

'boundaries' will cause addition of chains in a more irregular, less parallel fashion than in the early stages.

It has not been possible so far to examine the spectrum of 'basic' particles, nor does the work suggest the reason why the production of primary particles ceases. Nevertheless, this comparatively simple experiment in

Raman spectroscopy suggests an interesting picture for the build-up of PVC particles.

REFERENCES

- 1 Cotman, J. D., Gonzalez, M. F. and Claver, G. C. *J. Polym. Sci. (A-1)* 1967, **5**, 1137
- 2 Robinson, M. E. R., Bower, D. I. and Maddams, W. F. *Polymer* 1978, **19**, 773
- 3 Robinson, M. E. R., Bower, D. I. and Maddams, W. F. *Polymer* 1976, **17**, 355
- 4 Krimm, S. *J. Polym. Sci. (C)* 1964, **7**, 3
- 5 Baruya, A., Booth, A. D., Maddams, W. F., Grasselli, J. G. and Hazle, M. A. S. *J. Polym. Sci. (Polym. Lett. Edn)* 1976, **14**, 329
- 6 Pohl, von H. U. and Hummel, D. O. *Makromol. Chem.* 1968, **113**, 190, 203
- 7 Shipman, J. J., Folt, V. L. and Krimm, S. *Spectrochim. Acta* 1962, **18**, 1603

Prediction of swelling of polymers in 2 and 3 component solvent mixtures

Z. Rigbi

Department of Chemical Engineering, Technion-Israel Institute of Technology, Haifa, Israel
(Received 22 March 1978; revised 2 May 1978)

Froehling *et al.*¹ have shown how the vector concept of Hildebrand's solubility parameter may be used to predict the proportions in which two solvents should be mixed in order to obtain maximum swelling of a given polymer. In the present Note, the concept is formalized and extended to mixtures of three solvents. As methods of vector algebra will be employed to this end, they will first be applied to Froehling's problem, and a simple formula stated for the composition of the mixture of two solvents, or of a solvent and non-solvent, which will give maximum swelling.

Hansen² considered the solubility parameter to be the resultant of three components due to dispersion forces, to polar forces and to forces arising out of hydrogen bonding. The three components are not arithmetically additive, but lie as vectors along orthogonal axes. The end-point of the radius vector thus represents Hildebrand's solubility parameter in the three-component space. Using the value of the components given by Hansen² and by Koenhen and Smolders³, and the equation:

$$(\delta_i)_m = \phi_1(\delta_i)_1 + \phi_2(\delta_i)_2 \quad i = p, d, h \quad (1)$$

Froehling calculated the components of the solubility parameter of a mixture of two solvents.

In studying the swelling of polymers in such mixtures, Froehling compared

the proportion of solvent mixture imbibed by the polymer with the distance Δ between the points in space representing the solubility parameter of the polymer (such as P in *Figure 1*), and the point representing the solubility parameter of the mixture such as X . Comparison of the two showed that, in general, the composition of a mixture which gives a maximum imbibition corresponds to a minimum Δ . This situation exists when the mixture is defined by M such that PM and AB are perpendicular.

The notation which we shall use in the following makes for simplicity and ease of writing. Instead of the subscripts d , p and h , we shall use 1, 2 and 3. The solubility parameters will be referred to by the lower case letter corresponding to the solvent component in the mixture, or the mixture itself, or the polymer. Thus a_1 is the dispersion component of the solubility parameter of solvent A , m_2 is the polar

component of the parameter of mixture M , and p_3 is the hydrogen bonding component of the parameter for polymer P . Values for these components may be found in refs 2 and 3.

For our present purposes, use is made of Froehling's *Figure 1* with the δ_d , δ_p (1 and 2 in our notation) axes rotated by a right angle. Since PM and AB are orthogonal, the scalar or dot product of the vectors lying along the lines must vanish and therefore (see *Figure 1*):

$$\begin{aligned} (m_1 - p_1)(b_1 - a_1) + \\ (m_2 - p_2)(b_2 - a_2) + \\ (m_3 - p_3)(b_3 - a_3) = 0 \quad (2) \end{aligned}$$

For the line AB , we have:

$$\frac{m_1 - a_1}{b_1 - a_1} = \frac{m_2 - a_2}{b_2 - a_2} = \frac{m_3 - a_3}{b_3 - a_3} \quad (3)$$

