Studies of Polymer–Polymer Solubility Using a Two-Dimensional Solubility Parameter Approach

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Synopsis

The two-dimensional solubility parameter approach has been applied to the prediction of solubility of one polymer in another. The solubility parameters of a number of polymers have been calculated and the second dimension shown to improve the agreement between the calculated solubility and that measured using a ternary solution technique. The method proved most useful for predicting the effect of small structural modifications on solubility, and several examples of changing solubility, monitored by calculations and measurements, are given. Structural modifications included copolymer ratio variations and substitutions to affect polymer density or reduce polarity of functional groups. The effects of temperature and molecular weight on solubility are discussed in terms of regular solution theory, which could not account for the decrease in solubilities with increased temperature observed for several polymer–polymer systems.

INTRODUCTION

For years, the coatings industry has used a simple and gratifyingly useful scheme for correlating, interpolating, and predicting the "compatibility," or phase behavior, of solvents and resins.[1,2] The scheme is based on the regular solution theory of Hildebrand and others[3] which presumes that phase behavior is determined by two factors: (1) a combinatorial entropy term which is ideal, depending only on volume fraction of each component in the phase, and (2) an enthalpy term which depends on the difference between like and unlike interactions. The latter is always positive or zero if the further assumption is made that the unlike interactions are just the geometric mean of the two like interactions. · Thus, if the two components have similar interaction energies, the enthalpy term is zero and the components will have maximum compatibility. This means that each resin and solvent could be simply characterized by one number, the solubility parameter, which should define its solubility in every other solvent. For solvents, the solubility parameter is readily determinable from heats of vaporization, and extensive lists have been compiled.[2,4] For resins, the solubility parameter is most often determined empirically.

In order to improve the workability of the solubility parameter approach to phase behavior, several refinements have been forwarded. Gardon,[5]

Hansen,[6] and others[7,8] have argued that one parameter is not enough for components possessing a significant dipole moment, because the dispersion and polar forces which comprise most of the interaction term are not interchangeable. By way of example, acetone, a polar liquid with a solubility parameter of 9.9 $cal^{1/2}/cm^{3/2}$, is a nonsolvent for polystyrene, a nonpolar polymer with a solubility parameter of 9.1; whereas nonpolar carbon disulfide, solubility parameter = 10.0, is a solvent.

The extension of solubility parameter to polymer–polymer systems has been attempted,[9,10] but the results have been less successful because the combinational entropy term decreases as the size of the molecule increases, other energy terms[11] may dominate as all terms decrease in magnitude, and solubility parameters for polymers are difficult to measure directly, usually being inferred or calculated. Furthermore, polymer–polymer phase behavior itself is difficult to study and even imprecisely defined.[12] In this work, an attempt has been made to apply the two-component solubility parameter approach to a very limited range of polymeric structures, attempting to predict relative, rather than absolute, behavior. In many applications, this is all that is required because there are often overriding practical and economic restrictions on any major structural changes which can be made to achieve soluble polymer systems.

THEORETICAL

A regular solution is one in which the entropy of the components is that of an equal, ideal solution.[3] This implies that a component 1 will have a distribution of 1 and 2 as neighbors and will have the opportunity of experiencing like and unlike interactions. The relative strength of these interactions then determine the solution's deviation from ideal behavior.

Many pairs of organic liquids and solids form regular solutions the properties of which can be predicted fairly well from component properties, namely, cohesive energy density and molar volume. The cohesion of a polymer, on the other hand, is not due to the interaction of one entire molecule with another, but to one segment of some intermediate size with another segment of similar size. The cohesive energy density cannot be easily measured in the solid state and values determined empirically from swelling or viscosity measurements with low molecular weight components might have little bearing on phase behavior with high molecular weight "solvents," because the latter cannot interact with as small a section of the solute polymer. It was felt that computations of cohesive energy density would provide a consistent *relative* placement of similar polymer structures which would aid in prediction of *changes* which could be made to improve solubility. If it is assumed that a regular solution can be formed with two polymer components and that the basic interaction segment is approximately the size of a repeat unit, then consistent calculations of phase behavior and, therefore, the thermomechanical behavior are possible.
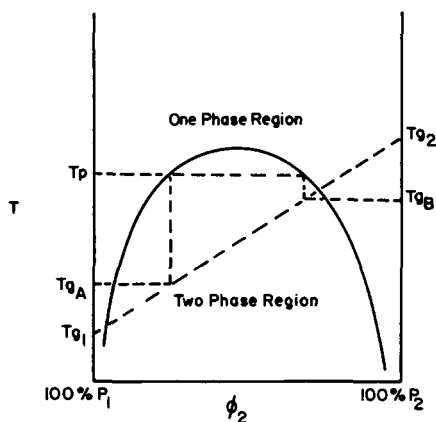
Fig. 1. Polymer–polymer phase diagram.

The differential energy balance for polymer 1 in phase A and phase B according to the familiar Hildebrand-Scratchard-Flory-Huggins equation[3] is
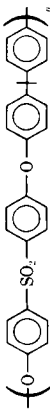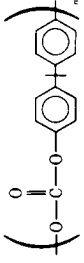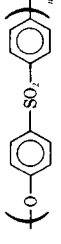
$$\ln \phi_{1A} + \left(1 - \frac{V_1}{V_2}\right) \phi_{2A} + V_1 \frac{(\delta_1 - \delta_2)^2}{RT} \phi_{2A}{}^2$$

$$= \ln \phi_{1B} + \left(1 - \frac{V_1}{V_2}\right) \phi_{2B} + V_1 \frac{(\delta_1 - \delta_2)^2}{RT} \phi_{2B}{}^2. \quad (1)$$
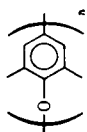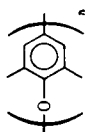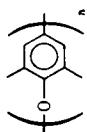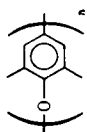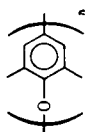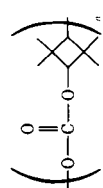
A similar equation can be written for polymer component 2. In this equation, ϕ is volume fraction, V is the molecular volume, and δ is the solubility parameter, the square of which is the cohesive energy density. The first two terms on each side of eq. (1) are regular mixing entropies while the third terms are due to interactions. As written, any *entropy* change due to interaction has been neglected, but would probably have to be included if specific interactions were present. It is generally necessary for polymer–solvent systems.[11] A beauty (and shortcoming) of eq. (1) is its ability to predict phase behavior from pure component properties only, allowing solubility predictions for untested and unmade compounds.

The phase diagram in Figure 1 is the type obtained from eq. (1). In this diagram, the miscible region for mixtures of 1 and 2 is located at high temperatures and separated from the two-phase region at low temperatures by the curved line. This curve is symmetrical, according to eq. (1), about the 50% polymer 1 (P_1), 50% polymer 2 (P_2) axis only if $V_1 = V_2$. In Figure 1, polymer 1 has been assigned a lower glass transition temperature (T_{g_1}) than polymer 2, which has a T_g equal to T_{g_2}.

