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X-ray high pressure study of polyvinylidene fluoride

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An X-ray high pressure study at room temperature of both phase I and phase II crystal structures of polyvinylidene fluoride has been carried out. At room temperature both phases are stable up to pressures greater than 14 kbar. The variation of lattice compressive strains with pressure could be fitted to the Tait equation with little scatter and the variation of the unit cell parameters with pressure computed. The bulk lattice compressibilities of both phase I and phase II was found to be considerably less than that of polyethylene with the lowest compressibility being found for the phase I structure. The linear lattice compressibilities are extremely anisotropic with the lowest compressibility being in the chain direction as expected. However, at the highest pressures, for the case of phase II it was observed that this anisotropy was greatly reduced. Applications of these data to the unique piezo-electric activity of PVF_2 are pointed out.

1. Introduction

In recent years, high pressure X-ray studies of several polymers have been carried out by various workers. An investigation of polyethylene at room temperature at pressures up to 4 kbar was made by Ito [1]. A phase transition occurring in polytetrafluoroethylene at room temperature and 7.2 kbar was studied by Flack [2]. The crystallization of polyethylene under conditions of high pressure at high temperatures was investigated by Bassett *et al.* [3] using X-ray methods. In this laboratory high pressure studies of polyethylene [4, 5] and nylon 11 [6] at room temperature and at elevated temperatures has been made. An X-ray study of the crystallization of polyethylene at high pressures has also been made by Yasuniwa *et al.* [7]. A recent review of X-ray high pressure studies of polymers has been made by Ito [8].

Crystallization studies of polyvinylidene fluoride (PVF_2) at high pressures and temperatures have been carried out by several investigators. Doll and Lando showed that pressure crystallization of PVF_2 gave rise to a new X-ray pattern which they designated as phase III, but later they demonstrated that this phase was a mixture of phase I and phase II [9, 10]. The effect of heat treatments at high pressure on the three crystalline forms of PVF_2 was studied by Hasegawa, Kobayashi and Tadokoro [11] who concluded that phase II was the most stable at ambient pressure, phase I was formed under special conditions, while phase III was an intermediate modification between I and II. On the other hand a third crystal phase, phase III was reported by Hasegawa, *et al.* [12] to be obtained by casting from a solution of dimethyl sulphoxide. Heating of unoriented phase II under high pressure gave rise to a mixture of phase I and phase III. More recently a study of melting and crystallization under high pressure has been made by Matsushige and Takemura [13] using a high pressure DTA cell.

The question of the relative stabilities of phases I, II and III appears to be unsettled at the present time. Investigations at atmospheric pressure, of samples subjected to various heat treatments and pressures, do not elucidate crystal structures present at high pressures without ambiguity, since reversible solid state phase transitions may occur with increasing or decreasing pressure and have been reported for other polymers [2, 3, 5–7]. More-

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over, studies with a high pressure DTA cell at this laboratory do not confirm in all respects the study of Matsushige and Takemura [13]. Unambiguous phase determination at high pressure can only be made using high pressure X-ray techniques.

PVF_2 is also interesting from the stand point of its unusual piezo-electric activity. The mechanism for the piezo-electricity and pyro-electricity observed in poled films of oriented phase I PVF_2 is not completely understood at the present time, but it now appears probable that dipole orientation in crystallites is most important. If the piezoelectric effect arises from changes in dipole moment per unit volume caused by lattice compression, then the magnitude of the peizo-electric coefficient should be directly related to the lattice compressibility. High pressure X-ray diffraction can be used to measure lattice compressibility at different pressures and temperatures.

For these reasons PVF_2 has been studied both at room temperature and at higher temperatures using high-pressure X-ray methods: These data have been supplemented with high-pressure quenching crystallization experiments and high pressure DTA studies. Here the results obtained using high pressure X-ray methods at room temperature are presented. Both phase I and phase II crystal structures were studied.

