polymer papers

The 'crystallinity' of PVC

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Examination of the solid state structure of PVC plasticized with deutero-di-n-octylphthalate using small-angle neutron scattering (SANS) combined with studies using SAXS (synchrotron X-ray source) and thermal mechanical analysis (TMA) gives new information about the 'crystallinity' of PVC. This is compared with the behaviour of a poly(ethylene terephthalate) copolymer with a similar level crystallinity. The latter serves as a model system which describes the thermal and mechanical behaviour of polymers with crystallinities in the region of 15%. A second model system is the polymer formed by addition of chlorine to poly(1,4-butadiene). This is head-to-head PVC and completely amorphous.

(Keywords: neutron scattering; X-ray scattering; poly(vinyl chloride); poly(ethylene terephthalate); crystallinity)

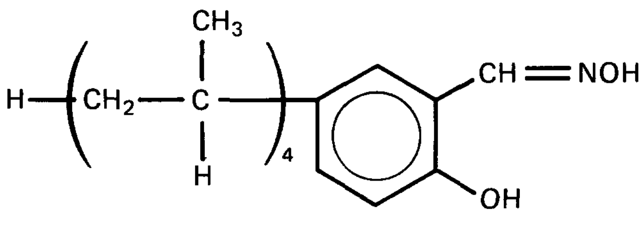
INTRODUCTION

The structure of PVC in the solid state has been a subject of much debate, the details of which have been summarized recently by Blundell[1] and Walsh[2]. When heated above its glass transition temperature, the flow behaviour of fluidized PVC resembles a lightly crosslinked gel. The origin of these crosslinks was associated with an anomaly in the polymerization. It is not uncommon in radical polymerizations for some branching to occur due to radicals removing atoms from the main chain which then become initiating centres. Under some circumstances termination of branched propagating centres can lead to crosslinking and gel formation.

A second and less widely held view is that the crosslinks are physical in origin and are due to low levels of crystallinity. The crystallite, if present, would bond together fragments of several discrete macromolecules leading to a three dimensional network. The crystallinity determined by classical X-ray scattering techniques is given as 10–15% and SAXS studies give a *d*-spacing of about 150 Å[2]. Reports about the possible crystallinity of PVC appeared in ICI internal reports of the mid-sixties and were reported in a review by Charles Bunn in 1973[3]. Detailed studies carried out by Wenig[4], Blundell[1] and Walsh[2] have also demonstrated a SAXS peak for PVC. However, Straff and Uhlmann[5] consider that the SAXS peak is not due to the crystallinity of PVC. Wendorff and Fischer[6] have pointed out that heterogeneties in bulk amorphous polymers can give rise to small-angle scattering. The X-ray technique is not wholly satisfactory due to the high absorption of X-rays by the material due to the presence of chlorine atoms. Also X-ray studies of polymeric materials in which the crystallinity is less than 20% are difficult to execute even when this high absorption is absent. Consequently there is very little background information derivable from related systems.

In 1982 G. D. Wignall described to one of us (DGHB) an unusual observation made on the SANS equipment at the Oakridge facility[7]. Addition of 33% by weight of deuterated nitrobenzene to PVC gave a sample which scattered neutrons in such a way as to give a well defined peak at a *Q*-value of 0.05. It was suggested that the peak derived either from the presence of crystallites in the partially deuterated matrix or was due to a specific type of phase separation within the amorphous matrix. In 1978, Herchenroder observed a similar peak using SANS[8].

At the time work was in progress in our laboratory on a study of the amorphous regions in polyethylene and nylon-6,6 copolymers. Of particular significance was the experiment with polyethylene. It had been found that polyethylene, which had been produced with highly active catalysts and had a large surface area, could absorb liquid hydrocarbons such as the tetramer of propylene. The latter was labelled with a Salicylaldoxime group to give a molecule with the structure **1**. The latter has a high affinity for metals and forms complexes with a variety of transition metals. Using the molecule has proved a very useful method of labelling the amorphous regions for electron microscopy. Sections of polyethylene treated in this way, gave electron micrograph in which the amorphous regions are 'highlighted' by the heavy metal hafnium.



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In the latter it was clearly seen that there was a periodicity and that the crystalline phase (light region) was remarkably uniform (*Figure 1*). The *d*-spacing obtained from the electron micrograph agreed with that found by SAXS and was 150 Å. The two geographically separated observations demonstrated that it was possible to study polymers with different degrees of crystallinity by 'labelling' the amorphous regions with atoms which had a significantly higher scattering cross-section than the crystalline regions.

