polymer reviews

A practical guide to polymer miscibility

Michael M. Coleman*, Carl J. Serman, Dorab E. Bhagwagar and Paul C. Painter
Department of Materials Science and Engineering, The Pennsylvania State University, University Park, PA 16802, USA
(Received 12 June 1989; accepted 13 September 1989)

In this paper a general guide to polymer miscibility is presented. The view taken here is that in many polymer systems mixing can be predicted on the basis of a simple balance between unfavourable 'physical forces', described in terms of non-hydrogen bonded solubility parameters, and favourable specific interactions. In essence, the closer the values of the two solubility parameters and the greater the relative strength of the potential intermolecular interactions present between the polymeric components of the blend, the greater the probability of miscibility. This is discussed in terms of critical values of the interaction parameter, χ_{Crit}, and the upper limits of the non-hydrogen bonded solubility parameter difference, $\Delta\delta$. It is then demonstrated that this approach can be applied to the prediction of trends in miscibility for a wide range of binary polymer blend systems.

(Keywords: miscibility; solubility parameters; intermolecular interactions; polymer blends)

INTRODUCTION

First a caveat. The title of this paper is a Practical guide to polymer miscibility and it is just that—a guide. It is not intended to be (nor do we have the temerity to consider it) a 'unified' theory encompassing all known miscible polymer blend systems involving intermolecular interactions ranging from purely dispersive forces to very strong hydrogen bonds. Rather, it is intended to assist the reader in predicting major trends in the gross phase behaviour of polymer blends using a few very simple concepts.

The basic idea is derived from a natural extension of our work on theoretical and experimental studies of the mixing of polymers that involve relatively strong intermolecular interactions (hydrogen bonds)[1–9] where the free energy of mixing was described by the equation[2,4]

$$\frac{\Delta G^{\mathrm{M}}}{RT}=\frac{\Phi_{\mathrm{A}}}{N_{\mathrm{A}}}\ln\Phi_{\mathrm{A}}+\frac{\Phi_{\mathrm{B}}}{N_{\mathrm{B}}}\ln\Phi_{\mathrm{B}}+\Phi_{\mathrm{A}}\Phi_{\mathrm{B}}\chi+\frac{\Delta G_{\mathrm{H}}}{RT} \qquad (1)$$

Following normal custom Φ_{A} and Φ_{B}, and N_{A} and N_{B}, are the volume fractions and degrees of polymerization of A and B, respectively; χ is the polymer–polymer interaction parameter. This is the well known Flory–Huggins relationship, but with an added term, $\Delta G_{\mathrm{H}}/RT$, to account for the presence of favourable intermolecular interactions; most commonly, but not necessarily, hydrogen bonds. It is important to recognize that we are not simply adding the effect of non-random hydrogen bonding contacts to a random mixing theory, although we do assume that the formation of hydrogen bonds is unaffected by their covalent linkage into polymer chains. The complexes (hydrogen bonded *n*-mers) are treated as distinguishable species and then these are permitted to randomly mix (see reference 3 for a detailed description of the theory).

The first three terms of equation (1) correspond to the change in free energy of mixing two polymers assuming that there are no significant favourable intermolecular interactions involved. Because we are dealing with high molecular weight polymers the negative contribution from combinatorial entropy expressed by the two log terms contributes little, in absolute terms, to the free energy of mixing. We stress that the polymer–polymer interaction parameter, χ, as defined here, is restricted to values that are $\geqslant 0$. Hence, the $\Phi_{\mathrm{A}}\Phi_{\mathrm{B}}\chi$ term is generally unfavourable to mixing, reflecting only the contribution of what we will call 'physical' forces. The $\Delta G_{\mathrm{H}}/RT$ term, on the other hand, represents favourable contributions to the change in the free energy of mixing arising from the presence of specific intermolecular interactions (hydrogen bonds and the like) and assumes values that are $\leqslant 0$. Therefore, in its most simple form, the free energy of mixing essentially reduces to a balance between the $\Phi_{\mathrm{A}}\Phi_{\mathrm{B}}\chi$ and $\Delta G_{\mathrm{H}}/RT$ terms.

According to equation (1), in the absence of favourable intermolecular interactions (i.e. when $\Delta G_{\mathrm{H}}/RT=0$), molecular mixing of two high molecular weight polymers can only occur when χ is very close to zero. An excellent example of such a blend is that reported recently by Trask and Roland[10]. The value of the Flory–Huggins interaction parameter for a blend of *cis*-1,4-polyisoprene with atactic poly(vinyl ethylene) was estimated to be $<1.7\times10^{-4}$. Krause[11] has discussed the limits of the value of χ for the Flory–Huggins case in an extensive review, but the salient features deserve repetition because they impact substantially upon our forthcoming arguments. A critical value of the polymer–polymer interaction parameter, χ_{Crit}, which sets the upper limit for miscibility across the entire composition range, may be determined using:

$$\delta^2[\Delta G^{\mathrm{M}}/RT]/\delta\Phi_{\mathrm{A}}^2=\delta^3[\Delta G^{\mathrm{M}}/RT]/\delta\Phi_{\mathrm{A}}^3=0 \qquad (2)$$

This leads to

$$\chi_{\mathrm{Crit}}=\frac{1}{2}\left[\frac{1}{N_{\mathrm{A}}^{0.5}}+\frac{1}{N_{\mathrm{B}}^{0.5}}\right]^2 \qquad (3)$$

---

* To whom correspondence should be addressed

0032-3861/90/071187-17

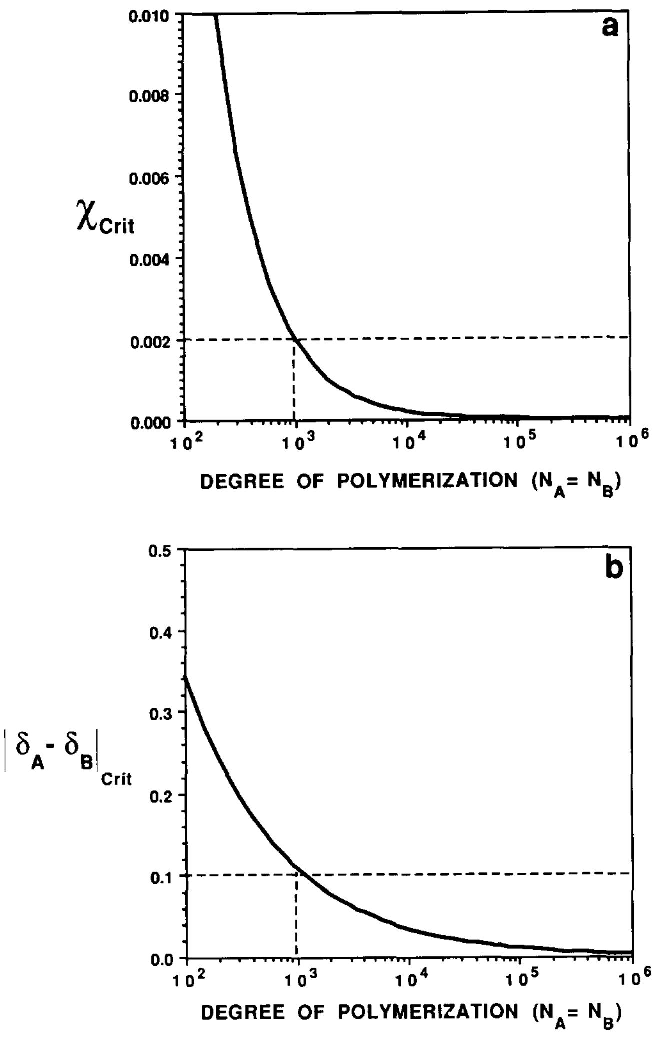


Figure 1 Effect of the degree of polymerization on (a) the critical value of the interaction parameter, χ_{Crit}, and (b) the critical difference between the solubility parameters, $\Delta\delta = |\delta_A - \delta_B|_{Crit}$, for the Flory–Huggins case

Figure 1a illustrates graphically the dramatic effect of the degree of polymerization on χ_{Crit} for the special case where $N_A = N_B$. Consider, for example, two polymers having $N_A = N_B = 1000$ (roughly a molecular weight of 100 000 in most cases). In order to achieve molecular mixing the value of χ needs to be <0.002 (and this is before other unfavourable effects, such as 'free volume', are taken into account). Because here we are dealing with weak interactions (van der Waals forces) we can relate χ to the Hildebrand solubility parameters of the two polymers using the equation[11]:

$$\chi = \frac{V_r}{RT}[\delta_A - \delta_B]^2 \tag{4}$$

Assuming a reference volume, $V_r = 100\,\mathrm{cm^3\,mol^{-1}}$, a critical value of the solubility parameter difference, $\Delta\delta_{Crit}$, may be calculated (see *Figure 1b*). Again, for the case of a polymer blend containing two polymers having $N_A = N_B = 1000$ the difference in the solubility parameters must be less than about 0.1 $(\mathrm{cal\,cm^{-3}})^{0.5}$ to ensure molecular mixing. Accordingly, it is necessary to measure or calculate the solubility parameters of polymers to an accuracy of better than ± 0.05 $(\mathrm{cal\,cm^{-3}})^{0.5}$ in order to obtain any reasonable prediction of miscibility in these types of polymer blends. As we will see later, this requirement is beyond the capabilities of any known method of determining the solubility parameters of polymers.

Polymer–polymer miscibility becomes more plausible when favourable intermolecular interactions occur between the components. These intermolecular interactions may be categorized from relatively weak (e.g. dipole–dipole) to relatively strong (e.g. hydrogen bonding). This distinction is somewhat arbitrary and is probably best described in terms of the magnitude of energies involved. *Figure 2* shows the results of a simple calculation using Maxwell's distribution law to determine the fraction of molecules (or, for our case, interacting units) that have energies greater or equal to the energy of dissociation at a given temperature. Above interaction strengths of about $3\,\mathrm{kcal\,mol^{-1}}$ less than 1% of the interacting units would have sufficient energy to dissociate at any particular instant. This is the realm of the (relatively) strong hydrogen bonding interactions typical of the polyamides, polyphenols and polyacids. Here we cannot assume random contacts of functional groups, because the interactions are directional and specific. We can, however, treat the contribution to the free energy of mixing with association models[3] (the chains or complexes of hydrogen bonded units are treated as distinguishable species and these groupings are allowed to randomly mix). Conversely, below, say, $1\,\mathrm{kcal\,mol^{-1}}$, there is a substantial fraction of interacting units that have energies $\geqslant \Delta E$ and it is appropriate to assume random mixing and a mean field. This corresponds to the case where there is little or no contribution from the $\Delta G_H/RT$ term and weak favourable interactions are perhaps best handled by including them in the χ parameter. Between these two poles, i.e. ΔE values of between approximately $1\text{–}3\,\mathrm{kcal\,mol^{-1}}$, we have an intermediate case where things are not so clear cut. Polymer blends that are known to involve intermolecular interactions in this strength range have been described in terms of binary interaction models[12–14] where several distinct interaction parameters are defined in such a manner that overall negative values of χ are permitted. We have taken a somewhat different tack in our approach to such systems, consistent with the generalized approach embodied in equation (1).

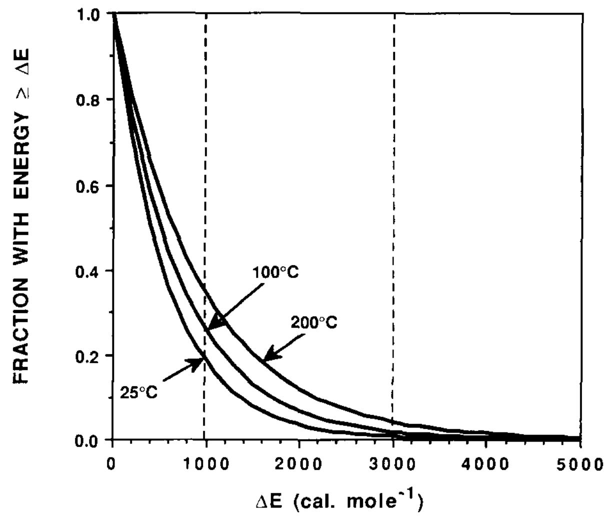


Figure 2 Calculation of the fraction of interacting units that have energies $\geqslant \Delta E$ at three different temperatures

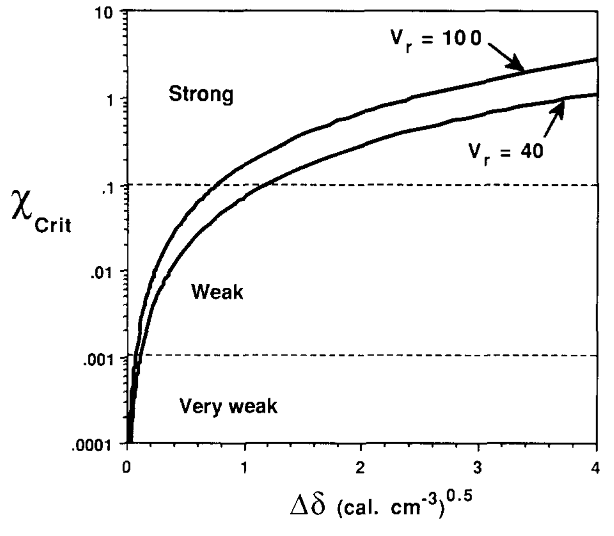


Figure 3 Plot of χ_{Crit} *versus* $\Delta\delta$ calculated from equation (4) using reference volumes of 40 and 100 cm^3 mol^{-1}

Because χ, as defined in equation (1), assumes only positive values, we conceptually separate out the favourable (negative) contributions in the $\Delta G_H/RT$ term. This model is most appropriately applied to those systems where the favourable interaction can be identified with specific localized parts or functional groups in the molecules. Simply put, the presence of such favourable intermolecular interactions then effectively increases the magnitude of χ_{Crit} and permits the toleration of a greater difference in the non-hydrogen bonding solubility parameters of the two polymers, $\Delta\delta$. This is illustrated schematically in *Figure 3* which shows a plot of $\Delta\delta$ *versus* χ calculated from equation (4) assuming a range of reference volumes of between 40 and 100 cm^3 mol^{-1} at a temperature of 298 K (the rationale for choosing this range will become clear later). As noted above, for very weak or 'repulsive' interactions χ values of $<10^{-3}$ are necessary for miscible blend systems, which correspond to $\Delta\delta$ values of <0.1 (cal cm^{-3})$^{0.5}$. However, if certain functional groups contribute relatively weak to intermediate strength favourable interactions between about 1 and 3 kcal mol^{-1} (*Figure 2*) χ values of up to about 0.1 may be tolerated, corresponding to an upper $\Delta\delta$ value of close to 1 (cal cm^{-3})$^{0.5}$. To complete the picture, when much stronger interactions are involved (>3 kcal mol^{-1}) χ values of greater than 0.1 can be tolerated and miscible blends are possible even when $\Delta\delta$ exceeds 1 (cal cm^{-3})$^{0.5}$.