2. Experimental details

2.1. Sample preparation

Capacitor grade Kureha KF-film was obtained from Kureha Chemical Industries Co. Ltd., Japan. To prepare unoriented samples with phase II crystal structures, the film was melted and slowly cooled to room temperature. The resulting film was annealed at 120° C for one hour. To prepare samples of phase I crystal structure the film was drawn at 50° C to a draw ratio of ~5:1.

2.2. X-ray diffraction high pressure camera

A high-pressure X-ray diffraction camera designed and constructed in this laboratory and based on the diamond piston-anvil method was used. The sample was contained by a gasket, and surrounded with silicone oil so that a hydrostatic pressure on the sample was generated. The sample was mixed with hexamethylene tetramine (HMT) which could be used as an internal standard to determine the applied pressure [14]. Filtered molybdenum radiation was used from a Rigaku-Denki rotating anode 6.3 kW X-ray generator. X-ray patterns were recorded on flat film. The film to specimen distance was determined from the X-ray diffraction from the HMT at atmospheric pressure.

2.3. Phase II crystal lattice

A typical X-ray diffraction pattern taken at ~5 kbar of a phase II sample is shown in Fig. 1. The sample is unoriented so that complete Debye–Scherrer rings are obtained. Two rings from HMT, (1 1 0) and (2 1 1), are present together with some lines determined as originating from the gasket material. Large Laue spots from the diamond crystals are also evident. Three strong reflections (1 1 0), (0 2 1), and (0 0 2) from PVF_2 can be seen together with a fourth strong reflection (0 2 0) partially obscured by the (1 1 0) reflection from HMT. A sample containing no HMT was studied and the (0 2 0) reflection was easily observed.

According to Hasagawa *et al.* [12], phase II is

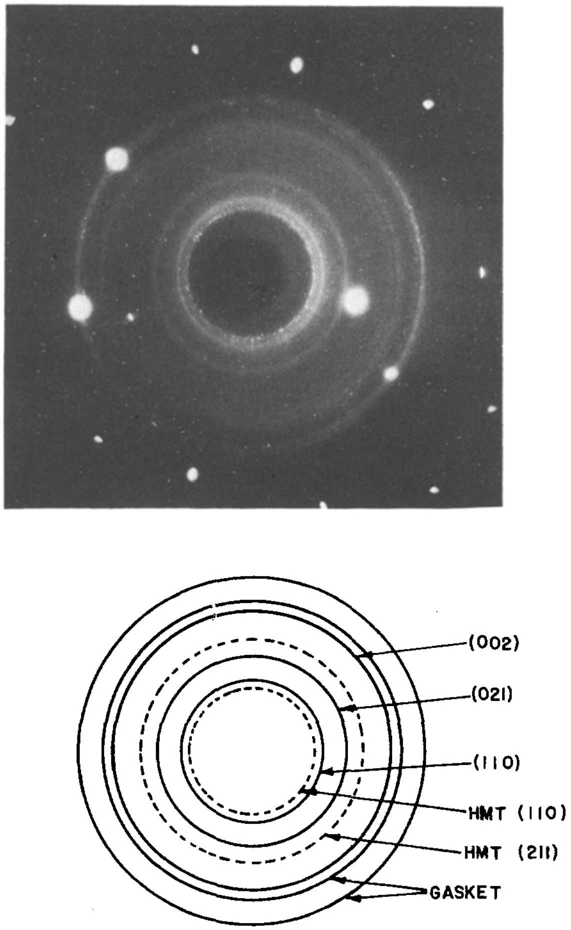

Figure 1 X-ray diffraction pattern of PVF_2 phase II at ~ 5 kbar (specimen–film distance = 6.88 cm).

monoclinic but pseudo-orthorhombic; $a = 4.96$ Å, $b = 9.64$ Å, $c = 4.62$ Å and $\beta = 90°$. No indication that the structure should be considered as monoclinic is indicated from the lattice, which is orthorhombic to within the experimental accuracy of the data. The space group cannot be assigned with complete confidence at the present time and both monoclinic and triclinic space groups are possible. Tadokoro and co-workers suggest the space group $P2_{1/c}$ (C^5_{2h}) which is monoclinic.