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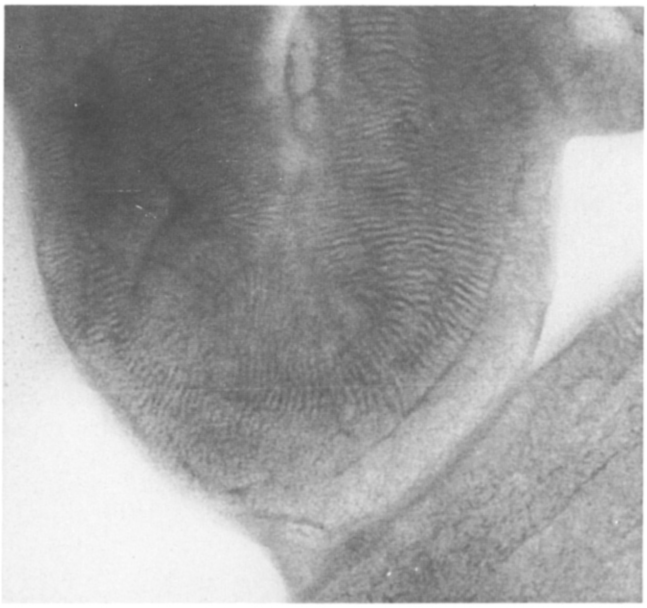

Figure 1 Electron micrograph of polyethylene treated in the manner as described in the text (magnification 75 000)

In this paper we report our studies of PVC in which the amorphous regions are 'highlighted' by di(n-D^{17}-octyl) phthalate, which is a known plasticizer for this polymer. This information is combined with that from very intense X-ray sources from the Synchrotron Radiation Facility which makes it possible to overcome the limitation of the high X-ray absorption by the chlorine atoms of PVC. These techniques have been used to study the crystallinity of PVC.

EXPERIMENTAL

Plasticized PVC for SANS and SAXS studies

The PVC used in this study was ICI Corvic Grade S60/104. This is in the form of a white powder which is formed in the polymerization reactor at 80°C and dried in the usual way at temperatures of 120°C. The molecular weight is about 77 000 (29 % syndiotactic, 21 % isotactic, 50 % heterotactic). Also the powder is microporous and consists of aggregates of particles 200 Å in diameter.

Di-n-octyl phthalate (DOP) or its deuterated analogue was dissolved in acetone and the appropriate amount of PVC powder added to it. The plasticizer was totally absorbed by the powder and the residual solvent removed in a stream of dry nitrogen. The powder was heated to 180°C and held at this temperature for 3 min. This was then compressed into plaques 1.0 mm thick and 15 mm diameter using a pressure of 10 tons for 1 min. They were then cooled to room temperature under pressure.

Di(n-D^{17}-octyl) phthalate

Di-(n-D^{17}-octyl) alcohol (Aldrich Chemicals) was mixed with the appropriate amount of phthalic anhydride in the presence of sulphuric acid which catalyses the esterification.

SANS studies of plasticized PVC

All SANS experiments were carried out using the small-angle scattering instrument on the PLUTO reactor at AERE Harwell, Berkshire, England. The wavelength used was 6 Å giving a Q-range of 1.8×10^{-2} to 0.26 $(\text{Å})^{-1}$ and a flux of 2.8×10^4 n cm^2 s^{-1}.

SAXS studies of plasticized PVC

The small-angle X-ray scattering patterns of the PVC samples were obtained using the SERC Synchrotron Radiation Source (SRS) located at Daresbury, Cheshire, England. There are several advantages for using the SRS over a laboratory camera but the most notable is speed of measurement. It is estimated that the time required to perform the experiments in the lab. would be in the region of 10 h for comparable signal-to-noise ratios. The integration times at Daresbury were 2 to 10 min depending on the thickness of the samples which varied between 0.11 to 1.13 mm.

The spectra were obtained with photons of $\lambda = 1.608$ Å and a sample-to-detector distance of 2.3 m. The scattering was recorded using a linear 1-D detector, i.e. all are measured simultaneously. The data shown have been corrected for the detector response but the curves have not been normalized to absolute intensity or corrected for background scattering. The intensity below $Q = 0.007$ Å^{-1}, i.e. the 'sharp peak', is to be ignored since this is an instrumental artefact.

Thermal analysis

The dynamic mechanical analysis was carried out on a Polymer Laboratories PL-DMTA. The thermal mechanical analyses were carried out using a Mettler TMA 300.

RESULTS AND DISCUSSIONS

Studies of mixtures of PVC with deuterated di-n-octyl phthalate using SANS and SAXS

Figure 2 depicts the result of SANS on a sample of PVC with 40 % deuterated DOP plasticizer. The existence of a large correlation peak can be explained by a non-uniform distribution of plasticizer. This non-uniform distribution