The glass transition temperature of a one-phase mixture of polymer components 1 and 2 will reflect the amount 1 and 2 contained in the phase in a roughly proportional fashion, as suggested by the straight diagonal line connecting T_{g_1} with T_{g_2}. This behavior has been observed for some totally miscible systems.[19,20] In systems involving two phases (A and B in Fig. 1),
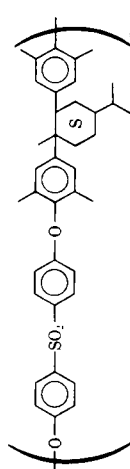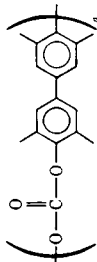
TABLE I
Polymer Components

Name and structure	Source	Abbreviation	Reduced viscosity, dl/g (0.2 g/dl in CH$_2$Cl$_2$)	Density	δ_d	δ_p
Polystyrene	Union Carbide, SGN-3000	PS	0.85	1.053	9.1	0.1
Poly(styrene-co-acrylonitrile), 28% acrylonitrile	Union Carbide RMD-4511	S/AN(28)	1.15	1.079		
Poly(oxy-1,4-phenylenesulfonyl-1,4-phenyleneoxy-1,4-phenyleneisopropylidine-1,4-phenylene)	Union Carbide, P-1700 polysulfone	PSF	0.409	1.241	8.7	5.9
Poly(oxycarbonyloxy-1,4-phenyleneisopropylidene-1,4-phenylene)	GE, Lexan 101 polycarbonate	Bis A/C	0.855	1.19	9.5	0.4
Poly(methyl methacrylate)	du Pont, Lucite 140	PMMA	0.415	1.19	8.6	2.9
Poly(2-vinylpyridine)	expr. polymer	PVP	1.095		4.5	8.6
Poly(oxy-1,4-phenylenesulfonyl-1,4-phenylene)	expr. polymer	Bis S	0.054	1.347	8.0	9.4
Poly[oxy(2,6-dimethyl-1,4-phenylene)]	GE	PPO		1.06	8.9	0.33

Poly(chlorostyrene), mixed isomers	expr. polymer	P(Cl-S)	0.639	1.242	9.5	1.5
Poly(dichlorostyrene), mixed isomers	expr. polymer	P(Cl$_2$-S)	0.647	1.401	10.4	0.9
Poly(styrene-co-acrylonitrile), 6.8% acrylonitrile	expr. polymer[a]	S/AN (7)	0.954			
Poly(styrene-co-acrylonitrile), 12.7% acrylonitrile	expr. polymer[a]	S/AN (13)	1.195			
Poly(styrene-co-acrylonitrile), 18.0% acrylonitrile	expr. polymer[a]	S/AN (18)	1.523			
Poly(styrene-co-acrylonitrile), 20.6% acrylonitrile	expr. polymer[a]	S/AN (21)	1.694			
Poly(styrene-co-acrylonitrile), 24% acrylonitrile	expr. polymer[a]	S/AN (24)	0.822			
Poly(styrene-co-acrylonitrile), 33% acrylonitrile	expr. polymer[b]	S/AN (33)	1.026			
Poly(styrene-co-acrylonitrile), 35% acrylonitrile	expr. polymer[b]	S/AN (35)	0.687			
Poly(styrene-co-acrylonitrile), 42% acrylonitrile	expr. polymer[b]	S/AN (42)	0.604			
Poly[oxycarbonyloxy(2,2,4,4-tetramethyl-1,3-cyclobutylene)]	expr. polymer	CB/C	1.17	1.07	6.7	0.38

TABLE I (continued)

Name and structure	Source	Abbreviation	Reduced viscosity, dl/g (0.2 g/dl in CH₂Cl₂)	Density	δ_d	δ_p
Poly[oxy(tetrachloro-1,4-phenylene)oxy-1,4-phenyleneisopropylidene-1,4-phenylene]	expr. polymer[a]	Bis A/HCB	0.45	1.375	9.8	2.4
Poly[oxy-1,4-phenylenesulfonyl-1,4-phenyleneoxy(2,6-diisopropyl-1,4-phenylene)isopropylidene(3,5-diisopropyl-1,4-phenylene)]	expr. polymer[d]	Tetraisopropyl Bis A/Bis S		1.055	8.5	3.6
Poly[oxy-1,4-phenylenesulfonyl-1,4-phenyleneoxy(2,6-dimethyl-1,4-phenylene)(1-methyl-4-isopropyl-1,2-cyclohexylene)(3,5-dimethyl-1,4-phenylene)]	expr. polymer[e]	TM Bis L/Bis S	0.9	1.098	8.7	3.8

+ other isomers

Polymer		Designation				
Poly[oxycarbonyloxy(2,6-dimethyl-1,4-phenylene)isopropylidene(3,5-dimethyl-1,4-phenylene)]	expr. polymer[c]	TM Bis A/C	0.62	1.085	8.6	0.17
Poly[oxy(2,5-dimethyl-1,4-phenylene) sulfonyl(2,5-dimethyl-1,4-phenylene)oxy-1,4-phenyleneisopropylidene-1,4-phenylene]	expr. polymer[a]	Bis A/TM Bis S	0.32	1.186	9.2	4.5
Polyacrylonitrile	PAN			~1.2	6.6	11.6
Poly(methacrylonitrile)	PMAN			~1.1	5.7	9.3
Polyacrylamide	P(ACR)			~1.3	7.6	11.4
Poly(vinyl chloride)	PVC			~1.4	7.4	6.1

[a] Synthesized by Dr. P. Fritze, Union Carbide Corporation.
[b] Synthesized by Mr. T. Gibb, Union Carbide Corporation.
[c] Synthesized by Dr. J. Kawakami, Union Carbide Corporation.
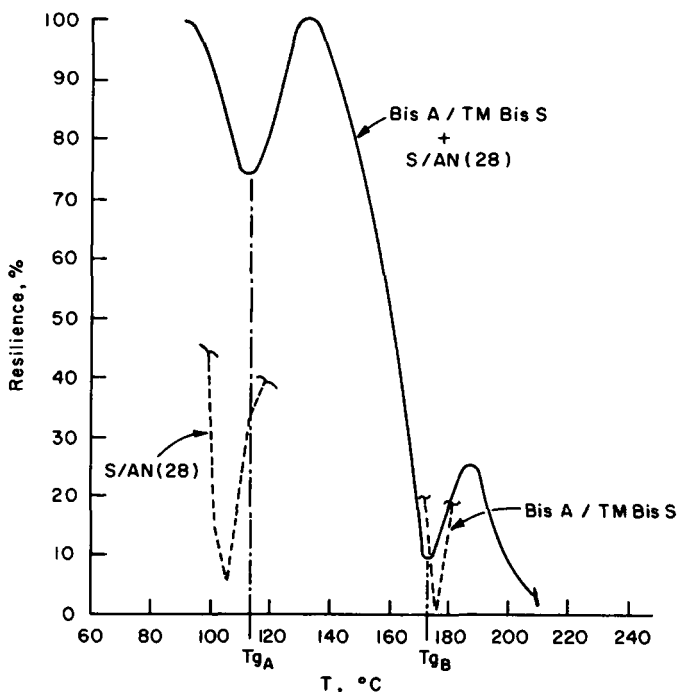[d] Synthesized by Dr. A. Farnham, Union Carbide Corporation.

