Small-angle scattering studies of melting and recrystallization in poly(vinyl chloride)

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The melting and recrystallization behaviour of the microstructure in both plasticized and rigid poly(vinyl chloride) (PVC) has been examined using temperature-dependent small-angle X-ray scattering and small-angle neutron scattering. PVC plaques plasticized using dioctyl phthalate have been studied within the temperature range 90–195°C. The results are interpreted in terms of the fringed micelle model.

(Keywords: poly(vinyl chloride); small-angle scattering; X-ray)

INTRODUCTION

The microstructure of poly(vinyl chloride) (PVC) has attracted much interest in the literature. This is because it is known that the polymer, in both rigid and plasticized form, usually exhibits a heterogeneous structure that comprises ordered domains in an amorphous matrix[1]. The presence of these ordered domains is known to influence directly the physical and mechanical properties[2-4]. They are often described as being crystalline, although their exact form has not been fully established. Estimates from wide-angle X-ray scattering (WAXS) measurements have indicated that commercial PVC, which is polymerized in the range 50–70°C, has a crystallinity of 5–10%. The exact value is difficult to determine as it relies on having a totally amorphous sample as a reference; something which is very difficult to accomplish. WAXS measurements on unplasticized PVC have shown that the unit cell of the ordered phase is similar for all PVC types and is of an extended syndiotactic structure[5-7]. For commercial PVC, the syndiotacticity is ~50%. In dried PVC gels (originally 10% PVC), the existence of crystallinity has been inferred from their mechanical behaviour, small-angle X-ray scattering (SAXS)[8,9] and WAXS[7,10]. The limited extent to which PVC gels will swell on the addition of increasing amounts of plasticizer has been presented as evidence that the crystallites act as physical crosslinks between polymer molecules[11]. Additionally the storage modulus of PVC gels has been observed to increase as they age[9]. This has been correlated with SAXS results to indicate that this effect is due to an increase in the number of molecules forming these crosslinks.

The evidence presented above indicates that the structure of PVC comprises ordered domains, predominantly formed by the syndiotactic sequences within the polymer chain architecture, that are held together by a three-dimensional network of tie molecules. The ordered or crystalline structure, therefore, seems to resemble a particular type of fringed micelle[7,9-11]. SAXS is frequently carried out on plasticized samples due to the enhanced electron density difference between the crystalline and amorphous regions which results[11]. These studies indicate that the ordered or crystalline domains are separated by a characteristic distance of between 100 Å and 350 Å, depending on the level of plasticizer in the sample. The reason for the existence of a microstructure of such regularity is not well understood. Additionally, very little is known about the mechanism by which the ordered domains melt or crystallize and the microstructures formed at elevated temperatures.

SMALL-ANGLE SCATTERING

In small-angle scattering experiments the scattered intensity is measured as a function of **Q**, the momentum transfer vector. This parameter depends on the wavelength of the incident radiation and the angle at which the scattered radiation is detected and is reciprocally related to the spatial distances probed within the sample. By definition,

$$\mathbf{Q} = 4\pi \sin(\theta/2)/\lambda \tag{1}$$

where θ is the angle between the incident and scattered radiation and λ is the wavelength of the incident radiation. Conventional small-angle scattering facilities typically measure **Q** values within the range 0.005–1.0 Å^{-1}, providing structural information within the range ~10–1000 Å.

There are many different types of small-angle scattering model that have been developed in order to fit each of the diverse structures that have been examined. For regular morphologies, a correlation peak may be observed in the data. The **Q** value of the peak maximum and the peak width provide information on the inter-domain separation and its polydispersity. The simplest method

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for obtaining an approximate inter-domain spacing, or *d*-spacing, is to treat the peak as a simple diffraction phenomenon and use Bragg's law:

$$d = 2\pi/\mathbf{Q}_{\max} \qquad (2)$$

where $\mathbf{Q}_{\max}$ is the **Q** value of the peak maximum.

A Lorentz correction must be applied to the data in order to determine the correct value of the one-dimensional *d*-spacing[12]. Thus, the value of $\mathbf{Q}_{\max}$ is determined from a plot of $I\mathbf{Q}^2$ *versus* **Q**, which is the form in which the data are illustrated here.