The procedure adopted was to take a large number of X-ray diffraction photographs at various pressures up to 14.6 kbar. The pressures were determined to within 0.2 kbar using the reflections from HMT. At each pressure the unit cell dimensions were determined from the *d*-spacings of (1 1 0), (0 2 1) and (0 0 2) reflections, assuming lattice orthogonality remained at higher pressures. Two separate sequences of measurements were made on two different samples to obtain a large number of data, to provide an indication of the actual scatter of data points, and to test for systematic errors.

2.4. Phase I crystal lattice

Fig. 2 shows an X-ray diffraction photograph taken using the oriented phase I sample at approximately 5 kbar. Laue reflections from the diamonds, and Debye–Scherrer rings from HMT and gasket material are present as before. Four reflections from the PVF_2 fibre are clearly visible; two equatorial reflections and two first-layer line reflections.

Although all reflections from phase I can be indexed on the basis of a hexagonal lattice, Lando *et al.* [15] have pointed out that space group Cm2m considerations indicate that the cell is orthohombic with a space group Cm2m (C^{14}_{2v}). Using the orthohombic cell as a basis for assigning indices, all reflections except (0 0 1) correspond to at least two different sets of indices. The four most intense reflections from PVF_2, visible on Fig. 2 are {(2 0 0), (1 1 0)}, {(3 1 0), (0 2 0)}, {(1 1 1), (2 0 1)} and (0 0 1). A sequence of photographs was taken at different pressures up to 14.1 kbar, and the *d*-spacings measured at each pressure level.

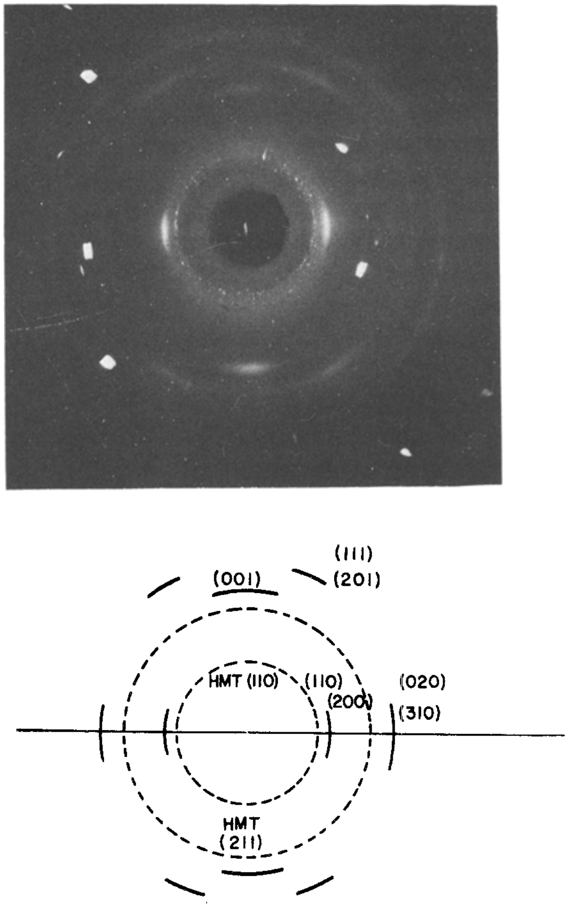

Figure 2 X-ray diffraction pattern of PVF_2 phase I at ~ 5 kbar (specimen–film distance = 6.88 cm).