We may combine (2) with (3) and simplify to obtain the expressions:

$$m_1 = a_1 + \frac{(p_1 - a_1)(b_1 - a_1) + (p_2 - a_2)(b_2 - a_2) + (p_3 - a_3)(b_3 - a_3)}{(b_1 - a_1)^2 + (b_2 - a_2)^2 + (b_3 - a_3)^2} (b_1 - a_1)$$

and substituting in (1), we have

$$\Phi_a = 1 - \frac{(p_1 - a_1)(b_1 - a_1) + (p_2 - a_2)(b_2 - a_2) + (p_3 - a_3)(b_3 - a_3)}{(b_1 - a_1)^2 + (b_2 - a_2)^2 + (b_3 - a_3)^2} = 1 - \Phi_b \quad (4)$$

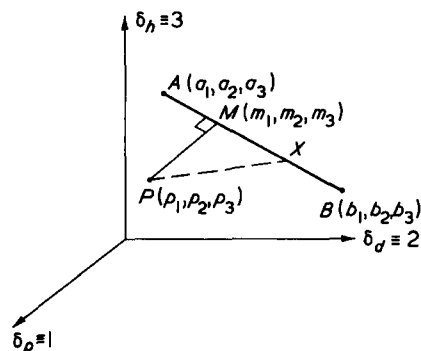


Figure 1 Spatial representation of 2 component solvent mixture - polymer interaction

where Φ_a is the volume fraction of solvent A in the mixture M of A and B . Strict attention must be paid to the signs of these differences.

Three component mixtures

Extending these considerations to mixtures of three non-interacting solvents or non-solvents, see Figure 2, we note that the vectors representing the lines joining M to each of the vertices of the triangle A, B and C must be coplanar, while simultaneously PM must be orthogonal to any two sides of the triangle. (The orthogonality to the third side is accounted for automatically. In other works $MA \cdot (\overline{MB} \times \overline{MC}) = 0$. $PM \cdot AB = 0$ and $PM \cdot BC = 0$. These may be manipulated into the following simple forms:

$$\begin{vmatrix} m_1 & m_1 & m_1 \\ b_1 & b_1 & b_1 \\ c_1 & c_2 & c_3 \end{vmatrix} + \begin{vmatrix} a_1 & a_2 & a_3 \\ m_1 & m_2 & m_3 \\ c_1 & c_2 & c_3 \end{vmatrix} + \begin{vmatrix} a_1 & a_2 & a_3 \\ b_1 & b_2 & b_3 \\ m_1 & m_2 & m_3 \end{vmatrix} = \begin{vmatrix} a_1 & a_2 & a_3 \\ b_1 & b_2 & b_3 \\ c_1 & c_2 & c_3 \end{vmatrix} \quad (5)$$

$$m_1(a_1 - b_1) + m_2(a_2 - b_2) + m_3(a_3 - b_3) =$$

(6)

$$m_1(a_1 - c_1) + m_2(a_2 - c_2) + m_3(a_3 - c_3) =$$

$$p_1(a_1 - c_1) + p_2(a_2 - c_2) + p_3(a_3 - c_3) \quad (7)$$

The length Δ of the line PM is an inverse measure of the interaction between the solvent mixture and the polymer, and is easily calculated.

For calculations by hand or pocket calculator, equation (5) must be expanded. m_1, m_2 and m_3 for the 'best' mixed solvent having been determined, we may now proceed to determine ϕ_a, ϕ_b and $\phi_c (= 1 - \phi_a - \phi_b)$ from*:

$$\begin{aligned} \phi_a a_1 + (\phi_b + \phi_c)(\phi_b b_1 + \phi_c c_1) &= m_1 \\ \phi_a a_2 + (\phi_b + \phi_c)(\phi_b b_2 + \phi_c c_2) &= m_2 \\ \phi_a a_3 + (\phi_b + \phi_c)(\phi_b b_3 + \phi_c c_3) &= m_3 \end{aligned} \quad (8)$$

RESULTS AND DISCUSSIONS

Table 1 presents data and calculated results for mixtures of optimum solubility (or swelling) towards specified polymers. For the purpose of this paper, optimum solubility implies merely the shortest distance between P and the plane of ABC ; it does not mean that there is real solubility for the given mixture, or that solubility is not equally observed with other proportions of the individual solvents. Furthermore, no suggestion is made that solutions of the polymers in the solvent mixture will have a low viscosity; on the contrary, there is good reason to believe that the viscosity of such solutions is very nearly the maximum attainable.

