter (eq 16) for polyethylene[a,b,b,b] (PE), polyisobutylene[a,d,d,d] (PIB), polystyrene[f,g,h,e] (PS), and poly(dimethylsiloxane)[a,i,j,k] (PDMS). The first reference gives the experimental data, the second the compressibility or P^*, the third the thermal expansion coefficient or T^*, the fourth the density for use with the parachor. Parachor values are obtained from the group contributions of O. R. Quayle, *Chem Rev.*, **53**, 439 (1953). The references are found in the caption to Figure 2.

by ref 5 to be inversely proportional to $\tilde{V}^{1.1}$ gives $\delta^2 = P^*/\tilde{V}^{2.1}$ so that eq 4 becomes

$$\gamma = 0.095 P^{*2/3} T^{*1/3}/\tilde{V}^{2.1} \qquad (16)$$

Most liquids have $\tilde{V} \sim 1.2$ and hence the modified solubility parameter equation (16) is consistent with expression 14. The variation with temperature, however, would only be half as large

$$\gamma^{-1} \mathrm{d}\gamma/\mathrm{d}T = -2.1\alpha \qquad (17)$$

We conclude that the three approaches are very similar, as will be seen by the comparison of the theoretical expressions with experiment. In each case the dependence of γ on molecular weight and temperature is through the free volume, *i.e.*, the expansion of the liquid above its close-packed volume, represented by $\tilde{V}$. We note that the solubility parameter had its origin as a means of evaluating intermolecular forces in liquids, making no explicit mention of free volume. Its success, however, in treating polymer systems seems due in large measure to a dependence of δ on free volume.[16]

Detailed Comparison of Theory and Experiment

Temperature Dependence of γ. Figure 1 shows literature values of $\gamma(T)$ for liquid high polymers together with values predicted from the corresponding states theory, eq 10–13, the modified solubility parameter theory, eq 16, and the parachor relation, eq 7. The Schonhorn prediction, eq 6, does not give as good results; however, there are no adjusted parameters in his equation. The values of P^* and T^* for use in the above were obtained using standard techniques[11] from equation of state data, given as a function of temperature except for the compressibility of polystyrene which was only obtainable at a single temperature. The values of P^* and T^* were found to vary slightly with temperature, but the curves of Figure 1 would be negligibly changed by taking P^* and T^* to be fixed at one temperature. The absolute values of γ are given reasonably well by all three correlations, but its temperature dependence is too small in the solubility parameter theory (*cf.* eq 8 and 17). It is notable that none of these theories introduces any special effect at the surface of a polymer liquid, such as a restriction in the number of configurations which would lower the surface entropy and also $\mathrm{d}\gamma/\mathrm{d}T$. The success of the corresponding states and parachor approaches in predicting $\mathrm{d}\gamma/\mathrm{d}T$ implies that the restriction of polymer configurations at the surface plays a relatively minor role in establishing the surface tension, as noted by Roe.[9]

Molecular Weight Dependence of γ. Figure 2 shows the experimental dependence of γ on molecular weight

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(16) J. Biros, L. Zeman, and D. Patterson, to be published.