In small-angle scattering the invariant can be defined by:

$$J = \frac{1}{2\pi^2} \int_0^\infty I(\mathbf{Q})\mathbf{Q}^2\, d\mathbf{Q} \qquad (3)$$

J is the mean square variance in electron density within the sample. It measures the total scattering power of the sample and is sensitive both to changes in the contrast between the two phases and to changes in their respective volume fractions. For semicrystalline polymers the value of the invariant is, therefore, sensitive to changes in the overall level of crystallinity.

EXPERIMENTAL

PVC sample preparation

The following rigid and plasticized PVC plaques were prepared for examination by real time X-ray scattering:

Dioctyl phthalate (DOP) plasticized PVC. The formulation used was 100 parts suspension polymerized PVC ('Corvic' S71/102, EVC (UK) Ltd), 100 parts DOP, 2 parts 17 tin stabilizer (Irgastab 17MOK, Ciba). Four plaques were made by pressing this formulation at temperatures of 130, 150, 170 and 190°C, respectively. All samples were pressed for 2 min at head pressure, then 2 min at 2 MPa and finally cooled to 50°C at 2 MPa. The samples were pressed between poly(ethylene terephthalate) sheets (250 μm thick) to produce plasticized PVC plaques (~390 μm thick).

Rigid PVC—solution cast. Suspension polymerized PVC was dissolved in tetrahydrofuran and then placed in an oven at 50°C to evaporate off the solvent. The sample was pressed into a plaque (<1 mm thick) at a temperature of 82±2°C.

PVC powders in DOP. PVC polymer grains, as polymerized, plus 10 wt% deuterated dioctyl phthalate (dDOP, deuterated octyl chains only) were sealed into disc-shaped aluminium containers of diameter 12 mm with a wall thickness of 200 μm and with a path length of 2 mm. The containers were then subjected to chosen thermal treatments and subsequently examined by small-angle neutron scattering (SANS).

Small-angle X-ray scattering

A Mettler DSC was used to provide the temperature ramps required for these experiments. The experiment was carried out using beamline 2.1 at the Daresbury Synchrotron Laboratory. The high intensity incident X-ray flux, of wavelength 1.54 Å, enabled the beam to be substantially collimated to form a 2 mm by 1 mm area on the sample without reducing its intensity to an unacceptably low level. The modified Mettler DSC was inserted into the path of the X-ray beam and mica sheets (10 μm thick) were used to contain the sample and provide a window through which the beam could pass. A quadrant detector, located in a vertical plane and covering an angle of 76° was used to detect the scattered radiation. It was located 2.5 m from the sample position, giving a measurable **Q** range of 0.013–0.03 Å^{-1}, enabling spatial features within the regime of 20–500 Å to be probed.

SAXS curves were collected sequentially over time intervals of 10 s as the temperature of the sample was heated or cooled at a specific rate. The recording of SAXS curves was started at the same instant as the d.s.c. scan to facilitate temperature calibration. The temperature was changed at either 10 or 20°C min^{-1}; rates commonly employed for d.s.c. measurements. Care was taken to ensure that the samples were never subjected to temperatures in excess of 195°C in order to minimize sample degradation.

The raw SAXS data were corrected for X-ray absorption and fluctuations in the incident X-ray flux by using an ionization chamber placed directly after the sample. The spectrum recorded from an ^{55}Fe source was used to correct for differences in the efficiency of individual detector elements. The **Q**-axis was calibrated from the diffraction peaks of wet rat tail collagen.

Small-angle neutron scattering

SANS data were recorded using the LOQ spectrometer at the Rutherford Appleton Laboratory. Measurements were carried out over a **Q** range of 0.005–0.22 Å^{-1}. Data reduction/manipulation was carried out using the standard LOQ software, COLLETTE[13].

RESULTS AND DISCUSSION

PVC plaques—melting and recrystallization studies

Plasticized PVC plaques. DOP plasticized PVC plaques pressed at 130, 150, 170 and 190°C were taken through a melting/recrystallization cycle which entailed heating the samples to 182°C at 10°C min^{-1}; holding them at that temperature for 4 min and then cooling them back down, also at 10°C min^{-1}, to 45°C. SAXS curves were successively collected for each of the samples over these temperature cycles, with each curve recorded over a 10 s period. The *d*-spacings were determined from the Lorentz corrected SAXS curves using Bragg's law, as described. The invariants were determined approximately by evaluating the integral [equation (3)] over the experimental **Q** range yielding a measure of the total scattering power of the sample. Examples of the experimental SAXS data and the information that was extracted are presented here in detail only for the plaque pressed at 150°C for the sake of brevity.