This is the key to our simple guide to polymer miscibility and centres on the questions: how do we estimate the value of χ and what potential favourable intermolecular interactions exist in the system?

THE ESTIMATION OF χ FROM SOLUBILITY PARAMETERS

The uses and abuses of solubility parameters are legendary. On the one hand, they are extensively applied and highly valued by the polymer chemist confronted by specific practical problems, such as those found in the surface coatings industry; on the other, they are disdained by many theoretically inclined polymer scientists on the compelling grounds of their many experimentally demonstrable inadequacies. Introduced by Hildebrand and Scott[15], solubility parameters in their original form are only applicable to molecules that are dispersive in nature, where the heat of mixing is $\geqslant 0$. Many attempts, most notably those of Burrell and Hansen, have been made to extend the solubility parameter concept into systems that involve hydrogen bonding and other significant intermolecular interactions[16]. While these approaches have been useful as guides for polymer solubility in low molecular weight solvents, they have not been very useful in the prediction of polymer–polymer miscibility.

In contrast to low molecular weight compounds, where solubility parameters can be directly calculated from heat of vaporization measurements (i.e. from $\delta=[\Delta E/V]^{0.5}$, where ΔE is the energy of vaporization to a gas at zero pressure), polymer solubility parameters have to be determined indirectly, either by experiment (e.g. swelling measurements of a slightly crosslinked polymer in a series of solvents of known solubility parameters) or by calculation from molar attraction constants. The errors inherent in the indirect experimental methods used to determine polymer solubility parameters are too large to be useful in the prediction of polymer miscibility (a cursory glance at the wide range of reported values for typical polymers listed in table 8.3 of van Krevelen's book[17] should be sufficient confirmation). A common method used to estimate polymer solubility parameters involves calculation through the use of group molar attraction constants[17–19]. At first glance, it appears a trivial task to calculate the solubility parameter of a polymer. One only has to consider the groups present in the repeat unit of the polymer, refer to tables of molar attraction constants (F) attributed to either Small[19], Hoy[18] or van Krevelen[17], and use the relationship:

$$\delta=\sum F_i/V \qquad (5)$$

Table 1 shows the results of such a calculation for two polymers, poly(methyl methacrylate) (PMMA) and poly(ethylene oxide) (PEO). All three methods give very similar results for the solubility parameter of PMMA ($\delta=9.1\pm0.2$ (cal cm^{-3})$^{0.5}$) and the choice of molar volume makes little difference (i.e. V_{expt} from density measurements of the polymer, or V_r and V_g which are the rubbery and glassy molar volumes, respectively, calculated from a correlation determined separately by van Krevelen (Table 4.6 in ref. 12). This appears fine, but consider now the calculated solubility parameters for PEO. The values range from 8.1 to 10.3 (cal cm^{-3})$^{0.5}$ depending upon which set of molar attraction constants is employed and, of equal importance, which value of the molar volume is used. Discrepancies, in general, are particularly acute for polymers containing small repeat units. Incidentally, blends of PMMA and PEO are reported to be miscible[20] and although they are both polar polymers is it reasonable to assume that any favourable interactions between them are relatively weak.

Table 1 Calculated solubility parameters

Polymer	Molar volume cm^3 mol^{-1}	Calculated solubility parameter (cal cm^{-3})$^{0.5}$ Small[19]	Hoy[18]	van Krevelen[17]
PMMA	$V_{expt}=85.6$	9.1	9.2	9.3
	$V_r=87.8$	8.9	9.0	9.1
	$V_g=86.5$	9.0	9.1	9.2
PEO	$V_{expt}=38.9$	8.6	9.7	10.3
	$V_r=41.4$	8.1	9.1	9.6

Accordingly, if one were trying to 'prove' the necessity of closely matched solubility parameters for the miscibility of this particular blend, a jaundiced selection of molar attraction constants and molar volumes can be easily found to substantiate this hypothesis. This is hardly a satisfactory situation, however, and we decided to review the underlying assumptions made and the errors involved in determining solubility parameters from group molar attraction constants.

Determination of group molar attraction and molar volume constants

Data pertaining to the liquid molar volumes (v) and solubility parameters (δ) of selected organic compounds that were deemed particularly appropriate as models for polymeric materials, were obtained from the data bank compiled by Daubert and Danner at Penn State University[21]. After several preliminary studies a final data set of 210 compounds was chosen such that its members exhibit little if any predilection towards self-association; this set includes 54 linear and branched aliphatic hydrocarbons; 33 mono-, di- and tri-alkyl substituted aromatic hydrocarbons; 51 linear and branched unsaturated, unconjugated, aliphatic hydrocarbons; 35 aliphatic and aromatic esters; 16 ethers; 11 ketones; 6 mixed ether/ester/ketones and 4 tertiary amines. In addition, after it was determined that inclusion of organic compounds that are known or suspected to be weakly self-associated did not materially affect the final results, 12 primary and secondary chlorides; 10 nitriles and 23 primary and secondary amines were added to the data set. It is important to emphasize that no compounds were included that contain groups known to strongly self-associate, such as alcohols and substances containing carboxylic acid, amide, urethane or similar groups. Details of the specific compounds chosen and a summary of their properties are included in the thesis of Serman[22].

A 255 x 18 matrix, **M**, was prepared using the Mac II MATLAB program (The MathWorks Inc., Sherborn, MA 01770, USA) for use on a Macintosh II computer. The 18 columns contained the number of the following chemical groups in each of the model compounds: $-CH_3$, $-CH_2-$, $>CH-$, $>C<$, C_6H_3, C_6H_4, C_6H_5, $CH_2=$, $-CH=$, $>C=$, $-COO-$, $-CO-$, $-O-$, $-Cl$, $-CN$, $-NH_2$, $>NH$ and $>N-$. We settled upon this particular group subdivision, which is almost identical to that employed by Small[19] in 1952, after the results of many preliminary calculations had convinced us that the errors inherent in the correlation method employed by Hoy[18] did not warrant further reduction. There are simply not enough data on model compounds with the appropriate structural subtleties to determine their group contributions with sufficient confidence.

Two additional 255 x 1 matrices were formed from the experimental values of the molar volumes (**V**) and the product of molar volumes and solubility parameters (**F**). Orthogonal (or QR) factorization was performed to solve the overdetermined set of linear equations. A best solution, in the least squares sense, was computed by matrix division[23] $\mathbf{V^*} = \mathbf{M}\backslash\mathbf{V}$ and $\mathbf{F^*} = \mathbf{M}\backslash\mathbf{F}$. Accordingly, **V*** and **F*** each represent 1 x 18 solution vectors that contain the molar volume and molar attraction constants, respectively, for the chemical groups mentioned above.

Table 2 Unassociated groups

Group	V* (cm^3 mol^{-1})	F* (this work) ((cal cm^3)$^{0.5}$ mol^{-1})	F (Small[19])
$-CH_3$	31.8	218	214
$-CH_2-$	16.5	132	133
$>CH-$	1.9	23	28
$>C<$	−14.8	−97	−93
C_6H_3	41.4	562	–
C_6H_4	58.8	652	658
C_6H_5	75.5	735	735
$CH_2=$	29.7	203	190
$-CH=$	13.7	113	111
$>C=$	−2.4	18	19
$-OCO-$	19.6	298	310
$-CO-$	10.7	262	275
$-O-$	5.1	95	70
$>N-$	−5.0	−3	–

Table 3 Weakly associated groups

Group	V* (cm^3 mol^{-1})	F* (this work) ((cal cm^3)$^{0.5}$ mol^{-1})	F (Small[19])
$-Cl$	23.9	264	260
$-CN$	23.6	426	410
$-NH_2$	18.6	275	–
$>NH$	8.5	143	–

The results are displayed in *Tables 2* and *3* together with the F contributions that were determined previously by Small[19]. The correspondence between our values of the molar attraction constants and those determined previously by Small is striking. Only the values for the ether group differ appreciably, which does have significance in our subsequent calculations of the solubility parameters of polyethers. Although it is gratifying to have independently confirmed Small's values, this would be trivial were it not for the recognition of a fundamental assumption inherent in the determination of group molar attraction constants that has important ramifications. The molar attraction constants are determined from experimental data of the solubility parameter of the model liquids multiplied by their respective molar volumes (i.e. $\sum F = \delta \times v$). Accordingly, we contend that subsequent calculations of the solubility parameter for an unknown organic liquid or polymer must also be based upon a correlation using the same set of experimental molar volumes. In other words, using our molar attraction constants (or those of Small, Hoy or others) with some arbitrary experimental or calculated molar volume to determine the solubility parameter of a polymer is specious. It is necessary to have both **V*** and **F*** from the same set of model compounds to be consistent in calculating the solubility parameter of a polymer. The data listed in *Tables 2* and *3* should allow us to determine just how accurately we can do this.

Calculation of solubility parameters and the errors involved

Multiplication of the matrix **M** with **V*** (or **F***) yields a set of calculated values of the molar volumes (or total F) for the model organic liquids based upon the respective group contributions (*Tables 2* and *3*). *Figure 4* shows a graph of the calculated molar volumes plotted against the experimental values of the 255 organic liquids employed in the original data set. A least squares fit of the data reveals an excellent correlation (a perfect correlation, of course, would be an intercept of zero and a slope and correlation coefficient of unity). The standard

Table 4 Groups determined by addition or subtraction

Group	V* ($cm^3 mol^{-1}$)	F* ($(cal\,cm^3)^{0.5} mol^{-1}$)
$-C_6H_2-$[a]	34.1	475
$-C_6H_{10}-$[a]	81.2	687
$-C_5H_4N-$[a]	66.5	766
–CO–O–CO–[b]	30.3	560
–O–CO–O–[b]	24.7	393
–NH–CO–[b]	19.2	405
–N–CO–[b]	5.7	259
–NH–CO–O–[b]	28.1	441
–N–CO–O–[b]	14.6	295

[a] Limited number of compounds ($\leqslant 6$) determined by difference using group contributions from *Table 2*

[b] Estimated by simple addition of group contributions listed in *Tables 2* and *3*

error of estimate was determined to be $1.9\,cm^3\,mol^{-1}$. A similar result, albeit slightly less perfect, is seen in the graph of the calculated *versus* experimental values of total F (*Figure 5*). Here the corresponding standard error of estimate was calculated to be $24\,((cal\,cm^3)^{0.5}\,mol^{-1})$.

Of primary relevance to our studies of polymer blends, however, is the comparison of the experimental and calculated solubility parameters, which is presented graphically in *Figure 6*. There is considerable scatter in the results as $\delta = \sum F / \sum v$ and the errors in molar volume and F compound. The standard error of estimate was determined at $0.21\,(cal\,cm^{-3})^{0.5}$. This is a very important result. We have alluded to the fact that for high molecular weight polymer blends, in the absence of favourable intermolecular interactions, miscibility is only feasible when the solubility parameters of the two polymers are within about $0.1\,(cal\,cm^{-3})^{0.5}$ of one another. If the error in calculating solubility parameters is approximately ±four times this figure (at the 2σ, 95% confidence level), it is little wonder that solubility parameters have been poor predictors of the phase behaviour of polymer blends.

Finally, it is instructive to calculate the molar volumes of polymer repeat units and compare them to the experimental densities of amorphous polymers (or the amorphous component of a semicrystalline polymer) reported at 25°C. Obviously, we have to take into account the glass transition temperatures of the amorphous polymers. Van Krevelen, for example, has reported different correlations for glassy and rubbery molar volumes of polymers at 25°C (Table 4.6 in ref. 17)). However, we again emphasize that if we wish to estimate the solubility parameter of a polymer from a set of molar attraction constants we must be consistent and employ a correlation based upon the same set of molar volumes from which it was derived. We should add that for our purposes we are really only concerned with polymers in blends that are liquid-like, as our model for the free energy of mixing of polymers necessitates equilibrium conditions. Because V* was determined from organic liquids it is in closer accord with polymers in the rubbery state. We thus appear to be restricted to a comparison between amorphous polymers that have T_g values below room temperature. It is possible, however, to estimate a rubbery molar volume from the experimental densities of glassy amorphous polymers at 25°C using the empirical relationships $\alpha_l T_g \approx 0.16$[24] and $(\alpha_l - \alpha_g) T_g \approx 0.115$[25] where α_l and α_g are the liquid and glass volume coefficients of thermal expansion, respectively.

