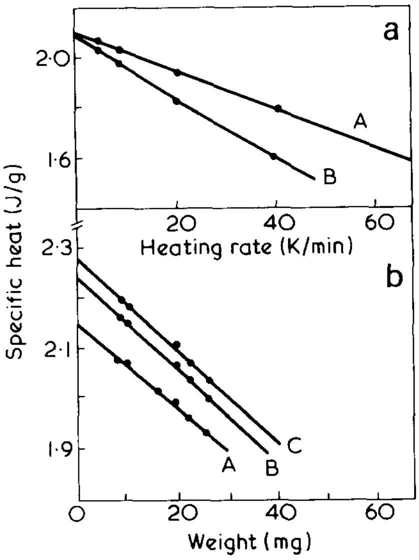

Figure 1 Dependence of the specific heat of PS 2 (a) on sample size A, 12 mg; B, 20 mg at 400K and (b) rate of heating. A, 430 K; B, 440 K ; C, 450 K

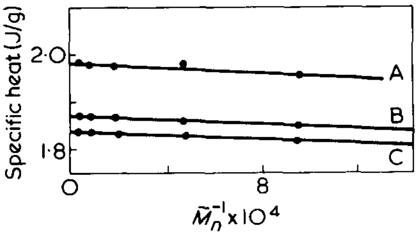

Figure 2 Molecular weight dependence of the specific heat of polystyrene. A, 420 K; B, 410 K; C, 400 K

polating to zero weight and zero rate were similar, and the two trends were consistent with thermal lags which increased with sample size and rate of heating. It was also consistent with the thermal lag correction applied previously[1] of 10K for a sample of 25 mg and a heating rate of 10 K/min.

The extrapolated specific heats, to zero weight and to zero rate, listed in *Table 1*, have been corrected for thermal lag. Both agree within the reproducibility of the determinations and so must represent the optimum values which can be measured by d.s.c. for this thermoanalytical standard. It would be meaningful to compare these values with those obtained by precision calorimetry in order to see if there are any systematic errors in d.s.c. measurement of specific heats.

Variations will be observed in the specific heats of different polystyrene samples. Accordingly monodisperse polystyrene samples (see ref 1, *Table 1*) were examined in the range 300–450K, in exactly the same manner as above. A small dependence of the specific heat on end-group concentration was observed, see *Figure 2*, consistent with equation (1) used previously[1]:

$$S = S_m + C_{p,e}/\bar{M}_n \qquad (1)$$

in which S and S_m are the specific heats observed and for the monomer repeat unit, and $C_{p,e}$ the average heat capacity for the end-groups. $C_{p,e}$ was found to be 20 ± 10 J/mol. $C_{p,e}$ must reflect the nature of the terminal units of the chain and so the mode of initiation, and will vary with polystyrene prepared by other methods.

CONCLUSIONS

Temperature corrections are required in measuring accurate specific heats of polymers by d.s.c., but conventionally these effects are masked by the limitations in accuracy of the determinations (±2%) imposed by the recorder used to detect the heat flow. A substantial improvement can be achieved if this is replaced by digital detection.

ACKNOWLEDGEMENT

The author wishes to thank Perkin–Elmer Ltd, Beaconsfield for the loan of equipment which made the measurements possible.

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Raman spectroscopic study of poly(vinyl chloride) particles

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(Received 19 April 1978)

INTRODUCTION

It has been shown[1] that when the growing chain of poly(vinyl chloride) attains a length of about 20 monomer units, it begins to precipitate from the liquid monomer. The chains agglomerate into so-called 'basic particles' which eventually reach about 200 Å in diameter. At this stage the basic particles form into clusters of diameter between 1000 and 2000 Å, called 'primary particles'. The polymer now begins to grow in a rather different way. No new primary particles appear, but the existing primaries slowly increase in size, not by further clustering, but by surface growth of successive polymer layers, rather like onion skins, until eventually polymerization ceases by monomer starvation. The change in the mode of growth of the polymer particles after the formation of primaries suggests that there may be an accompanying change in either the configuration or conformation of the polymer chain, or both, at this stage.