The Lorentz corrected SAXS data for the first melting cycle, from 87 to 182°C, and the first recrystallization cycle, from 182 to 87°C, are shown in *Figures 1a* and *b*, respectively, for the plaque pressed at 150°C. For clarity, only one in three of the recorded SAXS curves is displayed. Therefore, the curves represent the scattering at 5°C temperature intervals. As *Figure 1* indicates, during the melting cycle the correlation peak decreases as the temperature is increased until at 180°C it has almost completely disappeared. During the cooling cycle a correlation peak reappears at a different **Q** value and

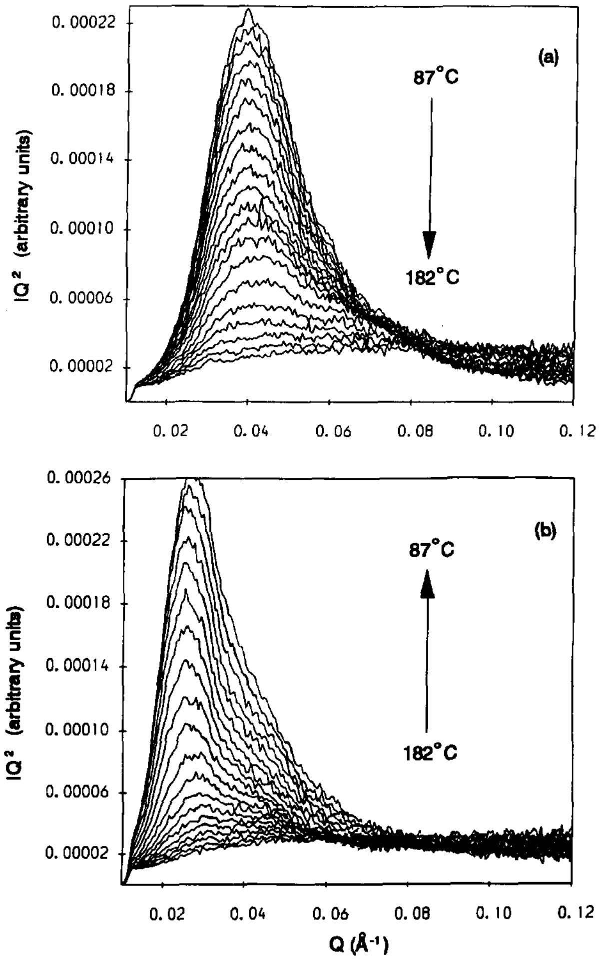

Figure 1 Lorentz corrected, temperature-dependent (heating rate, 10°C min^{-1}) SAXS data for plasticized PVC sample preseed at 150°C as described in the text. (a) Data for the melting cycle and (b) the subsequent recrystallization cycle. The direction of the arrow on these and all other such plots shown here relates to whether the SAXS peak intensity increases or decreases over the indicated temperature change

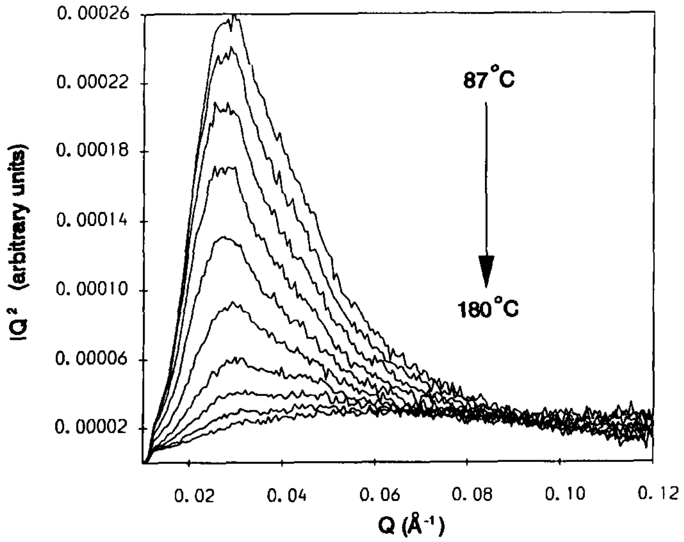

Figure 2 Lorentz corrected, temperature-dependent (heating rate, 20°C min^{-1}) SAXS data for melting cycle 2 of the same sample as in *Figure 1*