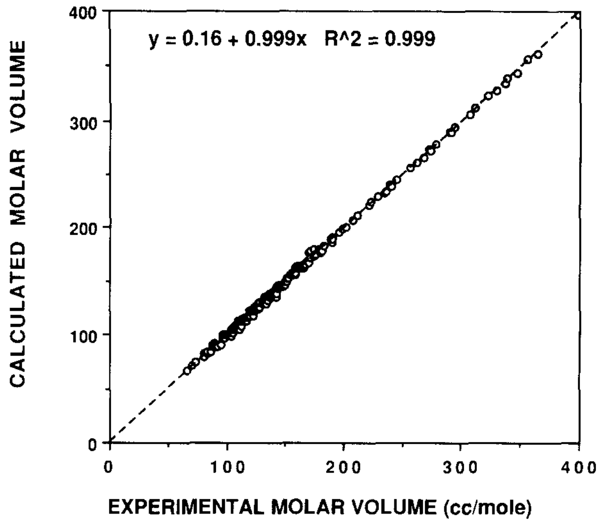


Figure 4 A plot showing the comparison of the experimental and calculated (*Tables 2* and *3*) molar volumes of the model organic compounds employed

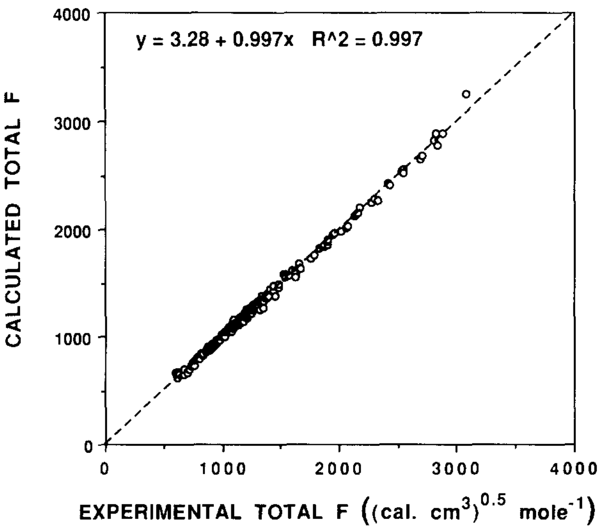


Figure 5 A plot showing the comparison of the experimental and calculated (*Tables 2* and *3*) molar attraction constants, F, of the model organic compounds employed

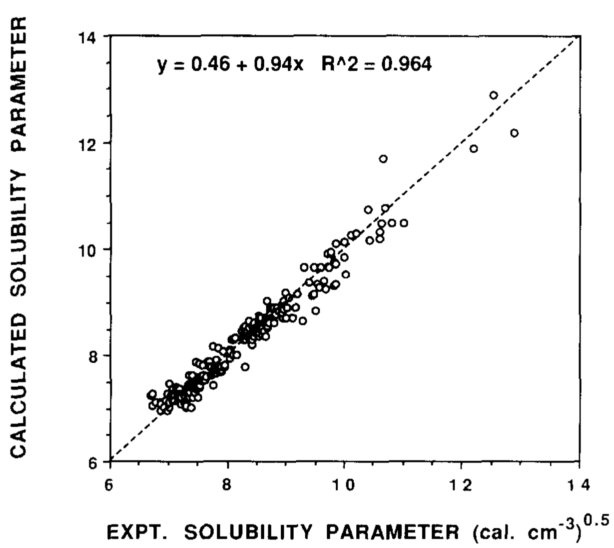


Figure 6 A plot showing the comparison of the experimental and calculated (*Tables 2* and *3*) solubility parameters, δ, of the model organic compounds employed

Figure 7 shows a comparison between the calculated (using *Tables 2* and *3*) and the experimental molar volumes at 25°C of 98 polymers of widely different chemistries obtained from density measurements reported in numerous sources in the literature[22]. About one third of the polymers have T_g values $\geqslant 25°\mathrm{C}$ and their glassy molar volumes were corrected to give rubbery molar volumes, using the relationships mentioned above. (For example, polystyrene has a T_g of 100°C and a density of $1.065\,\mathrm{g\,cm^{-3}}$ at 25°C. This corresponds to a glassy molar volume of $97.8\,\mathrm{cm^3\,mol^{-1}}$ which when corrected, yields a rubbery equivalent of $95.6\,\mathrm{cm^3\,mol^{-1}}$.) The agreement between the calculated and experimental polymer molar volumes appears quite reasonable, as shown by the fine least squares fit of the data. Only eight examples were found to differ by $\geqslant 5\%$. A standard error of estimate of $2.8\,\mathrm{cm^3\,mol^{-1}}$ was determined. This is twice that determined for the analogous organic liquids.

Table 5 shows a comparison of the experimental[17] and our calculated solubility parameters of some representative weakly self-associated and essentially non-hydrogen bonding polymers. We contend that as we have been consistent and have used molar volume and attraction constants derived from the same set of model data (*Tables 2* and *3*) that this is the best we can do and we have to accept a potential error of at least $\pm 0.4\,(\mathrm{cal\,cm^{-3}})^{0.5}$.

Table 5 Comparison between experimental and calculated polymer solubility parameters

Polymer	Solubility parameter $(\mathrm{cal\,cm^{-3}})^{0.5}$ δ_{Expt}[17]	δ_{Calc}
Polyethylene	7.7–8.4	8.0
Polypropylene	8.2–9.2	7.4
Polyisobutene	7.8–8.1	7.2
1,4-polybutadiene	8.1–8.6	8.1
1,4-polyisoprene	7.9–10.0	8.1
Polystyrene	8.5–9.3	9.5
Poly(vinyl chloride)	9.4–10.8	9.9
Poly(vinyl acetate)	9.4–11.1	9.6
Poly(methyl acrylate)	9.7–10.4	9.6
Poly(ethyl acrylate)	9.25–9.4	9.3
Poly(propyl acrylate)	9.05	9.1
Poly(butyl acrylate)	8.8–9.1	8.9
Poly(isobutyl acrylate)	8.7–11.0	8.7
Poly(methyl methacrylate)	9.1–12.8	9.0
Poly(ethyl methacrylate)	8.9–9.2	8.9
Poly(butyl methacrylate)	8.7–9.0	8.7
Poly(isobutyl methacrylate)	8.2–10.5	8.5
Poly(benzyl methacrylate)	9.8–10.0	9.8
Polyacrylonitrile	12.5–15.4	13.8
Polymethacrylonitrile	(10.7)	11.9
Poly(methylene oxide)	10.2–11.0	10.5
Poly(tetramethylene oxide)	8.6	8.8
Poly(propylene oxide)	7.5–9.9	8.5
Poly(ethylene terephthalate)	9.7–10.7	11.5

Estimation of the solubility parameters of strongly associated polymers

We have separated the molar attraction and molar volume contributions into two parts (*Tables 2* and *3*) to emphasize a point. *Table 2* contains the values for groups that we can confidently assume do not self-associate to any appreciable extent. Those group contributions listed in *Table 3*, however, were derived from model organic compounds that are known to weakly self-associate. This may not be too significant, but it is a matter of degree and when we consider strongly self-associating groups, such as alcoholic and phenolic hydroxyls, amide, urethane and carboxylic acid groups, the problem becomes acute. Model organic compounds containing such groups were not included in our calculations of molar attraction constants. Why is this? We can again use *Figure 2* to illustrate the problem. Experimental solubility parameters of model organic compounds are calculated primarily from vapour pressure data (i.e. $\delta = [\rho\,\Delta E_{\mathrm{vap}}/M]^{0.5}$). If the energy of self-association is less than say $1\,\mathrm{kcal\,mol^{-1}}$, a large fraction of molecules have energies equal to or greater than the dissociation energy. Accordingly, at the boiling point of typical low molecular weight compounds of this type, individual molecules are the predominant species and M is simply the molecular weight of a 'monomer'. In contrast, for energies in excess of say $3\,\mathrm{kcal\,mol^{-1}}$, a significant fraction of the molecules remain associated at the boiling point and may be thought in terms of a distribution of n-mers. In any event, the determination of the solubility parameter is equivocal as M is no longer just the molecular weight of the monomer but some larger value reflecting an average molecular weight of the associated species. This is exemplified in the hydrogen bonded dimer formation of carboxylic acids and was recognized by Hoy[18].

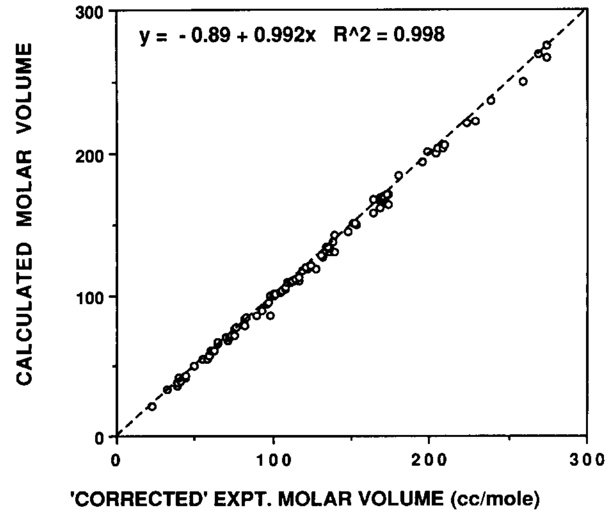


Figure 7 A plot showing the comparison of the 'corrected' experimental (see text) and calculated (*Tables 2* and *3*) molar volumes of polymers

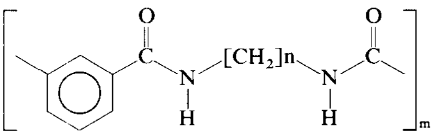
However, because we use a model that separates the repulsive physical forces, embodied in the interaction parameter χ, from the favourable attractive forces, contained in the $\Delta G_{\mathrm{H}}/RT$ term of equation (1), what we really require is an estimation of the non-hydrogen bonded solubility parameters of strongly self-associated polymers, such as poly(4-vinyl phenol) (PVPh), phenoxy and polyamides. In other words, we need the solubility parameters of these polymers assuming that they did not strongly self-associate through hydrogen bonding. This is not a trivial problem. One approach has been to calculate the solubility parameter of a closely related but non-hydrogen bonding polymer. For example, substitution of a methyl group for the labile proton in a polyamide, polyurethane or polyphenol has been attempted, but the methyl group itself causes a significant perturbation, especially if the repeat unit is relatively small, and this leads to a serious underestimation of the value

Table 6 Calculated non-hydrogen bonded solubility parameters for polyamides

Polyamide	Solubility parameter (cal cm^{-3})$^{0.5}$ [CO+NH]	[CO+N]	Polyamide	Solubility parameter (cal cm^{-3})$^{0.5}$ [CO+NH]	[CO+N]
Nylon 2-I	13.3	13.9	Nylon 3	12.8	13.5
3-I	12.7	13.1	4	11.7	11.9
4-I	12.2	12.5	5	11.0	11.0
5-I	11.8	12.0	6	10.5	10.4
6-I	11.5	11.6	7	10.1	10.0
7-I	11.2	11.3	8	9.9	9.8
8-I	11.0	11.0	9	9.7	9.6
9-I	10.8	10.8	10	9.5	9.4
10-I	10.6	10.6	11	9.4	9.3
12-I	10.3	10.3	12	9.3	9.1

of the solubility parameter. We prefer to employ the following procedure.

Table 6 lists estimated non-hydrogen bonded solubility parameters for a series of polyamides: aliphatic polycaprolactams (denoted nylon 6 etc.) and aromatic polyisophthalamides (denoted nylon n-I—see below)[8].



Nylon n-I

There are two sets of results. The first are calculated using a combination of the individual –CO– and >N–H group contributions (**F*** and **V*** in *Table 4*) for the amide (–CO–NH–) group. The rationale here is that these individual –CO– and >N–H group contributions were determined from compounds that are polar but not strongly self-associated and as such represent the non-hydrogen bonded contributions to the amide group. The second set are calculated for an analogous hypothetical polyamide molecule, but without the N–H proton. In effect we calculate the solubility parameter using a combination of the individual –CO– and >N– group contributions (**F*** and **V*** in *Table 4*) for the amide group. In this case the rationale is that the errors involved in eliminating the proton are reasonably small, especially when the repeat unit is relatively large and, again, both the –CO– and >N– group contributions were derived from essentially unassociated model compounds. It is pleasing to see that the two sets of results are in close agreement to one another. Using the same principles the non-hydrogen bonded solubility parameter of the amorphous polyurethane (APU) employed in our previous studies was calculated[6]. Comparable values of 11.2 and 11.3 (cal cm^{-3})$^{0.5}$ were determined for APU using the [–OCO–+>N–H] and [–OCO–+>N–] group contributions for the urethane group, respectively (see *Table 4*).

In contrast to the polyamide and polyurethane polymers, for hydroxyl containing polymers (PVPh, phenoxy and PVOH) we do not have the luxury of being able to dissect the O–H group into two group contributions that are derived from essentially unassociated molecules. Nevertheless, we can calculate the solubility parameter for hypothetical analogues that are missing the hydroxyl proton by employing the ether group contributions, both **F*** and **V***, for the hydroxyl group. *Table 7* summarizes the results of such an exercise.

Table 7 Non-hydrogen bonded solubility parameters

Polymer	Solubility parameter (cal cm^{-3})$^{0.5}$
Poly(4-vinyl phenol)	11.0
Poly(vinyl alcohol)	10.6
Phenoxy	10.2
Amorphous polyurethane[a]	11.2

[a] Reference 6

Estimating the non-hydrogen bonded solubility parameters in this manner is rather crude and subject to considerable error, especially for relatively small polymer repeat units. We have reason to be confident that this approach has merit, however. This is based upon the argument that we have successfully predicted the gross phase behaviour of a wide variety of PVPh[5,9], polyamide[8] and polyurethane[6] blends using values of the non-hydrogen bonded solubility parameters close to those given in *Tables 6* and *7*.