Fig. 2. Thermal-mechanical analysis of a partially soluble mixture.

with each phase containing some of each component, the glass transition temperature of each phase should follow the same relationship.   In Figure 1, for example, the components could be equilibrated at processing temperature T_p which would in turn fix the composition of phases A and B at the positions denoted by the dotted, vertical lines of the diagram.   If the glass transition behavior of this mixture were then observed, transitions at T_{g_A} and T_{g_B}, higher and lower than T_{g_1} and T_{g_2}, respectively, would be found.

This behavior is seen often with polymer mixtures, as illustrated by Figure 2, where the resilience minimum for poly(styrene–co-acrylonitrile), S/AN (component 1), has been raised about 10°C by mixing with a high-T_g, substituted   polysulfone: poly[oxy(2,5-dimethyl-1,4-phenylenesulfonyl-(2,5-dimethyl-1,4-phenylene)oxy-1,4-phenyleneisopropylidene-1,4-phenyl-ene] (Bis A/TM Bis S, Table I).   Equation (1) requires that solubility will increase as T_p is raised and correctly predicts the extremely low mutual solubility of high molecular weight (V large) substances with any but a slight difference in cohesive energy densities.

If the mixing of two polymer components occurs with the entropy allowed by eq. (1), regardless of structure, then the enthalpy term will determine the composition of the phases and their T_g's.   As written, the enthalpy term $(\delta_1 - \delta_2)^2$ has one parameter for each polymer: its total energy of cohesion. Implied is a cohesion between polymer 1 and polymer 2 proportional to $\delta_1\delta_2$, which should be a close approximation in the limit of spherical, polariz-

able volumes (giving dispersion energy proportional to $\alpha_1\alpha_2$; α = polariz-ability) containing centrally located dipole moments, μ (giving dipole–dipole interactions proportional to $\mu_1{}^2\mu_2{}^2$). This is the geometric mean rule for nonspecific interactions. The spherical volumes must be equal in size and equally spaced in components and mixtures (no volume change). The induction energy (proportional to $\alpha_1\mu_2{}^2 + \alpha_2\mu_1{}^2$) will not follow the geo-metric mean rule but is generally a small fraction of the total energy.[5] The dipole–dipole interaction will decrease proportionally with temperature for freely rotating volumes, but dipoles on polymer chains lack complete freedom and the temperature dependence probably should be less. The polarization energy, $\alpha\alpha$, is sensitive to temperature only insofar as the centers between the volumes move with sample expansion.

If the interaction energy is assumed to be solely due to dispersion and dipole–dipole contributions, the enthalpy can be written as proportional to
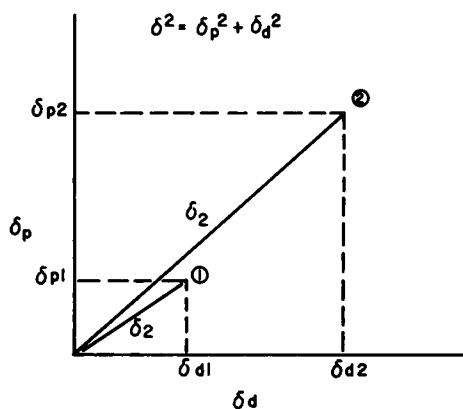

Fig. 3. Two-dimensional plot, illustrating relationship between total solubility parameter and the polar and dispersive components.

$(\delta_{d1} - \delta_{d2})^2 + (\delta_{p1} - \delta_{p2})^2$, where subscripts d and p stand for dispersive and polar, respectively. Then, a good match between the polar *and* dispersive components of the cohesive energies of both polymers is required for high solubility. The importance of such a match has been demonstrated for polymer–solvent systems[6,7] and presumably will be equally important for two-polymer mixtures.

The "two-component" solubility parameter can be conveniently plotted in the manner depicted in Figure 3. Each structure is a point in the δ_d, δ_p plane, and the solubility of one structure in another will be inversely related to the distance between the points. Variation of the copolymer composi-tion will move the δ along this line, while movement about the plane will require a terpolymer. This minimum requirement is important: a given structure requires at least a terpolymer second component for perfect solubility. In addition, two appropriate copolymer components can be made soluble by choosing the correct copolymer ratio for each in order to

match the polar and dispersive contributions.   These requirements will be discussed further in the experimental section with reference to real examples.

The polar and dispersion contributions for structures can be consistently calculated by the method outlined by Gardon.[5]   As a first step, the total solubility parameter is calculated using Small's method of group contributions.[13]   The total parameter is then proportioned according to eq. (2):

$$\frac{\delta_p{}^2}{\delta^2} = \frac{2\mu^4/3kT}{2\mu^4/3kT + 3I\alpha^2/4 + 2\alpha\mu^2} \tag{2}$$

where μ and α are the dipole moment and polarizability, respectively, and I is the first ionization potential; assumed constant at 10 eV.   Polariz-
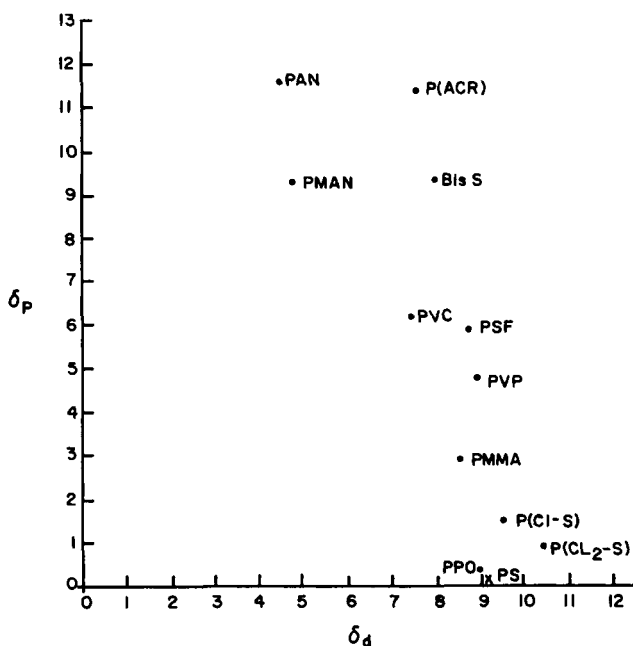

Fig. 4. Calculated components of the solubility parameter for a number of homopolymers.

ability is calculated via the Lorentz equation and group contributions to molar refractivity, while a dipole moment is assigned after examination of measured moments for structurally similar, low molecular weight compounds.   As the dispersive component is given by $\delta_d{}^2 = \delta^2 - \delta_p{}^2$, it contains automatically the small $2\alpha\mu^2$ induction term.

Using the method described, the solubility parameter components for a number of actual and imaginary polymers were calculated.   Some examples are displayed in Figure 4.   Experimental verification of the calculations was attempted by the solubility measurements described below.

