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Kinetic aspects of the IV–II phase transformation in PTFE

Kenneth S. Macturk
Battelle Memorial Institute, Polymer Product Group, 505 King Avenue, Columbus, OH 43201, USA

and R. K. Eby*
Department & Institute of Polymer Science, The University of Akron, Akron, OH 44325-3909, USA

and B. L. Farmer
Department of Materials Science & Engineering, The University of Virginia, Charlottesville, VA 22903-2442, USA

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Kinetic aspects of the transformation of poly(tetrafluoroethylene) (PTFE) from phase IV to phase II at 19°C and atmospheric pressure were studied using wide angle X-ray diffraction (WAXD) following a rapid decrease in temperature from 24.7 to 14.5°C. Information relating to changes in molecular packing was obtained from the position of an equatorial peak. Changes in the amount of disorder present were characterized by measuring the integrated intensity of peaks on the second layer line. Within the limits of error, the molecular packing and disorder changes occurred simultaneously as the transformation occurred. The kinetics of the transformation were evaluated following the approach of Avrami. The results indicate one-dimensional crystal growth in agreement with theory. The results from this study are discussed with respect to implications for the transformation mechanisms and previous work in this area. Copyright © 1996 Elsevier Science Ltd.

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INTRODUCTION

The study of phase transformations seeks to understand the relationship between molecular structure, physical properties and mechanisms of the transformations. Controlling phase behaviour can have a great influence on material properties which, in turn, can have technological implications. The properties of PTFE in the three phases which exist near room temperature at atmospheric pressure are well known. Much less is known about the mechanisms of the transformations with respect to the relationship among changes in molecular conformation, molecular packing, unit cell type and the amount of disorder present. Improved understanding of the transformations will provide important insight into the phase behaviour of PTFE and other polymer systems.

Below 19°C at atmospheric pressure, PTFE is in phase II. The molecular conformation approximates a 54/25 helix. Phase II exhibits a triclinic unit cell which is three-dimensionally ordered and comprised of two molecules of opposite hand[1,2]. Between 19 and 30°C PTFE is in phase IV, and the molecular conformation is a 15/7 helix. X-ray diffraction results suggest the unit cell is metrically hexagonal and comprised of only one molecule[3,4]. N.m.r. and WAXD data indicate the structure is rotationally disordered by angular displacements of molecular segments about the axis of the molecule[4,5]. The disorder can be both intramolecular, in the form of helical defects, and intermolecular, via rotation of one helix relative to another. Modelling results indicate the ideal lowest energy unit cell is larger than that found experimentally and contains at least two molecules of opposite hand, similar to that found in phase II[1,6]. The disorder can eliminate reflections from the larger cell and resolve the discrepancy with the experimental X-ray results, which indicate a single molecule in the smaller unit cell.

The effect of the rotational disorder on the diffraction pattern of PTFE has been discussed in detail[7]. It has the effect of reducing intensities on the upper layer lines in the diffraction pattern. The reduction in intensity has the form:

$$I_i = I_0 \exp(-n^2 \varphi^2) \tag{1}$$

where I_i is the integrated intensity on layer line i, I_0 is the integrated intensity on layer line i with no disorder present; n is the order of Bessel function controlling the intensity on layer line i; φ^2 is the mean square rotational disorder. Rotational disorder, therefore, has no effect on the intensity of peaks on the equator since $n = 0$.

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* To whom correspondence should be addressed

However, it reduces the intensity on all layer lines where *n* is large.

Investigations of the molecular motion in PTFE at temperatures well below 19°C gave a discrepancy between n.m.r. results, which show large amounts of angular disorder below 19°C, and WAXD results, which show less disorder[8,9]. Helix reversals[10] were proposed as a means of allowing dynamic angular displacements of the molecules about the chain axis with little effect on the diffraction pattern[8]. Such helix reversals, with one dihedral angle in the *trans* position between segments of opposite hand, were argued to be energetically feasible. The defects could be generated either at chain ends or in pairs in the crystal without disrupting the translational symmetry of the molecules in the crystal. Planes of defects normal to the molecular axis could form boundaries between sections of the molecules of opposite hand. (In view of the structure below 19°C[2], it should be remembered that the regions of the crystal separated by the defect planes contain molecules of both hands.) Motion of the defect planes would then allow all molecules to change hands and still produce the same diffraction pattern. The authors proposed that the defect planes could move in a coordinated manner changing the local handedness of the molecules while leaving the overall handedness unaffected. This mechanism would seem to resolve the discrepancies between n.m.r. and WAXD results at temperatures near 0°C.