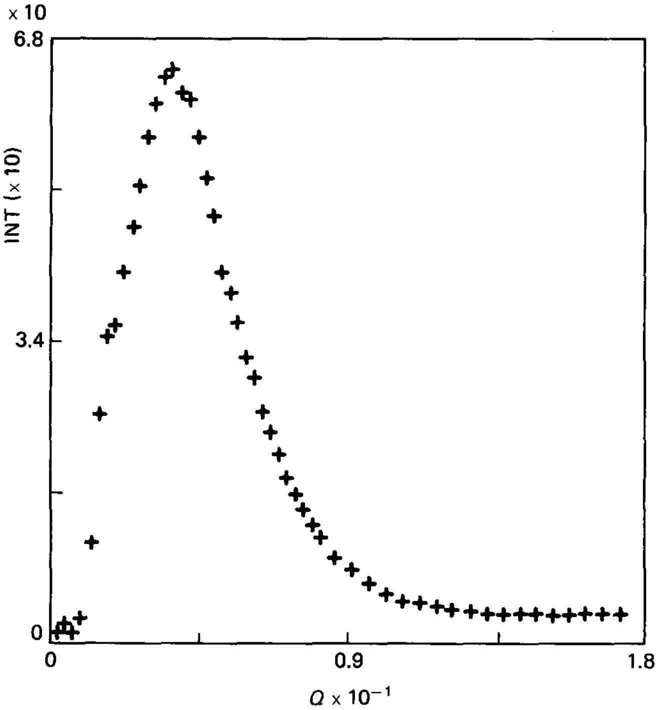

Figure 2 SANS curve of PVC + 40 % deuterated DIOP

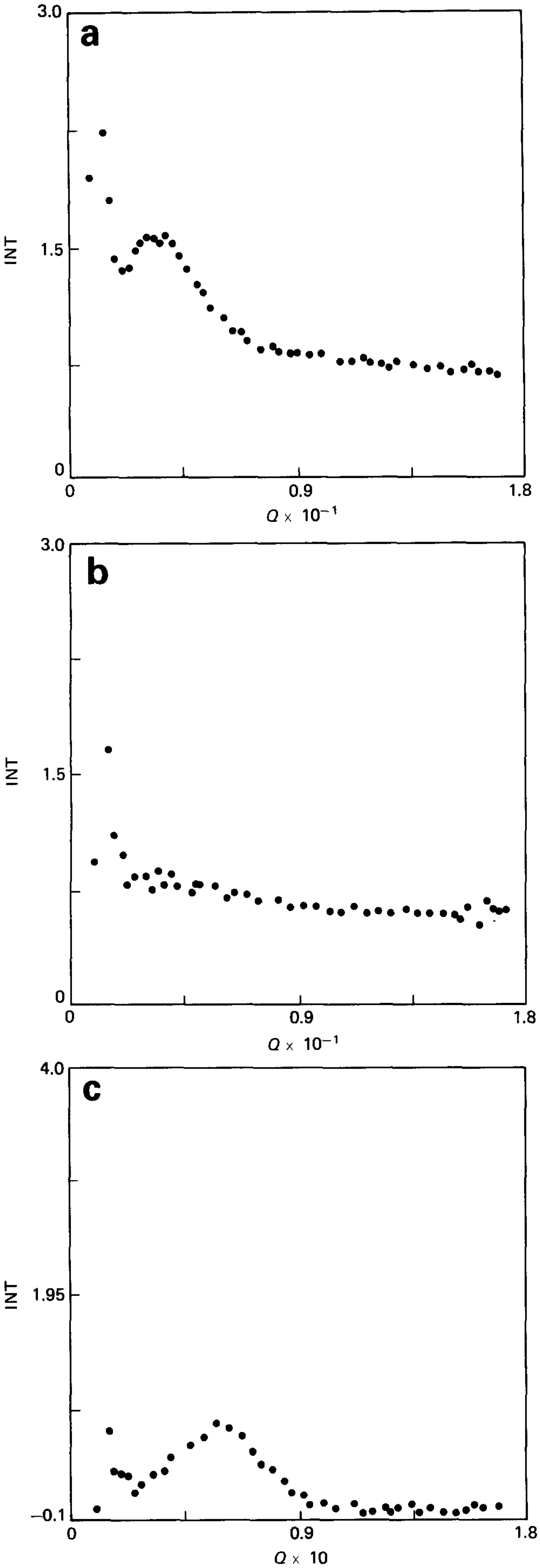

Figure 3 (a) SANS of PVC+10% d-DIOP. (b) Sample heated to 220°C for 1 min and then quenched. (c) The same sample annealed at 110°C for 5 h

of plasticizer suggests the presence of domains from which the plasticizer is excluded. The position of the neutron correlation peak corresponds to a long spacing of 169 Å.

Formulations of PVC with only 10% plasticizer added yield a product with a T_g higher than room temperature (30°C) and are therefore more convenient to study. The corresponding weaker scattering peak obtained from such a sample is shown in *Figure 3a*. This sample was then heated to 220°C and held at that temperature for one minute whereupon it was quenched into methanol and dry ice mixture. The resulting scattering produced (*Figure 3b*) shows the complete elimination of the domains. Subsequent annealing of the sample for 5 h at 110°C, produced a material in which the correlation peak has been restored (*Figure 3c*). The corresponding spacing for this peak is 109 Å. Thus it can be seen that the elimination of these domains is fully reversible and that PVC can be annealed giving rise to a variable long spacing.

The greater sensitivity of this technique over the classical SAXS studies afforded an opportunity of studying the melting characteristics of PVC. The results of heating to 180°C, 190°C, 200°C and 210°C and then quenching in methanol as before are shown in *Figure 4*. It is evident the domains from which the plasticizer is excluded disappear between 200 and 210°C (*Table 1*).

Inspection of the density data in *Table 1* confirms that there is no loss of plasticizer during heating. This data further indicates that the percentage crystallinity decreases with increasing temperature.

A parallel set of experiments was also carried out with the high intensity X-ray source available from the synchrotron. The same set of samples was employed as those in the neutron scattering experiments. In *Figure 5* is shown the scattering curve obtained for annealed samples. It is evident that there is a well defined correlation peak at $Q = 0.0578$, the same value obtained with SANS. In *Figure 6* is SAXS information obtained with samples used in the experiments described in *Figure 4*. It is evident that there is substantial agreement with the neutron scattering data that domains are present which disappear on heating.