EXPERIMENTAL

Materials

The source, structure, density, reduced viscosity, and abbreviation of the polymeric components used for the phase studies are listed in Table I. Included are calculated values of the polar (p) and dispersive (d) contributions to the solubility parameter, the source of which was discussed in the theoretical section. These polymers are all primarily amorphous, contain no hydrogen bond-donating capabilities, and cover a fairly wide range of polarities and total cohesive energy densities. Poly(vinyl chloride), PVC, is considered to be a hydrogen bond donator, either intra- or intermolecularly, showing solubility in a wide range of polymers, many of which are insoluble in each other. Therefore, PVC was not included in the study, although a calculation was run on the structure (Fig. 4).
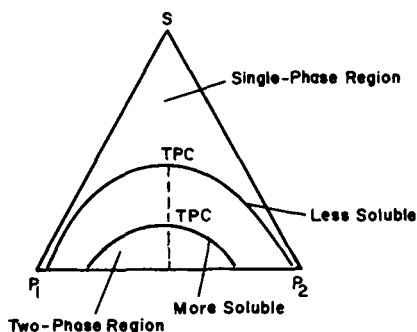
Measuring Solubility

As the solubility of polymer 1 in polymer 2 could be predicted using the two-parameter, cohesive energy density approach, combined with regular solution equations, it was felt desirable to test the results by actual solubility measurements. But first the development of a routine method for measuring solubility was necessary in order to gather sufficient data for a significant test.

The most meaningful, practical measure of solubility is probably the T_g's of the equilibrium phases relative to the pure components. The upward, low-T_g shift (Fig. 2) tends to be slightly self-correcting for the molecular weight of the solute because of the combination of inverse T_g and solubility dependence on molecular weight. Often the correction is inadequate, most pairs passing through a maximum "T_g solubility" as the molecular weight is increased.

Glass transition shifts are not useful, of course, when the mutual solubility of two-polymer components with similar T_g's is desired. Also, equilibration is difficult and uncertain, and measurement may be time consuming. A method based upon ternary (2 polymers, 1 solvent) phase behavior was, therefore, explored and adopted. Methylene chloride was chosen as the solvent because of its manipulative ease (high volatility), lack of high hydrogen-bonding capabilities, and solvency for a wide range of polymers.

Scott[14] has shown that the critical point concentration for a ternary system should be related only to interactions between the two polymers and independent of polymer–solvent interactions, if the latter are equal for the two-polymer components. This may be a very good approximation if the polymers are close to being mutually soluble. A typical polymer 1, polymer 2, solvent phase diagram is illustrated in Figure 5. The threshold point concentration (TPC)[10] denoted in the figure was used in place of the critical point concentration because the latter is exceedingly difficult to measure.

$$TPC_{12} = \frac{RT}{\langle V \rangle_{12} \ (\delta_1 - \delta_2)^2}$$

Fig. 5. Illustration of ternary phase behavior for system polymer 1 + polymer 2 + solvent.
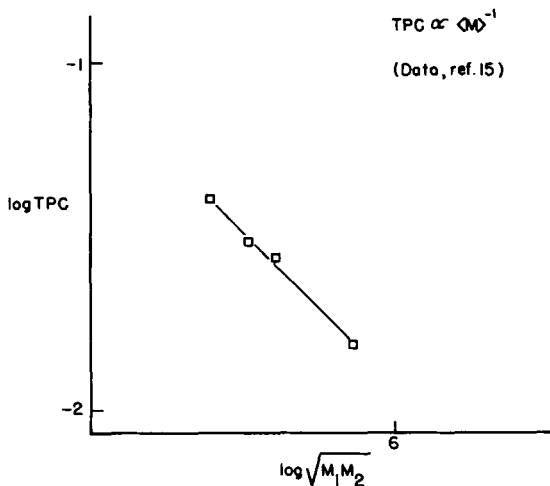

Fig. 6. Variation of threshold point concentration with average molecular weight of components (cellulose acetate + polyvinylacetal).

The two are usually quite close if the molecular weights of the polymers are similar.

The relationship of interest is

$$TPC_{12} \ \propto \ \frac{RT}{\langle V \rangle_{12} \ (\delta_1 \ - \ \delta_2)^2} \tag{3}$$

where TPC stands for the polymer concentration at the threshold point, $\langle V \rangle$ is an average polymer molar volume, and $(\delta_1 - \delta_2)^2$ is the cohesive energy density term.

The effect of molecular weight (volume) is illustrated in Figure 6. The plot is designed to show that the geometric mean molecular weight is an acceptable average, giving a straight line of slope negative one as predicted
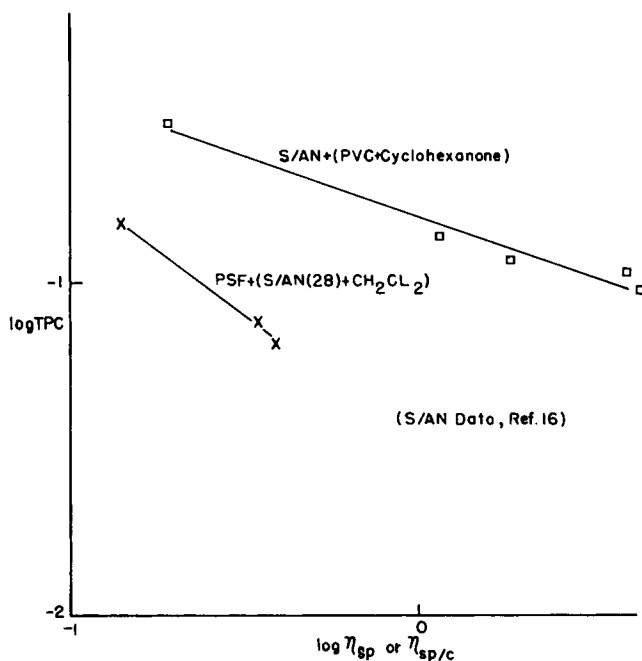
Fig. 7. Variation of threshold point concentration with solution vicosity of one polymer component.

by eq. (3). The molecular weights which led to these data covered nearly a decade.[15] As will be seen in the experimental results and discussion section below, a separable molecular weight effect on the TPC allows multiplicative corrections to be made on the experimentally determined solubility of a polymer pair, an important practical consideration.

The method can be further simplified by considering the variation of the TPC with the experimental solution viscosity of one polymer component. Typical results are shown in Figure 7. As expected, the negative slopes were less than one, varying from 0.5 to 0.7 (extremes illustrated). A value of 0.6 has been used to correct the TPC data (as in Fig. 11, for example) and appears to remove most of the scatter due to molecular weight variations.

RESULTS AND DISCUSSION

Test of Solubility Calculations

Seven homopolymers were chosen to test the solubility calculations described previously. The mutual solubilities of all combinations were calculated, then measured using the TPC method. Figure 8 contains the data (circles) as a log–log plot of solubility ratios, which should tend to eliminate molecular weight effects if the proportional corrections discussed above are realistic, without the necessity of measuring the components' molecular weights or solution viscosities. This can be easily seen using eq. (3) if the
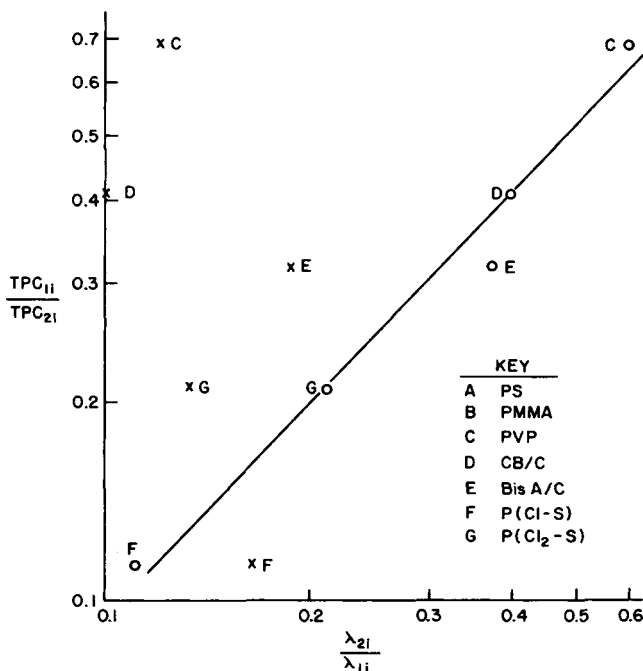
Fig. 8. Correlation of measured with calculated solubility for homopolymer components PS–PMMA baseline.