More recent WAXD results have shown a small amount of disorder may exist in phase II in the 15–19°C temperature range[9]. This is consistent with the idea that an increase in intermolecular spacing which occurs with increasing temperature can disrupt the cooperative motion of the helices leading to the random disorder seen experimentally just below the transformation temperature and in greater amounts in phase IV.

A mass-gravimetric apparatus was used to study the kinetics of the 19°C transformation[11]. A modified Avrami treatment of the data indicated nearly one dimensional growth of the crystals occurs during the transition ($n \approx 1.2$). A model similar to that described above was used to explain the experimental results. The rate of transformation was shown to be proportional to the (001) surface area of the crystals. The (001) surface is a logical place for the transformation to begin since they are the areas of highest energy in the solid. Clearly, as the author stated, other mechanisms are possible.

In this study, the relationship between disorder and molecular packing at the transformation from phase IV to phase II at 19°C was examined using WAXD. Molecular packing distances were obtained from the position of equatorial diffraction peaks present in both phases. The amount of disorder present was obtained from the measurements of the integrated intensities of peaks on the second layer line. Both were measured as a function of time after a rapid temperature decrease from phase IV to phase II. The implications of the data for the transformation mechanisms were analysed.

EXPERIMENTAL

The sample consisted of an oriented bundle of PTFE fibres which was also used in earlier work[9,12]. A rotating anode source was used at settings of 40 kV, 200 mA. A 0.3 mm pinhole collimator system and Ni filtered CuK$_\alpha$ radiation were used. The sample to detector distance was 15.2 cm, resulting in a detector resolution of 0.07°/pixel. The temperature of the WAXD samples was regulated to within ±0.2°C in the temperature range of approximately 15.0–30.0°C used in these experiments. The experimental apparatus has been more completely described elsewhere[9]. The sample temperature was equilibrated at 24.7°C for over 1 h. The experiment began with a rapid temperature decrease from 24.7 to 14.5°C at a rate of 2.0°C min^{-1}. Diffraction patterns were taken every 30 min for the first 2 h, every hour for the next 2 h, and then every 2 h until 42 h after the temperature decrease.

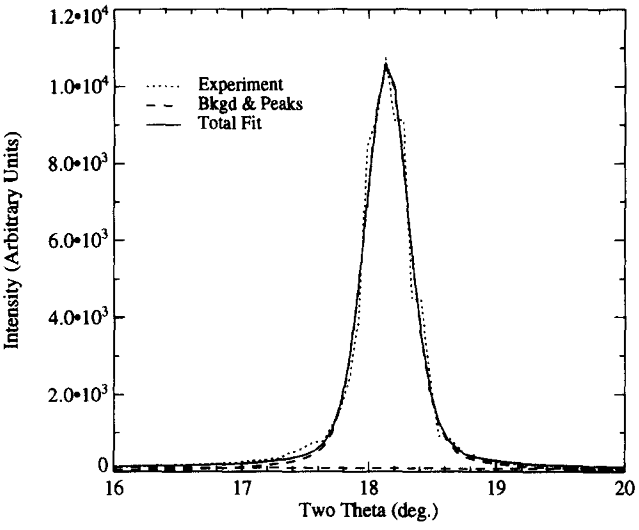

Figure 1 Typical plot of the intensity vs 2θ for the (200) equatorial peak 16 h after the transformation began. Fit of the curve is also shown

The experiment was performed a second time with a fine focus filament installed in the X-ray source. The rotating anode source was set at 40 kV and 30 mA with the 0.3 mm collimator. The exposure time was increased to 1.5 h so that the total counts on the detector per diffraction pattern were similar to the first experiment. The increased exposure time was needed to obtain good signal to noise ratios on the peaks and to allow for reliable comparison of the integrated intensities. Diffraction patterns were taken every 1.5 h for the first 6 h, then every 2 h until 42 h after the temperature decrease.