It is well known that both the configuration and conformation of a synthetic polymer chain may often be revealed by studying the vibrational spectrum. In vibrational studies of PVC, interest has centred particularly on the υ C–Cl (stretching) frequencies (see ref 2 and publications cited therein). By comparing the spectra of samples of different but known tacticity (i.e. of different molecular configuration) it has been possible to relate the appearance of υ C–Cl vibrations at particular frequencies to the presence of isotactic or syndiotactic sequences and, for the

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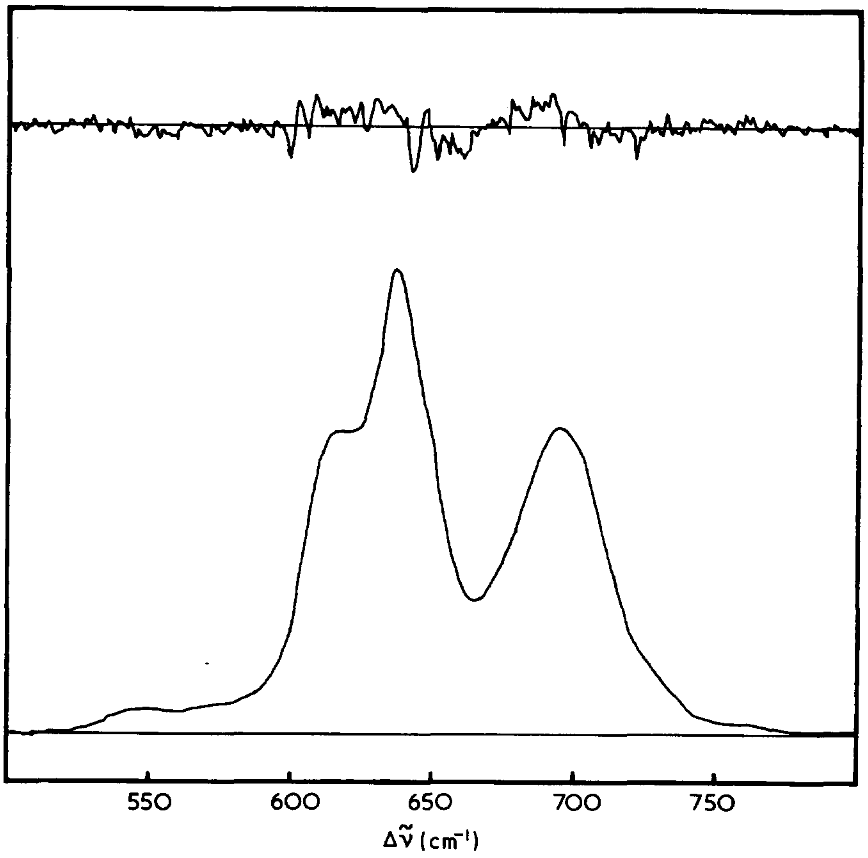

Figure 1 Difference between two spectra from the 36% conversion sample, run on different days illustrating the degree of reproducibility of the spectra. The full line corresponds to one of the spectra and the difference between the two spectra (X5) is shown above it

syndiotactic species, particular υC–Cl bands may be associated with the crystalline form[3]. In order to characterize particular conformational isomers, comparison has been made[4] between spectra of PVC and those of particular chlorocarbons which, because of their chemical structure, can each exist in only a small number of molecular conformations. These conformations are described, in the usual nomenclature for rotational isomers, by the two atoms (which may be either hydrogen or carbon) which are *trans*-substituents on the carbon atoms on either side of the C–Cl group in the polymer chain. As a result of this extensive background work, it is possible to establish in considerable detail the conformation and configuration of the PVC chain.

The C–Cl stretching modes of PVC may be observed in both the infra-red and the Raman spectrum. To record the infra-red spectrum it is necessary to convert the polymer sample, either by solution or by hot pressing, into a film. While this does not affect the molecular configuration, the effect on the molecular conformation may be substantial. It is possible by Raman spectroscopy, however, to examine the polymer particles just as they are produced. This should therefore be a powerful method of investigating the conformation and configuration of the polymer during the various stages of formation of PVC particles. In this study, we have halted the polymerization, by monomer starvation, at the primary particle formation stage, and then at various stages up to 50% conversion.

