Disorder in the crystal structures of phases I and II of copolymers of tetrafluoroethylene and hexafluoropropylene

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X-ray diffraction patterns for oriented and unoriented copolymers of tetrafluoroethylene and hexafluoropropylene are presented. They show a transition between 229 and 243K for a copolymer with about 3.4 CF_3 per hundred main chain carbon atoms. The lower temperature phase (II) appears to be similar to that of the homopolymer. A primary difference is the presence in the copolymer crystals of small longitudinal displacements of the molecules caused by the randomly located CF_3 groups. The displacements increase with increasing CF_3 concentration. The higher temperature phase (I) is similar to that of the homopolymer with a difference again being the longitudinal disorder of the copolymer. The difference disappears at higher temperatures as longitudinal disorder is introduced thermally in the homopolymer. At 296K (phase I) the molecular stems in a copolymer with about 3.4 CF_3 per hundred main chain carbon atoms are at an angle of 37.1 degrees with respect to the normal to the basal plane of the lamellas. In phase II, this number is the same within the limits of error.

INTRODUCTION

The phase diagram of polytetrafluoroethylene and some copolymers of tetrafluoroethylene with hexafluoropropylene exhibits three solid phases at one atmosphere[1]. Above 303K, the homopolymer is in phase I, which analysis of X-ray diffraction measurements shows to be metrically hexagonal with the molecules in a 15/7 $=2.1429$ units/turn conformation and strongly rotationally disordered[2-4]. With increasing temperature, the molecular helices untwist and develop variability of pitch, tending toward an average of planar zig-zag[5,6]. Phase IV, which exists only in the narrow range between about 292 and 303K, is metrically hexagonal with the 15/7 molecules being slightly rotationally disordered[2,3]. Below 292K, phase II exhibits well developed triclinic order with the molecules in a conformation of approximately $473/219=2.1598$ units/turn[7,8].

The corresponding phases in the copolymers have not been investigated in detail. Previous X-ray powder diffraction measurements have suggested that phases I and II are similar to those of the homopolymer with the presence of longitudinal and possibly rotational disorder[9]. However, various reflections are superimposed in the powder patterns, and it is difficult to make an unambiguous interpretation.

This article resolves the problem by presenting copolymer fibre patterns for phases I and II. These were examined and compared with the patterns for the corresponding phases of the homopolymers. Portions of this work have been presented previously[10]. Phase IV, which exists in only a narrow range[1] of temperature, pressure, and CF_3 concentration, is not discussed.

EXPERIMENTAL

In a previous study, a number of samples were investigated by calorimetry[1]. Samples with CF_3 concentrations of 0, 0.8, 1.8, 2.5, and 6.9 per hundred main chain carbon atoms were chosen from that work and used to obtain powder patterns. They are samples 20, 14, 1, 2, and 23, respectively, of ref. 1. Sample no. 15 of ref. 1 was an oriented fibre with a diameter of 0.5 mm and a CF_3 concentration of approximately 3.4 per hundred main chain carbon atoms. The hompolymer fibre used for comparison is equivalent to that used in ref. 2.

A cylindrical camera with a diameter of 57.3 mm was used with nickel-filtered copper radiation to obtain fibre diffraction patterns at temperatures from 97 to 343K. Temperature regulation was achieved below 300K by the use of nitrogen gas boiled from a Dewar flask of liquid nitrogen at a rate sufficient to give the desired temperature. Above 300K, heated air was used. The fibre samples, which have rotational symmetry about the fibre axis, were mounted on the axis of the camera with a 1 cm long, thin-walled (10^{-2} mm) capillary to insulate them from the goniometer. A calibrated thermocouple was used to monitor the temperature. The accuracy of this arrangement was determined at 216K by melting pure n-octane[11] mounted in similar fashion. The melting temperature as measured by diffraction exposures was within 0.5K of the value given in the literature. Temperature fluctuations during the two hours or less of exposure were less than ±0.2K. In addition to normal exposures with the fibre axis parallel to the camera axis, a series was made with a very short length of fibre with its axis at right angles to the camera axis in an oscillation mode. Powder camera patterns at low temperatures were obtained in the manner described previously[12]. The powder camera temperature cell was also fitted to a small-