SIMPLE RULES GOVERNING MISCIBILITY IN POLYMER BLENDS

In the following discussion it will be convenient to consider three different categories of polymer blends, as delineated in *Figure 3*; those involving very weak (Case I), weak (Case II) and 'strong' (Case III) intermolecular forces. (The adjective 'strong', as applied here, encompasses a range of hydrogen bond strengths that, in turn, could be subdivided into categories ranging from the intermediate to the very strong. At this point it is not important to make such semantic distinctions.) However, in general, if the reader accepts the arguments presented so far and wishes to search for new miscible polymer blend systems, then the first rule of thumb is to minimize χ which, in turn, necessitates looking for closely matched non-hydrogen bonded solubility parameters. This is hardly a new concept, except that we have extended it into the realm of polymer mixtures involving strong favourable intermolecular interactions by separating out the physical contributions into an interaction parameter, χ, which is estimated from the non-hydrogen bonded solubility parameters. In a nutshell, if χ is close to zero, the favourable intermolecular interactions present will drive the system towards miscibility. Just how close the non-hydrogen bonded solubility parameters have to be to one another depends upon the type and relative strength of the intermolecular interactions.

Case 1: very weak or non-existent favourable intermolecular interactions

It is apparent that the solubility parameters of polymers cannot be determined with sufficient accuracy to adequately predict the phase behaviour of polymer blends of this type. Nevertheless, solubility parameters may be employed to discern significant trends in the phase behaviour of systematically chosen sets of polymer blends, ones in which there are variations in copolymer composition or where a homologous series of polymers is considered.

Borrowing a concept used extensively for gauging polymer solubility in the surface coatings industry, and restricting ourselves (for now) to the absence of significant favourable intermolecular interactions, consider the case of blending a homopolymer having a solubility parameter, δ_A, with a random copolymer composed of two repeat units that individually have values of solubility parameters of δ_B and δ_C, respectively, that span δ_A. As discussed by Scott[26], a random copolymer of a given composition can be considered in terms of an average solubility parameter, $\bar{\delta}_{BC}$, which if matched to δ_A could potentially predict a miscible blend system (note that the use of an average solubility parameter precludes the possibility of a 'repulsion' effect and hence a negative overall χ). Butadiene-*co*-acrylonitrile (BAN) polymers, whose solubility parameters span a wide range from approximately $\delta = 8.1$ to $13.8\,(\mathrm{cal\,cm^{-3}})^{0.5}$, represent fine examples in this category. What might we anticipate if we were to blend BAN copolymers of varying copolymer composition with a non-polar homopolymer, such as polystyrene (PS), which has a solubility parameter within this range ($\delta = 9.5\,(\mathrm{cal\,cm^{-3}})^{0.5}$)?

Figure 8a shows the calculated solubility parameter of BAN as a function of wt% acrylonitrile (AN) in the copolymer. An estimate of χ for BAN–PS blends using equation (4) with a reference volume of $100\,\mathrm{cm^3\,mol^{-1}}$ is shown graphically in *Figure 8b*. The narrow parabolic shaped variation of χ as a function of BAN copolymer composition has a minimum value of $\chi = 0$ at approximately 30% AN. Recall that for $N_A = N_B = 1000$, in the absence of favourable intermolecular interactions, the critical value of $\chi \cong 0.002$. Accordingly, there is a very narrow range of BAN composition ($\approx$30–34% AN in this case) over which there is the best chance of finding a miscible blend of BAN and PS. This allowed composition range is actually more restrictive than this, because unfavourable 'free volume' effects have not been taken into account[27] and this would further narrow the range. Moreover, recognizing the errors involved in determining individual solubility parameters, the 'true' curve may be significantly displaced on either side of the minimum value shown on the x-axis of *Figure 8*. The overall shape of the curve would be the same but finding the 'window' could be difficult!

To summarize, for the case of polymer blend systems in which the absence of favourable intermolecular interactions can be assumed:

(1) The probability of finding a miscible blend of two homopolymers of high molecular weight is exceedingly low since this implies the almost perfect matching of solubility parameters ($\Delta\delta \leqslant 0.1\,(\mathrm{cal\,cm^{-3}})^{0.5}$).

(2) As the error in estimating polymer parameters far exceeds the accuracy required to predict miscibility, it makes more sense to use the method to eliminate potential candidates. For example, blends of PS and polyisoprene ($\delta = 9.5$ and $8.1 \pm 0.4\,(\mathrm{cal\,cm^{-3}})^{0.5}$, respectively) are readily rejected as a potentially miscible pair, because the difference between the solubility parameters, even if one assumes the most favourable values at the error limits, significantly exceeds $0.1\,(\mathrm{cal\,cm^{-3}})^{0.5}$. Furthermore, one can assume that it is very unlikely that a non-polar homopolymer such as PS will mix with a copolymer of styrene and any other non-interacting comonomer (e.g. poly(styrene-*co*-acrylonitrile) (SAN), SBR, etc.) because the difference in the solubility parameters becomes increasingly larger the greater the concentration of the comonomer.

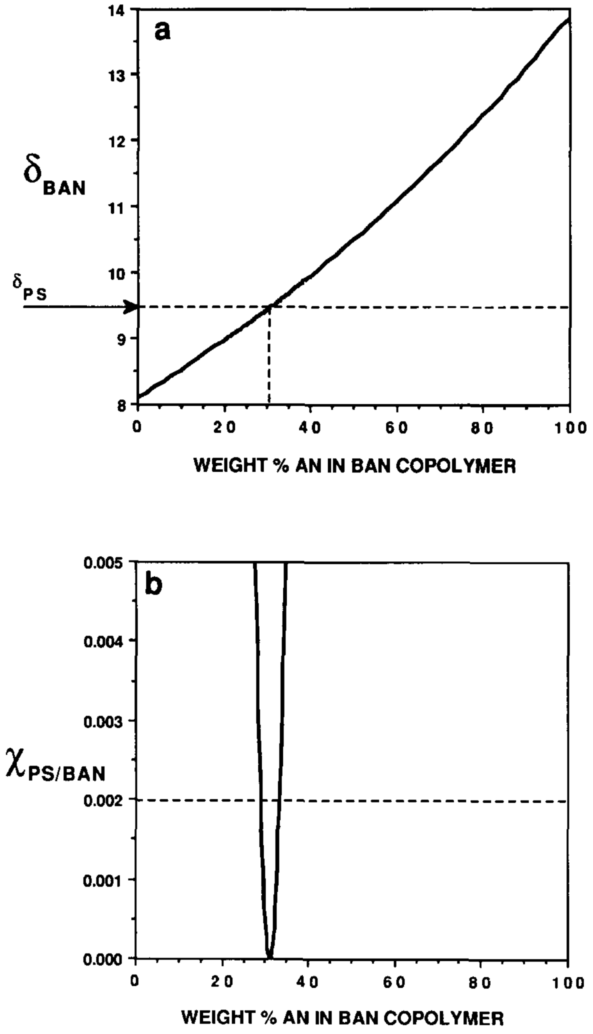


Figure 8 (a) A plot of the calculated values of the solubility parameter for butadiene-*co*-acrylonitrile (BAN) polymers as a function of acrylonitrile content. (b) Calculated values of χ (equation (4)) for polystyrene–BAN blends

(3) If the object is to find a miscible blend of a given non-polar homopolymer a good strategy might be to employ the 'mixed solvent' approach described above. An experimental approach of trial and error might be necessary to find the rather narrow window defining the limits of miscibility, because of the inherent errors involved in estimating solubility parameters.

Case 2: relatively weak favourable intermolecular interactions

Examples of miscible binary polymer blends that fit into the category of relatively weak favourable intermolecular interactions include PMMA–PEO[20];

PVAc–PEO[28]; PS–PVME[29]; PS–poly(phenylene oxide) (PPO)[30] and poly(butylene terephthalate) (PBT)–polyarylate[31]. Keeping in mind the errors involved in estimating polymer solubility parameters, the difference between the solubility parameters of these polymer pairs is $\Delta\delta = 0.3$, 0.2, 1.0, 0.3 and 0.1 $(\mathrm{cal\,cm^{-3}})^{0.5}\,\mathrm{mol^{-1}}$, respectively. Poly(vinyl chloride) (PVC) blends with polar polymers containing ester, acetate and acrylic groups also fit into this category and because there has been a number of systematic studies of these blends we will now concentrate our attention on these systems. PVC may be classified as a moderately self-associated polymer. The precise nature of the intermolecular interactions involved between the chemical moieties of PVC, be they dipolar, relatively weak hydrogen bonds or a combination of both, is the subject of debate. For our purposes here, however, this is not important.

Consider first the PVC–SAN blend system. PVC is neither miscible with PS nor polyacrylonitrile (PAN) but is miscible with SAN copolymers containing 11.5 to 26% acrylonitrile[32]. Paul and his coworkers[32] attribute the miscibility of the PVC–SAN blends to the intramolecular repulsion of the styrene and acrylonitrile units within the SAN copolymer chain, which they interpret according to their hypothesis of a binary interaction model[14]. These authors also discuss possible favourable intermolecular interactions occurring between chlorinated compounds and aromatic rings. Other possibilities also exist, involving the acrylonitrile unit (we have observed, for example, that the carbonyl group shifts to lower frequency in miscible polycaprolactone (PCL)–SAN blends suggesting that the carbonyl group is involved in a specific interaction with presumably the α-hydrogen of the acrylonitrile unit[33]). The precise nature of the intermolecular interactions is again not important to our arguments here, only the fact that they exist and that they are, on our scale, relatively weak.

Figures 9a and *9b* show the calculated solubility parameter of SAN as a function of acrylonitrile content and an estimate of χ for PVC–SAN blends, respectively, using equation (4) with a reference volume corresponding to the PVC repeat unit $(42.4\,\mathrm{cm^3\,mol^{-1}})$, the molar volume of the self-associated polymer (see reference 3). PVC has a solubility parameter $(\delta = 9.9\,(\mathrm{cal\,cm^{-3}})^{0.5})$ that is intermediate between that of PS ($\delta = 9.5$) and PAN ($\delta = 13.8$). As in the previous figure, the curve of χ *versus* SAN copolymer composition resembles a parabola in shape and goes through a minimum value of zero at a composition of about 10% acrylonitrile. If there were no favourable intermolecular interactions (i.e. $\chi_{\mathrm{Crit}} < 0.002$) and the estimated values of the solubility parameters are reasonably accurate, this immediately implies a 'miscibility window' for blends of PVC with SAN containing between about 7 and 15% acrylonitrile. However, the presence of the relatively weak favourable intermolecular interactions serves to open the compositional range for miscibility. Employing the experimental range of miscibility determined by Paul and coworkers[32] for PVC–SAN blends, it appears that a χ_{Crit} value of about 0.02 is appropriate. This is an order of magnitude greater than the case involving no favourable interactions. Let us not lose sight of the fact, however, that by simply considering the solubility parameters of PVC and SAN copolymers and recognizing that relatively weak favourable intermolecular interactions exist in this system, we have predicted with reasonable accuracy the most probable range of miscibility without recourse to the postulation of a 'repulsion' effect.

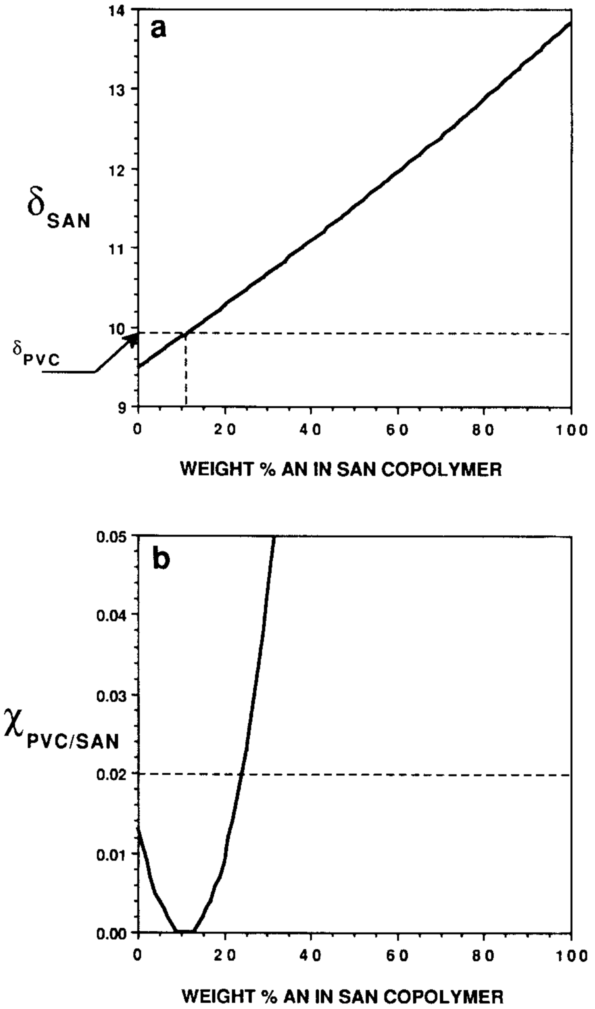


Figure 9 (a) A plot of the calculated values of the solubility parameter for styrene-*co*-acrylonitrile (SAN) polymers as a function of acrylonitrile content. (b) Calculated values of χ for poly(vinyl chloride) (PVC)–SAN blends

To illustrate that the above is not an isolated fortuitous result, let us now consider PVC–BAN blends. Zakrzewski[34] found that BAN copolymers having acrylonitrile contents between 23–45% were miscible with PVC over the entire range of blend compositions. Using the data in *Table 2*, the solubility parameter of 1,4-polybutadiene is calculated to be 8.1 $(\mathrm{cal\ cm^{-3}})^{0.5}$. *Figures 10a* and *10b* show the calculated solubility parameter of BAN as a function of acrylonitrile content and an estimate of χ for PVC–BAN blends, respectively. The curve of χ *versus* BAN copolymer composition again has a parabolic shape, but this time goes through a minimum value of zero at a composition of about 40% acrylonitrile. With no favourable intermolecular interactions (i.e. $\chi_{\mathrm{Crit}} < 0.002$) a 'miscibility window' for blends of PVC with BAN containing between about 35 and 42% acrylonitrile is indicated. However, the presence of the relatively weak favourable intermolecular interactions, corresponding to a χ_{Crit} value of about 0.02 as suggested by the PVC–SAN results mentioned in the previous paragraph, leads to a predicted miscibility window for blends of PVC with BAN copolymers containing from about 27–48% acrylonitrile. This is in remarkable agreement with experimental observation.