Fits of peaks on the diffraction curves were done with the PEAKFIT program from Jandel Scientific (San Rafael, CA). The peaks are assumed to have a combined Gaussian–Cauchy functional form given by[13]:

$$I(2\theta) = f_t G_t + (1 - f_t) C_t \qquad (2)$$

where f_t is the profile fraction parameter, G_t is the Gaussian function, C_t is the Cauchy function. The Gaussian function has the form:

$$G_t = A_0 \exp\{-\ln 2[2(X - A_1)/A_2]^2\} \qquad (3)$$

where A_0 is the peak amplitude (arbitrary units), X has the value of 2θ (°), A_1 is the peak position (°), A_2 is the width of peak at half maximum (°). The Cauchy function is:

$$C_t = A_0/\{1 + [2(X - A_1)/A_2]^2\} \qquad (4)$$

The fitting procedure provided f_t, A_0, A_1, A_2 and their standard deviations for each experimental diffraction peak. The value of the integrated intensity for the diffraction peaks on each layer line was also calculated at each temperature. A linear term plus a constant were

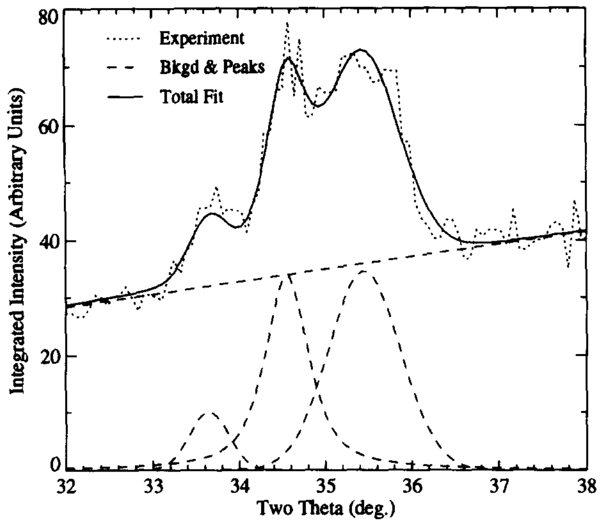

Figure 2 Typical plot of the intensity vs 2θ for the second layer line 16 h after the transformation began. Fit of the curve is also shown

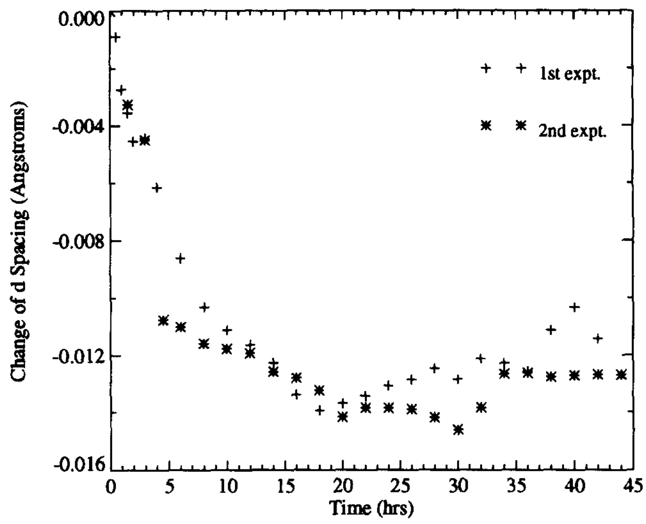

Figure 3 Comparison of changes in equatorial d-spacing vs time after the rapid temperature decrease for the two transformation experiments. The standard deviation is approximately ±0.002 Å

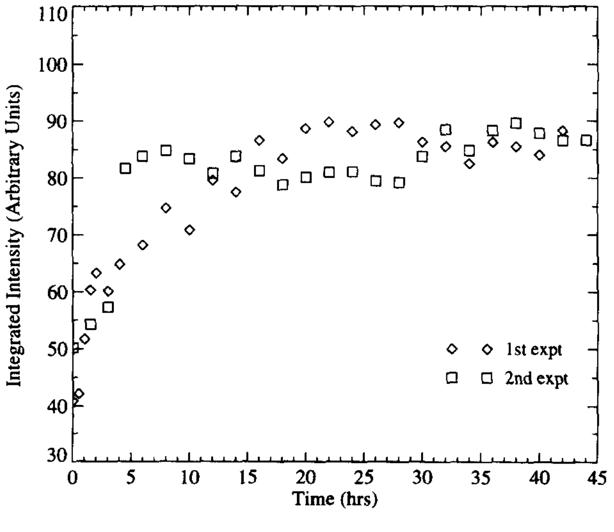

Figure 4 Comparison of integrated intensity of second layer line vs time after the rapid temperature decrease for the two transformation experiments. The standard deviation for each point is approximately ±10 (arbitrary units)

used to fit the background. Addition of a quadratic term to the background resulted in aphysical variations of the background intensity from one diffraction pattern to the next.