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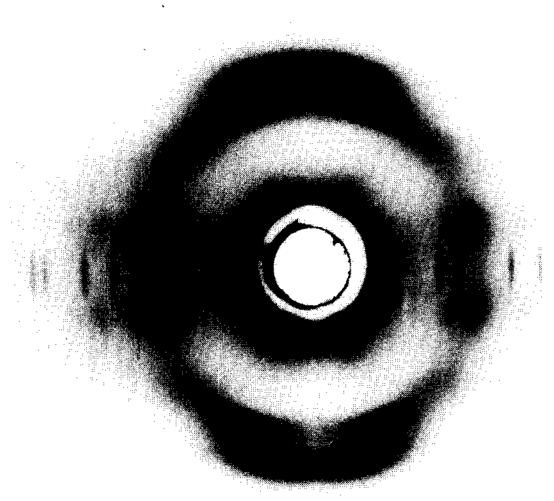

Figure 1 Fibre pattern obtained at 117K with a copolymer with about 3.4 CF_3 groups per hundred main-chain carbon atoms. The fibre axis is vertical

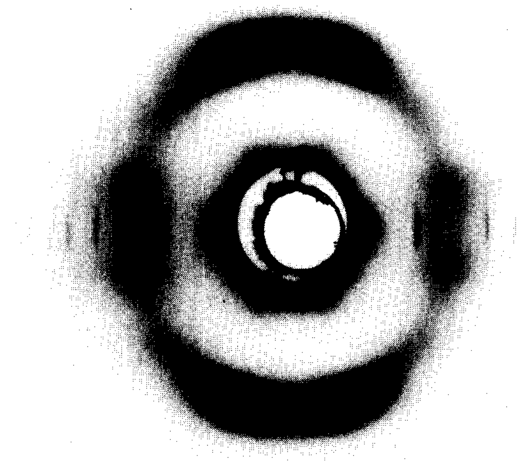

Figure 2 Fibre pattern obtained at 268K with the copolymer of *Figure 1*

angle camera with pinhole collimation to obtain small-angle diffraction patterns for the fibre. The sample to film distance was 417.6 mm. Densitometer measurements of the films were made with a Joyce, Loebl and Co.[13] instrument.

RESULTS AND DISCUSSION

The normal fibre diffraction pattern for a copolymer with about 3.4 CF_3 groups per hundred main-chain carbon atoms is shown in *Figure 1* for 117K and in *Figure 2* for 268K. It is clear from the nominal second layer line (the first visible one adjacent to the zero layer line) that a disordering transition has taken place between the two temperatures. Patterns recorded at a series of temperatures show the transition to occur between 229 and 243K in qualitative agreement with data obtained by differential scanning calorimetry[1]. The X-ray results also agree with the calorimetric data in that only one transition can be resolved over the entire temperature range.

In *Figure 1*, the pattern for phase II of the copolymer exhibits less order than phase II of the homopolymer at 268K (*Figure 3*). The comparison shows clearly in the nominal 5th, 6th, and 7th layer lines which exhibit sharp reflections in the homopolymer and only a diffuse continuum in the copolymer. (The 6th and 7th lines may appear sharp because of the characteristics of the eye and film. However, they are broad and diffuse). The nominal second layer line of the copolymer pattern exhibits the major features of the homopolymer but with considerable broadening. This is confirmed by the densitometer curves given in *Figure 4*. The top curve is a trace along the nominal second layer line of the copolymer and the