increases steadily in intensity as the temperature is reduced. Apart from the step change in the position of the peak, the **Q** values of the peak maxima are observed to remain reasonably constant, particularly for the melting cycle. The average *d*-spacings have been measured for both the melting and recrystallization cycles over most of this temperature range. By Bragg's law, the peak for the melting cycle corresponds to 157 Å compared with 242 Å for the recrystallization cycle.

A second temperature cycle, 2 min after the first, was additionally applied to only the 150°C sample. A temperature ramp of 20°C min^{-1} was used instead of the 10°C min^{-1} employed for cycle 1. The Lorentz corrected SAXS data are displayed in *Figure 2* for melting cycle 2 for 87 to 180°C. The *d*-spacings were found to be very similar to those found during the recrystallization cycle.

After the melting cycle 2, the temperature of the plasticized PVC sample was reduced from 180 to 150°C at 20°C min^{-1} and then the sample was held at that temperature for 3 min. The sample was then cooled further at the same rate to a temperature of 130°C and held again for 6 min. The SAXS data recorded during this experiment are displayed in *Figures 3a, b* and *c*. This figure clearly indicates the simultaneous presence of the two different *d*-spacings and the relative growth of the peak at lower **Q** (the longer *d*-spacing) both isothermally as a function of time and as the sample is cooled. *Figures 4a* and *b* plot the variation in the value obtained for the scattering invariant for both cycles. This indicates how, to a good approximation, the final level of crystallinity after thermal cycling is the same as that of the nascent polymer.

Table 1 shows the *d*-spacings that were determined from SAXS measurements on the plasticized PVC samples that were pressed at 130, 150, 170 and 190°C. They were measured for each plaque at room temperature, before any temperature gradient had been applied, and then again at this temperature after the sample had been subjected to a melting/recrystallization cycle.

It is clear from *Table 1* that the *d*-spacings change considerably for the 130 and 150°C plaques after the first melt cycle has been performed. This is due to the fact that the samples had not been subjected to high enough temperatures at any stage during their fabrication to melt fully the nascent PVC crystal structure. During the first melt cycle, however, temperatures of at least 180°C are applied and the nascent structure appears to melt completely. In the melt, the mobile polymer chains are free to form a more favourable ordered structure on subsequent cooling. This new ordered structure has a different characteristic inter-domain spacing to that measured originally for these samples.

The 170 and 190°C plaques had been subjected to temperatures at which the microstructure formed during the manufacture of the PVC powder had already been substantially melted out. Consequently, the *d*-spacings recorded for these plaques before and after the first melt cycle are similar.

Table 1 Summary of SAXS results for plasticized PVC

Pressing temperature (°C)	Original *d*-spacing (Å)	Final *d*-spacing (Å)
130	150	262
150	157	242
170	203	203
190	209	228

