A SANS study of the structure of plasticized PVC

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The structure and crystallinity of plasticized poly(vinyl chloride) (PVC) has been examined using small-angle neutron scattering (SANS) and a deuterated plasticizer. The scattering curve, which shows a prominent peak at a Bragg spacing of ~11 nm, has been interpreted using a two-phase model where the phases are assumed to be plasticized amorphous material and unplasticized, probably crystalline, material. The volume fraction of the PVC that was unplasticized was obtained from the SANS invariant. The value found, 0.29, was relatively insensitive to the assumed amorphous density and consistent with the dependance of the scattering peak height on the fraction of the plasticizer that was deuterated.

(Keywords: PVC; SANS; plasticization; structure)

INTRODUCTION

The microstructure of both plasticized and unplasticized PVC is surprisingly little understood considering the technical importance of the polymer. PVC is generally considered to be slightly crystalline with the crystallites forming the junction points of a network that is important in giving the plasticized material its useful mechanical properties. The degree of crystallinity and form of the crystallites is not clear however. Among the reasons for this lack of understanding of the morphology of such an important polymer are the poor thermal stability of the material, which makes the melt inaccessible, and also the high absorption of X-rays, which adds difficulties to X-ray experiments. For these reasons neither the density nor the wide-angle X-ray scattering (WAXS) patterns are well known for amorphous PVC. This makes the measurement of crystallinities by either wide- or small-angle X-ray scattering (SAXS) rather uncertain.

Nonetheless, a considerable amount of both wide- and small-angle X-ray scattering work has been published on PVC. The use of highly syndiotactic material has permitted the determination of the crystal structure and density[1]. Attempts have been made to measure crystallinities by combining this information with densities and scattering patterns obtained from materials that have been quenched from high temperatures and are presumably amorphous[2,3]. Values of ~10–15% have typically been obtained in this way. A fairly similar value was found by Blundell[4], who assumed a two-phase model and obtained a crystallinity from the absolute SAXS invariant.

There is no direct information available on the crystallinity of plasticized PVC but both spectroscopic and thermal analysis techniques have been used to examine the change of crystallinity on plasticization. Tabb and Koenig[5] used *FT*i.r. to show that the bands which were characteristic of straight syndiotactic sequences and presumably came from the crystallites did not change in position or amplitude with plasticization. These bands have been used by Witenhafer[6] to follow crystallization after quenching. Brown *et al.*[7] used thermal analysis techniques to examine in more detail the effect of plasticization on crystallinity and showed that the maximum crystallinity obtainable was little affected by the addition of up to 50 phr (parts per 100 PVC) of plasticizer. WAXS has also been used to obtain the same conclusion[8].

SAXS studies combined with replica transmission electron microscopy (TEM) work have been used extensively to examine the effects of processing and plasticization on the morphology of PVC[9,10]. The interpretation of these results is rather problematic, however, as there are reproducibility and interpretation difficulties with this TEM technique and the SAXS data had a low signal-to-noise ratio. However it was concluded that the material was in a nodular form with a crystallite probably forming the core of each nodule.

The problems connected with the absorption of X-rays and the amorphous density uncertainties can be considerably alleviated by the use of a deuterated plasticizer and small-angle neutron scattering (SANS). The scattering length difference between the plasticized and unplasticized regions is not very sensitive to the assumed density of the amorphous PVC as it is controlled mainly by the large scattering length difference between the hydrogenated polymer and deuterated plasticizer.

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Also the scattering from this system is strong so that it is far less sensitive to 'dirt' in the polymer than is the case for the equivalent SAXS experiment. Another advantage of the SANS technique is that contrast matching methods can be used to test the validity of the assumed model. The aim of this paper is to describe an investigation of the structure of plasticized PVC using the SANS technique.

EXPERIMENTAL TECHNIQUE

The PVC used was IUPAC PVC No. 9, a suspension polymerized material with an M_n of 49 200 and M_w of 114 900 Daltons. This was plasticized with 33% by weight (50 phr) of mixtures of hydrogenated and deuterated nitrobenzene. Nitrobenzene was chosen because it is commercially available in a deuterated form. The plasticized samples were made by dissolving both the polymer and plasticizer in THF then slowly drying the sample to produce a film about 0.5 mm thick.

The SANS experiments were performed using at the 10 and 30 metre machines at the National Center for Small-Angle Scattering (NCSASR) at Oak Ridge. The data were corrected for absorption and background in the usual way and converted to absolute units using a polystyrene standard. This standard consisted of a mixture of monodisperse hydrogenated and deuterated polymer of known molecular weight whose scattering was fitted accurately as a Debye coil.