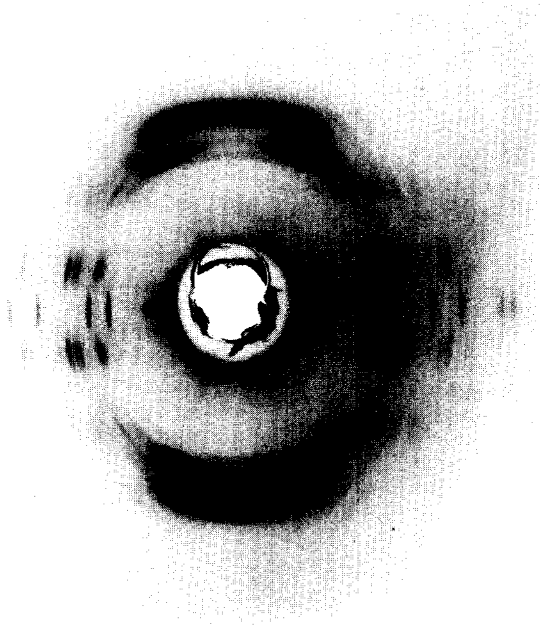

Figure 3 Fibre pattern obtained at 268K with polytetrafluoroethylene

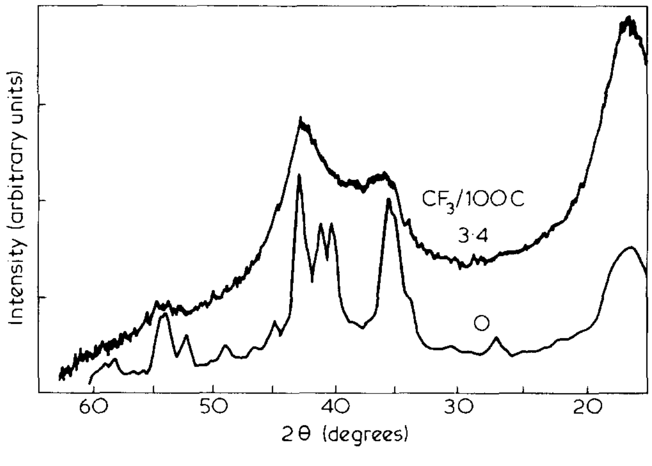

Figure 4 Densitometer trace of the nominal second layer line of *Figure 1* (top). Densitometer trace of the nominal second layer line of *Figure 3* (bottom). The copolymer curve has been shifted slightly to larger angles to allow for the larger cell dimensions of the copolymer

