Small-angle scattering studies of PVC and PVC blends

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Small-angle X-ray and small-angle neutron scattering studies have been carried out on poly(vinyl chloride) (PVC), and blends of PVC with solution-chlorinated polyethylene (SCPE) and poly(butyl acrylate) (PBA). The PVC used was commercial (suspension-polymerized) or bulk-polymerized. The blends of PVC with PBA were prepared by solvent-casting and those with SCPE by *in situ* polymerization. PVC samples show shoulders in the scattering spectra, presumably due to crystallites, which persist even in samples which have been solvent cast. Blends of PVC with PBA also show a peak but at a higher '*d*' spacing. The blends with SCPE which were prepared by *in situ* polymerization show no such peak. This suggests that the method of preparation prevents the formation of crystallites. An increase in scattering of the PBA blends was observed when the samples were heated to the temperature of phase separation. Neutron scattering studies were also carried out using 2% deuterium labelled PVC in PVC and in the blends. In the PVC this showed chain dimensions in good agreement with predicted values. In the blends, dimensions of the same order were obtained, confirming a molecular dispersion of chains in the single phase, but there was an apparent reduction in the chain dimensions. This could be explained by a true reduction in dimensions or a non-zero A_2 value in the blends.

INTRODUCTION

Low-angle scattering techniques are often used in the characterization of polymer microstructures, and the theory has been reviewed by a number of authors[1-2].

The degree of crystallinity of poly(vinyl chloride), PVC), has been measured by these techniques and values between 0 and 20% have been found. Some small-angle X-ray (SAXS) studies have found no evidence for diffraction peaks[4]. Others have found Bragg peaks in the signal[5], said to originate from crystalline lamellae with a *d*-spacing of about 150 Å. This result depended on the history of the sample and especially its original method of polymerization[5]. In interpreting these results we need to bear in mind recent disagreements over the structure of amorphous polymers. Some authors have interpreted transmission electron microscopy (*TEM*) micrographs as showing paracrystalline nodules[6]. Others have interpreted the corresponding SAXS signal as due to 'frozen-in' thermal density fluctuations[7].

Preliminary investigations of PVC by small-angle neutron scattering (SANS) have found a broad peak in the scattering function suggesting some structure in the polymer[8].

Scattering techniques can also be used to examine polymer blends and polymer mixtures[2]. SAXS and SANS can be used to obtain information about the size of polymer domains in two-phase polymer systems. SANS can also be used to determine the dimensions of the polymer coils in one-phase polymer mixtures.

The intensity of small-angle X-ray scattering is proportional to the mean square fluctuation of the electron density. For a two-phase system this is given by:

$$\overline{(\rho-\bar{\rho})^2}=(\rho_2-\rho_1)^2\varphi_1\varphi_2 \qquad (1)$$

where φ_1 and φ_2 are the volume fractions of phases with densities ρ_1 and ρ_2 respectively, ρ being the actual density at any point. The total integral of the scattered intensity for an infinite slit is defined by:

$$\mathbf{\Omega}=\int_0^\infty sI(s)\mathrm{d}s \qquad (2)$$

where $s=2\sin\theta/\lambda$, θ is half the scattered angle, λ the wavelength, and I the absolute intensity. If the signal is measured relative to a standard, it is possible to obtain absolute intensity values.

One of the problems in assessing the results has been the correction of the SAXS signal for the finite slit used in the camera. Various procedures for normalization and correction of the signal for desmearing have been reported[9,10].

For neutron experiments a 'contrast factor', K. for a two-component mixture may be defined in a similar way to equation (1) as:

$$K=\left[\frac{\Sigma_1 b}{v_1}-\frac{\Sigma_2 b}{v_2}\right]^2 \qquad (3)$$

where $\Sigma_1 b$ and $\Sigma_2 b$ are the total neutron scattering lengths for the nuclei in components 1 and 2, respectively, and v_1 and v_2 are the specific volumes. To obtain an exact analogy with equation (1), K must be multiplied by a volume fraction, or, in the case of a solution of polymer chains, by the molecular weight $\bar{M}_w$ and concentration c.

If the forward scattering intensity $I(\theta=0)$ is given by the usual expression[2]:

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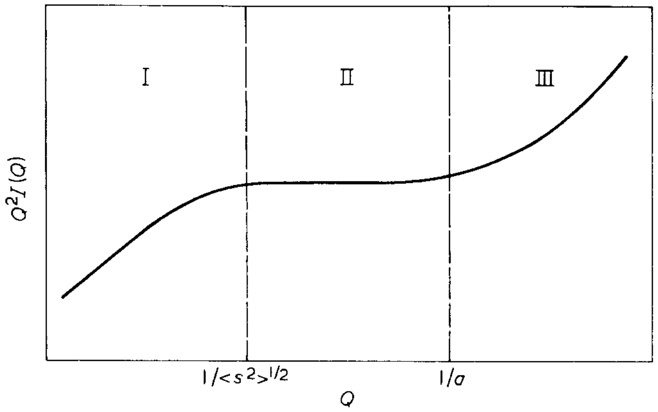

Figure 1 Plot of $Q^2I(Q)$ against Q for a Gaussian chain in solution showing the three main scattering regions

$$\frac{K^*c}{I(\theta=0)}=\frac{1}{\bar{M}_w}+2A_2c \tag{4}$$

and if (1) refers to a polymer segment and (2) to a solvent molecule in equation (3), then:

$$K^*=\frac{KN_a}{m} \tag{5}$$

where m is the mass of a monomer segment, c is the concentration in wt %, N_a is Avogadro's number and A_2 the virial coefficient.