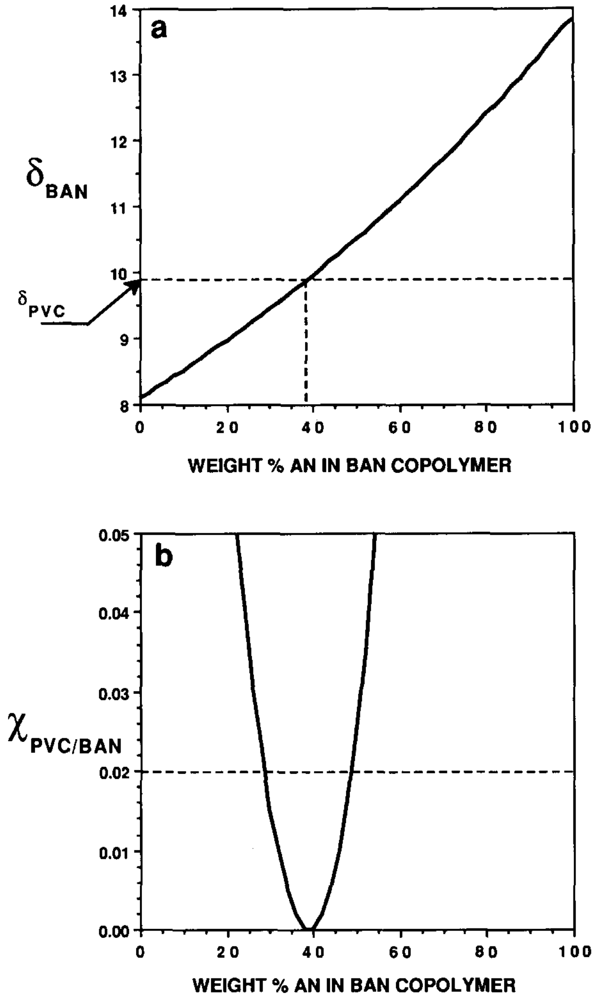


Figure 10 (a) A plot of the calculated values of the solubility parameter for BAN polymers as a function of acrylonitrile content. (b) Calculated values of χ for PVC–BAN blends

Infrared evidence for the presence of specific interactions involving PVC and the carbonyl group of polymers containing ester, acetate and acrylate groups has been reviewed by our group[35]. The debate still rages as to whether this interaction should be described as a relatively weak hydrogen bond between the carbonyl group and the methine proton of PVC, as we still favour, or a dipole-induced dipole interaction involving the carbonyl group and the C–Cl bond of PVC, or a Lewis acid–base type of interaction[36]. However, the precise nature of the interaction is not important to the arguments presented here. Judging from the comparatively minor frequency shifts ($<6\,cm^{-1}$) in the carbonyl band of miscible polyester (or polyacetate or polyacrylate) blends with PVC[35], we are still in the range of our so-called relatively weak interactions. Nevertheless, these intermolecular interactions are expected to be significantly stronger than those occurring between PVC and the SAN or BAN polymers.

Woo, Barlow and Paul[37] reviewed the previous literature on PVC blends with aliphatic polyesters. Following their studies these authors concluded, in essence, that linear aliphatic polyesters with CH_2/COO ratios of less than between 3 and 4 were immiscible with PVC. At greater CH_2/COO ratios, miscible systems are observed but phase separation at elevated temperatures becomes apparent at ratios greater than 10. Judging from the trends in their cloud point curves (Figure 7 in ref. 37) and assuming that equilibrium conditions can be achieved, PVC forms miscible blends at ambient temperature with linear aliphatic polyesters having CH_2/COO ratios of up to about 15–18. This PVC–polyester 'miscibility window' was described by Woo *et al.*[14] in terms of the binary interaction model and the strong unfavourable interactions between the CH_2 and COO groups of the polyester. However, as we will describe below, our simple concept of a balance between unfavourable physical forces and favourable specific interactions, which is the main theme of this paper, leads to the same conclusion.

Figures 11a and *11b* show the calculated solubility parameter of aliphatic linear polyesters (using the data in *Table 2*) as a function of the number of methylene units in the polyester repeat unit defined so as to contain one COO group, and an estimate of χ for PVC–polyester blends, respectively. The curve of χ *versus* the number of methylene units has the familiar shape of a potential energy diagram and goes through a minimum value of zero at about 3.5 methylene groups. Below 3 methylene groups χ rises very sharply. In contrast, above 4 methylene groups χ increases, but much more gradually and at a decreasing rate with increasing number of methylene groups. This has a familiar ring to it and is

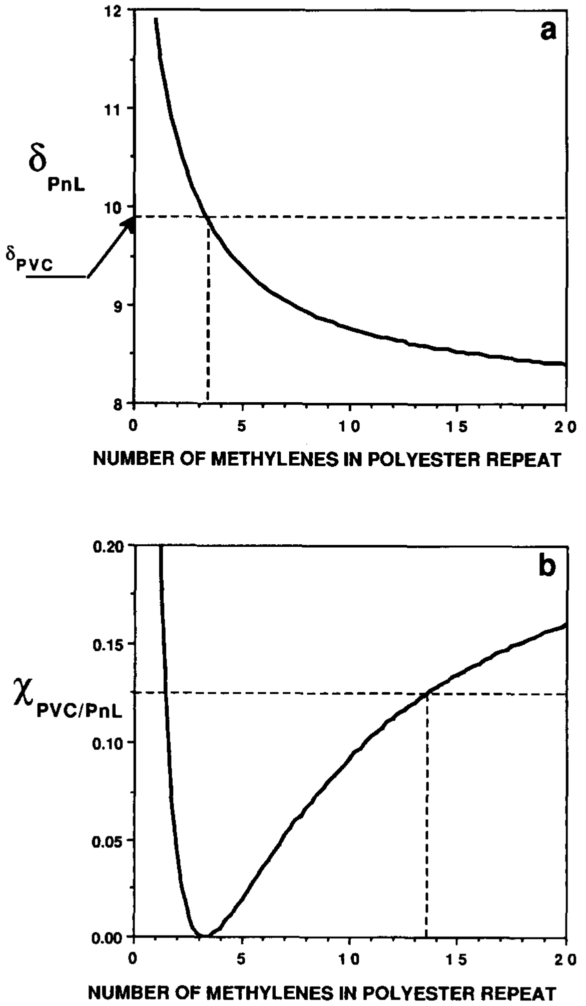


Figure 11 (a) A plot of the calculated values of the solubility parameter for linear aliphatic polyesters (PnL) as a function of the number of methylene groups in the chemical repeat. (b) Calculated values of χ for PVC–PnL blends

in accord with the description of the sharp and diffuse divisions between miscibility and immiscibility of these blends at low and high CH_2/COO ratios, respectively[37]. Once again, the presence of the relatively weak favourable intermolecular interactions serves to increase the range of miscibility. Employing the experimental range of miscibility determined by Woo and coworkers, it appears that a χ_{Crit} value of between 0.10 to 0.15 is appropriate, suggesting that the favourable interaction here is about 5 to 7.5 times that found between PVC and the acrylonitrile containing copolymers. This is at the outer edge of our categorization of relatively weak intermolecular interactions and corresponds to an upper limit of about $1\,(\mathrm{cal\,cm^{-3}})^{0.5}$ for the solubility parameter difference, $\Delta\delta$ (*Figure 3*). While not perfect, we have predicted with reasonable accuracy the most probable range of miscibility for PVC blends with linear aliphatic polyesters by simply considering the solubility parameters of PVC and polyester 'copolymers' and recognizing that relatively weak favourable intermolecular interactions exist in this system.

Systematic studies of PVC blends with a series of linear polymethacrylates[38] and polyacrylates[38,39] have been performed by Walsh and his coworkers. There is less uncertainty concerning the phase behaviour of the former and we will rely on these experimental studies for our purposes here. In summary, Walsh and McKeown[38] found that PVC was miscible with all the linear polymethacrylates up to poly(*n*-pentyl methacrylate). Poly(*n*-hexyl methacrylate) appears to be on the edge of the miscibility window, as it phase separated at temperatures below 125°C.

Figures 12a and *12b* show the calculated solubility parameter of the polymethacrylates as a function of the number of methylene groups in the polymer repeat, together with the estimate of χ for PVC–poly(alkyl methacrylate) (PAMA) blends. PVC ($\delta = 9.9\,(\mathrm{cal\,cm^{-3}})^{0.5}$) has a calculated solubility parameter that lies outside the range of both PMMA ($\delta = 9.1$) and PE ($\delta = 8.0$); the limit when there are an infinite number of methylene units in the repeat. Accordingly, the estimated value of χ always exceeds χ_{Crit} for the case of a polymer blend involving no favourable intermolecular interactions. The smallest value of χ corresponds to the blend of PVC and PMMA. Increasing the number of methylene units in the side chain increases the value of χ. At what point does the value of χ negate a reasonable estimate of favourable intermolecular interactions? If we use the observations of Walsh and McKeown[38] we arrive at a value of χ_{Crit} of between 0.10 and 0.15. This result is identical to that found above for the PVC–polyester blends. We do not believe that this is merely serendipitous.

The last PVC blend example concerns ethylene-*co*-vinyl acetate (EVA). There are unfortunately many conflicting reports in the literature concerning the miscibility of these blends. Two of the more recent papers that painstakingly document the prior literature pertaining to these blends are those of Rellick and Runt[40] and Cruz-Ramos and Paul[41]. Sample preparation, a strong $\Delta\chi$ effect[27], relatively low lower critical solution and degradation temperatures conspire to make the system difficult to study. Nonetheless, the PVC–EVA system has been featured prominently as an example supporting the binary interaction model. Shiomi *et al.*[42], using samples cast from THF solution experimentally determined that a wide compositional range of EVAs containing from about 45% to 85% VAc are miscible at ambient temperature.

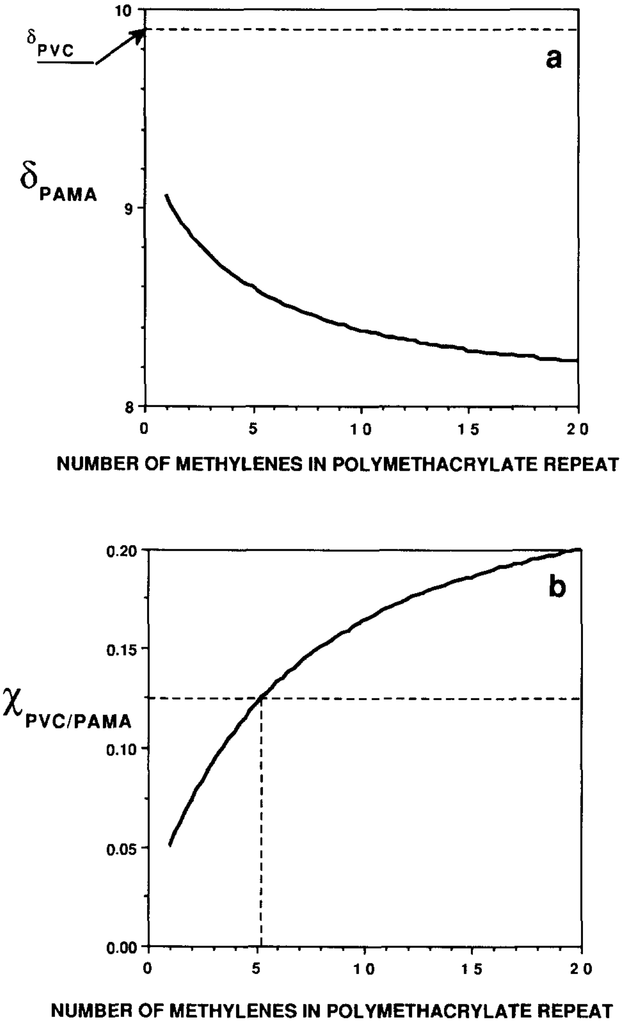


Figure 12 (a) A plot of the calculated values of the solubility parameter for poly(alkyl methacrylates) (PAMA) as a function of the number of methylene groups in the chemical repeat. (b) Calculated values of χ for PVC–PAMA blends

Figures 13a and *13b* show the calculated solubility parameter of EVA as a function of vinyl acetate content together with the estimate of χ for PVC–EVA blends. This is another example where the solubility parameter of PVC lies outside the range of both PVAc ($\delta = 9.6$) and PE ($\delta = 8.0$). The smallest value of χ corresponds to the blend of PVC and PVAc. If we assume that the interactions between PVC and acetate groups are roughly equivalent to those occurring between PVC and ester or acrylate groups considered above, then it would require a χ value of greater than about 0.10 to 0.15 to overwhelm the favourable intermolecular interactions. Our simple calculation predicts, therefore, that PVC should be miscible with EVA copolymers containing from about 45 to 100% VAc. This is at variance with the experimental results quoted above and was the impetus that led us to reexamine the PVC–PVAc blend system. While we confirmed that films cast from THF were invariably multiphased, apparently arising from a powerful $\Delta\chi$ effect, a simple change of solvent to methyl ethyl ketone produces a sample that exhibits only one intermediate T_g consistent with a miscible blend[43], supporting our simple predictions.