One aim of this work was to calculate the small-angle scattering invariant, Q, given by

$$Q=\int_0^\infty \frac{d\Sigma}{d\Omega}(q)d^3q$$

where $d\Sigma/d\Omega$ is the coherent scattering cross-section and the magnitude of the scattering vector q is related to the scattering angle 2θ and the neutron wavelength λ by

$$q=\frac{4\pi}{\lambda}\sin\theta$$

It was therefore necessary to subtract the incoherent background from the measured intensities and extrapolate the measured data to zero and infinite q. The incoherent background was estimated from the specimen transmission using the equation given by Jacrot[11] who suggested that the apparent incoherent scattering cross-section is given by

$$\left(\frac{d\Sigma}{d\Omega}\right)_{\text{inc}}=\frac{(1-T_{\text{inc}})g}{4\pi}$$

where for water $g=1.37$ at the relevant wavelength. It is to be expected that g will depend slightly on the detector and also on the mobility of the sample. A value of 1.43 has been found for water at Oak Ridge and a comparison of water and fully hydrogenated polystyrene suggests a value of 1.30 for polystyrene. As the mobility of plasticized polystyrene is intermediate between that of polystyrene and water a value of 1.37 was used for PVC. To obtain the required incoherent scattering transmission factor T_{inc} it was necessary to correct the measured transmission for the transmission caused by neutron absorption in the sample. The measured sample transmissions were found to agree well with that calculated from the known incoherent and absorption cross-sections and the incoherent scattering obtained was consistent with the observed high angle data. The data were extrapolated to high scattering angles by assuming conformity to the Porod law so that at high angles the intensity is given by

$$\frac{d\Sigma}{d\Omega}(q)=\frac{B}{q^4}$$

where B is a constant. This asumption is consistent with the use of a two-phase model with infinetely sharp phase boundaries which is implicit in the data analysis. The extrapolation to zero angle is relatively unimportant due to the low volume near the origin of reciprocal space and was done linearly to zero at the origin.

RESULTS AND DISCUSSION

Figure 1 shows experimental scattering curves for three deuteration levels of the plasticizer. The most noticeable feature of these curves is the massive peak with Bragg spacing of around 110 Å. This peak, though clear in the equivalent SAXS experiment[9], is much more distinct using the SANS technique for the reasons discussed in the Introduction. The 100% D data are shown in *Figure 2* as a plot of $(d\Sigma/d\Omega)q^4$ vs. q to test the Porod law assumption implicit in the data extrapolation. The scattering curve extended with the Porod tail is shown in *Figure 3*. It would appear from this figure that the extrapolation worked well.

The scattering curves were measured for the series 0%, 25%, 50%, 75%, 100% D plasticizer. The invariants for the 100% and 75% deuterated (D) material are shown in *Table 1*. The errors in Q are rather large for lower deuteration levels.

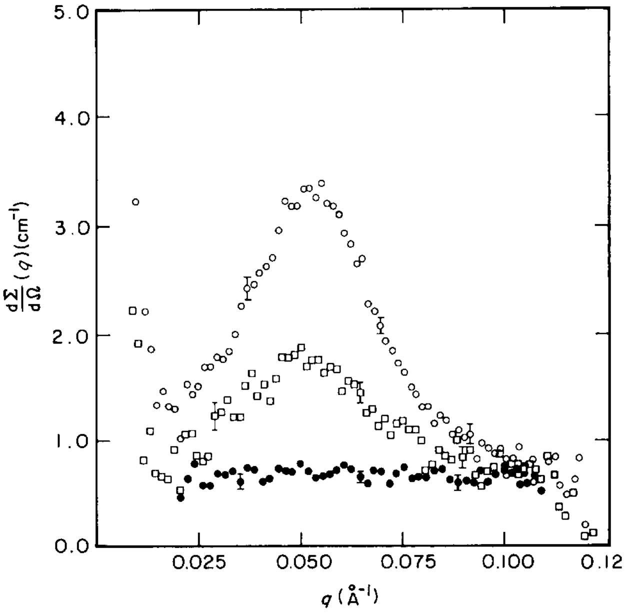

Figure 1 Total scattering cross sections (coherent and incoherent) for PVC plasticized by 33 wt% nitrobenzene: (○) 100% deuterated nitrobenzene; (□) 50:50 D- and H-nitrobenzene; (●) 100% H-nitrobenzene