Different scattering behaviour is observed in different regions of the scattering vector Q, given by:

$$Q=\frac{4\pi}{\lambda}\sin\frac{\theta}{2} \tag{6}$$

where λ is the neutron wavelength and θ the angle of scatter. For a Gaussian chain in solution the three main regions of interest are shown in *Figure 1*.

The regions are approximately divided into values of Q less than $1/\langle S^2\rangle^{1/2}$ where $\langle S^2\rangle^{1/2}$ is the root-mean-square radius of gyration; values of Q between $1/\langle S^2\rangle^{1/2}$ and $1/a$ where a is the persistence length; and values of Q greater than $1/a$.

Region I is the Guinier region where the scattering is dominated by the molecular size and:

$$\frac{K^*c}{I(Q)}=\frac{1}{\bar{M}_w}\left(1+\frac{Q^2\langle s^2\rangle}{3}\right)+2A_2c \tag{7}$$

Region II is the Kratky region. Here the Debye curve for a Gaussian polymer chain[1] becomes proportional to Q^{-2} so that a plot of $Q^2I(Q)$ against Q should reach a plateau, and

$$\frac{K^*c}{I(Q)}=\frac{1}{\bar{M}_w}\frac{Q^2\langle S^2\rangle}{2} \tag{8}$$

Deviations from Kratky behaviour have been observed for a number of amorphous polymers [in particular poly(methyl methacrylate)], and recent calculations have shown that these deviations are indications of local chain conformation detail, and not deviations from the randomness of the chain statistics[11].

In region III the local chain stiffness dominates the scattering. A simple Gaussian distribution of statistical segments of length L would give scattering as from a solution of rigid rods and:

$$\frac{K^*c}{I(Q)}=\frac{1}{\bar{M}_w}\frac{LQ}{\pi} \tag{9}$$

but here the simplicity of the model often breaks down in practice.

The particular advantages of the SANS method lie in the ease with which K can be manipulated by substituting deuterium for hydrogen in one component ($b_H=0.33\times10^{-12}$ cm but $b_D=0.66\times10^{-12}$ cm), and in the available wavelength range. By using 15 Å neutrons, much lower values of Q than are normally available in X-ray experiments can be obtained. Absolute normalization of the intensity at forward angles is therefore a more reliable process.

The phase diagram of PVC with solution-chlorinated polyethylene (SCPE) has been reported[12]. The two polymers are compatible and exhibit a lower critical solution temperature (*LCST*) at around 120°C. The two polymers, PVC and poly(butyl acrylate) (PBA), have also been reported as compatible[13]. 50/50 Mixtures are found to phase-separate at around 140°C. Here, we report the results of SAXS and SANS studies of PVC homopolymer, PVC/SCPE blends, and PVC/PBA blends.

EXPERIMENTAL

Preparation and purification of materials

Commercial poly(vinyl chloride). PVC suspension-polymerized homopolymer (supplied by ICI) was purified by dissolving in tetrahydrofuran, centrifuging at 10000 rpm for 1 h and casting the supernatent liquid as a film. The product was dried at 10^{-2} torr at 50°C for 24 h.

Polymerization of vinyl chloride. Industrial grade vinyl chloride monomer (VCM) was distilled on a vacuum line and subjected to two freeze–thaw–melt cycles to remove gaseous impurities. The VCM was then distilled in known quantities into clean, freshly-prepared thick-wall tubes. These quantities were measured knowing the volume of the apparatus, by measuring the gas pressure with a mercury manometer. the gas was then condensed into the ampoules which were then sealed under vacuum. Polymerization was carried out at 40°C using ^{60}Co(γ) radiation of 0.1 Mrad h^{-1} for 5 h. Post polymerization at 85°C for 6 h gave conversions of about 99%. The product was then evacuated for 48 h at 10^{-2} torr at room temperature.

Polymerization of deutero-vinyl chloride. Deutero (d_3) VCM (Merck, Sharpe & Dohme Ltd) was distilled on the vacuum line into two thick-wall tubes and sealed as before. One was polymerized by radiation as above. The other was preloaded with 0.1% (w/w benzoyl peroxide and the monomer polymerized at 60°C, followed by post-polymerization at 80°C for 6 h, to give a conversion of about 98%. The samples were then heated to 50°C at 10^{-2} torr for 1 h to remove residual monomer. Since the molecular weight of PVC homopolymer is a function of the temperature of polymerization only[14], the deuterated polymers were analogous to the normal hydrogenated polymers.