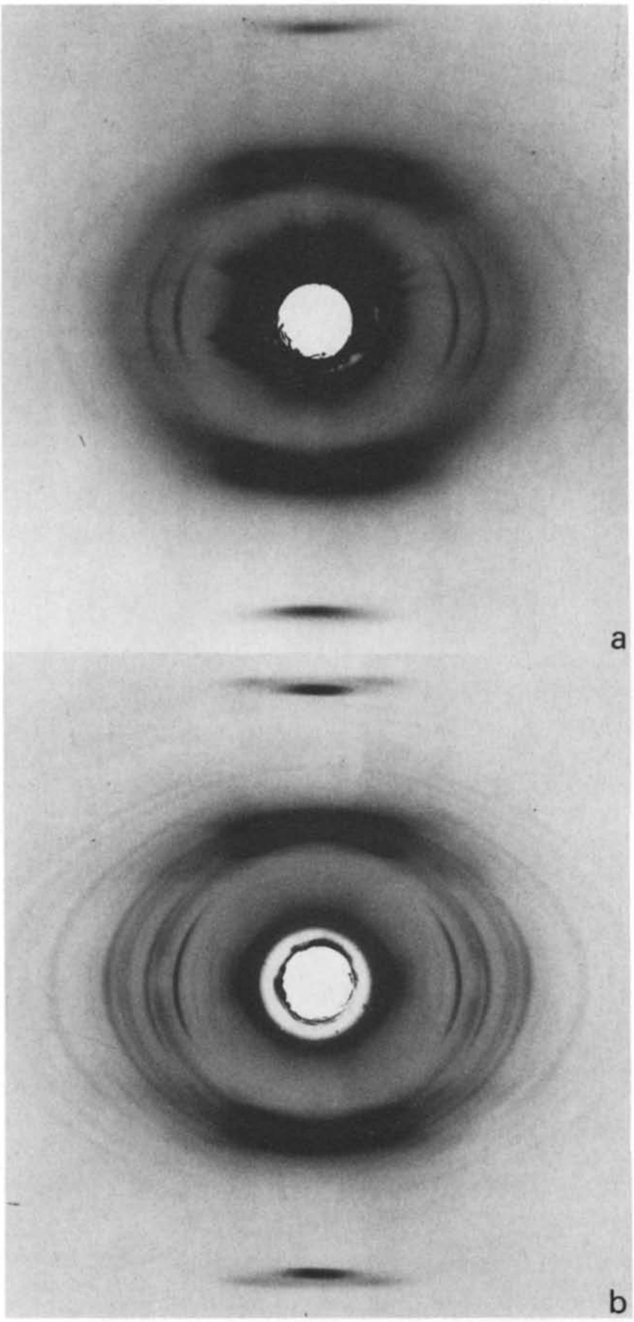

Figure 5 Oscillation pattern obtained at 125K with the copolymer of *Figure 1* (a). The fibre axis is perpendicular to the rotation axis in order to obtain the nominal 13th layer line. Pattern showing the nominal 13th layer line of the homopolymer at 265K (b)

bottom one is an equivalent trace for the homopolymer. If allowance is made for the slightly larger cell dimensions of the copolymer[9], it can be concluded that the nominal second layer line of the copolymer is a broadened version of that for the homopolymer imposed on a continuum. *Figure 5* shows oscillation patterns obtained for phase II with the fibre axis perpendicular to the camera axis. The nominal 13th layer line of the copolymer (top) at 125K is a diffuse continuum as compared with the homopolymer (bottom) which exhibits resolved reflections even at 265K. Finally, it should be noted that, in contrast to the differences, the zero layer line of the copolymer in *Figure 1* appears nearly identical to that of the homopolymer in *Figure 3*. The very slight splitting of the higher index reflections in the homopolymer cannot be resolved in the slightly broader lines of the copolymer. Thus, phase II of the copolymer appears to be similar in nature to that of the homopolymer except that there is a form of crystal disorder which has little effect on the zero layer, broadens the nominal second layer, and makes each of the higher layers a diffuse continuum.

Small longitudinal (axial) displacements of the molecules will reduce the intensity of the sharp Bragg reflections exponentially with increasing layer line number and introduce layer line continuua[14]. (Small screw displacements can have a similar effect depending upon their pitch.) If the displacements also increase with distance along the molecules, the half-width of the reflections will increase[15]. It is very likely the perfluoromethyl groups introduce such disorders through their effect on both the molecular conformation and the inter-molecular packing. The effect on conformation is suggested by molecular models. As shown in *Figure 6*, the CF_3 groups appear to interrupt the continuity of the helix. If the disorder is generated by the side groups, additional disordering should occur with increasing CF_3 concentration. This hypothesis is consistent with the increasing breadth and diffuseness of the diffraction pattern with increasing CF_3 concentration. *Figure 7* shows densitometer traces in the 2θ range, 30 to 45 degrees, for powder patterns obtained at 100K. In this range, which includes reflections from the layer lines discussed above, only the zero layer reflections remain relatively sharp as the comonomer concentration increases from 0 to 6.9 CF_3 per hundred main-chain carbon atoms. The other reflections change from relatively sharp to increasingly weak and broad. It is probably this longitudinal disorder which changes the energy of packing sufficiently to permit the two disordering transitions of the homopolymer to couple into a single transition with increasing CF_3 concentration[1].

In the pattern shown in *Figure 2* for phase I of the copolymer, the nominal second layer has also become a diffuse continuum, and only the zero layer, which results from the metrically hexagonal packing of the molecules,

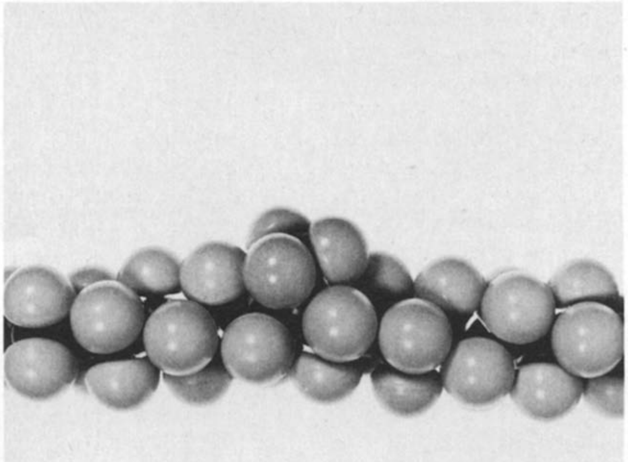

Figure 6 Molecular model of the polytetrafluoroethylene molecule with a CF_3 group incorporated