The *d*-spacings are accurate to within ~5% of the quoted values

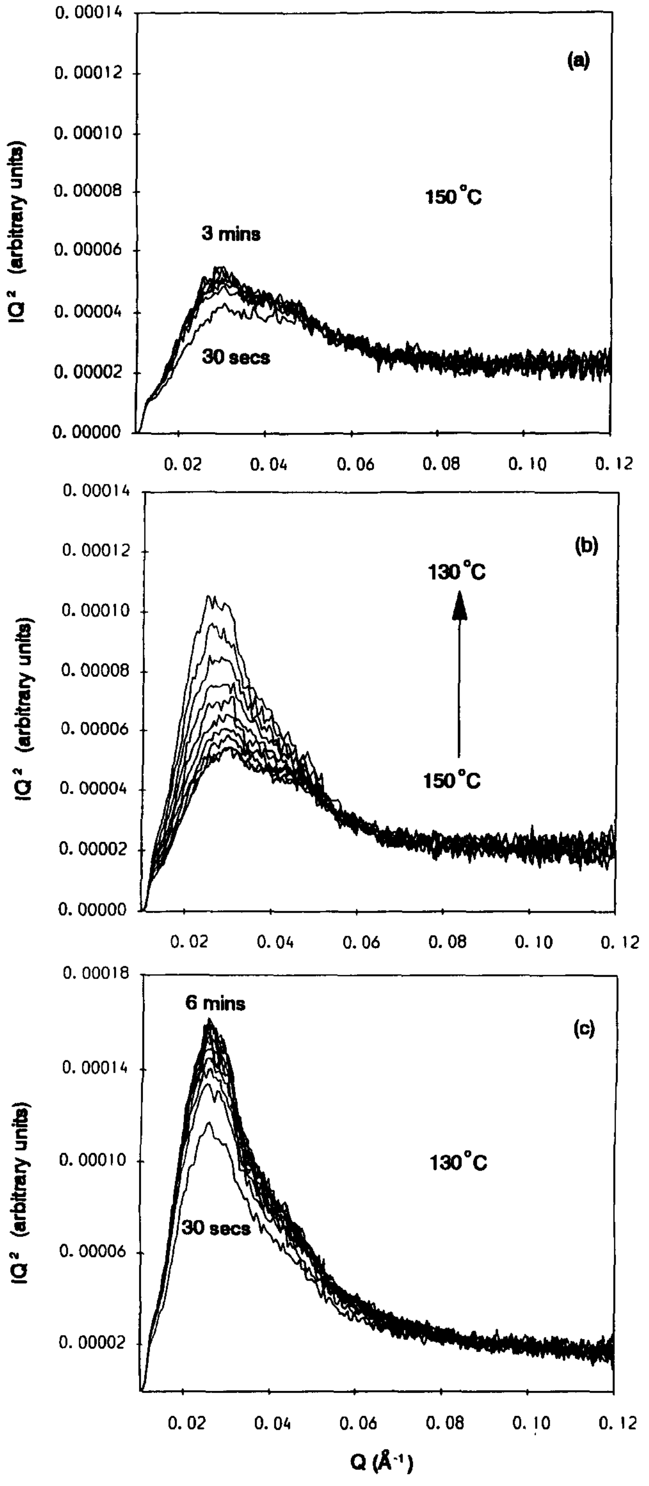

Figure 3 Lorentz corrected, temperature-dependent SAXS data for recrystallization cycle 2 of the same sample as in *Figures 1* and *2*. The sample was cooled at 20°C min^{-1} to 150°C and (a) held at that temperature for 3 min, then (b) cooled further at the same rate to 130°C and finally (c) held at that temperature for 6 min

Rigid PVC—solution cast. *Figures 5a* and *b* show Lorentz corrected SAXS curves for solution cast PVC during melting and recrystallization cycles, respectively. A temperature range of 40–180°C was used for these measurements. Due to the high level of noise on the data points, SAXS curves have only been plotted at temperature intervals of 20°C. The noise is attributable to the fact that the electron density difference between the ordered and disordered phases is much smaller in the absence of plasticizer. The *d*-spacings before and after the temperature cycles are measured approximately to be 97 and 124 Å, respectively. It appears that the correlation peak for the rigid polymer is somewhat broader than for plasticized polymer. This may indicate that the ordered domains in the solution cast PVC do not form as regular a morphology as observed in the plasticized PVC plaques. However, it is also possible that the correlation peak is bimodal. The data are too noisy to be certain but it is tempting to suggest that there are two peaks in the SAXS data at $Q = 0.065$ and 0.049 Å^{-1} corresponding to *d*-spacings of 97 and 128 Å, respectively. The noise on the data points and the width of the correlation peak prevent a detailed analysis of the melting and recrystallization behaviour from the SAXS data. There has not been very much work reported in the literature on microstructural studies of rigid PVC using SAXS because the electron density difference between the ordered and amorphous phases is often too small for standard laboratory equipment. In the work that has been performed[14,15], both the existence of a very weak correlation peak and its absence has been reported. Due to the high intensity of the Daresbury Synchrotron Source, it is possible to show clearly the presence of such a correlation peak.