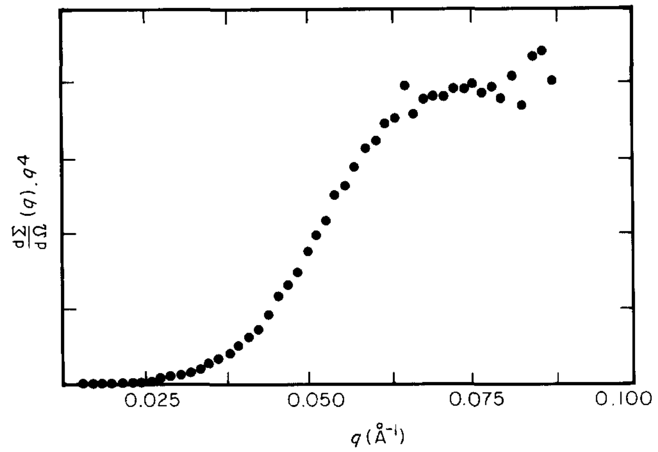

Figure 2 Porod plot of the data from the 100% D sample

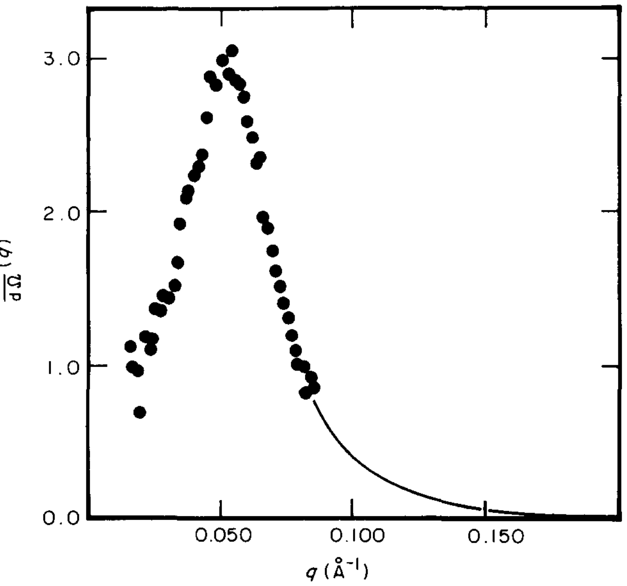

Figure 3 100% D data shown with the Porod tail extension

A primary aim of this work was to obtain information on the fraction of unplasticized, probably crystalline material in plasticized PVC. With certain assumptions this information can be obtained from the invariant, Q. For a two phase model

$$Q=(2\pi)^3 V_u(1-V_u)(\rho_{bp}-\rho_{bu})^2$$

where V_u is the volume fraction of unplasticized (assumed crystalline) material and ρ_{bp}, ρ_{bu} are the scattering length densities for the plasticized and unplasticized phases. The crystalline phase was assumed to have a density of 1.53 g/ml and the amorphous PVC was initially assumed to have a density of 1.35 g/ml, values consistent with previous published work[4]. Densities of 1.20 and 1.25 g/ml were assumed for the H- and D-nitrobenzene. Volume additivity was assumed in the amorphous phase. A weight fraction of the PVC, W_c, that was crystalline was assumed and from it the $V_u(1-V_u)$ calculated. In addition from the value of W_c it was possible to calculate the scattering length density of the plasticized phase. The scattering length density of the unplasticized phase was assumed constant, equal to the value for crystalline PVC. It was therefore possible to calculate another value of $V_u(1-V_u)$ from the invariant and the equation above. W_c was then varied to find the value such that the estimates of $V_u(1-V_u)$ were in agreement.

The value of W_c obtained in this way was 0.32, which corresponds to a volume fraction of PVC that is unplasticized and assumed crystalline of 0.29.

The dependence of crystallinity on assumed amorphous density was checked by recalculating an assumed density of 1.385, which is possibly the largest value in the literature. In this case W_c was found to be 0.31 so the method is not very dependent on the assumed amorphous density. The way that the invariant was obtained in these experiments assumes that the material is isotropic. The samples were made by drying from solution, a technique that produces films with planar orientation in glassy polymers; but nitrobenzene is a good plasticizer for PVC (the films were soft and rubbery), so that orientation seems unlikely.

Data were taken over a range of ratios of D- to H-nitrobenzene and the peak heights I_p obtained are shown in *Table 2*. If it is assumed that the morphology of the plasticized polymer is independent of deuteration level, an assumption that is reinforced by the fact that the scattering curves do not change in shape with deuteration level, then the scattered intensity is given by

$$I(q)=C(\Delta\rho_b)^2 S(q)$$

where C is a constant, $\Delta\rho_b$ is the difference in scattering length density between the two phases and $S(q)$ is a scattering function dependant only on the morphology. It follows that $I_p^{1/2}$ should vary linearly with deuteration. Clearly

$$I_p^{1/2}=R(\rho_{bp}-\rho_{bu})$$

where R is a constant. If the small difference in density between D- and H- nitrobenzene is ignored, then

$$\rho_{bp}=V_{pv}\rho_{bpv}+(1-V_{pv})\rho_{bn}$$

where V_{pv} is the volume fraction of the plasticized region that contains polymer and ρ_{bpv}, ρ_{bn} are the scattering length densities of the amorphous polymer and plasticizer. In addition