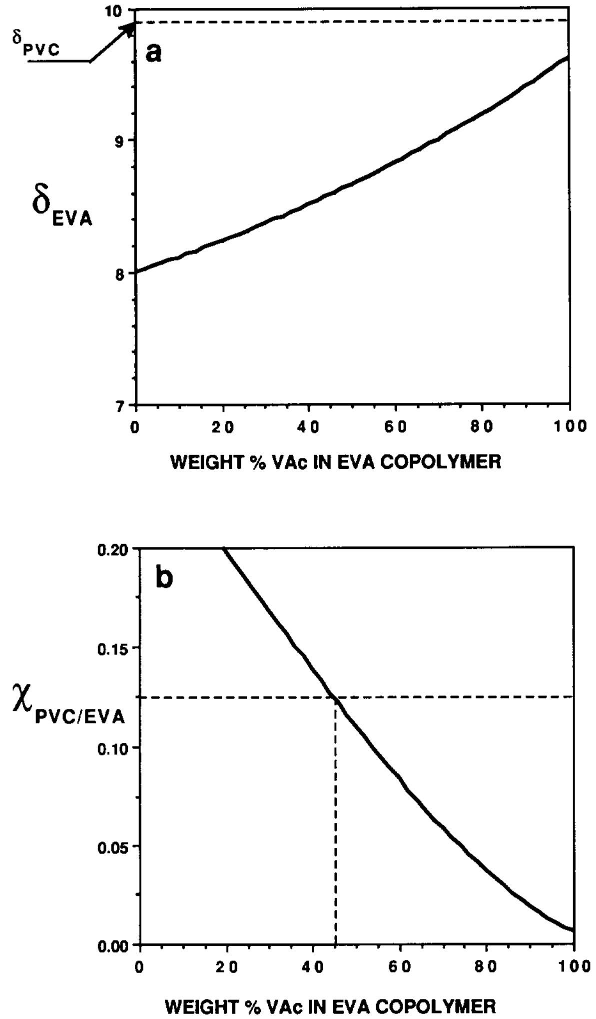


Figure 13 (a) A plot of the calculated values of the solubility parameter for ethylene-*co*-vinyl acetate (EVA) polymers as a function of vinyl acetate content. (b) Calculated values of χ for PVC–EVA blends

Finally, we should consider in this category another systematic series of blends that have been studied by Paul and his coworkers involving linear aliphatic polyesters with the polycarbonates, bisphenol A polycarbonate (PC) and tetramethylbisphenol A polycarbonate (PTMC)[44,45]. Cruz *et al.*[44] have found that PC is miscible with polyesters having CH_2/COO ratios of between 2 and 5 (with partial miscibility up to 7). Similarly, Fernandes *et al.*[45] have determined that PTMC is miscible with polyesters having CH_2/COO ratios of between 5 and 10 (with partial miscibility at 4). While the precise nature of the intermolecular interactions occurring between polycarbonates and polyesters is not crucial to the arguments presented here, it should be noted that the frequency shift of the carbonyl stretching mode of poly(ε-caprolactone) (PCL) in an amorphous miscible blend with PC is somewhat less ($\approx 3\,\mathrm{cm}^{-1}$) than that seen in analogous PCL–PVC blends suggesting a weaker intermolecular interaction of about half the strength[35,46,47].

Figure 14a shows the calculated solubility parameter of aliphatic linear polyesters as a function of the number of methylene units in the polyester repeat. Also included in this figure are broken lines representing the calculated solubility parameters of PC and PTMC (10.6 and 9.5 $(\mathrm{cal\,cm}^{-3})^{0.5}$, respectively) employing the group contributions given in *Tables 2* and *4*. (Note that the values of the group contributions for the carbonate group are subject to greater uncertainty because they were estimated from the addition of the values for ester and ether groups and not determined from model organic carbonate data.) χ as a function of the number of methylene groups in the polyester repeat for PC–polyester and PTMC–polyester blends is given in *Figure 14b*. (In this case there is no obvious self-associated polymer and we have assumed a value for V_r of $100\,\mathrm{cm}^3\,\mathrm{mol}^{-1}$. Any error caused by this assumption is only of scale and not in the shape or trends observed for χ as a function of the number of methylene units.) The overall form of the two curves is in accord with the experimental observations. In fact, if we assume a χ_{Crit} of between 0.05 and 0.075 (the rationale being that the strength of the intermolecular interactions is roughly half that of polyester–PVC blends), the breadth of the miscibility windows are predicted quite well. We could improve the correlation between the calculated predictions and experimental observations by adjusting the solubility parameters (especially those of the polycarbonates) within the bounds of known error, but this would detract from the elementary nature of this guide and we prefer to emphasize trends and not specifics.

To summarize for the case of polymer blend systems

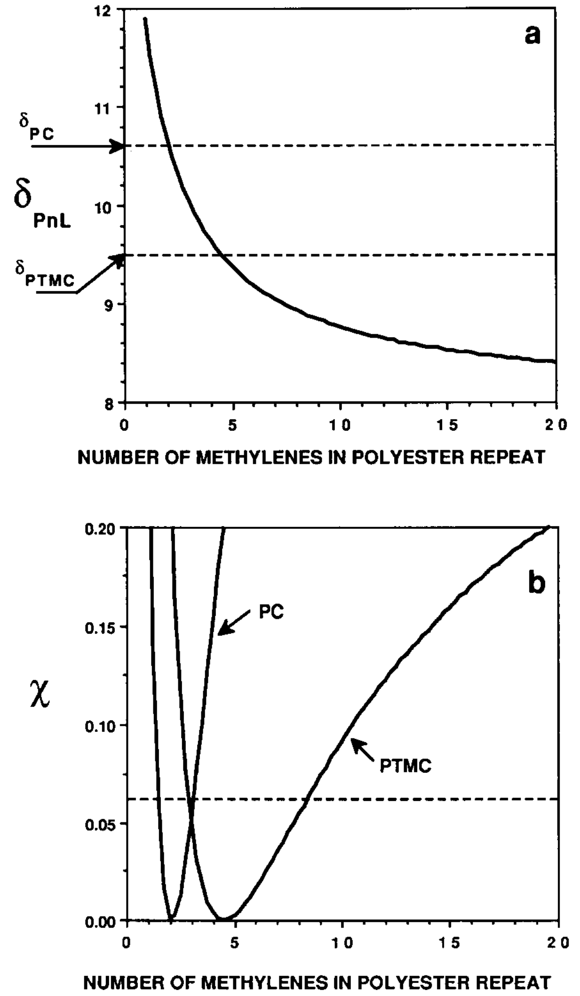


Figure 14 (a) A plot of the calculated values of the solubility parameter for linear aliphatic polyesters (PnL) as a function of the number of methylene groups in the chemical repeat. (b) Calculated values of χ for PVC–poly(bisphenol A carbonate) (PC) and PVC–poly(tetramethylbisphenol A carbonate) (PTMC) blends

in which there are relatively weak favourable intermolecular interactions:

(1) The presence of relatively weak favourable intermolecular interactions (i.e. those with dissociation energies of between about 1 and 3 kcal mol^{-1}) increases the probability of finding miscible blends of polar polymers over those that are purely dispersive in nature (Case 1).

(2) Simply stated, these favourable interactions serve to counteract the unfavourable contribution to the free energy of mixing expressed in the χ parameter. We may conveniently view this in terms of a larger value of χ_{Crit} which, in turn, is reflected by a greater tolerance in the solubility parameter difference of the two polymers (up to about 1 (cal cm^{-3})$^{0.5}$).

(3) The first rule of thumb for predicting polymer miscibility still remains the matching of the non-hydrogen bonded solubility parameters. We must still recognize the errors involved in calculating polymer solubility parameters, but now we have some room to work and are not required to be so stringent.

Case 3: relatively strong favourable intermolecular interactions

Examples of miscible binary polymer blends that fit into the category of relatively strong favourable intermolecular interactions include polymers containing amide, urethane, hydroxy and carboxylic acid groups, blended with polymers that have ether, acrylate, acetate, ester, oxazoline and pyridine groups present in their (average) chemical repeat. For these systems it is also possible to calculate $\Delta G_H/RT$ directly (equation 1), because infrared measurements can be used to obtain a measure of the number and strength of the hydrogen bonds formed in these mixtures. This work is reported in detail elsewhere[3,4] and here we will keep to our general discussion of the effects of steadily increasing the strength of the intermolecular interactions. We first consider blends of polyisophthalamides (nylon n-I) with two different polyethers, poly(ethylene oxide) (PEO) and poly(vinyl methyl ether) (PVME), that were the subject of a recent study[8]. In essence we found experimentally that nylons 8-I through 10-I (the upper limit of the polymers synthesized) were completely miscible in the amorphous state with PEO while nylon 6-I was on the edge of miscibility (partially miscible). PIPA polymers containing <6 methylene groups in the translational repeat became progressively less miscible. In contrast, blends of the PIPA polymers (nylons 2-I to 10-I) were all found to be immiscible with PVME. PEO and PVME have calculated solubility parameters (*Table 2*) of 9.4 and 8.5 (cal cm^{-3})$^{0.5}$, respectively. Using these values in conjunction with those given in *Table 6* for the various PIPA polymers, the interaction parameter, χ, may be estimated from equation (4). The reference volume, V_r, in this case is the molar volume of the average repeat unit containing one amide group of the polyisophthalamide in question (i.e. half the translational repeat)[3,8]. *Figures 15a* and *15b* show the calculated solubility parameter and estimate of χ, respectively, of the nylon n-I polymers as a function of the number of methylenes (n). A χ_{Crit} value of about 0.5 (~ 4 times that of the PVC blends with polyester and related polymers), which corresponds roughly to solubility parameter difference (*Figure 3*) of between 1.5 and 2.0 (cal cm^{-3})$^{0.5}$, is consistent with the experimental observations. Note that on this basis alone, one would require greater than 15 methylene units (i.e. a nylon 15-I) before the PIPA polymers would be predicted to be miscible with PVME. Also keep in mind that at this end of the interaction scale we have been able to calculate χ_{Crit} directly from a knowledge of $\Delta G_H/RT$ and this is not a *post facto* fitting of the data.

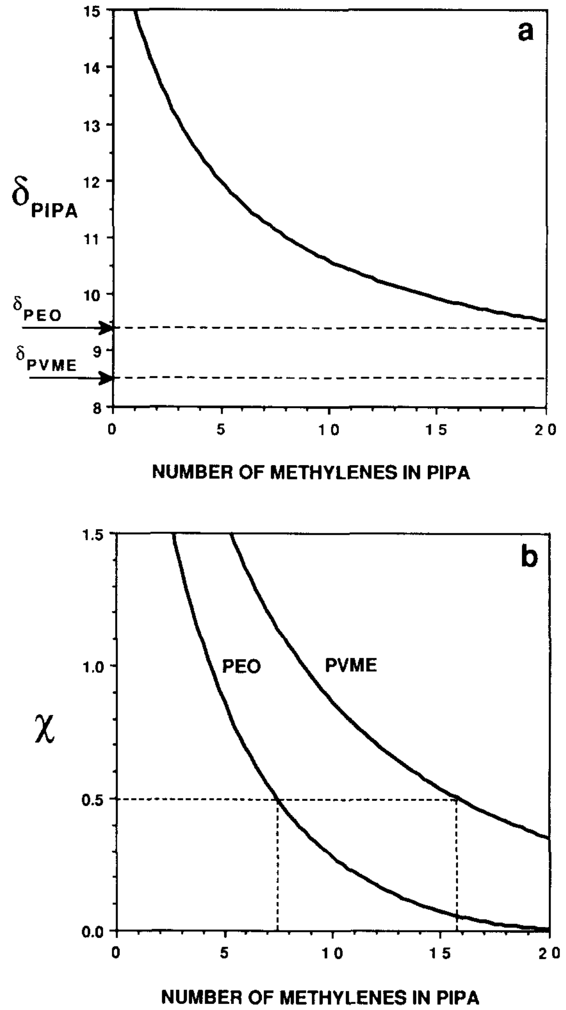


Figure 15 (a) A plot of the calculated values of the solubility parameter for polyisophthalamides (PIPA) as a function of the number of methylene groups in the chemical repeat. (b) Calculated values of χ for PIPA–poly(ethylene oxide) (PEO) and PIPA–poly(vinyl methyl ether) (PVME) blends

Turning now to hydroxyl containing polymers; we will first consider the poly(hydroxy ether of bis-phenol A) (phenoxy) blends with linear aliphatic polyesters. Harris *et al.*[48] have determined that phenoxy is miscible with aliphatic polyesters over a narrow range of 3–5 methylenes. In addition, we have reported *FT*i.r. studies pertaining to the relative strength of the interactions attributed to self-association of phenoxy and association between the phenoxy and poly(ε-caprolactone) (PCL)[49]. *Figure 16a* shows calculated solubility parameters for linear aliphatic polyesters as a function of the number of methylene groups in the polymer repeat. Note that the non-hydrogen bonded solubility parameter for phenoxy is estimated at 10.2 (cal cm^{-3})$^{0.5}$ (*Table 7*). *Figure 16b* shows the corresponding estimates of χ (equation 4) for the blends ($V_r = 241$ cm^3 mol^{-1}, the molar volume of phenoxy). The shape of the curve is very similar to the