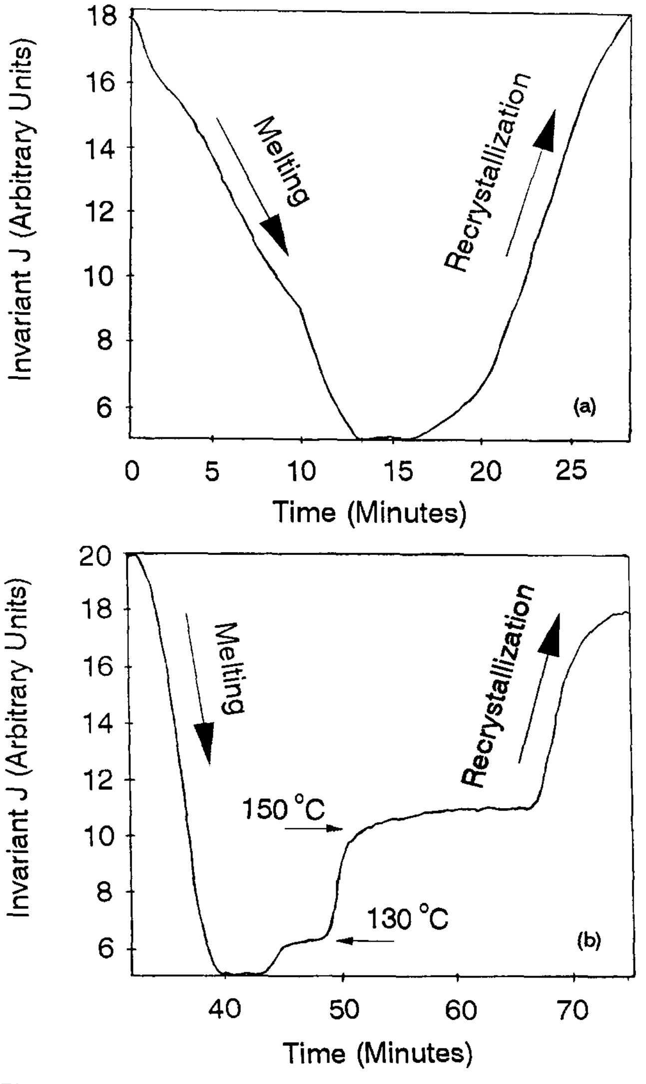

Figure 4 (a), (b) Variation of the value of the invariant calculated according to equation (3). The melting and recrystallization cycles as well as the isothermal periods to which the SAXS data shown in the preceding figures relate are indicated

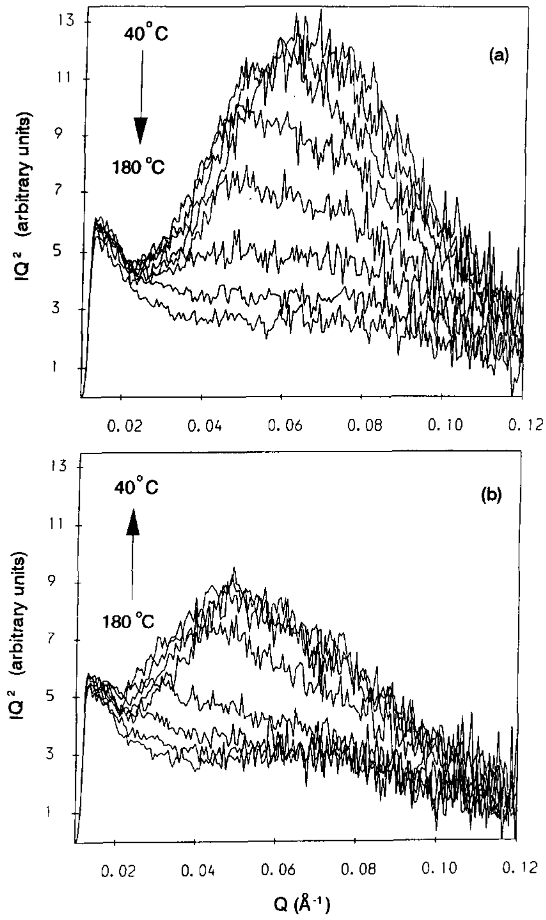

Figure 5 Lorentz corrected, temperature-dependent (heating rate, 10°C min^{-1}) SAXS data for rigid PVC sample prepared as described in the text. (a) Melting cycle and (b) recrystallization cycle