cohesive energy density term $(\delta_1 - \delta_2)^2$ is replaced by the two-dimensional term $(\delta_{p_1} - \delta_{p_i})^2 + (\delta_{d_1} - \delta_{d_i})^2$, which is just the square of the calculated distance between polymer 1 and i on the p,d plane. Combining this information with the relationships suggested by Figure 6 yields

$$TPC_{1i} \propto \frac{RT}{(V_1 V_i)^{1/2}[(\delta_{p_1} - \delta_{p_i})^2 + (\delta_{d_1} - \delta_{d_i})^2]}. \qquad (4)$$

The term in square brackets is called λ_{1i}^2 in Figure 8 for simplicity. A similar equation can be written for polymer pair $2i$. Dividing the two gives

$$\frac{TPC_{1i}}{TPC_{2i}} = \left(\frac{V_2}{V_1}\right)^{1/2}\left(\frac{\lambda_{2i}}{\lambda_{1i}}\right)^2 \qquad (5)$$

which upon taking logarithms of both sides provides the relationship plotted in Figure 8. Note that the molecular volume of polymer i has been eliminated. The ratio V_2/V_1 is constant for the diagram because polymer 1 and polymer 2, referred to as the "baseline," are not changed within the diagram. The baseline for Figure 8 is polystyrene (PS)–poly(methyl methacrylate) (PMMA) (polymers 1 and 2).

By way of example, the abscissa value for the first point, poly(chloro-styrene), P(Cl-S), in Figure 8 was calculated by dividing the distance λ between poly(methyl methacrylate) and poly(chlorostyrene) (polymer i) on
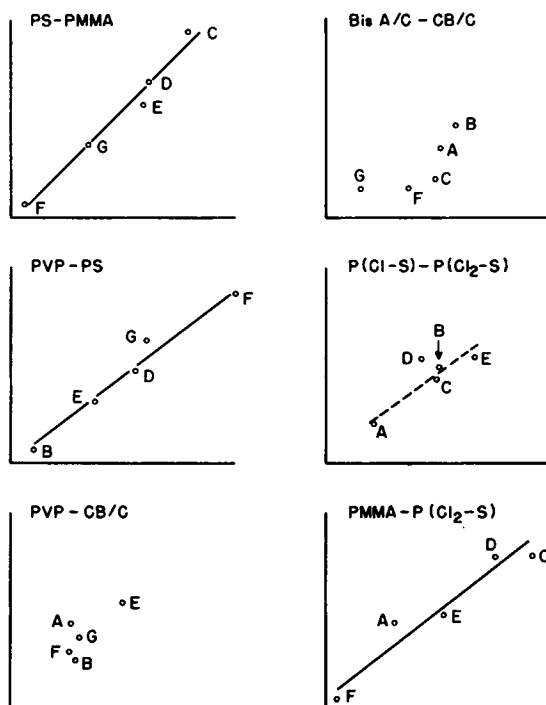
Fig. 9. Correlation of measured with calculated solubility for homopolymer components. Other baselines. Scales are same as in Fig. 8.

the δ_p, δ_d plane by the distance between polystyrene and poly(chlorostyrene). The ordinate for this point is the TPC for the pair polystyrene–poly-(chlorostyrene) divided by the TPC for poly(chlorostyrene) with poly-(methyl methacrylate). The other points are derived in a similar manner using data for the indicated resins. The data represented by the crosses are based on the same resins and the same TPC ratios, but the distance ratios $\lambda_{2i}/\lambda_{1i}$ were calculated using the absolute differences between the *total* solubility parameters.

As can be seen, the two-dimensional calculation gives a better correlation with the measured solubility than does the one-dimensional (crosses). Table I contains the structures corresponding to the abbreviations used in this figure.

Figure 9 displays the same data using other polymer 1–polymer 2 baselines. In some cases, especially with the polycarbonates, the correlation was not distinct. But the interesting outcome is that in all instances where correlation is good, the slopes are very near unity. (Note, however, that the plots are not completely independent.) Equation (5) suggests, contrarily, that the slope should be two. Evidently, the TPC is not independent of polymer–solvent interaction: the solvent reduces polymer 1–polymer 2 interaction more than by simply increasing the contact distance between the two polymers.

Examples of Partial Polymer–Polymer Solubility

The TPC method just described has proven most useful for measuring the relative solubility of a new polymer in a copolymer series, along with its point of maximum solubility. These results can then be used in connection with calculated locations on the δ_p, δ_d plane to predict changes which might improve solubility. This working relationship is represented graphically by Figures 10 and 11.

Figure 10 is an expanded version of Figure 4, detailing the vicinity around the dashed S/AN line. It is important to remember that this line does not represent S/AN of a particular styrene-to-acrylonitrile ratio (which should be a point) but is the locus of all copolymers ranging from 100% poly-
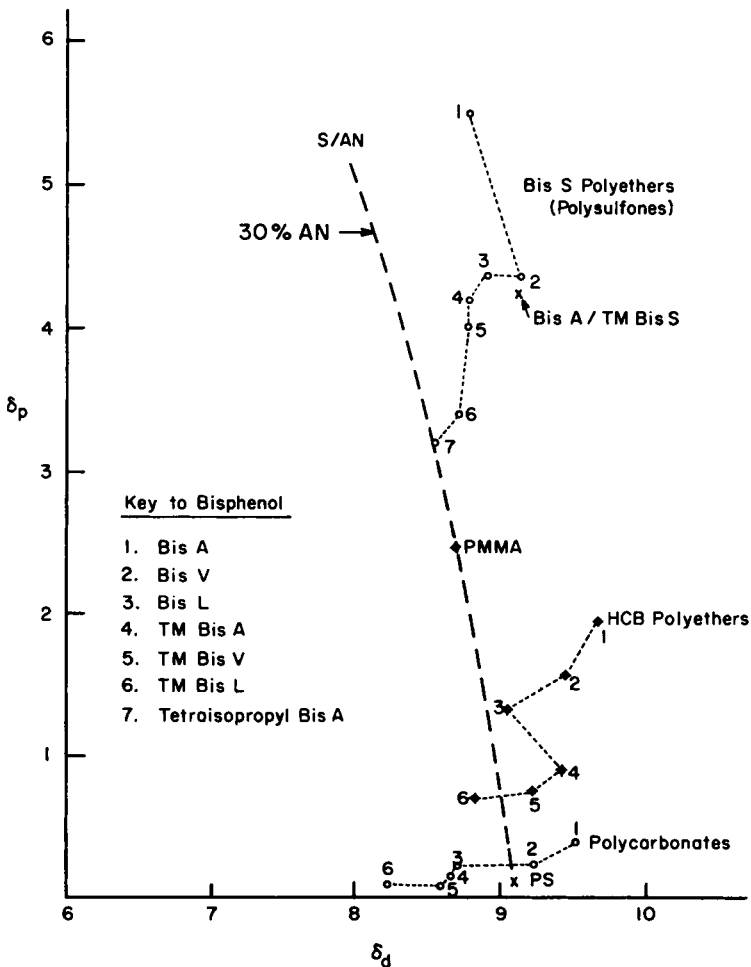

