Inter-lamellar crystallization in poly(tetramethylene oxide)

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(*Received* 9 *April* 1980; *revised* 16 *September* 1980)

High molecular weight poly(tetramethylene oxide) crystallizes isothermally from the bulk to a final crystallinity level of approximately 50%. Further crystallization can be induced in this material by cooling. This effect has been studied by differential scanning calorimetry (d.s.c.) and small angle X-ray scattering (SAXS). The additional crystalline material has a lower melting point than the original and its presence causes a pronounced decrease in the small angle spacing (correlation function maximum). The propensity to crystallize further at low temperatures decreases with increasing secondary crystallization under the original isothermal conditions. Additional crystallinity can also be induced, without temperature change, by cleaving chains by prolonged exposure to an X-ray source. These facts are explained in terms of the additional crystallinity occurring by growth of new thin lamellae between the original isothermally grown lamellae. The new lamellae grow preferentially in the thicker amorphous regions, which are reduced in size and number by secondary crystallization. The radiation damage effects indicate that amorphous chain constraint as well as available space is an important factor inhibiting crystallization between preformed lamellae.

INTRODUCTION

The contrast in crystallinity between poly(ethylene) and other linear polymers of high molecular weight such as the linear poly(ethers) is a matter of considerable interest. For example, high molecular weight poly(tetramethylene oxide), PTMO, although structurally similar to poly(ethylene)[1], PE, has a volume fraction crystallinity considerably less than 50%[2]. A major difference between the two polymers lies in the observations of very much faster lamellar thickening rates in PE[3] compared to PTMO[4] and this may partially explain the higher observed crystallinity in PE. However, it appears that the large amorphous regions in PTMO are under such constraints as to prevent further significant crystallization under isothermal conditions whereas the higher degree of mobility in PE crystals may relieve these constraints and allow further interlamellar crystallization. A similar process has been reported[5] for isotactic poly(styrene), a low crystallinity polymer, where the amorphous regions between lamellae undergo isothermal crystallization.

In this paper, we report the induction of further crystallinity in PTMO by low temperature treatment of previously isothermally crystallized polymer.

EXPERIMENTAL

Details of the polymerization and characterization of the PTMO studied have been given elsewhere[4].

The small-angle X-ray scattering equipment and techniques employed have also been detailed elsewhere[2,4] and the small-angle data were analysed using the correlation function approach of Vonk and Kortleve[6]. A low temperature cell was constructed for this work from poly(methylmethacrylate) sheets with double glazed 0.001″ thick 'Mylar' windows. Dry cold nitrogen was passed through the cell and with liquid nitrogen as a cooling medium, no difficulty was experienced in maintaining temperatures down to 220 K with control ±2. Sample temperatures were measured with a thermocouple placed directly on the sample out of the X-ray beam.

D.s.c. measurements were made with a Dupont 900 Thermal Analyser with a Dupont d.s.c. cell and a heating rate of 10 K min^{-1}. The temperature axis was calibrated using mercury and gallium calorimetric standards.

RESULTS AND DISCUSSION

Poly(tetramethylene oxide) which has been isothermally crystallized in the range 283–300 K generally melts between 300 and 330 K. However, d.s.c. measurements performed after cooling below ∼260 K show a broad endothermic continuum up to ∼300 K with a maximum ∼285 K. Two typical d.s.c. scans are shown in *Figure 1*.

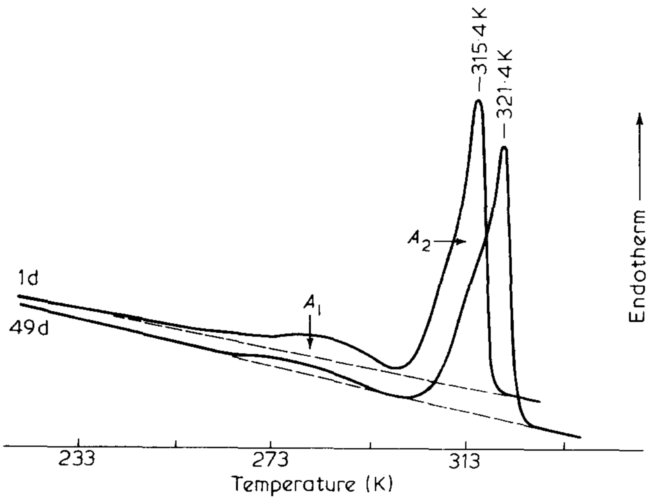

Figure 1 D.s.c. scans for PTHF isothermally crystallized at 293 K for 1 day and 49 days, cooled to 173 K at 25 K min^{-1} prior to scanning at 20 K min^{-1}

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0032–3861/81/101349–04$02.00

Table 1 Crystallization conditions and melting data

Sample	Crystallization time* at 293 K (h)	Rate of cooling (K min^{-1})	Minimum temperature reached (K)	Time held at 233 K (h)	Low temperature melting peak (K)	Relative area† A_1/A_2
A	24	5	233	2	287	0.12
B	24	30	233	2	287	0.12
C	24	1.3	143	0.25	287	0.19
D	24	25	173	–	287	0.18
E	24	15	233	2	287	0.12

* Primary crystallization (complete space-filling by spherulites) is complete in 5½ h at 293 K

† A_1 and A_2 represent the areas of low and high (normal) temperature melting peaks from d.s.c.