Table 1 Molecular weights of poly(vinyl chloride)

Polymer	$\bar{M}_n \times 10^{-3}$ (g.p.c.)	$\bar{M}_w \times 10^{-3}$ (g.p.c.)	$\bar{M}_n \times 10^{-3}$ (corrected)	$\bar{M}_w \times 10^{-3}$ (corrected)
PVC (radiation polymerized)	152	275	93	165
d-PVC (radiation polymerized)	150	280	90	170
PVC (commercial, ICI)	58	120	32	65
d-PVC (chemically-initiated)	60	123	33	60

Where necessary, samples were pressed without additives at 150°C for 5 min between aluminum sheets to the desired thickness and annealed.

Characterization of poly(vinyl chloride). The various PVC samples were analysed by gel permeation chromatography (g.p.c.) using 1% solutions in tetrahydrofuran and molecular weights were determined relative to monodisperse polystyrene standards. A universal calibration technique was used with values of K and α from the literature[15]. The corrected values are shown in *Table 1*.

Solution chlorinated polyethylene. SCPE was supplied by Du Pont (UK) Ltd as Hypalon 48. This contains 43% (w/w) chlorine, and analysis by g.p.c. gives $\bar{M}_w$ at 3.0×10^5 relative to polystyrene standards, and a polydispersity of 2.3. This was dissolved in dichloromethane, centrifuged, and the supernatent liquid cast as a film. The product was dried under vacuum at 10^{-2} torr for 48 h. The polymer also contains 1% S as SO_2Cl groups.

Poly(butyl acrylate). Butyl acrylate monomer was distilled under vacuum (boiling at 51°C at 11 torr) to remove inhibitors. It was polymerized by emulsion polymerization using distilled water (100 cm^3), monomer (50 g), sodium lauryl sulphate (1 g), and potassium persulphate (0.003 g). The ingredients were charged into a round bottomed flask, equipped with stirrer, reflux condenser, and thermometer well. The flask was flushed with nitrogen and heated to 90°C for 4 h. The latex was coagulated[16] by shaking with diethyl ether (5 cm^3) and 5% magnesium chloride solution (30 cm^3), then pouring slowly into a ten-fold excess of methanol. The polymer was filtered off and washed with hot methanol to remove the last traces of emulsifier. The polymer was then dissolved in butan-2-one, the solutions centrifuged at 10 000 rpm and the supernatent liquid reprecipitated into methanol. It was then dried in an oven at 80°C for 24 h. The number-average molecular weight of the polymer has been determined by osmometry[13] as 1.0×10^5.

Preparation of blends. Blends were prepared using different techniques for the different systems. 2% *d*-PVC in PVC was cast as a film from a 5% solution of the two polymers in dichloroethane, then dried under vacuum. A 50% blend of SCPE in PVC was prepared by *in-situ* polymerization. This technique requires freshly prepared thick-wall tubes of 15 mm internal diameter with an optically flat end. These are preloaded with the required weight of purified SCPE. The desired amount of monomer is then condensed into the vessel and the system is sealed under vacuum. After equilibration of the mixture for 24 h, the monomer is polymerized by $^{60}Co(\gamma)$ radiation exactly as for the homopolymer. The 2% deuterated PVC analogue was prepared by precasting the *d*-PVC with the SCPE elastomer from dichloroethane solution, then loading the ampoule with this mixture and proceeding as for an *in-situ* polymerization. A sample of 50% *d*-PVC/SCPE was prepared by *in-situ* polymerization using the deuterated VCM. This technique results in discs of about 15 mm diameter × 1 mm thickness which can then be accurately measured before further work.

Blends of PVC and PBA were prepared by casting films from solutions of the polymer mixtures in butan-2-one to the desired thickness of 1 mm, and drying the film at 10^{-2} torr at 20°C for 48 h. *In-situ* polymerization could not be used for these mixtures due to problems of grafting.

Small-angle X-ray scattering

A Siemens–Kratky apparatus (Queen Elizabeth College, University of London) was used with samples 1 mm thick at 20°C in a evacuated chamber. The detector was an electronic step–scan device. The scattered signals were corrected for slit smearing[17].

Small-angle neutron scattering

The D11 instrument at the ILL Grenoble was used as described previously[3]. Samples 12 mm in diameter and 1 mm thick were used. The signal was normalized for detector counts, detector efficiency and sample thickness, and corrected to give absolute intensities where necessary by the method of Girot[18].