3. Results

3.1. Phase II

The phase II crystal structure appeared to be stable at room temperature for increasing pressures up to 14.6 kbar. Fig. 3 shows the variation in strains on the (1 1 0) and (0 2 1) planes for various pressures, all data from different samples being included on the same figure. For purposes of comparison the lattice strain versus pressure variation for the (1 1 0) polyethylene lattice planes is shown. The solid lines represent the Tait equation $(-\epsilon = A \ln [1 + (P/B)])$ in the

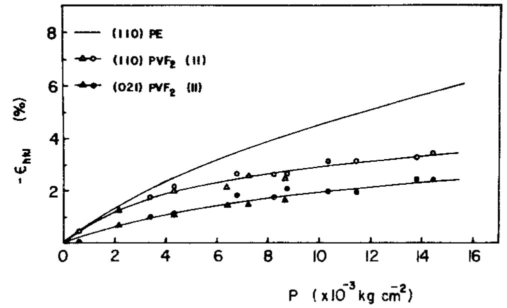

Figure 3 Comparison of phase II (1 1 0) and (0 2 1) lattice compressive strains versus pressure with polyethylene (1 1 0) planes.

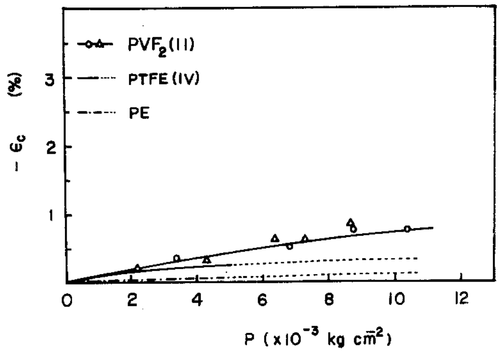

Figure 4 Comparison of lattice compressive strains in the chain direction for polyethylene, polytetrafluoroethylene, and PVF$_2$ phase II.

parameters chosen to best fit the data. The best fit parameters obtained were:

for (1 1 0) $A = 0.0138$, $B = 1.39 \times 10^3$ kg cm^{-2}

for (0 2 1) $A = 0.0147$, $B = 3.51 \times 10^3$ kg cm^{-2}

The Tait equation, with only two adjustable parameters appears to provide an excellent fit of the data. Moreover the data obtained from two completely different samples did not show appreciable differences.

Fig. 4 shows the corresponding data for the (0 0 2) planes. This data also was fitted to the Tait equation shown by the solid line in Fig. 4, the parameters obtained being $A = 0.0645$, $B = 50.00 \times 10^3$ kg cm^{-2}. Since the chain direction is perpendicular to the (0 0 2) planes this figure provides an indication of the compressibility of the lattice in the chain direction. It can be seen that the elastic strains are very small (less than 1% even at pressures above 10 kbar). The corresponding data obtained by Ito [16] for polyethylene and polytetrafluoroethylene are also shown. As expected the lower energy chain conformations for polyethylene and polytetrafluorothylene give rise to a lower compressibility parallel to the chain direction. This would indicate that the greater compressibility for the case of PVF$_2$ is obtained by incremental bond angle rotations giving rise to a twisting about the chain axis.

The data from Figs. 3 and 4 enable the lattice parameters *a*, *b* and *c* to be calculated as a function of pressure. The *c*-parameter can be obtained directly from (0 0 2) planes. If this is known the *b*-parameter can be calculated from (0 2 1) planes. The *a*-parameter can then be obtained from (1 1 0) planes. Fig. 5 shows the fractional variation in *a* and *b* parameters calculated from the Tait equation parameters. There is very little difference at lower pressures, but above 7 kbar the *b*-axis appears to show a greater compressibility.

3.2. Phase I

The phase I crystal structure appears to be stable at room temperature for increasing pressures up to 14.1 kbar. The changes in *d*-spacing for the (0 0 1) planes were so small even at the highest pressures that they could not be measured with reliability. The values actually obtained are shown in Fig. 6. The solid lines shown for polyethylene and polytetrafluoroethylene suggest that the compressibility in the chain direction for PVF$_2$ is comparable to these polymers. Since the phase I chain conformation is very close to planar zig-zag this would be expected. Certainly the compressibility in the chain direction for phase I is much less than is the case for phase II. The variation in strain with pressure for the other nonequatorial reflection [(1 1 1), (2 0 1)] is also shown on Fig. 6. Since strains on these planes also involve strains not perpendicular to the chain axis these strains are