Fig. 10. Two-dimensional plot of solubility parameter components. Enlarged about S/AN line, with calculated points of polysulfones, polyethers, and polycarbonates.
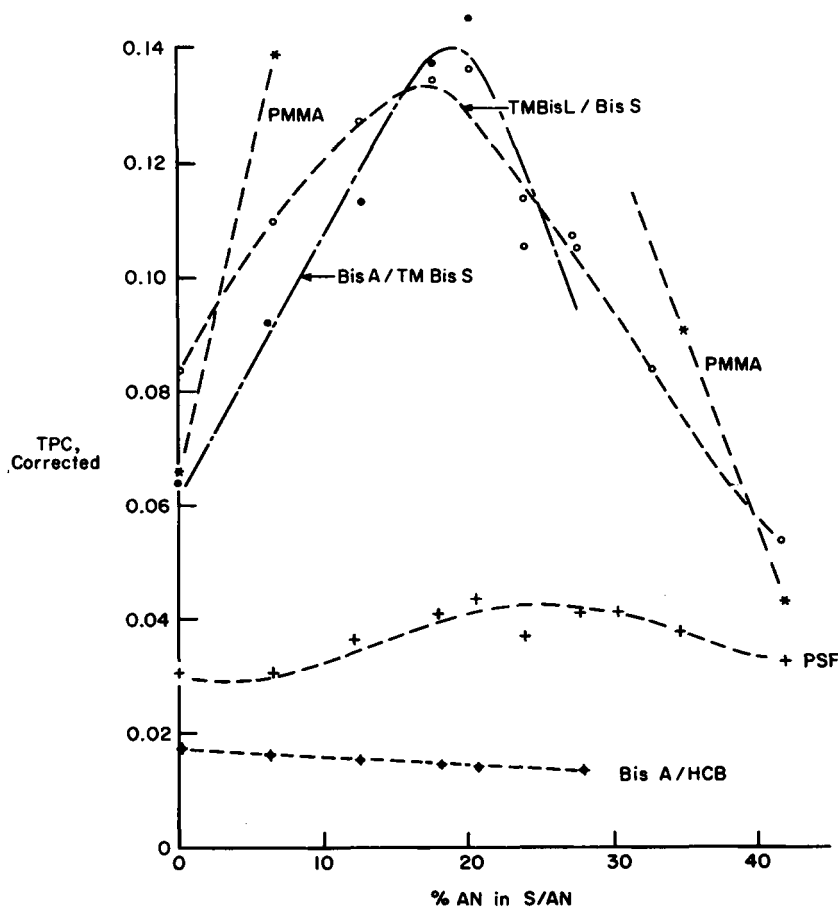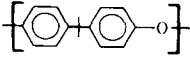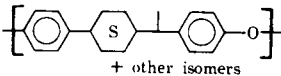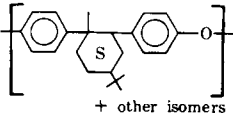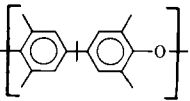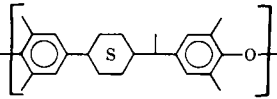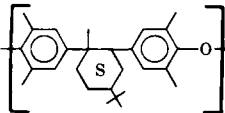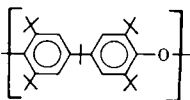
Fig. 11. Threshold point concentration for selected polymer components in a series of S/AN copolymers.

styrene to 100% polyacrylonitrile. The location of 30% AN is marked with an arrow on the S/AN curve, providing an approximate calibration of the curve. This line was calculated from certain copolymer compositions and must be curved to provide a monotonic increase in total solubility parameter as the AN content is increased. All other polymer points were located by calculations, with no corrections. The points connected by the dotted lines represent groups of high T_g polymers, based on the listed bisphenols, which would make interesting mixtures with S/AN. (The synthesis and detailed structural information for these bisphenols is given by Lee et al.[17]; segment structures are listed in Tables I and II.) This figure includes several structures which were not fully tested for solubility or even synthesized in some cases. It was designed more to show the predicted effects of consistently varied structures on the cohesion energy of important families of polymers. In general as the bulk of bisphenol in-

TABLE II
Structures of the Bisphenol-Derived Segments of Polymers Employed in the
Calculations for Figure 10

Abbreviation	Structure
Bis A	
Bis V	+ other isomers
Bis L	+ other isomers
TM Bis A	
TM Bis V	
TM Bis L	
Tetraisopropyl Bis A	

creases, the dispersive contribution decreases, much in proportion to density. Attachment of alkyl groups alpha to the polar ether linkage decreases polarity by about 0.2 debyes per group, probably due to electron donating properties of the alkyl substituent which establishes a countering dipole. Note the locations of PMMA, poly(oxy-1,4-phenylenesulfonyl-1,4-phenyleneoxy-1,4-phenyleneisopropylidene-1,4-phenylene) (PSF), poly-[oxy-1,4-phenylenesulfonyl-1,4-phenyleneoxy(2,6-dimethyl-1,4-phenylene)-(1-methyl-4-isopropyl-1,2-cyclohexylene)(3,5-dimethyl-1,4-phenylene)] (TM Bis L/Bis S), Bis A/TM Bis S, and poly[oxy(tetrachloro-1,4-phenylene)oxy-1,4-phenyleneisopropylidene-1,4-phenylene] (Bis A/HCB) relative to the S/AN line.

Figure 11 has the experimental TPC values for the aforementioned polymers in S/AN copolymers of various AN contents. PMMA shows a rapid increase in solubility on increasing the AN content, going beyond the capabilities of the TPC measurement until high AN contents are reached.

0   7   13   18   24   28
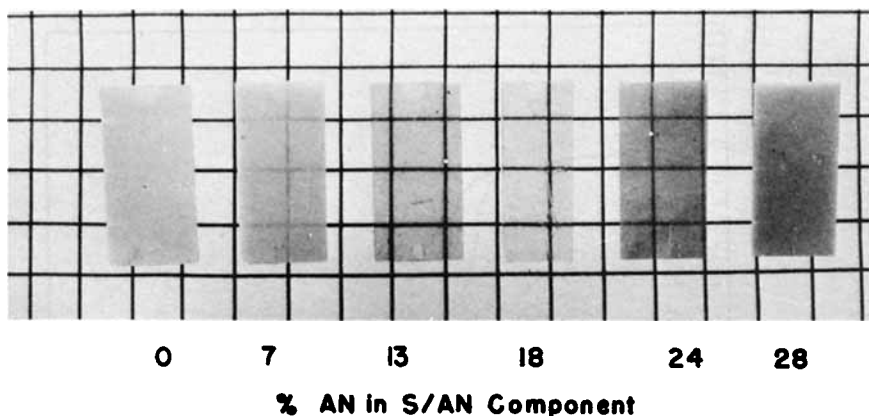
% AN in S/AN Component

Fig. 12. Photograph of 50:50 mixtures of Bis A/TM Bis S with a series of S/AN co-
polymers, illustrating solubility variation with AN content of copolymer.