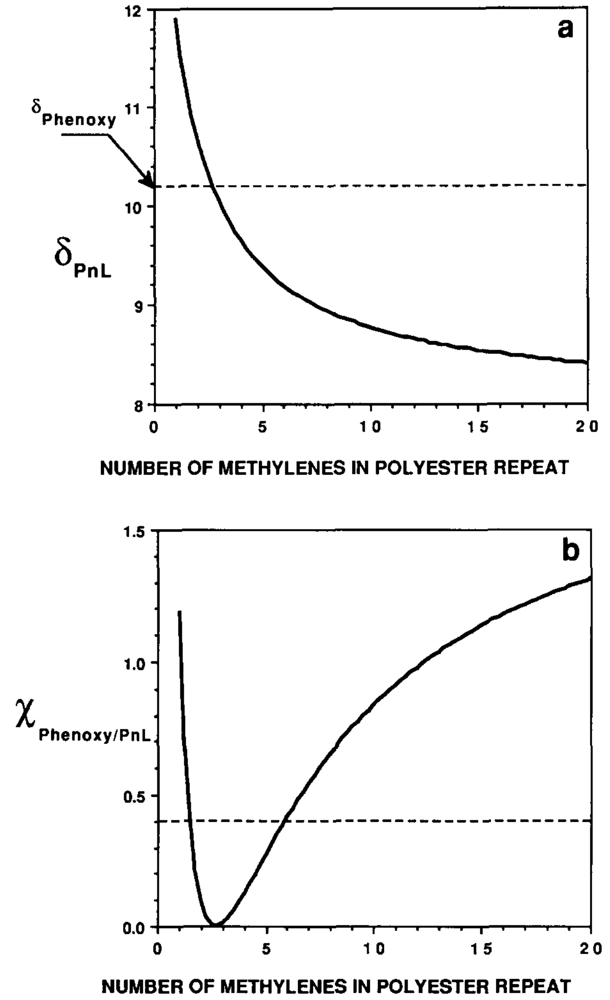


Figure 16 (a) A plot of the calculated values of the solubility parameter for linear aliphatic polyesters (PnL) as a function of the number of methylene groups in the chemical repeat. (b) Calculated values of χ for poly(hydroxyether of bisphenol A) (phenoxy)–PnL blends

PVC–polyester blend case (*Figure 11*). Below 2 methylenes χ increases precipitously from values close to zero, while above 4 methylenes, χ increases but in a more moderate fashion. In the absence of any favourable intermolecular interactions between phenoxy and the polyesters, these simple calculations predict that only the linear polyester, $-(CH_2)_3-COO-$, is likely to be miscible with phenoxy. The window of miscibility opens with the occurrence of favourable interactions, and the experimental range of 3 to 5 CH_2 molecules determined by Harris *et al.*[48] corresponds to a χ_{Crit} value of approximately 0.4. From a comparison of the frequency shifts of the PCL carbonyl stretching mode in miscible blends of phenoxy and PVPh[35] (approximately 13 and 26 cm^{-1}, respectively), it is evident that the relative strength of the intermolecular interactions in the case of the phenoxy blend is roughly half that of the analogous PVPh blend, and as we will see directly below, consistent with the doubling of the χ_{Crit} value.

The next four examples pertain to PVPh blends. From an infrared spectroscopic point of view, studies of PVPh blends with polyacrylates, polyacetates, polyesters and polymethacrylates[5,9,49,50] have been most rewarding, because it is possible to directly measure the fraction of hydrogen bonded carbonyl groups in the blends as a function of composition and temperature. PVPh is miscible with linear polyacrylates from poly(methyl acrylate) to poly(*n*-butyl acrylate) but only partially miscible with poly(pentyl acrylate) and the higher polyacrylates become increasingly more immiscible[5]. With linear polymethacrylates the first three of the series, polymethyl, ethyl and *n*-propyl methacrylates are essentially miscible with PVPh at ambient temperature. Poly(*n*-butyl methacrylate), on the other hand, is only partially miscible[9]. Furthermore, PVPh is miscible with poly(vinyl acetate) (PVAc) and EVA[70], partially miscible with EVA[45] and essentially immiscible with EVA[25][5,50,51].

Figure 17a shows calculated solubility parameters for linear polyacrylates and polymethacrylates as a function of methylene groups in the polymer repeat. *Figure 17b* shows estimates of χ (equation (4)) for the blends with PVPh ($V_r = 100\,cm^3\,mol^{-1}$, the molar volume of PVPh). In both cases, the value of χ increases with the number of methylene groups in the repeat as the difference between the solubility parameters of PVPh and the polyacrylates or polymethacrylates becomes increasingly larger. Taking advantage of the observations described in the last paragraph, we conclude that a χ_{Crit} of approximately 0.8 is consistent with these results. This corresponds to an upper limit in the non-hydrogen bonded solubility parameter difference, $\Delta\delta$, of about

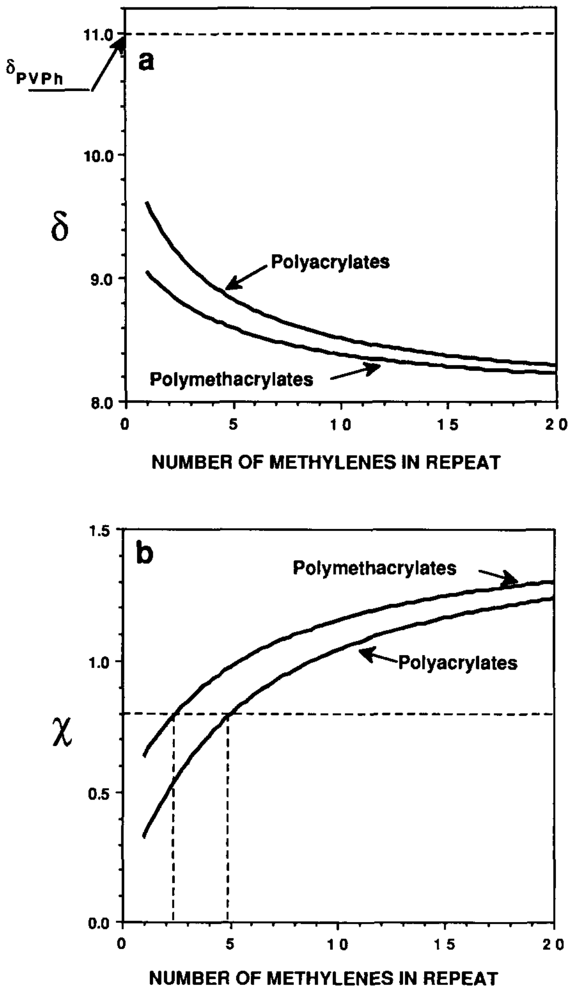


Figure 17 (a) A plot of the calculated values of the solubility parameter for poly(alkyl methacrylates) and poly(alkyl acrylates) as a function of the number of methylene groups in the chemical repeat. (b) Calculated values of χ for poly(vinyl phenol) (PVPh)–poly(alkyl methacrylate) and PVPh–poly(alkyl acrylate) blends

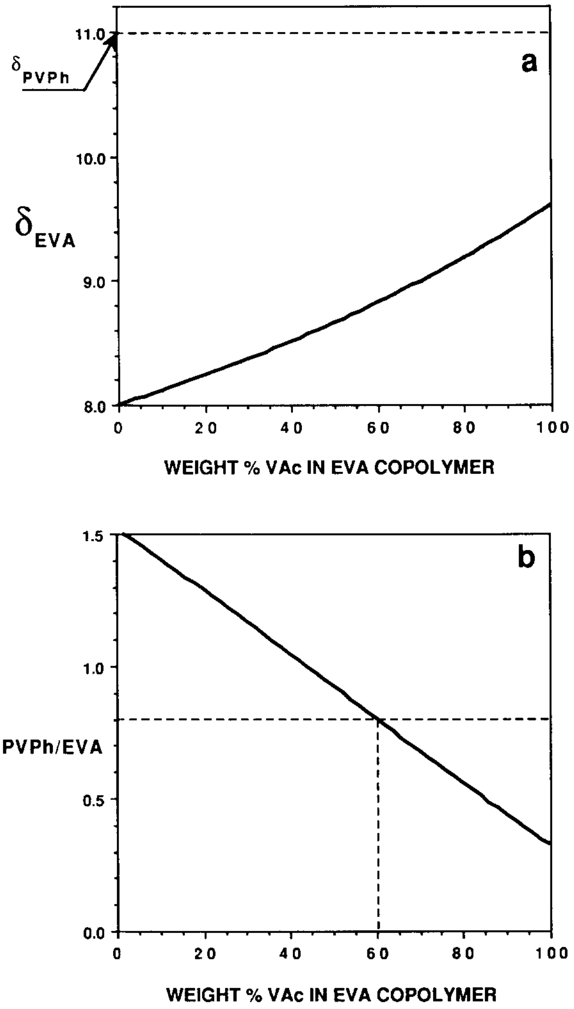


Figure 18 (a) A plot of the calculated values of the solubility parameter for EVA polymers as a function of vinyl acetate content. (b) Calculated values of χ for PVPh–EVA blends

2 (cal cm^{-3})$^{0.5}$. Not unexpectedly, this value of χ_{Crit} also appears to apply to the PVPh–EVA copolymer blends. *Figures 18a* and *18b* show curves representing the calculated solubility parameters of EVA copolymers as a function of the wt% of vinyl acetate based upon an average polymer repeat and the estimate of χ for PVPh–EVA blends, respectively. A χ_{Crit} of 0.8 leads to a prediction that a vinyl acetate content exceeding 60% is required for miscible PVPh–EVA blends; a gratifying agreement with experiment[51,52]. Note again that although this value of χ_{Crit} appears exceedingly large, the value of $\Delta G_H/RT$, calculated from experimental measurements, is sufficiently large to make this a reasonable figure.

Before we leave the class of PVPh blends with polymers containing ester type carbonyl groups consider the following: poly(methyl methacrylate) (PMMA) is immiscible with polystyrene (PS) (corresponding, in our terms, to a Case 1 situation because there are no obvious favourable intermolecular interactions to drive miscibility) but miscible, as discussed above, with poly(vinyl phenol) (PVPh). The question is, 'how many vinyl phenol (VPh) units would we need to incorporate into PS to render it miscible with PMMA?' Chen and Morawetz[53] recently reported that only approximately 1% was necessary in the case of PMMA and poly(ethyl methacrylate) (PEMA)[53]. Our theoretical calculations of the phase diagrams of PVPh and styrene-*co*-vinyl phenol copolymers (STVPh) blends with poly(alkyl methacrylates) successfully predict a wide window of miscibility[9]. Here, however, we wish to see if the simple scheme presented in this paper reveals such a trend. Assuming that styrene is an inert diluent, we can readily estimate the solubility parameters of the STVPh copolymers, which change in an essentially linear fashion with copolymer composition, as shown in *Figure 19a*. Estimates of the value of χ for the STVPh–PMMA blends may now be determined (equation (4)) where the molar volume of the STVPh repeat is employed as the reference volume, V_r. The results are summarized in *Figure 19b*. The value of χ as defined here is determined by two factors: the size of the reference volume V_r, which increases with increasing styrene content in the STVPh copolymer; and the difference in the solubility parameter of STVPh, $\bar{\delta}_B$, and its value relative to δ_A, the solubility parameter of PMMA. These two factors tend to offset one another over a wide range of STVPh copolymer composition. With decreasing concentration of VPh in the STVPh copolymer, however, a point is reached where the value of χ rises rapidly. Employing the value for χ_{Crit} of 0.8 (see preceding two paragraphs) leads to a prediction that PMMA should be miscible with STVPh copolymers containing from about 5 to 100% VPh units. This is a remarkably good prediction given the simplistic nature of our scheme.

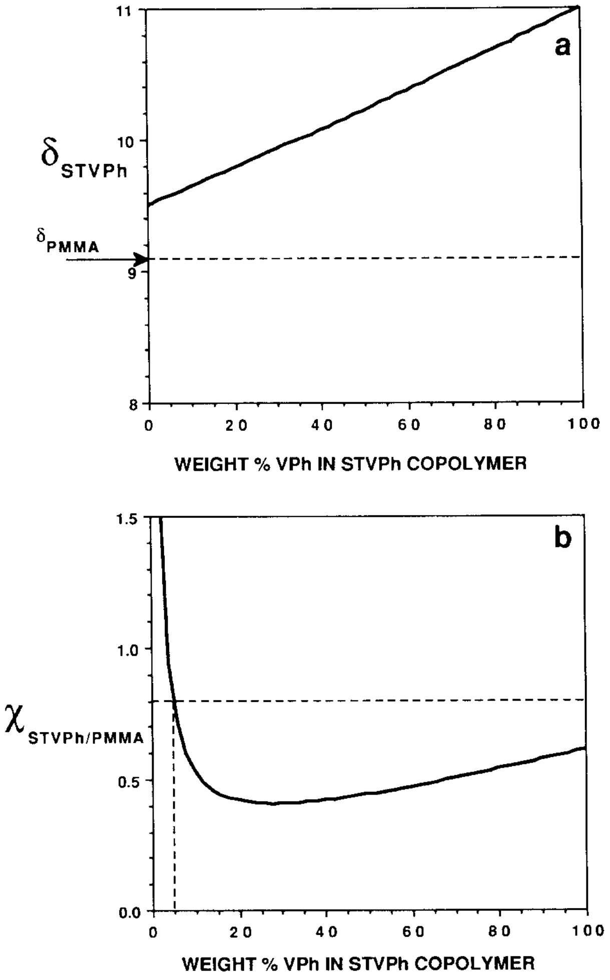


Figure 19 (a) A plot of the calculated values of the solubility parameter for styrene-*co*-vinyl phenol (STVPh) copolymers as a function of vinyl phenol content. (b) Calculated values of χ for STVPh–poly(methyl methacrylate) (PMMA) blends

Consider now PVPh blends with polyethers where the strength of the potential intermolecular interactions are even greater. The interaction between the phenolic hydroxyl and ether oxygen groups is considerably stronger than that occurring between PVPh and the ester type carbonyls considered above. This is readily observed in the infrared spectrum from the shift of the hydrogen bonded phenolic hydroxyl stretching mode relative to the 'free' (non-hydrogen bonded) frequency. Frequency shifts of between 200–325 cm^{-1} are observed in the former, while typically only 100 cm^{-1} shifts are seen in the latter[35,50]. There is only a limited amount of experimental data pertaining to the phase behaviour of PVPh–polyether blends and for the purposes of this work we will restrict ourselves to the trends observed in the PVPh blends with poly(vinyl alkyl ethers). In a nutshell, PVPh is miscible at ambient temperature with poly(vinyl methyl ether) (PVME; $\delta = 8.5\,(\mathrm{cal\,cm^{-3}})^{0.5}$) and poly(vinyl ethyl ether) (PVEE; $\delta = 8.4$) but immiscible with poly(vinyl isobutyl ether) (PViBE; $\delta = 8.0$). *Figures 20a* and *20b* show the calculated solubility parameters for linear poly(vinyl alkyl ethers) as a function of methylene groups in the polymer repeat together with the estimate of χ for the blends with PVPh. In this case χ_{Crit} is at least 1.2 because both PVPh blends with PVME and PVEE are miscible which corresponds to an upper limit in the non-hydrogen bonded solubility parameter difference, $\Delta\delta$, of about 2.5 $(\mathrm{cal\,cm^{-3}})^{0.5}$ (*Figure 3*).