It is evident from the breadth of the peak in *Figure 5* that if any crystallinity is present it is poorly defined. This makes precise definition of the controid of the peak uncertain. The *d*-values computed from peak maxima are summarized in *Table 2*.

Poly(ethylene terephthalate) copolymers

These were synthesized to compare their behaviour with PVC. Copolymerization of ethylene glycol with terephthalic acid and substituted terephthalate acids produced semi-crystalline copolymers with an annealed crystallization close to 15%[9]. A typical SAXS curve for this copolymer is shown in *Figure 7*. The maximum corresponds to a *d*-spacing of 280 Å (crystallinity 15%) considerably larger than the value of 180 Å (crystallinity 40%) for PET.

These polymers differed considerably from PVC in that the PET-copolymers crystals were visible in the polarizing microscope and spherulites were observed. The latter on annealing were clearly defined as is evident from *Figure 8*.

Another important difference between PVC and the PET-copolymer can be demonstrated by dynamic mechanical thermal analysis (DMTA). PET-copolymer

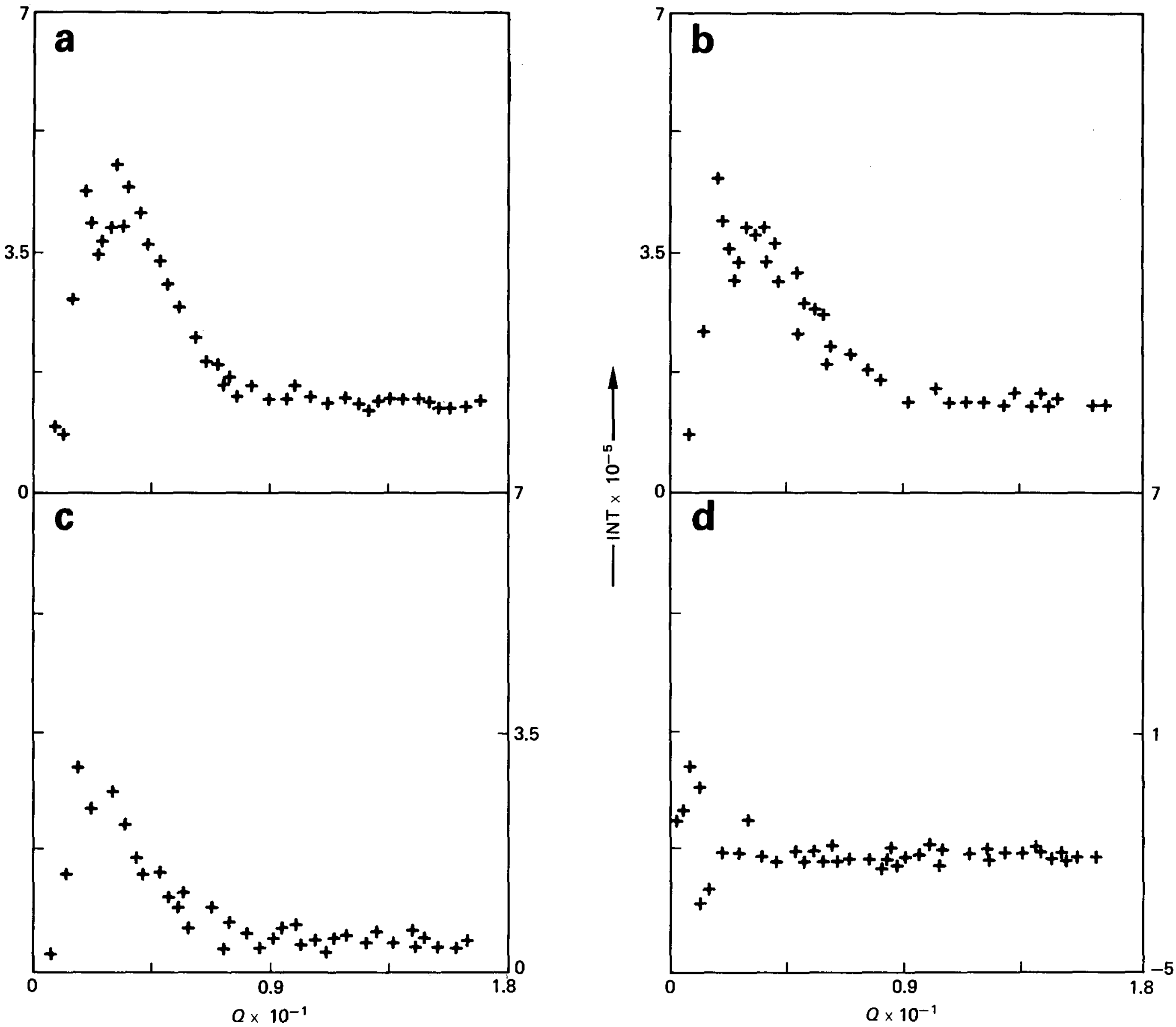

Figure 4 (a) SANS curve of PVC+10% d-DIOP quenched from 180°; (b) 190°C; (c) 200°C; (d) 210°C

Table 1 SANS results obtained from a range of deutero-plasticized PVC's quenched from various temperatures. Also shown are the SANS *d*-spacings obtained for plasticized PVC that had not been quenched from elevated temperatures as well as one sample which had been annealed at 110°C for 5 h