RESULTS AND DISCUSSION

X-ray scattering

Curves corrected for slit smearing were obtained from the various cast samples and are shown in *Figure 2*. The pure PVC shows a broad peak centred around 6.0×10^{-2} Å^{-1}, probably due to crystallites in the polymer. The PVC/PBA blends show much low-angle diffuse scattering, possibly due to electron density differences between the two amorphous components. They also show a shoulder presumably from the PVC crystallites which has moved to lower Q values. This could be attributed to increasing the separation of lamellar crystallites from 105 to about 180 Å with increasing concentration of the non-

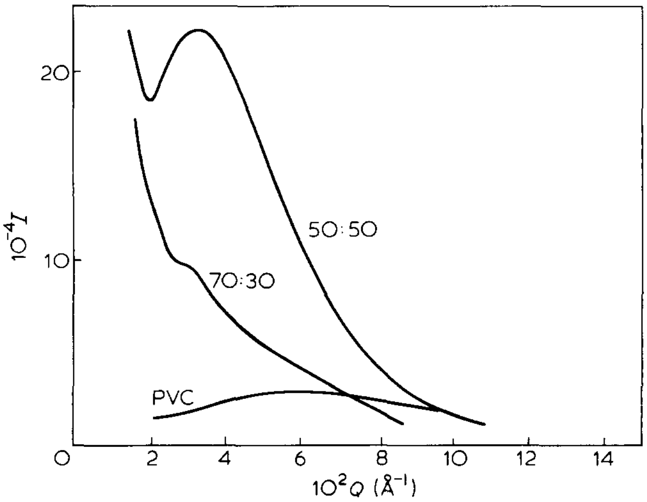

Figure 2 Small-angle X-ray scattering from cast samples. I vs. Q for pure PVC, and 50/50 and 70/30 PVC/PBA blends

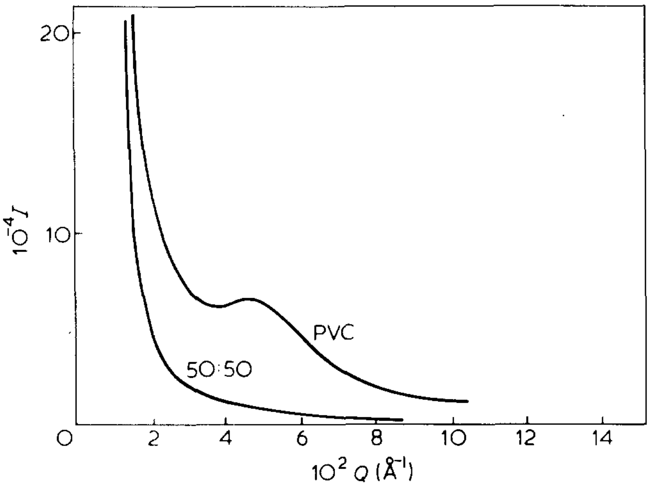

Figure 3 SAXS from an *in-situ* polymerized 50/50 blend and radiation polymerized PVC

crystalline component. The peak also has a much greater intensity, which can be explained by the increase in the intensity factor which results when the density of the matrix is changed. The electron density of crystalline PVC is $0.44(e^-/\mathrm{Å}^3)$ and the value for amorphous PVC is $0.42(e^-/\mathrm{Å}^3)$[19]. Assuming 15 wt% crystallinity this gives an intensity factor of 0.5×10^{-4}, and this is sufficient to produce the observed signal in the pure PVC. However, PBA has an electron density of $0.33(e^-/\mathrm{Å}^3)$, so a 50% blend of PBA and amorphous PVC would have a density of 0.375. If the same fraction of crystallites is present in the PVC, the intensity factor would be 2.3×10^{-4} which agrees with the observed increase in intensity.

Figure 3 shows the corrected results for PVC prepared by radiation polymerization and a blend prepared by *in-situ* polymerization. These samples show a large low-angle diffuse scattering, probably due to structural effects in the samples. Similar results have been found previously for bulk-polymerized PVC[5]. The solvent casting process clearly removes these effects as shown in *Figure 2* (or at least displaces them out of the Q range of observation). The PVC scattering function also shows a broad shoulder, presumably due to crystallites, but the PVC/SCPE blend shows only small-angle scattering. SCPE has an electron density of $0.4(e^-/\mathrm{Å}^3)$, and a blend with amorphous PVC would give 0.41 if the density is taken as the mean of the components. Assuming the proportion of crystallites is 15 wt% of the PVC, the intensity factor would be 0.6×10^{-4}. This should be observed at a similar intensity to that in PVC. The absence of any shoulder indicates the technique of preparation may have prevented the crystallites from forming. PVC is insoluble in its own monomer and precipitates out during polymerization. This probably does not occur in the presence of a compatible, preformed polymer. Entanglements with the other polymer chains also probably stop the PVC chains lining up into a crystalline structure.

Microstructure of PVC and blends from small-angle neutron scattering

The contrast mechanism for neutron scattering in polymers is dominated by the contribution from hydrogen atoms with their negative scattering lengths[2]. The contrast is often enhanced by replacing hydrogen by deuterium in selected regions. The contrast factor (K) is given by equation (3) and this may be calculated from the scattering lengths (Σb) values shown in *Table 2*. This results in values of K (probability of scatter per segment volume) for *d*-PVC/SCPE of 0.0059×10^{-24} and for *d*-PVC/PBA of 0.0080×10^{-24}. These are adequate contrast factors to observe the scattered signals in these blends. The use of *d*-PVC rather than *d*-PBA and *d*-SCPE was also preferable because the monomer is available commercially. Because of the lower density of PBA the value of K for non-deuterated PVC/PBA (0.0004×10^{-24}) is also adequate to observe scattering in this system without resorting to deuterated polymers.