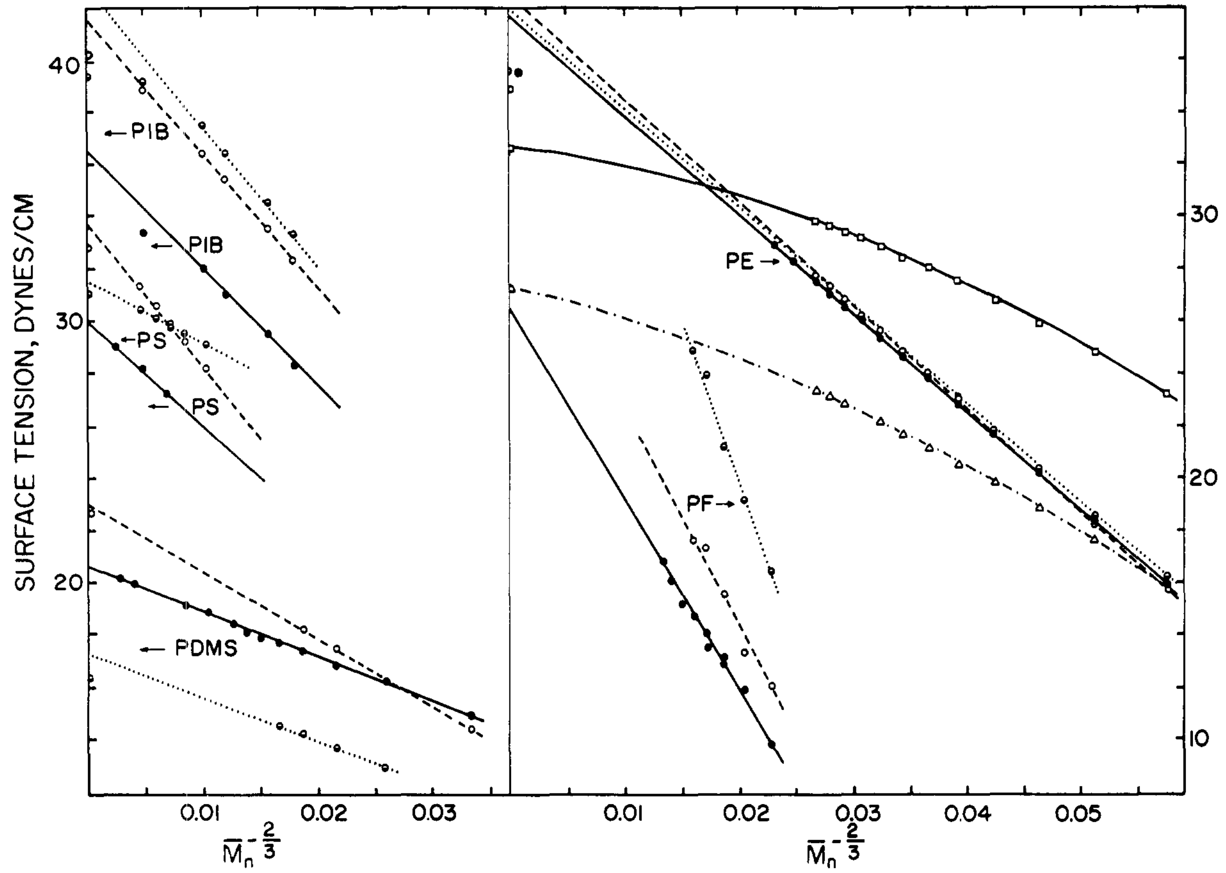

Figure 2. The surface tension of polymers as a function of molecular weight (the first reference gives the experimental data, the second the compressibility or P^*, the third the thermal expansion coefficient or T^*, the fourth the density for use with the parachor): ●, literature experimental values; dashed line, corresponding states theory (eq 10–13); dotted line parachor (eq 7) for oligomers of polyethylene[a,b,b,b] (PE), *i.e.*, *n*-alkanes at 20°, polyisobutylene[c,d,e,c] (PIB) at 24°; polystyrene[f,g,h,e] (PS) at 176°; poly(dimethylsiloxane)[i,j,j,k] (PDMS) at 30°; poly(tetrafluoroethyelene)[l,l,m,m] (PF) at 20°. Parachor values are obtained from the group contributions of Quayle (see caption to Figure 1). Curve for the *n*-alkanes obtained from the solubility parameter equation (16) and the Schonhorn equation (6) are indicated by a dot–dash line and □, respectively: [a] F. D. Rossini, *et al.*, "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds," Carnegie Press, Pittsburgh, Pa., 1953; R. J. Roe, *J. Phys. Chem.*, **72**, 2013 (1968). [b] R. A. Orwoll and P. J. Flory, *J. Amer. Chem. Soc.*, **89**, 6814 (1967). [c] D. G. LeGrand and G. L. Gaines, Jr., *J. Colloid Interfac. Sci.*, **31**, 162 (1969). [d] B. E. Eichinger and P. J. Flory, *Macromolecules*, **1**, 285 (1968). [e] T. G Fox and S. Loshaek, *J. Polym. Sci.*, **15**, 371 (1955). [f] G. W. Bender and G. L. Gaines, *Macromolecules*, **3**, 128 (1970). [g] G. Gee, *Polymer*, **7**, 373 (1966). [h] V. S. Nanda and R. Simha, *J. Phys. Chem.*, **68**, 3158 (1964). [i] H. W. Fox, P. W. Taylor, and W. A. Zisman, *Ind. Eng. Chem.*, **39**, 1401 (1947); G. L. Gaines, *J. Phys. Chem.*, **73**, 3143 (1969). [j] D. Patterson, S. N. Bhattacharyya, and P. Picker, *Trans. Faraday Soc.*, **64**, 648 (1968); G. Allen, G. Gee, D. Mangaraj, D. Sims, and G. J. Wilson, *Polymer*, **1** (4), 467 (1960). [k] T. Kataoka and S. Ueda, *Polymer Lett.*, **4**, 317 (1964). [l] G. H. Rohrback and G. H. Cady, *J. Amer. Chem. Soc.*, **71**, 1938 (1949); V. E. Stiles and G. H. Cady, *ibid.*, **74**, 3771 (1952); G. D. Oliver, S. Blumkin, and C. W. Cunningham, *ibid.*, **73**, 5722 (1951); H. M. Scholberg, R. A. Guenther, and R. I. Coon, *J. Phys. Chem.*, **57**, 923 (1953); R. N. Haszeldine and F. Smith, *J. Chem. Soc.*, 603 (1951). [m] R. D. Dunlap and R. L. Scott, *J. Phys. Chem.*, **66**, 631 (1962); R. D. Dunlap, C. J. Murphy, Jr., and R. G. Bedford, *J. Amer. Chem. Soc.*, **80**, 83 (1958); E. B. Smith and J. H. Hildebrand, *J. Chem. Phys.*, **31**, 145 (1959); L. L. Burger and G. H. Cady, *J. Amer. Chem. Soc.*, **73**, 4243 (1951).