EXPERIMENTAL

Preparation of samples

Polymers were produced in a stainless steel autoclave. Approximately 2 l of vinyl chloride monomer was heated to 50°C in the autoclave under autogenous pressure in the presence of 0.05% di-(t-butyl cyclohexyl) peroxy dicarbonate initiator. It was known, from previous experiments, that after about 10 min under these conditions, at a conversion of about 2%, primary particles would have been produced with very little secondary growth. Thus, after 10 min the polymerization was terminated by rapid cooling, and the residual monomer was removed, leaving the polymer particles remaining attached to the autoclave walls, from which they were carefully brushed. They were subsequently freed from the final traces of residual monomer by heating in vacuum at about 40°C for 24 h. This sample was then used, with no further treatment, in the Raman study. Further samples were made, corresponding to 17%, 36% and 49% conversion, producing primaries of increasing diameter, up to about 6000 Å at 49% conversion.

It would have been interesting to study the Raman spectra of basic particles, but under these experimental conditions the degree of conversion was so low that the amount of polymer left on the vessel wall proved too small to collect, and we had therefore to be content with examining primaries and primaries with subsequent growth.

Method of obtaining spectra, and their analysis

The Raman spectra of the powders were obtained from samples held in the open ends of glass capillary tubes. The laser beam was focussed into the open end and the Raman light was collected at 90° to the direction of the incident beam and analysed by means of a Coderg PHO spectrometer. No analyser or polarization scrambler were used in the spectrometer, since the Raman-scattered light from a powder is randomly polarized. The removal of these optical components allowed spectra with a higher signal to noise ratio to be obtained than would have been possible otherwise. The slit width used was equivalent to ~2 cm^{-1}.

The output from the spectrometer over the range 500–800 cm^{-1}, which includes the υC–Cl frequencies, was recorded digitally at 1 cm^{-1} intervals as described in an earlier paper[2] and was subsequently processed in the following way. A straight line joining the mean values of the first eleven and last eleven data points was computed and this was used as a preliminary baseline for the data. The total area under the remaining spectrum was then scaled to a standard value and the spectrum was plotted on a computer controlled graph-plotter. In order to check the reproducibility of the spectrum of a particular sample two spectra were run on different days and compared by plotting them, in the way described, together with the difference between the two. *Figure 1* shows a typical pair of spectra and indicates that the reproducibility