Figure 4 shows the SANS results for *d*-PVC (as-polymerized), *d*-PVC pressed at 150°C and annealed, and a sample of non-deuterated PVC, also pressed at 150°C. The 'as-polymerized' *d*-PVC shows a broad, diffuse, small-angle scattering signal which may be associated with a random arrangement of large particles[5]. This is reduced by annealing. The annealed *d*-PVC also shows a Bragg peak. Taking account of the diffuse nature of the peak, this gives a d spacing of about 142 Å which is similar to that calculated from the SAXS experiments with the annealed PVC. No peak is observable in the plot from the undeuterated PVC. This can be explained from the lower net scattering length of the hydrogenated polymer (see *Table 2*) which therefore gives a smaller scattering contrast between the crystalline and amorphous regions.

The results for scattering from 50/50 blends of PVC and PBA prepared by casting from solution in butan-2-one are shown in *Figure 5*. At room temperature a peak is evident with a d spacing of about 250 Å, similar to that

Table 2 Scattering lengths of deuterated and non-deuterated polymers

Polymer	Specific volume cm^3 per g segment mole	Hydrogenated $\times 10^{12}$ cm per segment	Deuterated $\times 10^{12}$ cm per segment
PVC	45	1.30	4.5
SCPE	39	0.9	4.3
PBA	128	1.35	13.9

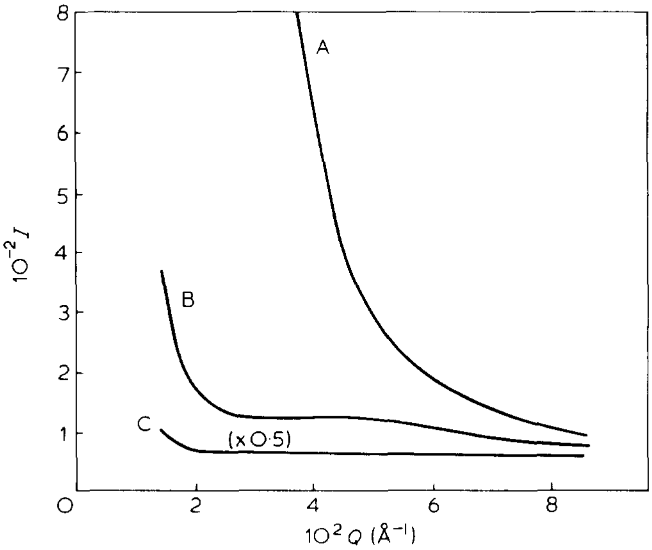

Figure 4 SANS for: A, *d*-PVC (as-polymerized); B, *d*-PVC pressed at 150°C and annealed, and C, *h*-PVC also pressed at 150°C

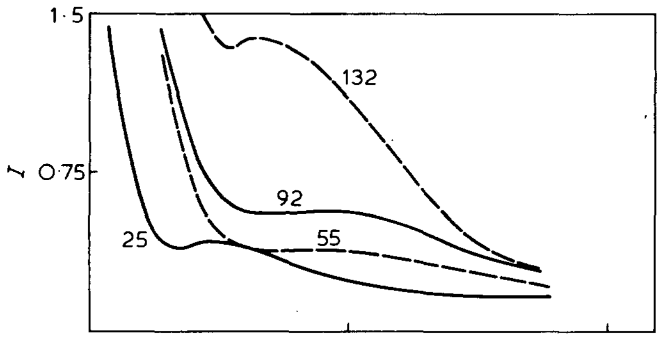

Figure 5 SANS from a blend of 50/50 PVC/PBA (solution cast) at 4 consecutive temperatures 25°, 55°, 92° and 132°C