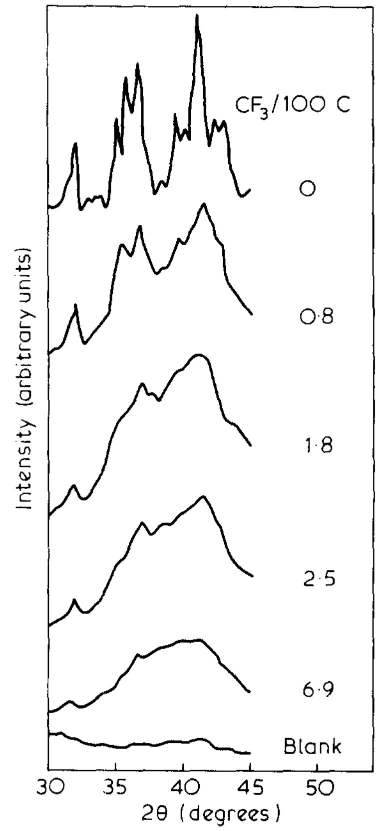

Figure 7 Densitometer traces in the 2θ range 30 to 45 degrees for powder patterns obtained at 100K. The figures indicate the number of CF_3 groups per hundred main-chain carbon atoms

exhibits sharp reflections. This change from phase II also occurs in the homopolymer (Figure 8) and can be explained in terms of rotational disordering of the molecules[14]. Thus, phase I of the homopolymer and copolymer appear to be similar except that the copolymers have the inherent longitudinal disorder induced by the perfluoromethyl groups. Longitudinal disorder is not apparent in the homopolymer until it is introduced thermally above 373K. Both the homopolymer[5,6] and the copolymer molecules also untwist and exhibit an irregular conformation with increasing temperature.

It could also be noted that at 147K, the copolymer fibre produces a four-point small-angle diffraction pattern. It corresponds to a long period of 23.4 nm and molecular tilt of 36.8 deg with respect to the normal to the basal plane of the lamellas. At 296K, these values become 22.8 and 37.1, respectively. The changes are within the limits of possible error. The angle of tilt at 296K corresponds approximately to a progressive displacement of 0.39 nm or three carbon atoms between molecules in the crystal planes separated by about 0.5 nm.

CONCLUSIONS

Phase II of a copolymer of tetrafluoroethylene and hexafluoropropylene with about 3.4 CF_3 per hundred main-chain carbon atoms appears to be similar to that of the homopolymer. A principal difference is the introduction of small longitudinal displacements of the molecules in the copolymer. These displacements appear to be caused by the CF_3 groups incorporated into the crystal and gradually increase with increasing CF_3 concentration. At higher temperatures, the copolymer undergoes a crystal disordering transition to phase I in which random rotational displacements of the molecules occur. This rotationally disordered structure is equivalent to that of the homopolymer, except for the longitudinal disorder of the molecules in the copolymer. This difference disappears at higher temperatures as longitudinal disorder is introduced thermally into the homopolymer crystal.

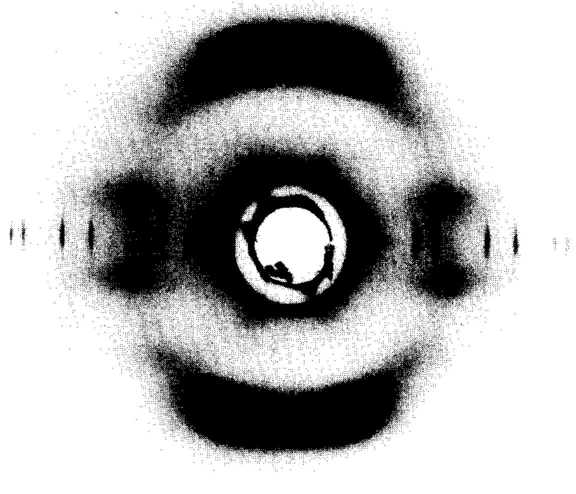

Figure 8 Fibre pattern obtained at 313K with polytetrafluoroethylene

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