Sample	Quenched from (°C)	Density	SANS *d*-spacing (Å)
PVC+10% DOP	210	1.3423	–
PVC+10% DOP	200	1.3450	200
PVC+10% DOP	190	1.3470	195
PVC+10% DOP	180	1.3465	182
PVC+10% DOP	170	1.3500	166
PVC+10% DOP	160	1.3512	145
PVC+40% DOP	–	–	169
PVC+10% DOP	–	–	186
PVC+10% DOP	220	1.3418	–
PVC+10% DOP	110 (annealed)	1.3590	106

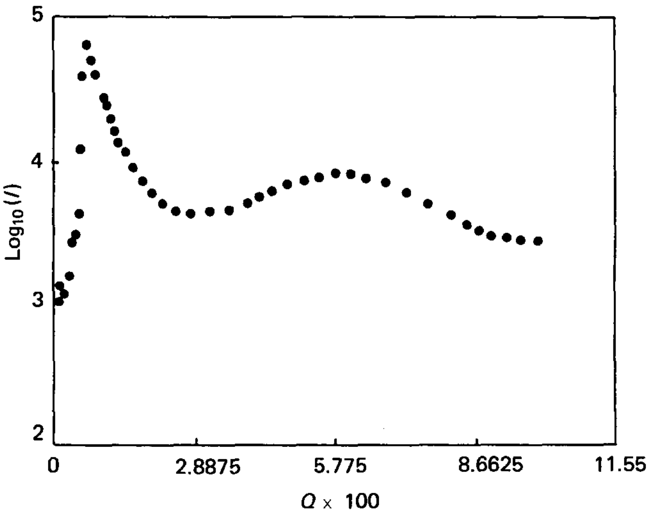

Figure 5 SAXS response to annealed PVC sample annealed at 110°C for 5 h

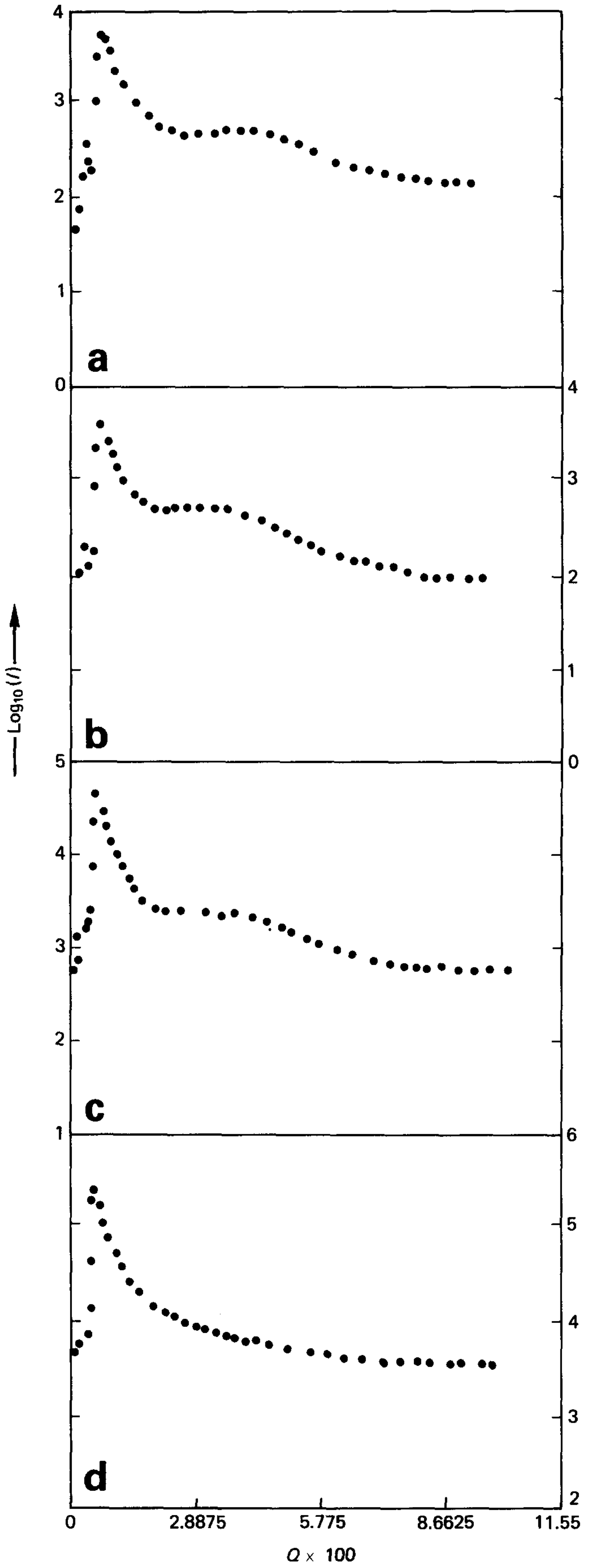

Figure 6 SAXS response to PVC+10% DIOP quenched from: (a) 160°C; (b) 170°C; (c) 180°C; (d) 220°C

Table 2 SAXS results obtained from a range of plasticized PVC's quenched from various temperatures

Sample	Quenched from (°C)	SAXS *d*-spacing (Å)
PVC+10% DOP	210	–
PVC+10% DOP	180	175
PVC+10% DOP	170	180
PVC+10% DOP	160	150