Particular attention must be paid to two points in interpreting the results. In the first place, there is considerable uncertainty in the values of solubility parameter components. Where the polar and dispersion components of two solvents are very close together, a small uncertainty in the value of the third component may cause very big differences in the values of m_1, m_2, m_3 and Δ calculated. Secondly, the individual

* An APL program which has been written by the author's associates, Mr B. Grinbaum and Mr G. Friedman, prints out the results as:

```
a1 a2 a3
b1 b2 b3
c1 c2 c3
p1 p2 p3  Δ m1 m2 m3 φa φb φc
```

The author will be pleased to save readers with access to APL both time and trouble by supplying this program on application.

solvents may interact, in which case the interpretation given does not hold. Froehling presents such an anomaly when he considers the mixture butyl acetate and nitromethane acting on PVC.

Inspecting case 1 in Table 1, we note that the optimum solvent ratios for toluene/hexane/chlorobenzene contains toluene in a *negative* quantity. From a geometrical point of view, this merely implies that M in on the opposite side of the line connecting the points for hexane and chlorobenzene as compared with the point for toluene. However, this can be given an interesting physical explanation when comparison is made with cases 4, 5 and 6. It appears that chlorobenzene is a considerably poorer solvent for polybutadiene than either toluene or hexane, and its addition reduces the solubility of a mixture of toluene and hexane towards polybutadiene (case 2).

Proceeding to PAN, and considering Δ as an (inverse) indicator of solubility, it will be seen that of the cases studied, mix 10 has the smallest value of Δ amongst the 3 component mixes. It would seem that a volume fraction of 0.015 n-propanol would not be very important, but if mix 10 is compared with mix 8 (the mixes being not very different in their main components) it will be seen that this very small quantity of alcohol increases solubility considerably. On the other hand, a small quantity (1.3 vol %) of n-butyl acetate increases the solubility only slightly (mix No 11).

Of the other combinations calculated, combination 17 must be taken with very great caution. Hansen² makes no claim for any accuracy whatsoever, and there is much doubt if the propanol/water mixture and trichlorethylene are mutually soluble.

PET appears to be soluble in several solvent combinations with little advantage of one over another.

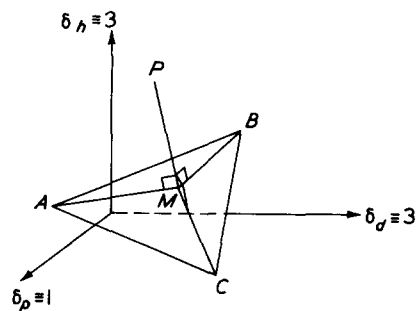


Figure 2 Spatial representation of 3 component solvent mixture - polymer interaction

Table 1 Calculated polymer/solvent mixture interactions: solvent fractions for minimum Δ . (This Table lists the polymers, 3, 2 and single component solvent mixtures with their solubility parameter components in the order $\delta_d, \delta_p, \delta_h$, the volume fractions ϕ corresponding to the minimum value of Δ and the Δ value. All solubility parameters in $J^{1/2}/cm^{3/2}$)