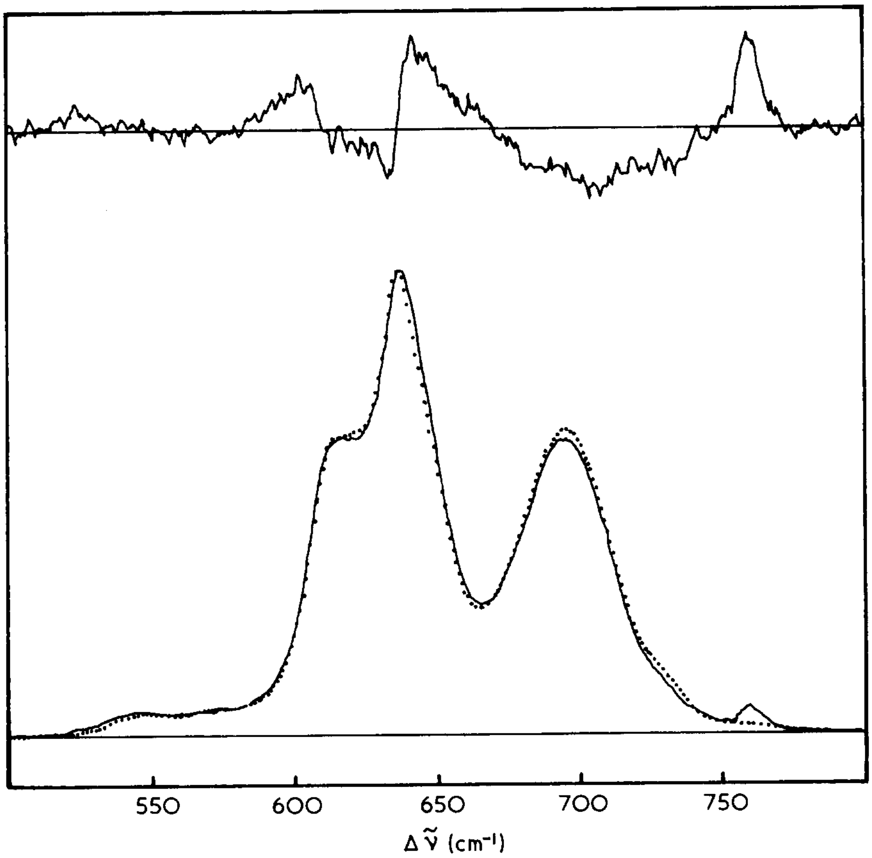

Figure 2 The spectrum of the 40% conversion sample (———) compared with that of the 2% conversion sample (· · ·). The difference between them (X5) is shown above the spectra

Table 1 Peak area as a percentage of total area in range 500–800 cm^{-1}

Peak position (cm^{-1})	% Conversion			
	2	17	36	49
545	2.8	2.6	2.6	2.9
571	0.4	0.8	0.7	0.6
609	7.1	6.9	6.5	6.2
615	5.5	5.8	5.9	6.5
623	9.8	9.8	9.6	9.1
634	9.2	8.6	9.8	11.2
638	11.8	11.5	10.8	10.3
647	13.8	15.3	13.7	12.7
682	8.7	8.7	9.4	9.1
694	17.7	17.1	17.6	17.7
706	12.5	12.4	13.0	13.5
728	0.2	0.4	0.3	0.4
760	0.6	0.0	0.0	0.0

was very good. (Each of the spectra compared is actually the average of two spectra run on the same day, as is every spectrum referred to below.)

The spectrum of each of the three powders corresponding to 17%, 36% and 49% conversion was then compared in a similar way with that of the powder corresponding to 2% conversion and the results of the comparison for the 49% conversion sample are shown in *Figure 2*. The differences between the spectra were small, but there appeared to be a systematic progression with increasing conversion. The most obvious changes were (i) a decrease in intensity near 608 and 638 cm^{-1}, (ii) an increase in intensity near 620 cm^{-1}, (iii) an increase in intensity of the broad peak at ~700 cm^{-1}, and (iv) a decrease in intensity of the small peak near 760 cm^{-1}, which almost disappeared by 17% conversion. The first three observations are consistent with a decrease of order, since the Raman spectrum of a highly ordered polymer prepared in a urea canal complex shows high intensity only near 608 and 638 cm^{-1} [3,5]. In an attempt to make a quantitative assessment of the differences between the spectra of the four samples we have fitted them with a set of overlapping Lorentzian peaks.

The method of fitting the spectra and the decision as to the number of peaks to be used were arrived at during an extensive study[2] of the νC–Cl regions of the Raman spectra of a large number of samples of PVC prepared in various ways. These included powders prepared in a urea canal complex and by more visual methods at various polymerization temperatures, together with sheets containing various concentrations of plasticizer. It was found necessary to use a total of nine major and four minor peaks to fit all the spectra in the region 500–800 cm^{-1}, although individual spectra could have been fitted well with fewer peaks. The positions of the peaks correspond closely to those found in the infra-red spectrum by Pohl and Hummel[6], with the exception of a peak at 608 cm^{-1}, and this discrepancy has been interpreted[3] as being due to correlation splitting in crystalline syndiotactic regions. In fitting the spectra a program was used which could fit four different spectra simultaneously and this has been used to fit the present four powder spectra.