Indeed, PMMA appears to form a truly soluble system with S/AN of
around 12–18% AN, as evidenced by phase microscope studies on the
appropriate mixtures. This is in agreement with the location of PMMA on
the S/AN line in Figure 10. Modulus-temperature measurements have
shown[21] that poly[oxy-1,4-phenylenesulfonyl-1,4-phenyleneoxy(2,6-diiso-
propyl-1,4-phenylene)isopropylidene(3,5-diisopropyl-1,4-phenylene)] (tet-
raisopropyl Bis A/Bis S), is also soluble in S/AN of AN content 13–16%
and is appropriately located along the S/AN copolymer line in Figure 10.

A polymer which lies off the S/AN series line will show a maximum S/AN
solubility at the AN content of closest approach, while the amplitude of the
maximum will depend on the proximity of the polymer to the S/AN line.
For example, compare TM Bis L/Bis S polyether with Bis A/Bis S poly-
ether (PSF). The TPC maximum for the former is much more pronounced,
corresponding to its relative closeness to the S/AN line, as depicted in
Figure 10.

Another close approach is registered by a slightly different aromatic
polysulfone, Bis A/TM Bis S. The TPC data (Fig. 11) are about the same
as for TM Bis L/Bis S, although the increase is sharper, implying perhaps a
closer approach to the S/AN line. (A TPC of 0.14 or greater becomes quite
difficult to measure, due to the high viscosity of the mixture, and data at
this level must be regarded as tentative. The slope at more reasonable
TPC values may, therefore, be a better indicator of a very close approach.)

The passage of the S/AN line past the Bis A/TM Bis S point is graph-
ically depicted in Figure 12. The polysulfone used to make these samples
was of a slightly lower molecular weight(R.V. = 0.25) than that used in the
TPC measurements to emphasize the solubility changes. The samples
pictured in Figure 12 were well-equilibrated 50:50 mixture of the Bis A/TM
Bis S with the S/AN samples, arranged in order of increasing AN content of
the S/AN component. The increase in clarity followed by a decrease is
evident, paralleling the TPC measurement, with a slight shift to lower AN
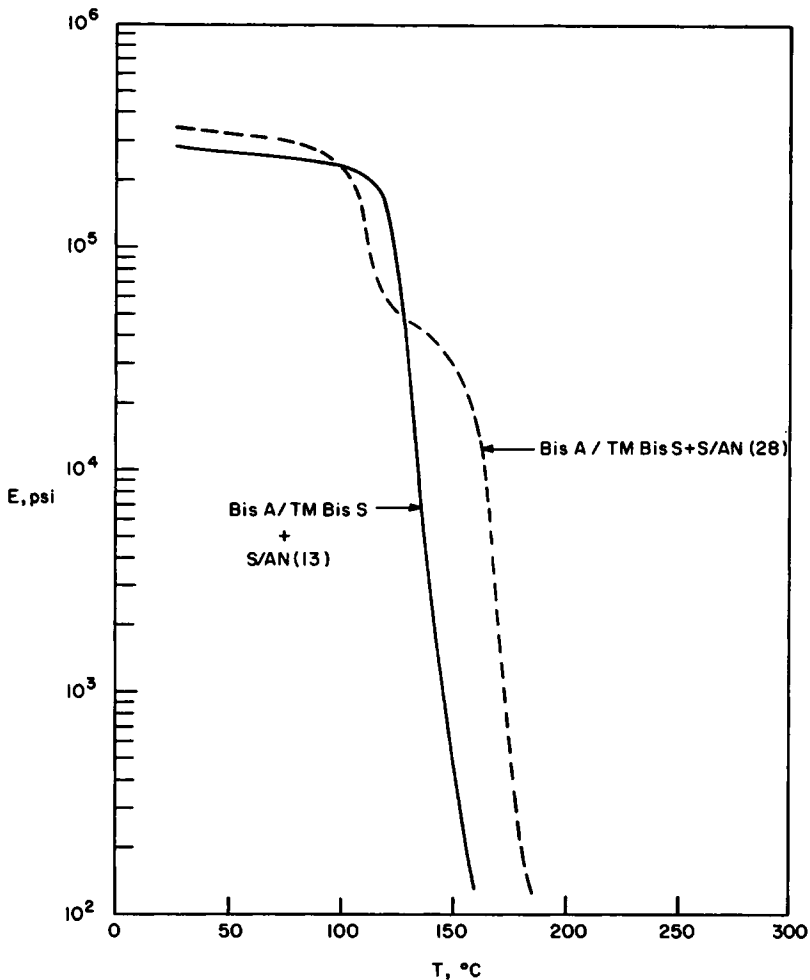
Fig. 13. Modulus vs. temperature for two mixtures from Fig. 12, showing single transition for Bis A/TM Bis S + S/AN (13) and two transitions for the two-phase Bis A/TM Bis S + S/AN (28) mixture.

content at maximum solubility in the case of the solid samples.   Figure 13 displays the modulus–temperature curves for two of these samples, containing S/AN (13) and S/AN (28), respectively.   These results support further the presence of a quite close approach at S/AN (13) wih this mixture, which shows one fairly narrow glass transition, indicative of a single phase.   The S/AN (28) mixture is definitely two-phase.

Bis A/HCB shows little change in solubility with increasing AN content, demonstrating that it is even farther away from the S/AN line than PSF. The calculations suggest slightly more solubility than is, in fact, found. The opposite is truc for poly [oxycarbonyloxy(2,6-dimethyl-1,4-phenylene)-isopropylidene(3,5-dimethyl-1,4-phenylene)], the polycarbonate based on

TM Bis A, abbreviated TM Bis A/C, which is quite soluble at room temperature in polystyrene in spite of a low solubility prediction. The reasons for the discrepancies are probably numerous, with some being the misassignment of a dipole moment, an unknown polymer 1–polymer 1 specific interaction, a steric problem which alters assumed interactions, or a complete breakdown of the regular solution theory assumptions. Pointedly, the method, as stated before, is most useful for following solubility changes rather than predicting the location of entire groups.