RESULTS AND DISCUSSION

Data in the form of intensity vs 2θ curves as a function of time for the equatorial peak reveal the peak position moved to larger values of 2θ with time after the rapid temperature decrease. As expected, this corresponded to a decrease in the molecular packing distance as the molecules moved closer together while the transformation proceeded from phase IV to phase II. The integrated intensity of the second layer line peaks increased as a function of time after the rapid temperature decrease. This followed the expected trend and indicated that the disorder originally present in phase IV was gradually removed to form the more ordered phase II.

The (200) equatorial reflection was fit using one peak. A comparison of the intensity vs 2θ curve and a fit of the equatorial reflection 16 h after the temperature decrease is shown in *Figure 1*. The three second layer line reflections were fit using three separate peaks. Since it was difficult to separate accurately the contributions of the three peaks, the intensities of the individual peaks were summed. An example of the intensity vs 2θ and a fit for the second layer line 16 h after the temperature jump is given in *Figure 2*.

Figure 3 shows the change in d-spacing of the equatorial peak vs time after the temperature decrease for both experiments. The differences between the two sets of data are within the uncertainties of approximately ±0.002 Å associated with the two sets of measurements. The molecular packing approaches the equilibrium value in phase II about 10–15 h after the transformation began.

The integrated intensity of the three reflections on the second layer line as a function of time after the transformation are shown in *Figure 4* for both experiments. Again, the uncertainties of approximately ±10 encompass the differences between the results from the two experiments. The sum of integrated intensity also approaches the equilibrium value for phase II approximately 10–15 h after the transformation started. The reproducibility of the results is especially pleasing in light of the complex nature of the experiments.

The values of d-spacing vs time and integrated intensity vs time were used to determine the values of fraction transformed. For the second layer line (f_{t2}):

$$f_{t2} = 1 - (A_f - A_i)/(A_f - A_s) \qquad (5)$$

where A_f is the integrated intensity at time = 42 h (arbitrary units), A_i is the integrated intensity at time i (arbitrary units), A_s is the integrated intensity at time = 0 h (arbitrary units).

The conversion to f_{te} for the equatorial peak has a similar form:

$$f_{te} = 1 - (d_i - d_f)/(d_0 - d_f) \qquad (6)$$

where $d_i = d-$ spacing at time i (Å), $d_f = d-$ spacing at time = 42 h (Å), $d_0 = d-$ spacing at time = 0 h (Å).

The average of the two experiments for the results of f_{te} are plotted against f_{t2} in *Figure 5*. If changes in molecular packing were occurring first, *Figure 5* would

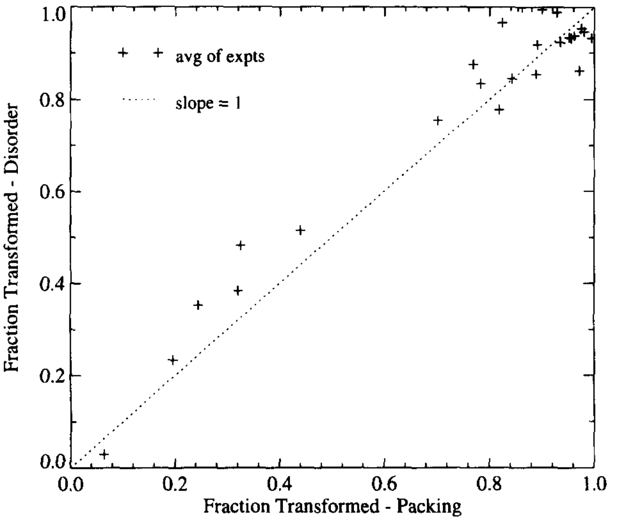

Figure 5 Average results for fraction transformed from changes in equatorial packing (f_{te}) vs fraction transformed from changes in disorder of the second layer line peaks (f_{t2})