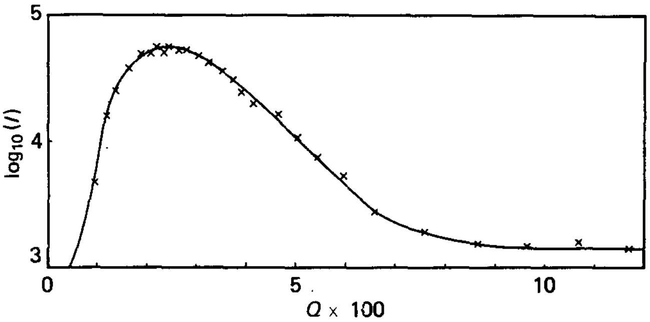

Figure 7 SAXS curve for copolymer of PET as described in the text ($\lambda = 1.54$ Å)

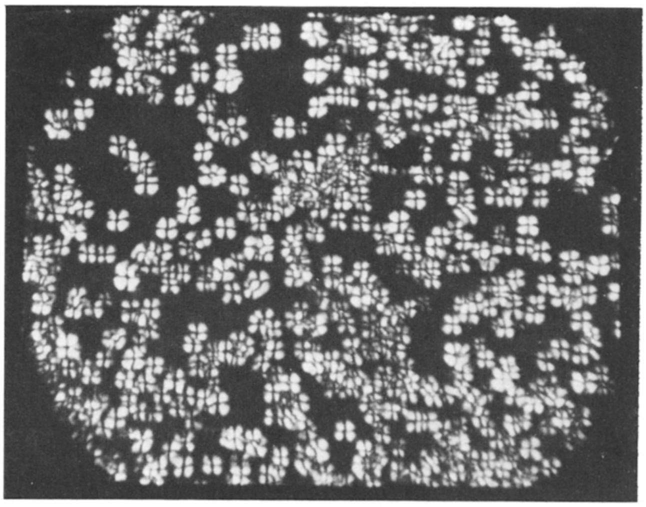

Figure 8 Optical micrograph using cross-polarizers of 15% crystalline PET copolymer annealed at 110°C for 5 h (magnification ×40)

quenched rapidly from 200°C is amorphous and gives rise to the DMTA curve depicted in *Figure 9*(*a*). The same material quenched at 130°C for 24 h gives rise to a DMTA curve noticeably different from the previous curve by the presence of a plateau region typical of semi-crystalline polymers. Contrast this with the equivalent pair of curves obtained from amorphous and crystalline PVC (*Figures 10*(*a*) and (*b*)). It is observed that the presence of crystalline regions in PVC has no apparent effect on the mechanical properties of the material.

Since the *d*-spacing determined by SANS and SAXS includes the amorphous regions the maximum computed thickness for the crystalline lamellae, if present, would be 25 to 30 Å. This compares with a value of 43 Å for the PET copolymer. The lamellae in the PET copolymer are formed in spherulitic clusters with average diameters of 10 μm and therefore visible in the optical microscope. On the other hand no such clusters are visible in PVC no

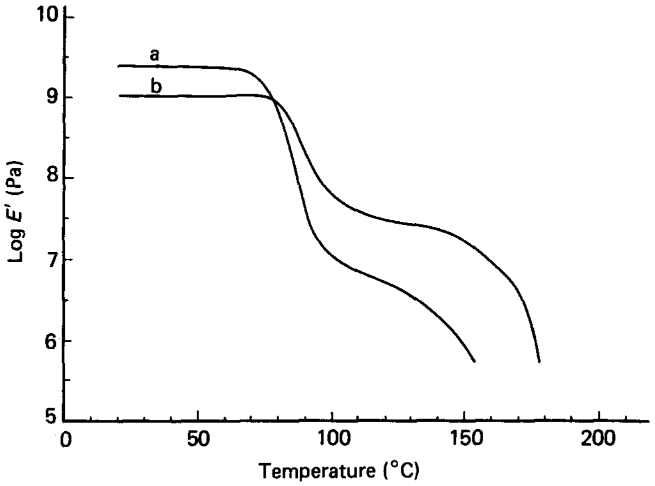

Figure 9 Dynamic mechanical thermal analysis curves for PET copolymers, heating rate 2 degrees per min. (a) Quenched from 200°C. (b) Annealed for 24 h at 130°C

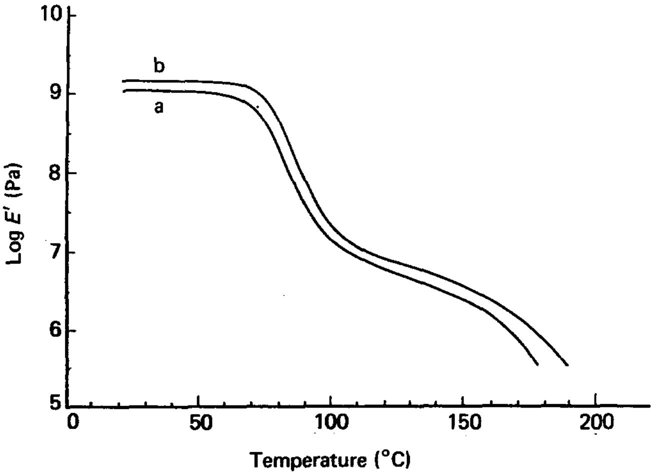

Figure 10 DMTA curves for unplasticized PVC, heating rate 2 degrees per min. (a) Quenched from 220°C. (b) Annealed at 110°C for 24 h

matter how carefully the system is annealed. It is evident therefore that the lamellae, if present, are discrete and cannot form visible assemblies.