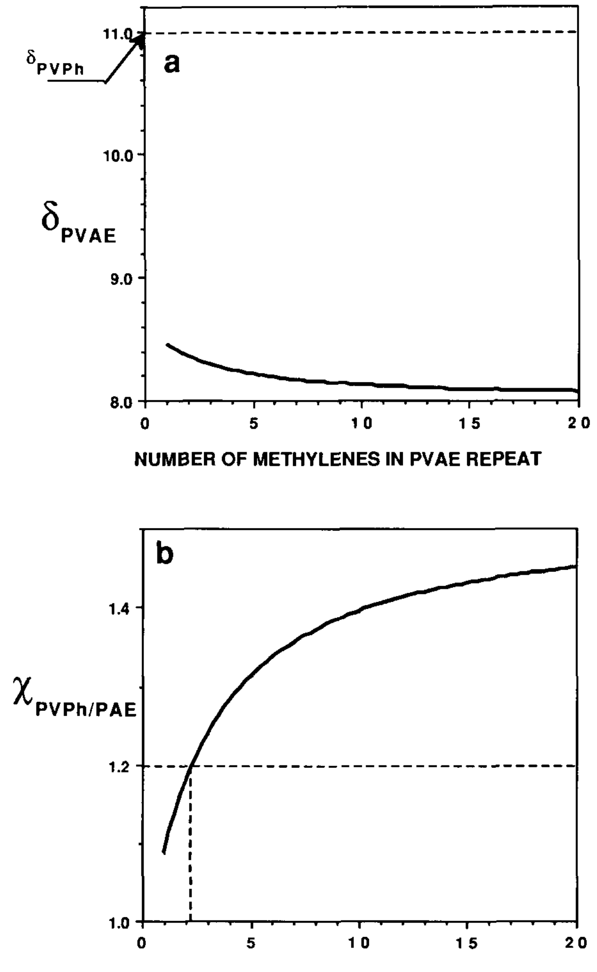


Figure 20 (a) A plot of the calculated values of the solubility parameter for poly(vinyl alkyl ether) (PVAE) polymers as a function of the number of methylene groups in the chemical repeat. (b) Calculated values of χ for PVPh–PVAE blends

Our final example before we summarize this section concerns blends of PVPh with poly(2-vinyl pyridine) (PVPy). Solutions of these two polymers dissolved in a common solvent (e.g. THF) immediately precipitate when mixed together, forming what is best described as a 1:1 polymer complex[54]. The interaction between the phenolic hydroxyl and pyridine nitrogen groups is much stronger than that occurring between PVPh and the ether oxygens, and is reflected in the very large shift ($\sim 500\,\mathrm{cm}^{-1}$) of the hydrogen bonded phenolic hydroxyl stretching mode relative to the 'free' (non-hydrogen bonded) frequency. Here we have the unusual case of a polymer blend of two homopolymers in which there are very strong favourable intermolecular interactions but where the calculated non-hydrogen bonded solubility parameters are almost identical ($\delta = 11.0$ and 10.9 $(\mathrm{cal\,cm^{-3}})^{0.5}$, respectively). For the purposes of a predictive rule of thumb for the molecular mixing of polymers this blend represents the epitome of factors favouring miscibility because we simultaneously have a large favourable hydrogen bonding term (equation 1), and a negligible contribution from the unfavourable $\chi\Phi_A\Phi_B$ term.

To summarize for the case of polymer blend systems in which there are relatively strong favourable intermolecular interactions:

(1) The presence of relatively strong favourable intermolecular interactions (hydrogen bonds) between the blend components (i.e. those with dissociation energies of between about 3 and 7 $\mathrm{kcal\,mol^{-1}}$) further increases the probability of finding miscible blends of polymers compared to those that are purely dispersive in nature (case 1) or are restricted to dipole–dipole or relatively weak hydrogen bonds (case 2).

(2) The favourable intermolecular interactions again serve to counteract the unfavourable contribution to the free energy of mixing expressed in the χ parameter. A larger value of χ_{Crit}, equivalent to upper limit of about 3 $(\mathrm{cal\,cm^{-3}})^{0.5}$ can be tolerated in the non-hydrogen bonded solubility parameter difference of the two polymers, $\Delta\delta$.

(3) The main principle for predicting polymer miscibility still remains the matching of the non-hydrogen bonded solubility parameters. However, now the errors involved in the calculation of non-hydrogen polymer solubility parameters are less important because there is a much wider range to work with.

CONCLUSIONS

We set out to provide a simple set of guidelines to qualitatively predict trends in polymer–polymer miscibility. This we believe we have accomplished using the ideas we have developed recently and which are embodied in equation (1). It is axiomatic in our scheme that the closer the match of the two non-hydrogen bonded solubility parameters and the greater the relative strength of the potential intermolecular interactions present between the polymeric components of the blend, the greater the probability of miscibility. This is summarized in *Table 8* in terms of critical values of χ and the upper limits of the non-hydrogen bonded solubility parameter difference, $\Delta\delta$. We do not expect such a rudimentary

Table 8 Summary of the critical values of χ and $\Delta\delta$

Intermolecular interactions involved	Polymer blend examples	Critical value of the interaction parameter χ_{Crit}	Critical value of the solubility parameter difference $\Delta\delta$ (cal cm^{-3})$^{0.5}$
Dispersive forces only	Polyisoprene–Poly(vinyl ethylene)	<0.002	<0.1
Dipole–dipole interactions	Poly(methyl methacrylate)–Poly(ethylene oxide)	0.002–0.02	0.1–0.5
Weak hydrogen bonds	Poly(vinyl chloride)–Polycaprolactone	0.02–0.2	0.5–1.0
Moderate hydrogen bonds	Poly(vinyl phenol)–Poly(vinyl acetate)	0.2–1.0	1.0–2.5
Strong hydrogen bonds	Poly(vinyl phenol)–Poly(vinyl methyl ether)	1.0–1.5	2.5–3.0

approach to predict all known miscible polymer blends. One obvious limitation is that the magnitude of the $\Delta G_H/RT$ contribution decreases with increasing concentration of inert diluent and this is not accounted for in this simple approach. We are confident that application of the guidelines presented in this paper can significantly reduce the time used in scouting for potential miscible polymer systems.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge the financial support of the National Science Foundation, Polymers Program, the Shell Foundation, E. I. du Pont de Nemours Company and ARCO Chemical Company.

REFERENCES

1 Coleman, M. M., Skrovanek, D. J., Hu, J. and Painter, P. C. *Macromolecules* 1988, **21**, 59
2 Painter, P. C., Park, Y. and Coleman, M. M. *Macromolecules* 1988, **21**, 66
3 Painter, P. C., Park, Y. and Coleman, M. M. *Macromolecules* 1989, **22**, 570
4 Painter, P. C., Park, Y. and Coleman, M. M. *Macromolecules* 1989, **22**, 580
5 Coleman, M. M., Lichkus, A. M. and Painter, P. C. *Macromolecules* 1989, **22**, 586
6 Coleman, M. M., Hu, J., Park, Y. and Painter, P. C. *Polymer* 1988, **29**, 1659
7 Coleman, M. M., Lee, J. Y., Serman, C. J., Wang, Z. and Painter, P. C. *Polymer* 1989, **30**, 1298
8 Hu, J., Painter, P. C., Coleman, M. M. and Krizan, T. D. *J. Polym. Sci., Phys. Edn.* 1990, **28**, 149
9 Serman, C. J., Xu, Y., Painter, P. C. and Coleman, M. M. *Macromolecules* 1989, **22**, 2015
10 Trask, C. A. and Roland, C. M. *Macromolecules* 1989, **22**, 256
11 Kraus, S. *J. Macromol. Sci., Revs. Macromol. Chem.* 1972, **C7(2)**, 251
12 Kambour, R. P., Bender, J. T. and Bopp, R. C. *Macromolecules* 1983, **16**, 753
13 ten Brinke, G., Karasz, F. E. and MacKnight, W. J. *Macromolecules* 1983, **16**, 824
14 Paul, D. R. and Barlow, J. W. *Polymer* 1984, **25**, 487
15 Hildebrand, J. and Scott, R. 'The Solubility of Non-Electrolytes', 3rd edn., Reinhold, New York (1949)
16 Burrell, H. in 'Polymer Handbook', 2nd edn., (Eds J. Brandrup and E. H. Immergut), Wiley-Interscience, New York, 1975
17 van Krevelen, P. W. 'Properties of Polymers', Elsevier, Amsterdam 1972, chapter IV, p. 135
18 Hoy, K. J. *J. Paint Technol.* 1970, **42**, 76
19 Small, P. A. *J. Appl. Chem.* 1953, **3**, 71
20 Martuscelli, E., Pracella, M. and Yue, W. P. *Polymer* 1984, **25**, 1097
21 Daubert, T. E. and Danner, R. P. 'Data Compilation: Tables of Properties of Pure Compounds', American Institute of Chemical Engineering, New York, 1989
22 Serman, C. J. *PhD Thesis*, The Pennsylvania State University, 1989
23 Moler, C., Herskovitz, S., Little, J. and Bangert, S. 'MATLAB User's Guide', The MathWorks, Inc., Sherborn, MA 01770, USA (1987)
24 Boyer, R. F. and Spencer, R. F. *J. Appl. Phys.* 1944, **15**, 398
25 Simha, R. and Boyer, R. F. *J. Chem. Phys.* 1962, **37**, 1008
26 Scott, R. L. *J. Polym. Sci.* 1952, **9**, 423
27 Patterson, D. and Robard, A. *Macromolecules* 1978, **11**, 690
28 Martuscelli, E., Silvestre, C. and Gismondi, G. *Makromol. Chem.* 1983, **186**, 2161
29 Bank, M., Leffingwell, J. and Thies, C. *Macromolecules* 1971, **4**, 44; Bank, N., Leffingwell, J. and Thies, C. *J. Polym. Sci.* 1972, **10**, 1097; Nishi, T. and Kwei, T. K. *Polymer* 1975, **16**, 285
30 Stoelting, J., Karasz, F. E. and MacKnight, W. J. *Polym. Eng. Sci.* 1970, **10**, 133; Schultz, A. R. and Gendron, B. M. *J. Appl. Polym. Sci.* 1972, **16**, 461
31 Kimura, M., Porter, R. S. and Salee, G. *J. Polym. Sci. Phys. Edn.* 1983, **21**, 367
32 Kim, J. H., Barlow, J. W. and Paul, D. R. *J. Polym. Sci. Phys. Edn.*, 1989, **27**, 2211
33 Varnel, D. F. *MS Thesis*, The Pennsylvania State University, 1980
34 Zakrzewski, G. A. *Polymer* 1973, **14**, 347
35 Coleman, M. M. and Painter, P. C. *Appl. Spectrosc. Revs.* 1984, **20**, 255
36 Vorenkamp, E. J. and Challa, G. *Polymer* 1988, **29**, 86
37 Woo, E. M., Barlow, J. W. and Paul, D. R. *Polymer* 1985, **26**, 763
38 Walsh, D. J. and McKeown, J. G. *Polymer* 1980, **21**, 1330
39 Walsh, D. J. and Cheng, G. L. *Polymer* 1984, **25**, 495
40 Rellick, G. S. and Runt, J. *J. Polym. Sci. Phys. Edn.* 1986, **24**, 279
41 Cruz-Ramos, C. A. and Paul, D. R. *Macromolecules* 1989, **22**, 1289
42 Shiomi, T., Karasz, F. E. and MacKnight, W. J. *Macromolecules* 1986, **19**, 2274
43 Bhagwager, D. E., Serman, C. J., Painter, P. C. and Coleman, M. M. *Macromolecules* 1989, **22**, 4654
44 Cruz, C. A., Paul, D. R. and Barlow, J. W. *J. Appl. Polym. Sci.* 1979, **23**, 589
45 Fernandes, A., Barlow, J. W. and Paul, D. R. *Polymer* 1986, **27**, 1799
46 Coleman, M. M., Varnell, D. F. and Runt, J. P. in 'Contemporary Topics in Polymer Science', Vol. 4 (Eds W. J. Bailey and T. Tsurata), Plenum, New York (1983)
47 Varnell, D. F., Runt, J. P. and Coleman, M. M. *Macromolecules* 1981, **14**, 1350
48 Harris, J. E., Goh, S. H., Paul, D. R. and Barlow, J. W. *J. Appl. Polym. Sci.* 1982, **27**, 839
49 Coleman, M. M. and Moskala, E. J. *Polymer* 1983, **24**, 251
50 Moskala, E. J., Varnell, D. F. and Coleman, M. M. *Polymer* 1985, **26**, 228
51 Moskala, E. J., Howe, S. E., Painter, P. C. and Coleman, M. M. *Macromolecules* 1984, **17**, 1671
52 Moskala, E. J., Runt, J. P. and Coleman, M. M. in 'Multicomponent Polymer Materials', (Eds D. R. Paul and L. H. Sperling), Ch. 5, Advances in Chemistry Series, **211**, ACS, Washington DC (1986)
53 Chen, C-T. and Morawetz, H. *Macromolecules* 1989, **22**, 159
54 Lee, J. Y., Moskala, E. J., Painter, P. C. and Coleman, M. M. *Appl. Spectrosc.* 1986, **40**, 991