In the fit, the positions and half intensity widths of corresponding peaks were constrained to be the same in the four spectra; only the peak heights were allowed to change from one spectrum to another. The positions, peak heights and half-widths of the minor peaks were fixed and were chosen by inspection, but those of the major peaks were determined by an iterative damped least squares fitting procedure. Three further constraints were imposed; the widths of the two peaks near 608 and 638 cm^{-1} were made identical, and their separation and the ratio of their intensities were fixed at the values 29.3 cm^{-1} and 1.67 derived from the fitting of the spectra of four powders of very different degrees of order, including the urea canal complex PVC. These peaks have been assigned[3], respectively, to the B_{3g} and A_g νC–Cl vibrations of crystalline syndiotactic PVC. In order to tidy up the fit of the minor peaks and to allow for the effects of this on neighbouring peaks a second fit to the four spectra was made in which the parameters of the peaks at 615, 623, 634 and 647 cm^{-1} were kept fixed at the values found in the first fit while those of the four minor peaks, the two crystal peaks and the peaks at 682, 694 and 706 cm^{-1} were refined by the least squares fitting procedure. An example of such a fitted spectrum is shown in *Figure 3* and the areas of the peaks for the four spectra are shown in *Table 1*. It should be noted that the fit is not very good in the region of 760 cm^{-1} because this region contains the tail of a peak at higher frequency which has not been allowed for.

We do not claim that the fits obtained are unique. It might be possible to obtain other fits which were as good, or almost as good, by changing the