The lack of effect on the dynamic modulus of the presence of crystallinity as shown in *Figure 10* was initially a surprising result. It implies that above the T_g the chains in 'crystalline' PVC have the same mobility as in the absence of the crystallites. The crystallites are obviously coherent to the extent that they exclude the plasticizer. Also it is a necessary requirement if the crystallites are to act as crosslinks and form a three-dimensional network that the crystallites contain segments of many chains.

One explanation for the similarity of the curves in *Figure 10* is that even in the amorphous state the polymer chains are closely associated. This is due to the C–Cl dipoles which will exert a strong attractive force between chains so that the amorphous state, though disordered as 'seen' by SAXS and SANS, is a close packed structure. Hence in *Figure 10* there is a marked plateau region above T_g even for the amorphous material. This explanation also has problems. Chlorinated poly(1,4-butadiene) of high molecular weight and unbranched is molecularly equivalent to PVC but has a totally head-to-head structure. In this polymer, notwithstanding the regular structure it is completely amorphous and very soluble in solvents such as chloroform and methylene chloride at room temperature[10]. If the properties of PVC in the solid state were attributable to the association between chains due to the C–Cl dipole, then the chlorinated butadienes should behave similarly. That they do not means that the dipolar interaction between chains cannot explain the solid state properties of PVC. The latter is insoluble in chloroform and most organic solvents. This is to be expected since most crystalline polymers are only sparingly soluble in solvents at temperatures far below the melting point. The melting point of PVC determined by the experiments described in this paper is 210°C, a temperature at which PVC decomposes if heated to for a prolonged time.

The explanation for the similarity of the DMTA curves in *Figure 10* is that PVC crystallizes rapidly at its T_g. This was determined by indirect density measurements using thermal mechanical analysis (TMA) equipment which measures changes in sample thickness with temperature. The results from such a measurement for unplasticized PVC which has been quenched from 210°C are depicted in *Figure 11*. It can be seen that rapid contraction due to crystallization occurs at the T_g of the polymer. The result for annealed unplasticized PVC is similarly depicted in *Figure 12*. This explains the similarity in the DMTA curves of *Figure 10*. The DMTA and TMA experiments were both conducted at the same heating rate of 2 degrees per minute and thus it can be seen that above T_g the samples rapidly become equivalent. It is worth speculating in passing that the rapidity with which PVC crystallizes and its failure to form spherulites suggests that the nucleation density of PVC is abnormally high.

Finally, TMA results for PVC + 10% DOP are shown in *Figure 13*. From these results it can be seen that the samples used in the SANS experiments which were carried out at room temperature were below T_g and could not therefore crystallize.

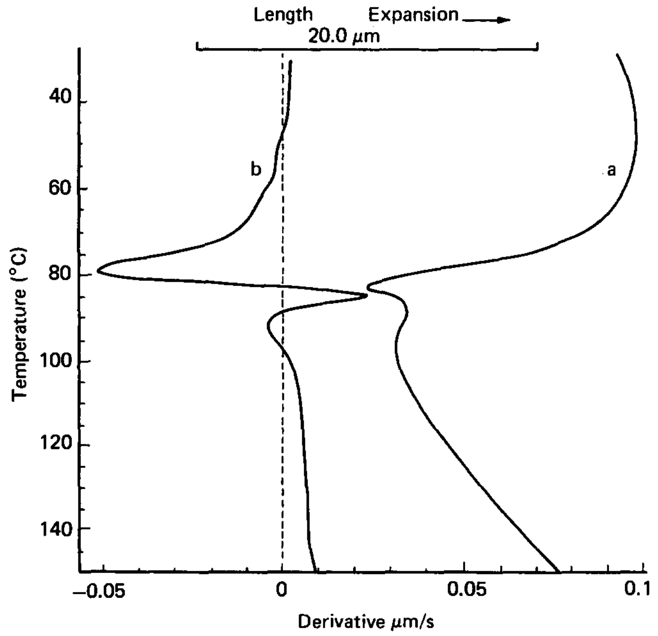

Figure 11 Thermal mechanical analysis curves of amorphous PVC quenched from 210°C. Heating rate 2 degrees per min. (a) Absolute change in thickness. (b) Derivative curve.