Case no.	Polymer	Solvents ^b	δ_d	δ_p	δ_h	Solvent volume fraction	Δ ($J^{1/2}/cm^{3/2}$)
1	Polybutadiene ^a 17.00 0 1.02	Toluene	18.05	1.4	2.0	-0.123	
		Hexane	14.78	0	0	1.068	0.522
		Chlorobenzene	19.00	4.3	2.0	0.055	
2		Toluene				0.546	0.884
		Hexane				0.454	
3		Toluene				1.561	0.168
		Chlorobenzene				-0.561	
4		Toluene				1.000	2.057
5		Hexane				1.000	2.399
6		Chlorobenzene				1.000	4.851
7	Polyacrylonitrile ^a 18.24 16.17 6.75	Ethyl acetate	15.23	5.3	9.2	0.022	
		Nitromethane	15.76	18.8	5.1	0.819	2.845
		Chlorobenzene	19.00	4.3	2.0	0.159	
8		n-Butyl acetate	15.70	3.7	6.3	0.013	
		Nitromethane				0.823	2.997
9		Chlorobenzene				0.164	
		n-Propanol	14.90	6.7	17.4	0.015	
10		Nitromethane				0.801	2.397
		Chlorobenzene				0.184	
		n-Butyl lactate	17.60	6.5	10.2	0.023	
11		Nitromethane				0.816	2.505
		Chlorobenzene				0.161	
12		Dimethylformamide	17.44	13.7	11.2	1.218	
		Nitromethane				0.024	1.848
13		Chlorobenzene				-0.242	
		Nitromethane				0.819	2.849
14		Chlorobenzene				0.180	
		Dimethyl formamide				0.417	2.069
15		Nitromethane				0.583	
		Dimethylformamide				1.000	5.191
16	Nylon-66 ^a 18.54 5.12 12.28	Nitromethane				1.000	5.518
		n-Propanol	14.90	6.7	17.4	0.040	
17		Water ^c	12.28	81.3	34.2	0.072	1.760
		Trichlorethylene	17.97	3.1	5.3	0.888	
		n-Propanol				0.551	1.760
18	Poly(methyl methacrylate) ^b 15.74 8.2 6.7	Trichlorethylene				0.449	
		Chloroform	17.70	3.1	5.7	0.000	
19		Benzene	18.32	1.0	2.0	0.088	0.397
		MEK	15.70	9.0	5.1	0.912	
20		MEK				1.000	1.838
		Benzene				1.000	8.953
21		Chloroform				1.000	5.668
		Chloroform	17.70	3.1	5.7	0.075	
22	PVC ^a 18.73 10.0 3.1	Tetrahydrofuran	16.82	5.7	8.0	3.400	0.426
		Butyl acetate	15.70	3.9	6.3	-2.475	
23		Chloroform	17.70	3.1	5.7	0.567	3.038
		Nitromethane	15.76	18.8	5.1	0.433	
24		Nitromethane	15.76	18.8	5.1	0.476	1.846
		Toluene	18.05	1.4	2.0	0.524	
25		Nitromethane	15.76	18.8	5.1	0.099	3.480
		MEK	15.90	9.0	5.1	0.990	
26		Tetrahydrofuran				1.000	6.800
		Nitromethane				1.000	9.510
27		MEK				1.000	5.635
28	Poly(ethylene terephthalate) 19.52 3.5 8.6	Chlorobenzene	19.00	4.3	2.0	0.125	
		Toluene	18.05	1.4	2.0	0.441	4.366
		Cyclohexanone	17.70	8.4	5.1	0.434	
29		Chlorobenzene				0.081	
		Toluene				0.681	3.232
30		Dimethylformamide	17.44	13.7	11.3	0.238	
		Chlorobenzene				0.035	
31		Toluene				0.301	3.183
		Tetrahydrofuran				0.664	
32		Chlorobenzene				0.099	
		Toluene				0.703	3.314
		Dimethyl sulphoxide	18.42	16.4	10.2	0.198	

^a Values from Koenhen and Smolders³ converted to SI units; ^b values from Hansen² converted to SI units; ^c note Hansen's² statement: 'The placement of water at 7.0, 8.0 and 20.9 ($cal^{1/2}/cm^{3/2}$) is perhaps more symbolic than reliable'. He later uses the figures given, presumably after recalculation

It must be noted that nothing is mentioned about the proportions of the components of the liquids *absorbed* by crosslinked or insoluble polymers which may be very different from that in the ambient mixture. Some reservations must also be made concerning the use of relative weight increases in view of the different densities of the pure materials involved; it is necessary, for a common basis, to express all

results as relative volume increase.

CONCLUSIONS

A method for the calculation of most efficient mixtures of three, two or single component solvents for resins has been developed. This method, because of its rapidity using modern computers, is capable of screening many

combinations. The best of these may then be tested experimentally.