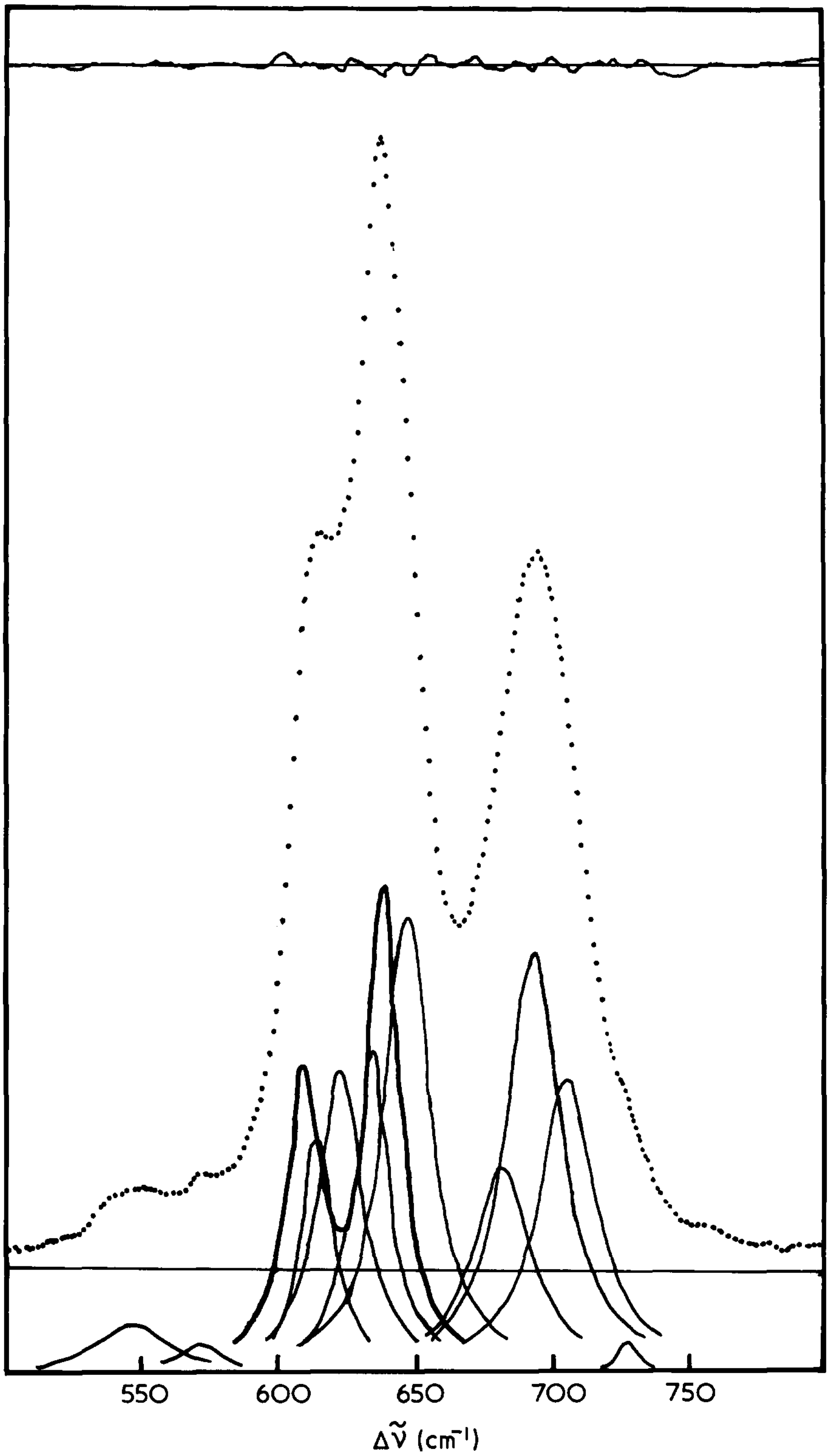

Figure 3 The spectrum of the 17% conversion sample with fitted Lorentzian peaks and linear background. The experimental intensities are shown (· · ·) and the deviation from the fit (X1) is shown near the top of the Figure

number of peaks or the constraints imposed upon them. The present fitting procedure does, however, permit a numerical comparison of the spectra of the four samples with each other and has the merit of being based on the experience of fitting a wider range of spectra than those involved in the present study.

DISCUSSION

The most obvious differences between spectra of different samples is the presence of the weak peak at 760 cm^{-1} in the spectrum of the 2% conversion sample which is almost completely absent from the spectra of samples of higher conversion. This feature is well clear of the main block of peaks in the spectra and the evidence for its presence does not depend upon any assumptions about peak separation. A peak at about this frequency in 3-chloro-2,2,4,4-tetramethyl pentane was assigned by Shipman *et al.*[7] to the νC–Cl mode in the S_{CC} chain conformation, in which the chlorine atom is *trans* to carbon atoms across both the adjacent C–C bonds and which involves a 'hairpin' bend in the molecular backbone. If this conformation is present in appreciable concentrations in the 2% conversion sample it strongly suggests that the chains may be folded in the early stages of formation of primary particles and that the tendency to folding is reduced at the later stages.

The other systematic change as polymerization proceeds, is a slight decrease in the crystallinity of the polymer; there appears, however, to be no significant change in the tacticity (see *Table 2*). The crystallinity is calculated as the sum of the fractional areas of the two crystal peaks at 609 and 638 cm^{-1}; the justification for this is discussed in ref 2. The absolute accuracy of the crystallinity values is probably no greater than ~ ±0.02, but because the spectra of the four powders were fitted simultaneously and because the spectra are so similar the changes of crystallinity from one sample to another are believed to be determined with rather greater precision than this. The method of estimating the syndiotactic content is also discussed in detail in ref 2, and similar remarks about absolute accuracy and precision in estimating differences between samples apply.

A qualitative description of the way in which a PVC particle grows may be suggested on the basis of these observations. At low degrees of conversion, folding of the chains allows syndiotactic segments to come together in crystalline register so that the centre of a basic particle consists of essentially parallel chains. As polymerization proceeds, further growth can take place on the existing nuclei without the need for as great a degree of chain folding. Eventually the accumulation of defects within the crystalline regions and at their

Table 2 Crystallinity and tacticity

Sample	Crystallinity*	Syndiotactic content*
2%	0.18_9	0.57_7
17%	0.18_4	0.58_7
36%	0.17_3	0.57_5
49%	0.16_5	0.56_8

* Evaluated as described in ref 2

'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.

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

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(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.

Hansen[2] 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 Hansen[2] and by Koenhen and Smolders[3], and the equation:

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

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 Froehlings *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*):

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

For the line AB, we have:

$$\frac{m_1 - a_1}{b_1 - l_1} = \frac{m_2 - a_2}{b_2 - a_2} = \frac{m_3 - a_3}{b_3 - a_3} \tag{3}$$

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

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

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