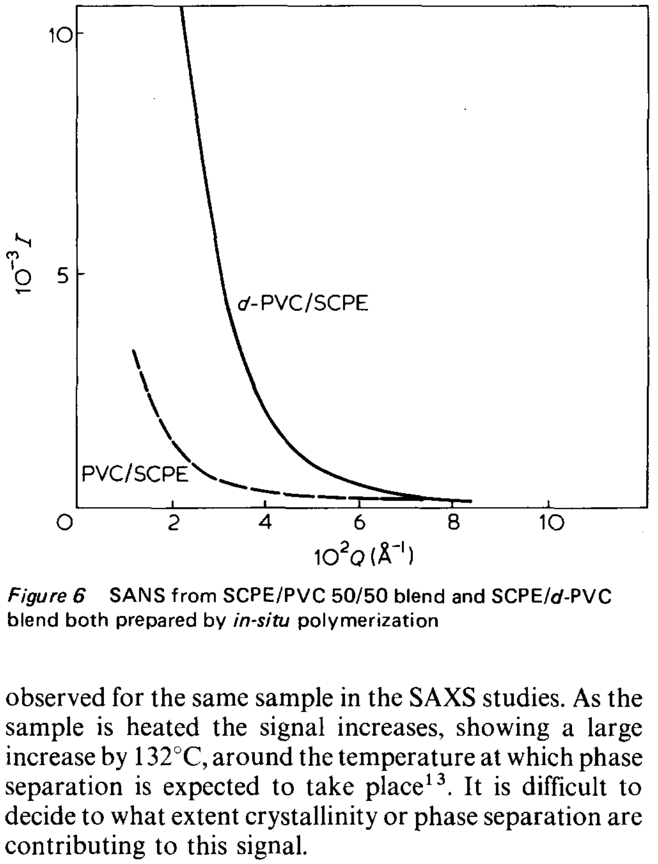

Figure 6 SANS from SCPE/PVC 50/50 blend and SCPE/*d*-PVC blend both prepared by *in-situ* polymerization

observed for the same sample in the SAXS studies. As the sample is heated the signal increases, showing a large increase by 132°C, around the temperature at which phase separation is expected to take place[13]. It is difficult to decide to what extent crystallinity or phase separation are contributing to this signal.

The results for scattering from a blend of PVC and SCPE, prepared by *in-situ* polymerization, are shown in *Figure 6*. In this case only a small-angle signal is observed with no diffraction peak which could be due to PVC crystallites. A similar 50% blend with *d*-PVC shown in *Figure 6* also shows no diffraction peak. A peak had been observed for pure *d*-PVC and in the blend the peak should have been much easier to see due to the enhanced contrast factor expected with the reduction in density of the matrix. This suggests that crystallites are not formed during *in-situ* polymerization with a compatible polymer, confirming the SAXS result.

Molecular dimensions of the polymer chains by SANS

A large number of measurements of single chain dimensions in the bulk state have been made[2,3]. The radius of gyration of polymer chains is obtained by analysing the signal from a dilute (~2%) dispersion of deuterated polymer in a hydrogenous matrix, having subtracted the signal due to the hydrogenous polymer alone. The analysis is carried through in the normal manner for polymer solutions as a Zimm plot, giving a weight-average molecular weight ($\bar{M}_w$), and the root-mean-square z-average radius of gyration $\langle s^2\rangle_z^{1/2}$. Two examples of these plots are given in *Figure 7*.

If we assume a Schultz distribution for the polymer molecular weight, the correction factor for a polydispersity of 2 if 0.67 for $\langle s^2\rangle_z^{1/2}$ [20]. This correction factor is applied to the values obtained.

PVC homopolymer. There were two methods of sample preparation used for the two different molecular weights investigated and the signals for the hydrogenous polymers themselves (*Figures 4* and *5*) already show differences in the small-angle range due to the sample preparation. The solution cast samples ($\bar{M}_w = 65\,000$) show some small-angle scattering but at low Q values, indicating fairly long-range density fluctuations, i.e. long correlation lengths. This, together with the lower molecular weight which allows Zimm analyses to extend to reasonably high Q values, gives a clean separation of the signals due to overall sample 'structure' and those due to the introduction of tagged (deuterated) chains. This is important because the introduction of these chains inevitably changes the contrast for the density fluctuations themselves so that background subtraction is never satisfactory in this Q range.

Figure 7 shows as the upper curve a Zimm plot for a sample of PVC prepared in this way containing 2% deuterated polymer. The signal of pure PVC has been subtracted. The residue of the density fluctuations is seen at low Q. Although this data extends to $Q\langle s^2\rangle^{1/2} \approx 3$ there is no sign of curvature, The $\langle s^2\rangle_z^{1/2}$ obtained is 115 Å, which corrected leads to a value of the ratio $(\langle s^2\rangle_w/\bar{M}_w)^{1/2}$ of 0.37 in good agreement with the Flory predicted value. This value is slightly higher than that obtained previously by neutron scattering, but is in good agreement with the value obtained by light scattering[2].

The $\bar{M}_w$ value obtained from the intercept is acceptable bearing in mind some uncertainty in the sample thickness. The high molecular weight samples ($\bar{M}_w = 170\,000$) which were pressed and annealed show small-angle scattering to higher Q values and because of the larger molecular

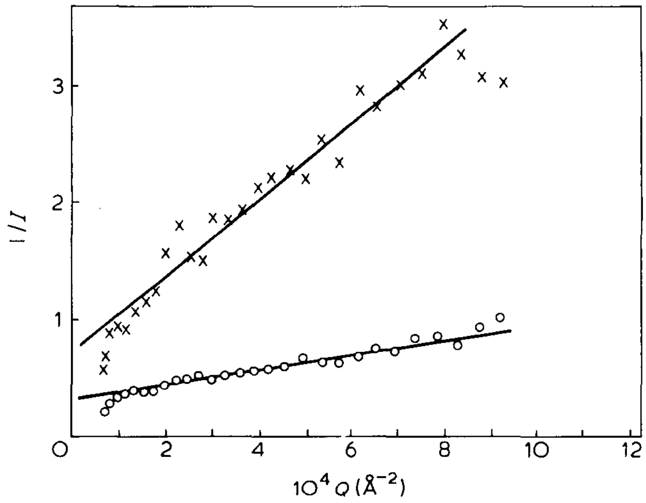

Figure 7 Plot of 1/*I*(*Q*) vs. Q^2 for 2% *d*-PVC in PVC (X) and for 2% *d*-PVC in 50/50, PVC/PBA blend (O) cast samples (*d*-PVC, $M_w = 65\,000$)