REFERENCES

- 1 Froehling, P. E., Koehnen, D. M., Bantjes, A. and Smolders, G. A. *Polymer* 1976, 17, 835
- 2 Hansen, C. M. *J. Paint Technol.* 1967, 39, 505
- 3 Koehnen, D. M. and Smolders, C. A. *J. Appl. Polym. Sci.* 1975, 19, 1163

Letters

The microstructure of polychloroprene determined by ^{13}C -nuclear magnetic resonance

The properties of polydienes are dependent upon the configurations of the diene units within the chains, the distribution of these units along the chain and upon the relative orientations of the units, i.e. whether they are in head-head, head-tail or tail-tail arrangements. ^{13}C nuclear magnetic resonance (^{13}C n.m.r.) spectroscopy can be used not only to distinguish between polybutadienes and polyisoprenes with regular microstructures¹ but also to determine the relative amounts and the distributions of diene units with different configurations within polymers of irregular microstructure²⁻¹². It has been shown also that for polyisoprenes, ^{13}C n.m.r. can be used to identify and measure the relative amounts of head-head, head-tail and tail-tail linkages involving 1,4- units^{11,12}.

For polychloroprenes, proton magnetic resonance spectroscopy can be used to detect head-head and tail-tail linkages between 1,4- units¹³ and also, if high field strengths are employed, to determine the relative amounts of *cis*-1,4- and *trans*-1,4- enchainment¹⁴. As yet, there have been no publications describing the use of ^{13}C n.m.r. to determine the microstructure of polychloroprenes, although the technique has been used to give some limited information regarding the microstructure of some chloroprene-methyl methacrylate copolymers¹⁵.

The Figure shows the methylene carbon resonances obtained at 20 MHz

(Varian CFT20 spectrometer) for a sample of polychloroprene prepared by bulk thermal polymerization under nitrogen at 25°C. The spectrum is the result of 30K pulses on a 10% w/v solution of the polymer in CDCl_3 with an acquisition time of 0.5 sec and a pulse width of 12 μsec (corresponding to a nuclear tip angle of $\sim 51^\circ$). There was no additional delay between pulses. 4096 data points were used in the accumulation of the spectrum over a spectral width of 4000 Hz, and the usual 'white noise' proton decoupling procedure was employed. The relative areas of the peaks in the spectrum were not affected by small changes in

pulse width and acquisition time and therefore the areas can be expected to give reliable quantitative results.

The pattern of methylene resonances is very like that observed for free radically prepared polyisoprenes^{11,12} showing the presence of both *cis*- and *trans*-1,4- units and a mixture of head-head, head-tail and tail-tail linkages. (The absence of any characteristic olefinic methylene carbon resonances in the full spectrum indicates that this polymer contains no 1,2- or 3,4- units). By analogy with polyisoprene spectra, the following assignments may be made for the methylene resonances:

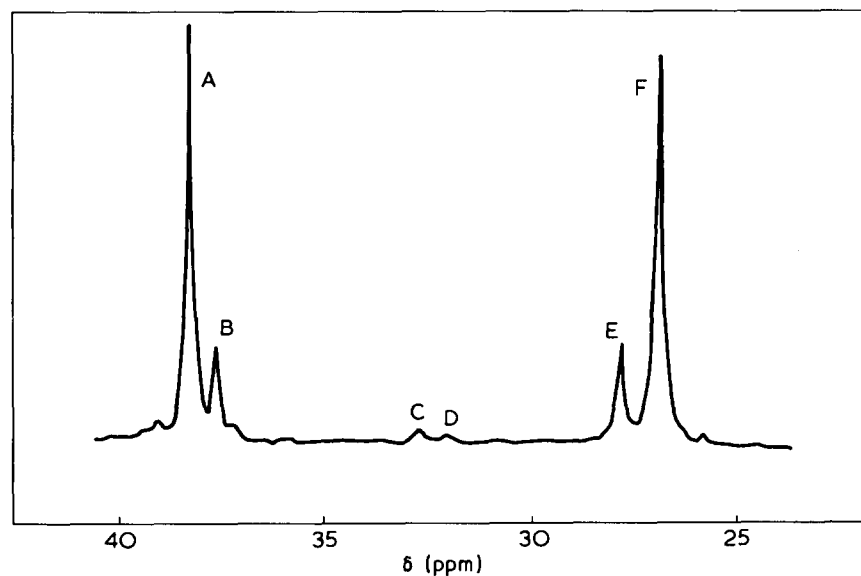


Figure 1 Methylene carbon resonances in polychloroprene (Peak assignments are given in the text)