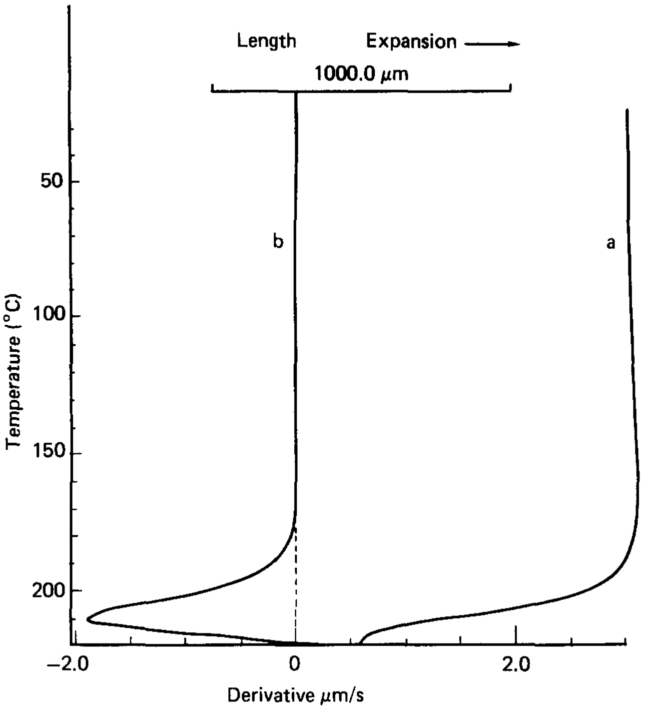

Figure 12 Thermal mechanical analysis curves of PVC annealed at 110°C for 5 h. (a) Absolute change in thickness. (b) Derivative curve

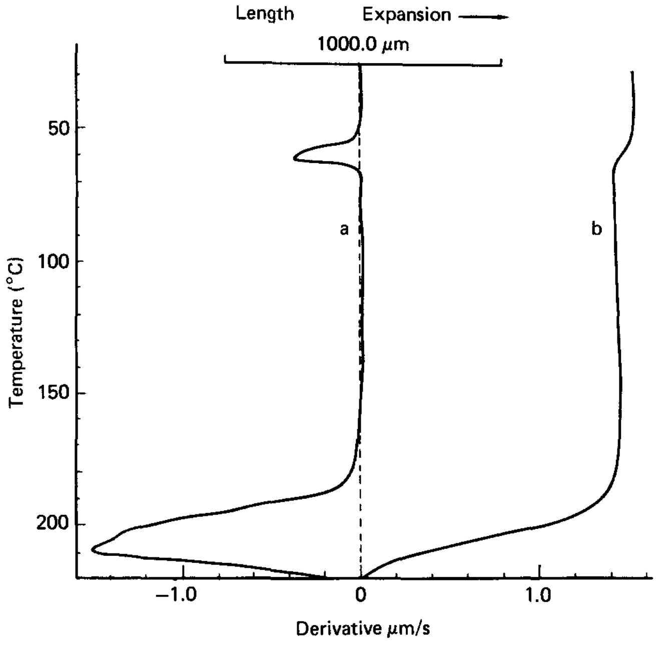

Figure 13 Thermal mechanical analysis curves of PVC+10% DOP quenched from 210°C. (a) Absolute change in thickness. (b) Derivative curve

Truly random copolymers of the PET type consisting of A crystallizable units described here, obey a simple thermodynamic law which relates melting point to comonomer content, which is

$$\frac{1}{T_m} > \frac{1}{T_{m0}} + \frac{R}{\Delta H} \ln X_A \qquad (1)$$

where T_{m0} is the melting temperature of the homopolymer containing only A units; T_m is the melting temperature of the copolymer; ΔH is the enthalpy of the A-units; X_A is the molar concentration of A units.

Equation (1) enables the minimum melting temperature of lamellae, consisting of homopolymer units will melt to be calculated. As the amount of comonomer increases the lamellae decreases in thickness and the melting point is reduced. If equation (1) is applied to the data for PVC and assuming it is a copolymer consisting of syndiotactic units interspersed with random atactic units then the computed melting point would be over 350°C. This is much too high and leads to the conclusion that the parts of the PVC chain which are present and able to crystallize are present as blocks.

CONCLUSIONS

(1) PVC is a crystalline polymer in which the crystallinity is about 15%.

(2) Comparing the crystallization behaviour of PVC with the random copolymer of PET of similar percentage crystallinity, shows that it differs in that PVC does not form spherulites and that it crystallizes much more rapidly.

(3) Further comparison of PVC with the completely amorphous head to head type polymer shows that it is markedly different. In particular, PVC is not soluble in dichlorinated hydrocarbons at ambient temperatures.

(4) The melting point of 10% plasticized PVC determined by SANS, SAXS and TMA is 210°C.

REFERENCES

1 Blundell, D. J. *Polymer* 1979, **20**, 934
2 Walsh, D. J., Higgins, J. S., Druke, C. P. and McKeown, J. S. *Polymer* 1981, **22**, 168
3 Turner-Jones, A., unpublished reported in a review 'Determination of Polymeric Structures by X-ray defraction methods', by C. W. Bunn, in 'Molecular Behaviour and the Development of Polymeric Materials', (Eds. A. Ledwith and A. M. North), Chapman and Hall, Ltd., London, 1974, p. 357
4 Wenig, W. *J. Polym. Sci., Polym. Phys. Edn.* 1978, **16**, 1635
5 Straff, R. S. and Uhlmann, D. R. *J. Polym. Sci., Polym. Phys. Edn.* 1976, **14**, 353
6 Wendorff, J. and Fischer, E. W. *Kolloid Z.Z. Polym.* 1973, **251**, 876
7 Wignall, G. D. and Brown, H. R., private communication
8 Herchenroder, P. *PhD Thesis* Mainz, 1978
9 Ballard, D. G. H. and Maskell, R. K., unpublished results
10 Ballard, D. G. H. and Courtis, A., unpublished results