for the oligomers corresponding to the polymers of Figure 1 plus the perfluoroalkane series. Equation 1 is seen to be obeyed. The corresponding states, eq 10–13, have again been used to calculate γ for the different series and the correct dependence on M is predicted. The value of P^* should vary little or not at all between members of an oligomer series. However, for the *n*-alkanes the P^* parameter was calculated for each member of the series using compressibility data; for the other series a constant value of P^* was used obtained from compressibility data of either the high polymer or one of the oligomers. Values of T^* vary considerably as the chain length of the oligomer changes and they were obtained for individual oligomers from thermal expansion coefficients. The points for the individual oligomers are shown in Figure 2. Both the corresponding state theory and the parachor give straight lines for low molecular weights, which do not extrapolate exactly to the high molecular weight value of γ. The solubility parameter theory, eq 16, and the Schonhorn equation (6) give a curved dependence of γ on $M^{-2/3}$ and the results are only shown for the *n*-alkanes. We conclude that both the corresponding states theory and the parachor yield satisfactory results for the molecular weight dependence of the surface tension, although possibly the former is more accurate.

It is surprising that a general relation should exist between the surface tension and the molecular weight which does not have a fundamental structural significance. Both the corresponding states and the parachor theories relate the decrease of γ with decreasing M to an increase of the free volume of the liquid, as represented by the reduced volume $\tilde{V}$ or the reduced temperature $\tilde{T} = T/T^*$. One would expect a relation to exist between the decrease of γ from γ_∞, *i.e.*, $\gamma(M)/\gamma_\infty - 1$ and the decrease of $1/T^*$ from $1/T^*_\infty$, *i.e.*, $T^*_\infty/T^* - 1$. We have found that for the polymers considered here, $\gamma(M)/\gamma_\infty - 1$ is directly proportional to $(T_\infty^*/T^* - 1)^{2/3}$. Elementary arguments stemming from the significance of T^* show that $T_\infty^*/T^* - 1$ should be very close to proportional to M^{-1}, and this has been found to be the case for the present systems. Thus $\gamma(M)/\gamma_\infty - 1$ is proportional to $M^{-2/3}$ which is equivalent to eq 1.

Conclusions

We draw the following conclusions from this study.

(1) The solubility parameter relation for γ gives poor results when V is replaced in eq 4 by the polymer repeat unit, but the modified form, eq 16, gives reasonable results. Nevertheless, the temperature dependence of γ is too small and the Gaines–LeGrand relation, eq 1, is not accurately predicted.

(2) Both the corresponding states and parachor theories give satisfactory predictions of the temperature and molecular weight dependences of γ. It is probably fair to consider the corresponding states approach as a justification of the more empirical parachor method. However, the parachor is clearly far superior as regards practical utility since it requires only density data, whereas the corresponding states theory requires thermal expansion coefficients, and compressibilities or CED data. We suggest that the comparison of the parachor and corresponding states theory predictions should be continued as equation of state and surface tension data become available for more polymers.

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Prediction of the χ Parameter by the Solubility Parameter and Corresponding States Theories

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ABSTRACT: Values of the polymer–solvent interaction parameter, χ, are predicted using the solubility parameter theory and the corresponding states theory in the form given by Flory and collaborators. The theories predict a similar effect on χ of changing molecular parameters such as the solvent chain length, polymer and solvent cohesive energy, and polymer flexibility. Surprisingly similar predictions are also given for the temperature and pressure dependence of χ. The corresponding states theory treats the changes of volume occurring in polymer and solvent during mixing. The simple solubility parameter theory can also take these changes into account, although this is not apparent in its derivation.

According to the solubility parameter theory[2] (SPT) the polymer(2)–solvent(1) interaction parameter, χ, is related to the difference between the solubility parameters, δ, of the two components through

$$\chi = \frac{V_1}{RT}(\delta_1 - \delta_2)^2 + \beta \tag{1}$$

$$= \frac{(\Delta E^{\mathrm{v}})_1}{RT}\left[1 - \frac{\delta_2}{\delta_1}\right]^2 + \beta \tag{2}$$

$$\delta = \left[\frac{\Delta E^{\mathrm{v}}}{V}\right]^{1/2} \tag{3}$$

Here ΔE^{v} and V are the molar energies of vaporization and molar volumes; β is an empirical constant absent in the original theory applied to mixtures of quasi-spherical molecules, but found necessary for polymer systems.[2a] These simple equations have been of great utility in predicting polymer solubility and other polymer properties. The success of the theory is attested by its continued development,[3,4] particularly for systems with polar and hydrogen-bonded solvents, and until recently it was the only theory used extensively.

In the last few years, however, the corresponding states theory (CST) of Prigogine[5] has attracted attention, particularly in the modified form of Flory and collaborators.[6a] This theory also gives[6b] the temperature and pressure dependence of the χ parameter which is generally considered to be beyond the powers of the SPT, and predicts a concentration dependence for χ which is completely ignored by the older theory. Fur-

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