Phase Behavior of the Two-Polymer System

The regular solution eq. (1) predicts certain basic phase behavior for the two-polymeric component system. With fixed interaction energy, the
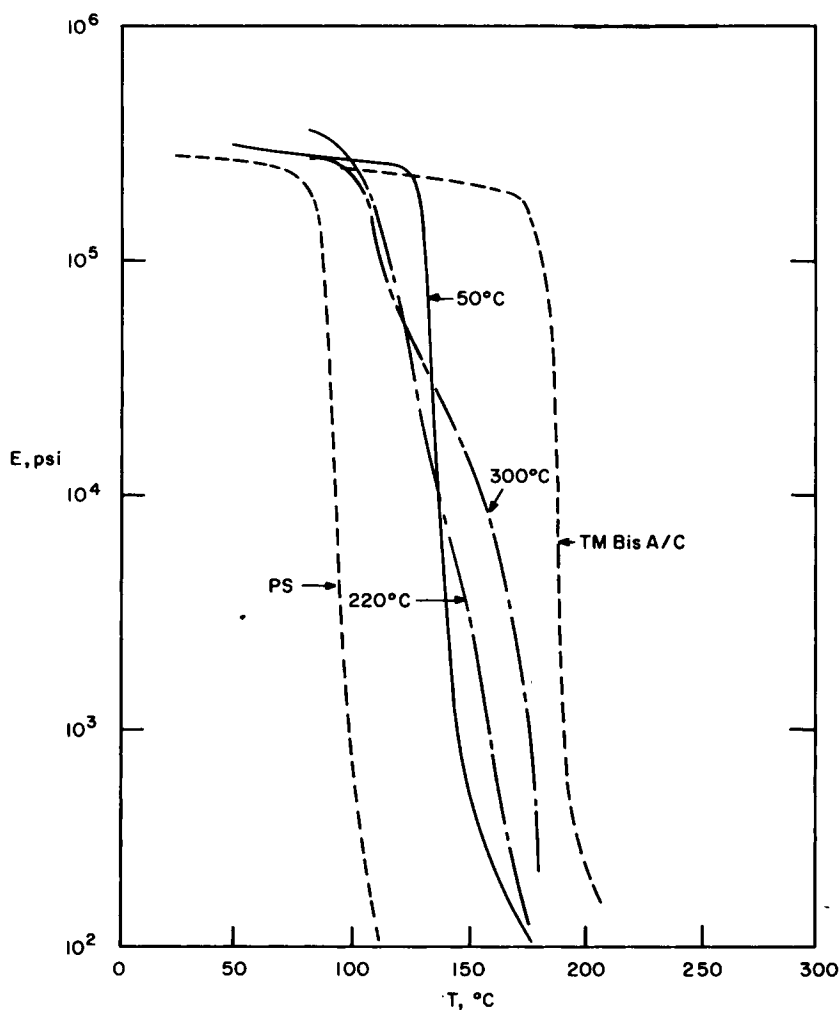

Fig. 14. Phase behavior of the system TM Bis A/C + PS as a function of equilibration temperature.

remaining variables are molecular volume (weight) and temperature. Increasing the former should decrease solubility and vice versa for the latter. On several systems these variables have been checked, with some strange results.

The molecular weight dependence of solubility has been tested on the following polymer pairs: TM Bis A/C + PS, Bis A/TM Bis S + S/AN,
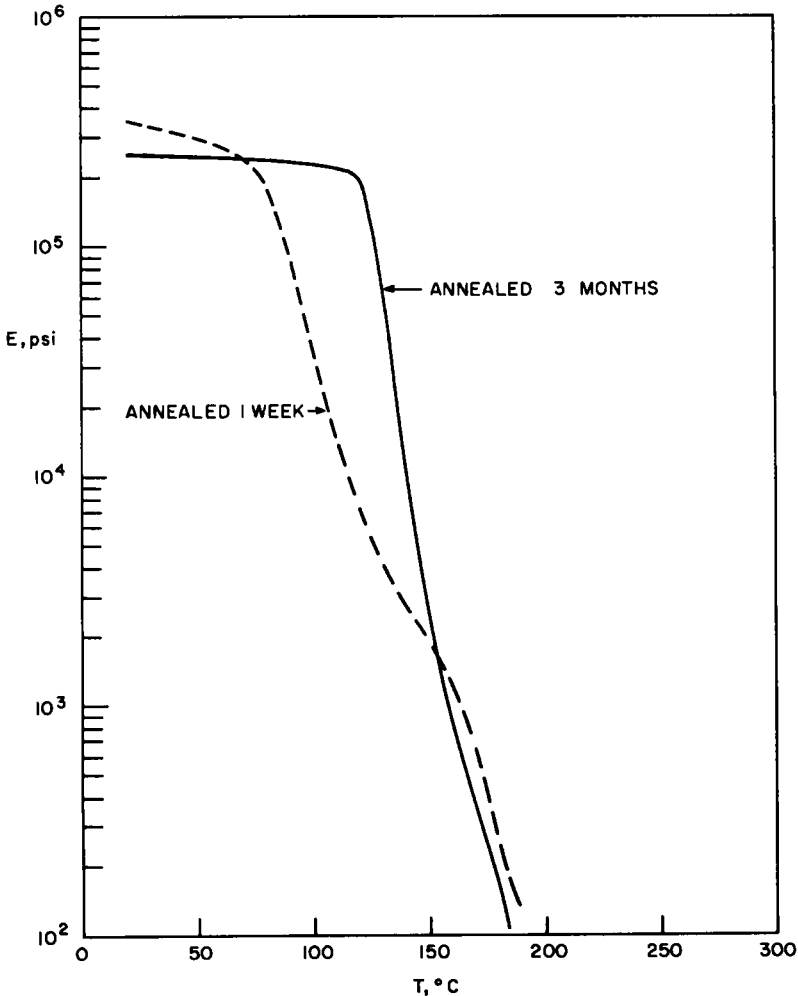

Fig. 15. The effect of annealing time at 100°C on the system PPO + PS.

and PSF + S/AN.   In every case, solubility decreased with increasing molecular weight, as required by eq. (1).

Temperature is a more complicated variable, pointing to the deficiencies of the simplest regular solution analysis or perhaps even calling for a completely different model of polymer–polymer "solutions" such as the corresponding states theory.[11,18]   A temperature investigation of the system

TM Bis A/C + PS is depicted in Figure 14. At the normal pressing temperature of 220°C, only fair solubility is observed, as evidenced by the gradual modulus change in the 125–175°C range (broken line). Increasing the temperature of equilibration to 300°C *decreases* the solubility to the point where fairly distinct phase transitions are observed. Casting at room temperature, followed by thorough solvent removal and equilibration at 50°C, results in a one-phase system with a sharp transition halfway between the two pure-component T_g's (solid line). These effects were all reversible.

The simplest explanation of this apparent lower critical solution temperature lies in the enthalpy of mixing, which may be a strong enough function of temperature to produce such an effect. The problem is that for every near-soluble system, there is at least even odds that an upper critical solution temperature will be found. As far as is known to date, no UCST has been found for any two-polymer system.[18] There has been some question[19] about the system poly[oxy(2,6-dimethyl-1,4-phenylene)] (PPO) + PS, but extensive annealing of this system at 100°C has not produced phase separation discernible by T_g measurement: On the contrary, a chloroform-cast film, which originally showed a broad transition, has been annealed at 100°C to the point where only one fairly sharp transition remains (Fig. 15).

An alternative explanation for the predominance of LCST's lies in the interaction entropy term, which is very important for solvent–polymer systems. Interaction of solvent molecules with a polymer chain invariably results in a drop in entropy regardless of the overall energetics. Patterson[11] views this entropy change as resulting from the free volume difference between solvent and polymer. For two polymers, this term must be very small; but when all energy terms are small, seemingly insignificant changes or temperature dependencies can have profound effects.[18]

Conclusions

Two-dimensional solubility parameters for polymers appear to improve the predictability of polymer–polymer solubility over the corresponding one-dimensional parameter. These simple predictions can be performed for structures which have not been synthesized.

Calculations and measurements of polymer–polymer solubility were most useful for monitoring the changes produced by small modifications to structure. The modifications which were effective included copolymer ratio variation, substitutions to change the density, and therefore the total cohesive energy of the polymer, plus substitutions designed to shield or reduce the polarity of functional groups. The modifications changed solubility in the predicted direction in most cases.

In the systems studied, solubility was shown to decrease with molecular weight of the components, as expected from regular solution theory, but to *decrease* with temperature, in contrast to theory.

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