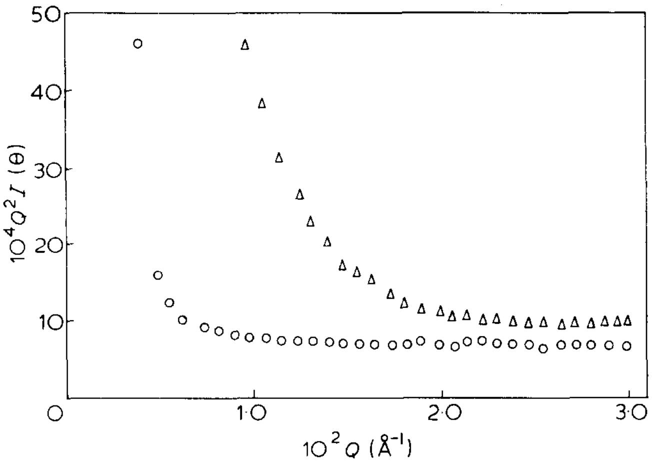

Figure 8 ○, $Q^2I(Q)$ vs. Q for 2% *d*-PVC in PVC. Pressed and annealed samples, (M_w = 170 000). Also shown: △, $Q^2I(Q)$ vs. Q for 2% *d*-PVC in a 50/50 *in situ* polymerized SCPE/PVC blend

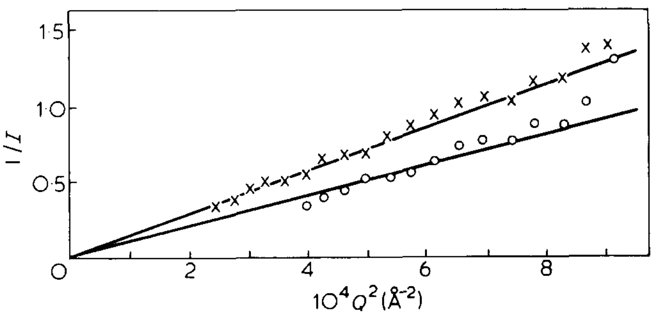

Figure 9 $1/I$ vs. Q^2 for 170 000 M_w samples of: X, 2% *d*-PVC in PVC and ○, in 50/50 SCPE/PVC blend

dimensions, it is not possible to disentangle the signal from single deuterated chains from that due to the overall structure in the Guinier range. However, *Figures 5* and *6* show that the structure scattering does die away at higher Q values in what should be the Kratky range. In this range, therefore, the signal should be separable. *Figure 8* shows a Kratky plot of $Q^2I(Q)$ vs. Q for a sample containing 2% *d*-PVC from which an *h*-PVC sample signal has been subtracted. At low Q an anomalous increasing signal is observed which is not seen in the cast samples. Above $Q = 1.5 \times 10^{-2}$ Å^{-1} a linear region is found. Accordingly it should be possible to extract a value for $\langle s^2 \rangle^{1/2}$ using equation (7). *Figure 9* shows $1/I$ plotted against Q^2 in this range for the pressed, annealed PVC. When the slope has been normalized for absolute intensity using scattering from a standard (water) and a known sample thickness, concentration and transmission[2], a value for $\langle s^2 \rangle_z^{1/2}$ of 141 Å^{-1} is obtained. The Flory ratio is then 0.28 which is lower than the value obtained for cast samples, but this probably simply reflects the error in determining the absolute scattering intensity necessary for analysing the Kratky region, but unnecessary for Guinier analysis.

PVC/PBA blends (*solution cast*). *Figure 7* also shows the Zimm plot for 2% *d*-PVC in a 50/50 blend of PVC/PBA. Even though the curves have not been normalized for the increased contrast in the blend sample and for differences in sample thickness and concentration, it is clear that the blend sample shows a much lower slope, and therefore a smaller value for $\langle s^2 \rangle$. Values for $\langle s^2 \rangle_z$ and $\langle s^2 \rangle_w$ extracted from the slope are listed in *Table 3*.

PVC/SCPE blends (in-situ *polymerization*). *Figure 8* shows Kratky plots for deuterated PVC in 50/50 blend samples. The structure scattering extends to higher Q values than for the pure PVC which is not surprising in view of the small-angle scattering (*Figures 5* and *6*) discussed for these blends. The region where the curves flatten has been plotted as $1/I$ vs. Q^2 in *Figure 9* for the blend. Again the lower slope clearly indicates the chains have smaller dimensions in the blend. Using the same normalization as for pure PVC but remembering the changed contrast, values of $\langle s^2 \rangle_z^{1/2}$ can be extracted from the slopes and these are listed in *Table 3*.