$$\rho_{bn}=\psi\rho_{bnd}+(1-\psi)\rho_{bnh}$$

where ψ is the fraction of deuterated plasticizer. Hence

$$I_p^{1/2}=R(A+B\psi)$$

where A and B are simple combinations of the densities

Table 1 Invariants for 100% and 75% deuterated material

% Deuteration	Invariant (cm^{-4})
100	10.4×10^{21}
75	7.4×10^{21}

Table 2 Peak heights for series

% Deuteration	I_p (cm^{-1})
100%	2.95
75%	1.82
50%	1.35
25%	0.42

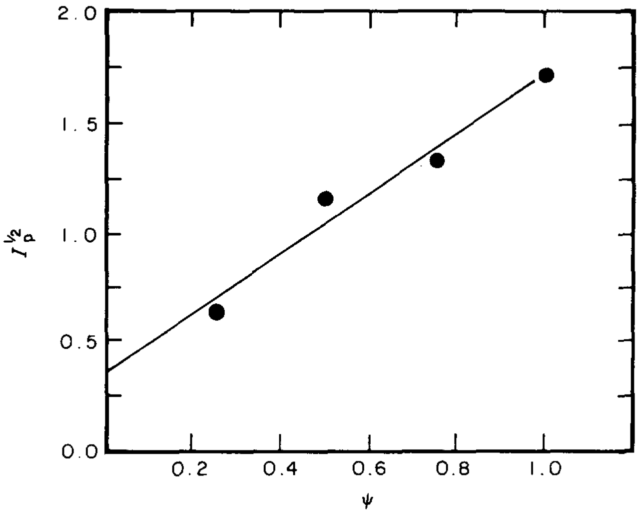

Figure 4 Plot of square root of the peak height against fraction deuteration of the plasticizer

and volume fractions. This suggestion is tested in *Figure 4* where $I_p^{1/2}$ is plotted against ψ. The excellent agreement observed helps to confirm the basic two-phase model and can be used to test the value of W_c obtained above. ψ, though defined as a volume fraction, is a variable that describes the scattering length density of the amorphous phase; it can be extended to negative values to represent a scattering length less than that of material plasticized by H-nitrobenzene. All the constants that go to make up A and B are known so it is possible to calculate from W_c the value of ψ at the intercept on the zero intensity axis. This value is -0.18, a number to be compared with the experimental value of -0.26 ± 0.15. The results of the contrast variation experiment are consistent with absolute invariant results described earlier.

This experiment basically measures the volume fraction of PVC than is unplasticized. This includes all the crystalline material and perhaps some highly constrained interfacial material. As little is known about the latter it will be ignored in the following discussion, though it may be very significant.

The value of 0.32 obtained in this experiment for weight fraction crystallinity of PVC is not in agreement with the majority of the literature on the subject, but there is considerable precedent for this sort of value. The most direct technique, WAXS, is very dependent on the shape chosen for the amorphous fraction, as discussed in some detail by D'Amato and Strella[3]. They tried two choices for this shape but could find no internal evidence that one was better than the other. Their choice *B*, which was similar to a previous choice by Lebedev[12], gave crystallinity values of ~0.35. Their preference, however, was for choice A, which gave values of about 0.15 for typical 55C suspension polymerized material. More recently Guerrero *et al.*[13], did some high temperature WAXS studies on PVC and obtained curves at 180°C distinctly different from those obtained by quenching and measuring at room temperature. Their material undoubtedly did suffer some degradation during the experiment but the particular peak that they ascribed to the noncrystalline fraction of the PVC appeared on heating and decreased again on cooling. From the shape of this curve they suggested that the PVC at 180°C showed a degree of intermediate order. They therefore argued that quenched material is probably microcrystalline, a suggestion that is in accord with its surprisingly high density.

The question of how PVC manages to obtain such high crystallinity while it is essentially atactic is still open[7]. It is hard to explain crystallinities of 0.10 with the crystals containing only straight chain syndiotactic sequences so if the crystallinity is 0.32 this could not be the case. Juijn *et al.*[14] have suggested that some isotactic dyads could be incorporated in the crystals; if enough of this happens maybe they should be considered more as nematic liquid crystals.

The most noticeable feature of the scattering curve is the existence of an extremely clear peak. Any number of models can be proposed to explain the origin of this peak. The peak has been observed in SAXS from gels containing only 10% polymer, therefore it must arise from more than just a volume exclusion correlation and, as such, the positions of the crystallites must be fairly well correlated. Work is currently underway using combined WAXS and SAXS in a temperature cell in a synchrotron, where the X-ray intensity decreases degradation problems, to gain more information on the origin of this peak.

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