Table 1 Comparison of Avrami constants with literature values

Source	$K \times 10^{-4}$	n
Equator	9.49 ± 1.36	0.70 ± 0.09
2nd layer line	3.68 ± 0.44	0.80 ± 0.09
Mass-gravimetry results[11]	1.54–8.44	1.16–1.23

be curved with an initial slope less than one and a final slope greater than one. On the contrary, if changes in the amount of disorder were occurring first, *Figure 5* would have an initial slope greater than one and a final slope less than one. Generally, the data at the earlier times suggest the latter result. However, scatter in the data yields standard deviations of 0.13 for the disorder fraction transformed and 0.29 for the packing fraction transformed. This precludes distinguishing whether the deviations from a slope of one are real. If not, the changes in molecular packing and disorder must be taken as occurring simultaneously. This places constraints on possible mechanisms of the transformation. There is nothing in the data to support the suggestion that packing changes precede the introduction of disorder. This is in agreement with previous work[9], but contrary to other published results[14].

Recall that the equatorial *d*-spacing is related to the intermolecular distance and that the integrated intensity of the second layer line is a measure of the amount of disorder present in the unit cell. This disorder can exist either intramolecularly in the form of helix reversals or changes of helical pitch as well as intermolecularly in the form of rotational disorder of one chain relative to another. Regardless of the type of disorder, the data in *Figure 5* imply that the disorder can be removed from the PTFE as it transforms to phase II *at molecular packing distances which approach the equilibrium values in phase II*. The barriers to remove the disorder must therefore be rather low. The need to remove the remaining disorder after the molecular packing distance has significantly decreased may explain the relatively long times necessary to complete the transformation from phase IV to phase II observed here and in earlier work[11,15,16].

The kinetics of the transformation were examined using the treatment developed independently by Kolmogoroff[17], Avrami[18–20] and Evans[21]. The approach relates f_t to time through the following equation:

$$\log[-\ln(1-f_t)] = \log K + n \log t \qquad (7)$$

where f_t is the fraction transformed, K is a constant related to number of nuclei and growth rate, n is the dimensionality of crystal growth. Thus, a plot of $\log[-\ln(1-f_t)]$ vs log(time) yields a line of intercept $\log(K)$ and slope n. The values of K and n from the equatorial peak and second layer line for the results averaged over the two experiments are given in *Table 1*. Published experimental results using a mass-gravimetric apparatus[11] are also given for comparison. The values of n for the equatorial and second layer line peaks are expected to be similar in light of the results in *Figure 5* which suggest the changes in molecular packing and disorder occur simultaneously as the transformation proceeds.

When the errors are considered, the values of K and n from this study are in the range of those from the mass-gravimetric results. Perhaps more importantly, the values of n are in approximate agreement with the value of $n = 1$ predicted for a predetermined number of nuclei and growth of rods in one dimension[22]. In PTFE, the number of nuclei are predetermined by the number of molecules present in phase IV. Growth during the transformation occurs along the length of the molecule in one dimension. The results of the Avrami plots are consistent with the proposed transformation mechanism consisting of motion of helical defects travelling along the lengths of the molecules which change the molecular conformation[8,11]. It is also possible that other mechanisms may exist which allow the transformation to occur along the length of the molecule.

An improved investigation of the transformation would required reducing the uncertainties in the *d*-spacing and integrated intensities. This could be achieved by using a higher power source, longer diffraction exposure times and a single fibre of PTFE. These improvements would allow for better signal to noise ratios leading to lower uncertainties in the fits. Use of a synchrotron X-ray source seems to be the best option to improve the results by reducing the uncertainty in measurements of the fraction transformed from the equator and second layer line.

CONCLUSIONS

WAXD experiments were used to investigate changes in molecular packing and amount of disorder as the transformation from phase IV to phase II occurred. It was not possible to distinguish unambiguously whether the changes in packing or disorder occurred first. Indeed, the data are consistent with their occurring simultaneously. Avrami kinetics were used to examine the transformation. The results are consistent with one-dimensional growth, matching both theoretical predictions and previous results from a different experimental technique. The data are consistent with a mechanism in which helical defects move in a coordinated manner along the molecular axis to change the molecular conformation. More study is needed to confirm this and to investigate other possible mechanisms which may also fit the data and exhibit the characteristics of the transformation.

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