The apparent reduction in the *d*-PVC dimensions in the blend samples must be treated with some care since for these systems the virial coefficient, A_2, will not be zero. In this case, interchain scattering effects have not been removed by extrapolation to zero concentration of marked chains. The concentrations used were low, however, so that this correction would be expected to be small. Without further experiments at varying concentrations of marked chains it is safe only to make two general observations about these results. Firstly, the chain dimensions obtained in the blend are clearly molecular, supporting other evidence that these polymers mix intimately at a molecular level. Secondly there is some evidence for a change from the pure PVC to the blend, reflecting the interactions between the polymers.

CONCLUSIONS

The microstructure of PVC and blends of PVC with SCPE and PBA has been examined by X-ray scattering and small-angle neutron scattering. Samples of PVC which have been polymerized in the bulk state show diffuse small-angle scattering due to structural effects in the samples, whereas solvent-cast samples do not show this in the range of observation. Samples also show a broad shoulder in the X-ray curve, presumably due to crystallites. This was also observed in neutron experiments with deuterated PVC but not with hydrogenous PVC, due to the smaller scattering contrast. This effect has been seen to persist even in samples which have been solvent cast.

Blends of PVC with PBA, prepared by solvent-casting, also show a peak, using both techniques, attributable to crystallites but at a higher *d* spacing, presumably due to increased separation of the crystallites. Blends of PVC with SCPE, which were prepared by *in-situ* polymerization, however, show no such peak. This suggests that

Table 3

Sample	$\langle s \rangle_z^{1/2}$ Å	$\langle s^2 \rangle_w^{1/2}$ (Values ±10%) Å	$(\langle s^2 \rangle_z / M_w)^{1/2}$ Å
2% *d*-PVC (M_w = 170 000) in PVC (annealed)	141	115	0.28
2% *d*-PVC (M_w = 170 000) in 50/50 PVC/SCPE (*in-situ* polymerized)	126	103	–
2% *d*-PVC (M_w = 65 000) in PVC (cast from butan-2-one)	115	94	0.37
2% *d*-PVC (M_w = 65 000) in 50/50 PVC/PBA (cast from butan-2-one)	78	62	–

the method of polymerization prevents the formation of crystallites.

Blends of PVC with PBA also show a large increase in the neutron scattering signal when the sample is heated to 132°C. This is close to the temperature at which phase separation is known to occur for this mixture.

Neutron scattering was also used to examine the molecular dimensions of the polymer chains in the blends. Experiments with 2% deuterated PVC in PVC showed chain dimensions in fairly good agreement with predicted values. Experiments using 2% deuterated PVC in blends of PVC with both SCPE and PBA showed chain dimensions of the same order as for the pure polymer confirming that there is a molecular dispersion in the single phase. An apparent reduction in the dimensions of the PVC chains needs to be confirmed by further experiments at varying concentration of marked chains since A_2 is expected to be non-zero in the blends.

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REFERENCES

1 Kratky, O. *Pure Appl. Chem.* 1966, **12**, 483

2 Higgins, J. S. and Stein, R. S. *J. Appl. Cryst.* 1978, **11**, 346

3 Maconnachie, A. and Richards, R. W. *Polymer* 1978, **19**, 739

4 Stratt, R. S. and Uhlmann, D. R. *J. Polym. Sci.* (*Polym. Phys. Edn*) 1976, **14**, 353

5 Wenig, W. *J. Polym. Sci.* (*Polym. Phys. Een*) 1978, **16**, 1635

6 Gezovich, D. M. and Geil, P. H. *Int. J. Polym. Mater.* 1971, **1**, 3

7 Wendorff, J. and Fischer, E. W. *Kolloid. Z. Z. Polym.* 1973, **251**, 876

8 Herschenroeder, P. Personal Communication, University or Mainz

9 Vonk, C. G. *J. Appl. Cryst.* 1971, **4**, 340

10 Schmidt, P. W. *Acta. Crystallogr.* 1967, **23**, 191

11 Yoon, D. Y. and Flory, P. J. *Macromolecules* 1976, **9**, 294

12 Doube, C. P. and Walsh, D. J. *Polymer* 1979, **20**, 115

13 Walsh, D. J. and McKeown, J. G. *Polymer* 1980, **21**, 000

14 Chapiro, A. 'High Polymers', Interscience, New York, 1962, Vol. XV, p 468

15 Evans, J. M. and Maisey, L. J. 'Industrial Polymers: Characterisation by molecular weight', Symposium at National Physical Laboratory, Transcripta Books, London, 1973

16 Haslam, J. and Willis, H. A. 'Identification and Analysis of Plastics', 2nd Edn, Iliffe, 1972

17 Lake, J. A. *Acta. Crystallogr.* 1967, **23**, 191

18 Jacrot, B. *Rep. Prog. Phys.* 1976, **39**, 911

19 Brandrup, J. and Immergut, E. H. 'Polymer Handbook', 2nd Edn, Wiley, 1975

20 Kirste, R. G., Kruse, W. A. and Ibel, K. *Polymer* 1975, **16**, 120