Plasticized PVC powders—SANS study

The aim of these experiments was to determine the effect of thermal history on the microstructure of PVC grains, as polymerized. PVC grains are porous particles, ~150 μm in diameter, which themselves have a complicated microstructure. Plasticizer is taken up into the grains by capillary action. Deuterated plasticizer was added to the polymer on the assumption that it would diffuse into the amorphous regions of the PVC, thereby, accentuating the difference in neutron scattering length density between this phase and the crystalline domains[16,17]. *Figure 6* shows the SANS curves recorded for the plasticized PVC powders with thermal histories of 30 min at 80°C, 10 min at 120°C and 5 min at 200°C. A correlation peak is present in all three of these curves, with the peak maximum for the first two centred at $\mathbf{Q}=0.036\ \text{Å}^{-1}$, corresponding to a d-spacing of 174 Å. The powder with the thermal history of 5 min at 200°C lies at a slightly lower **Q** value of $0.033\ \text{Å}^{-1}$, corresponding to a d-spacing of 190 Å (determined from the Lorentz corrected plot).

A comparison of the SANS data displayed in *Figure 6* shows that the intensity of the low **Q** scattering, $\mathbf{Q}<0.03\ \text{Å}^{-1}$, is reduced by nearly an order of magnitude for the PVC powder with a thermal history of 5 min at 200°C relative to those subjected to temperatures of 150°C or less. It has been ascertained that the low **Q** data for the latter decay monotonically as $\mathbf{Q}^{-4}$, within the range of $\mathbf{Q}=0.005\text{–}0.030\ \text{Å}^{-1}$ (see inset in *Figure 6*). This indicates that the scattering obeys Porod's law and is likely to originate from domains of >300 Å. It is possible therefore that the scattering is from the surfaces defining the boundaries of the primary particles in the PVC powder. Previous work indicates that they are likely to lie within the size regime of 5000–10 000 Å[18]. For the plasticized powder with a thermal history of 5 min at 200°C, the reduction in the low **Q** intensity indicates that the boundaries defining the primary particle surface have been melted out. This explanation would be consistent with previous work on PVC which states that at temperatures around 177°C the interactions of the primary particles with one another are increased as the two-phase microstructure network extends across particle boundaries, reducing and possibly destroying the primary particle boundary itself[11].

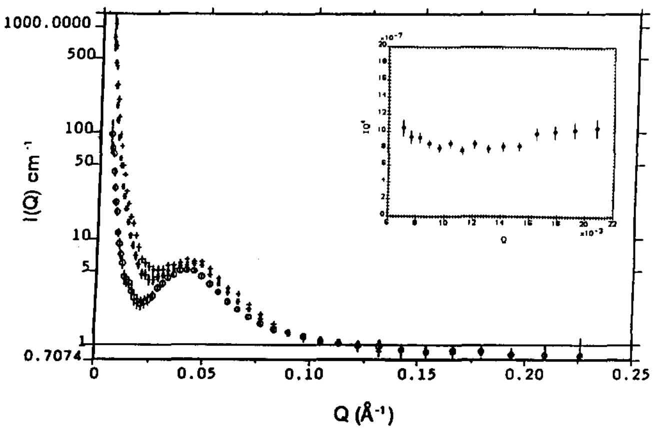

Figure 6 SANS data for PVC plasticized with dDOP. The different symbols relate to the thermal history of the sample: (+) 30 min at 80°C; (∗) 10 min at 120°C; (○) 5 min at 200°C. Error bars are superimposed on the data point symbols. The inset is a Porod plot (IQ^4 *versus* **Q**) of the data sets at low **Q** showing the $\mathbf{Q}^{-4}$ dependence

Further work is necessary to investigate the above effects in greater detail.

DISCUSSION

Real time SAXS data from polyolefins during the melting process indicate a peak which moves to lower **Q** as the temperature is increased[19]. This has been interpreted as being indicative of a process in which the thinner crystalline moieties melt out and may, in some cases, recrystallize onto larger, more stable lamellae giving rise to multiple endotherms[20].