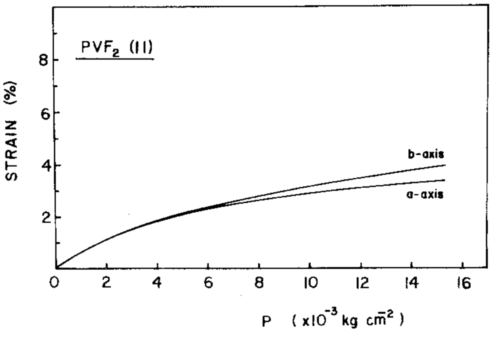

Figure 5 Phase II lattice parameter variation with pressure.

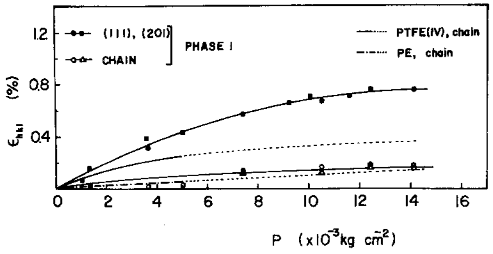

Figure 6 Comparison of lattice compressive strains in the chain direction for polyethylene, polytetrafluoroethylene, and PVF$_2$ phase I.

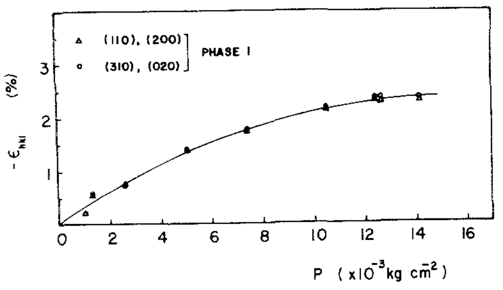

Figure 7 Lattice compressive strain variation with pressure for phase I.

also small. The solid line through these points represents the best-fit Tait function with parameters $A = 0.00506, B = 3.68 \times 10^3$ kg cm^{-2}.

Changes in the reflections from planes parallel to the chain axis were much larger and are shown in Fig. 7. If the hexagonal symmetry of the lattice is maintained at higher pressures then lattice compressibilities perpendicular to the chain direction should be isotropic, and this is observed. The solid line represents the best fit Tait function through the data, with parameters $A = 0.0157, B = 3.75 \times 10^3$ kg cm^{-2}.

4. Discussion

From the Tait equation parameters obtained for both phase I and phase II lattice compressive strains, the variation in unit cell parameters and unit cell volumes with pressure can be calculated. Volumetric data is shown for both phase I and phase II in Fig. 8 together with the volumetric data for polyethylene. Clearly phase I is considerably less compressible than phase II and both are less compressible than polyethylene. It is known that phase I is a more dense phase than phase II owing to a higher packing efficiency. The greater chain compressibility for the case of phase II has already been discussed. From these considerations the relative compressibilities of the two phases observed in Fig. 8 would be anticipated.

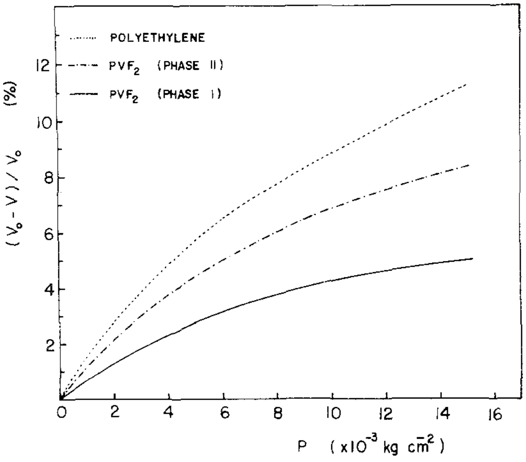

Figure 8 Comparison of volumetric strain variation with pressure for phase I, phase II and polyethlene.