In the case of PVC, the melting process has been shown here to be characterized as one in which the SAXS peak decreases steadily in intensity while remaining at the same position in **Q** right up to its final disappearance. This behaviour is quite different to that of polyolefins and serves to underline the differences between fringed micelle and lamellar morphologies. As mentioned in the Introduction, the majority of the SAXS intensity arises in plasticized PVC from the difference in electron density arising from the exclusion of plasticizer from the ordered domains. As the temperature is raised, plasticizer gradually begins to diffuse into the edges of these micelles, working its way further in as the temperature is increased towards the melting point. This is facilitated by increased polymer mobility at the edges of the micelles leading to an increase in free volume which, in turn, allows the ingression of plasticizer. In this way, the scattering contrast diminishes as the temperature is raised without giving rise to a change in the peak position. At the point at which the polymer finally melts, the plasticizer is evenly distributed throughout the sample and the scattering peak disappears. Therefore, the melting involves the gradual and uniform disappearance of the ordered domains rather than the selective melting of the thinner or less stable moieties which characterize polyolefin melting and gives rise to a change in the position of the scattering peak.

More perplexing is the recrystallization cycle in which a SAXS peak grows back at constant but quite different position in **Q** to the original peak position. When this morphology is subsequently melted again, the characteristics are the same in that the peak decreases steadily in intensity without moving in **Q**. The isothermal experiments performed on the final recrystallization show that, in fact, both peaks are present apparently in competition with one another, with the peak at lower **Q** relating to the favoured morphology.

First, it seems reasonable to accept that the nascent morphology in which there is a relatively higher domain nucleation density can revert to another form on subsequent melting and recrystallization. The nascent structure presumably does not represent the morphology favoured thermodynamically and given sufficient chain mobility, the polymer can adopt a lower energy state in which there are fewer, better developed, ordered domains. However, the isothermal experiments show that even after two melting cycles, there is a tendency initially still to produce both morphologies. The recrystallization process thus appears to be characterized by the presence of two crystal forms (type 1 and type 2) which differ in that one can form more readily but the other is preferred thermodynamically. In this way, slow cooling at normal (d.s.c.) rates will always produce the thermodynamically preferred type 2 low nucleation density form. It might be that it is necessary to go to much higher temperatures than these samples were subjected to in order to melt out fully the nascent morphology. thus, although at 180°C the small-angle scattering peak appears to have been melted out, vestiges of the structure might remain which act as seeds on cooling. In this way, the 'memory' of the nascent morphology is probably quite hard to remove completely.

There has been much work on the morphology of PVC gels in which it has been suggested that two different types of crystal morphology are formed[21]. It has been found that gels which have been stretched comprise small fringed micelles (type B) crystals intermixed with a larger lamellar (type A) form. The work presented here is either on highly plasticized PVC which is, of course, a gel or on solution cast rigid PVC which will have gone through a gel phase on drying. It is worth noting also that during polymerization, PVC/VC gels exist wherein the polymer is swollen by its monomer.

Whether the type A and type B crystal forms of reference 21 represent the two different types of nucleation site in our work is not clear. Certainly, there is no indication from the SAXS data of lamellar type melting as has already been discussed. Our data seem rather to suggest that both forms are based on fringed micelles. One can envisage a range of fringed micelle domains of varying stability and ease of formation depending on the length and purity of syndiotactic runs in the polymer chains that are available locally during crystallization. That they should fall into two reasonably distinct categories is surprising. It might suggest that there is a critical syndiotactic sequence length or similar requirement for type 2 morphology and that these conditions can be 'found' by the polymer if there is sufficient mobility and time. However, there are other looser associations that the polymer can adopt as an alternative which compete dynamically with the more stable form during the recrystallization process.

It has often been commented upon that the statistical probability of finding syndiotactic sequences of any length is extremely low unless one assumes that above some minimum sequence length, the distribution is no longer Bernoullian and that syndiotactic blocks become somehow preferred, leading to a syndiotactically blocky polymer. An alternative hypothesis is that complete syndiotactic purity is not a prerequisite for the formation of a fringed micelle. Below some critical purity, only the looser association is formed giving rise to domains containing several defects. However, above some critical local syndiotactic concentration, the more stable entity can form in which there are correspondingly fewer defects. The statistical requirements for such a scenario are much less exacting and one need not invoke unexpected and unexplained departures from Bernoullian statistical behaviour.

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