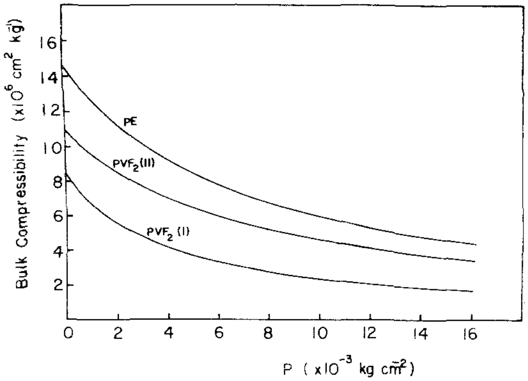

Figure 9 Variation of bulk compressibility with pressure for phase I, phase II and polyethylene.

It is, however, perhaps surprising that polyethylene with the excellent packing efficiency possible with a symmetric molecule, and a low energy all trans planar zig-zag molecular conformation should show a higher volumetric compressibility. The repulsive potential arising from the fluorine atoms may perhaps be responsible for the low volumetric compressibility observed for PVF$_2$ compared with polyethylene. In Fig. 9 the lattice bulk compressibilities for polyethylene phase I and phase II PVF$_2$ are shown as a function of pressure and confirm these observations.

In Fig. 10 the various lattice linear compress-

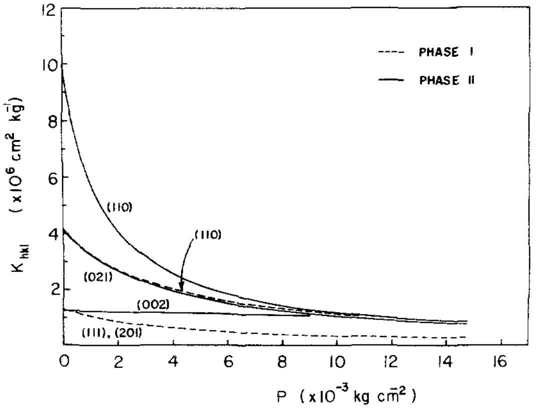

Figure 10 Linear compressibilities in phase I and phase II.

ibilities for both phase I and phase II are shown. It is interesting to observe that the compressibility of the (1 1 0) planes of the phase II structure is the greatest ($\sim 10 \times 10^{-6}$ cm^2 kg^{-1}) at atmospheric pressure. A very rapid decrease with pressure is observed, however, and at approximately 14 kbar the compressibilities on (1 1 0), (0 2 1) and in the chain direction are all identical ($\sim 1 \times 10^{-6}$ cm^2 kg^{-1}). Thus the anisotropy in lattice compressibility usually assumed for crystalline polymers has essentially disappeared at these pressures for phase II PVF_2. The decrease in lattice compressibility with pressure for phase I is also shown.

Some comment concerning the piezo-electric activity of PVF_2 is important since this polymer is unique in this respect. If we assume that piezoelectricity arises from lattice compression of dipoles then it should be noted that the lattice compressibility in the dipole direction is important. Phase I PVF_2 shows the greatest activity and the dipole direction is close to the *b*-axis direction. The lattice compressibility in the *b*-direction is calculated to be 4.2×10^{-6} cm^2 kg^{-1}. The lattice compressibility in the *a*-direction for phase II is calculated to be $\sim 11.4 \times 10^{-6}$ cm^2 kg^{-1}. The piezo-electric activity for phase II PVF_2 films is less than that observed for phase I films and this is usually attributed to the centrosymmetric lattice for phase II. The compressibility data obtained suggests a very great improvement in piezo-electric activity would be expected if the phase II crystal structure were non-centrosymmetric, since the piezo-electric coefficient should be roughly proportional to lattice compressibility parallel to the dipole direction. In fact, recent reports suggest that a polar phase II structure can be produced by poling films with very high poling voltages [17]. Of course, for the case of the phase II crystal structure the dipole direction is no longer perpendicular to the chain axis. Nevertheless, based on the data observed, we conclude that observations of the piezo-electric activity of polar phase II films may be very interesting.

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