In each case the polymer has been isothermally crystallized at 293.0 K and then cooled to 173 K prior to scanning.

In one case (1 day sample) the cooling has been initiated shortly after the end of primary crystallization (i.e. the time of complete spherulite impingement) whilst in the second case a considerable amount of isothermal secondary crystallization has been allowed before cooling.

To examine the effect of cooling rate and crystallization temperature, samples crystallized at 293 K were cooled in the d.s.c. cell at a constant rate and then held at 233 K (runs A and B in *Table 1*) prior to the d.s.c. melting experiment. The initial cooling rate has no effect on the final amount of low temperature melting material present. However, up to 20% additional crystallinity may be induced by lowering the temperature below 233 K (C and D). Optical micrographs of PTMO crystallized at 293 K show well formed volume-filling ringed spherulites. This suggests that the low temperature crystallinity occurs within existing spherulites by some infilling process. The possibilities are formation of new lamellae between existing lamellae either on surfaces or as separate inter-lamellar crystals. A further possibility is that the new crystalline phase occurs between bundles of lamellae as recently observed in PE[7].

In order to study the morphology of these systems, small-angle X-ray scattering was carried out at low temperatures and compared with that from an isothermally crystallized sample without cooling. The SAXS patterns from two samples, E and C, crystallized for 24 h at 293.0 K were determined at 293.0 K. (Complete space-filling by spherulite growth occurs in 5½ h at this temperature). Sample E was then cooled *in situ* to 233 K at ~15 K min^{-1} and maintained at that temperature for 2 h prior to re-scanning the SAXS at 233 K. Sample C was cooled to 143 K at a slower rate of 1.3 K min^{-1}, then maintained at 233 K whilst measuring the SAXS. Each scattering curve was de-smeared[8] and a $4\pi s^2$ Lorentz correction factor applied. The data were crudely assessed initially by applying Bragg's Law to the corrected curves shown in *Figure 2*. In each case, the peak maxima shifted to smaller spacings (245 Å to 192 Å for sample C) and the intensity of scattering corresponding to large Bragg spacings (400 Å to 1000 Å) was considerably reduced. Qualitatively, these results are compatible only with a model involving the growth of new lamellae within the original large amorphous areas known to be present between original lamellae.

In order to quantify the SAXS data, experimental correlation functions were calculated from all the scattering curves as shown in *Figure 3*. The correlation functions of E and C before cooling were typical of those reported earlier[2,4] and could be fitted by theoretical correlation functions based on Gaussian thickness distributions for the crystalline and amorphous layers. However, the experimental correlation function from C at 233 K showed a double maximum (*Figure 3b*) thereby suggesting that some regions were still present with the original periodicity but with a majority of spacings reduced to smaller values. This confirms the conclusions drawn from direct interpretation of the scattering curve and signifies that inter-lamellar growth has occurred. However, the persistence of the original periodicity indicates that inter-lamellar growth has not occurred in all the amorphous layers, such as the smaller regions or those under greater constraints.

The correlation function from E at 233 K shows only slight distortion of the first maximum and could be matched with a theoretical function in the usual manner. The derived structural information is listed in *Table 2*. It can be seen that the average periodicity ($C+A$) has been

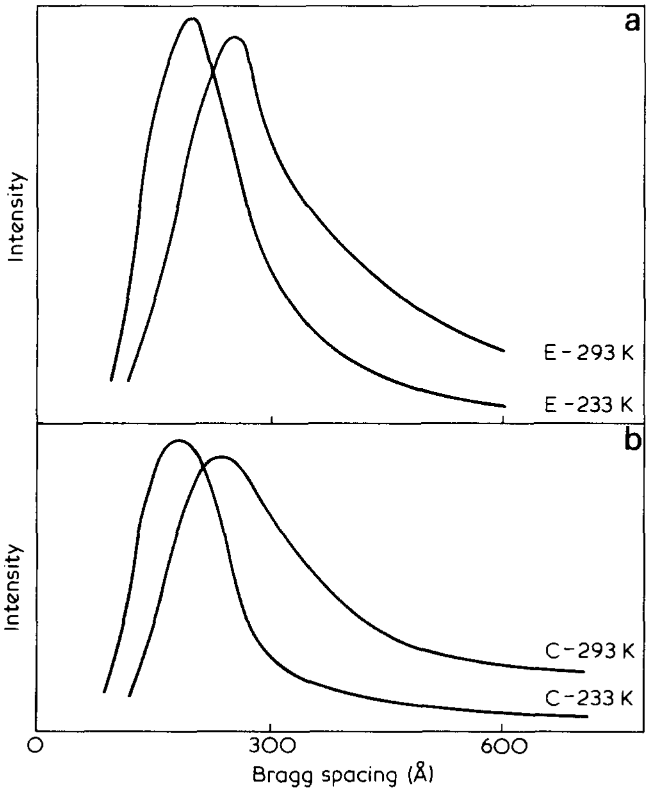

Figure 2 Desmeared and Lorentz corrected SAXS data for samples E and C. Both samples were crystallized at 293 K: E for 24 h followed by cooling at 15 K min^{-1} to 233 K for 2 h; C for 13 h followed by cooling to 143 K at 1.3 K min^{-1} and returning to 233 K for 15 min before scanning

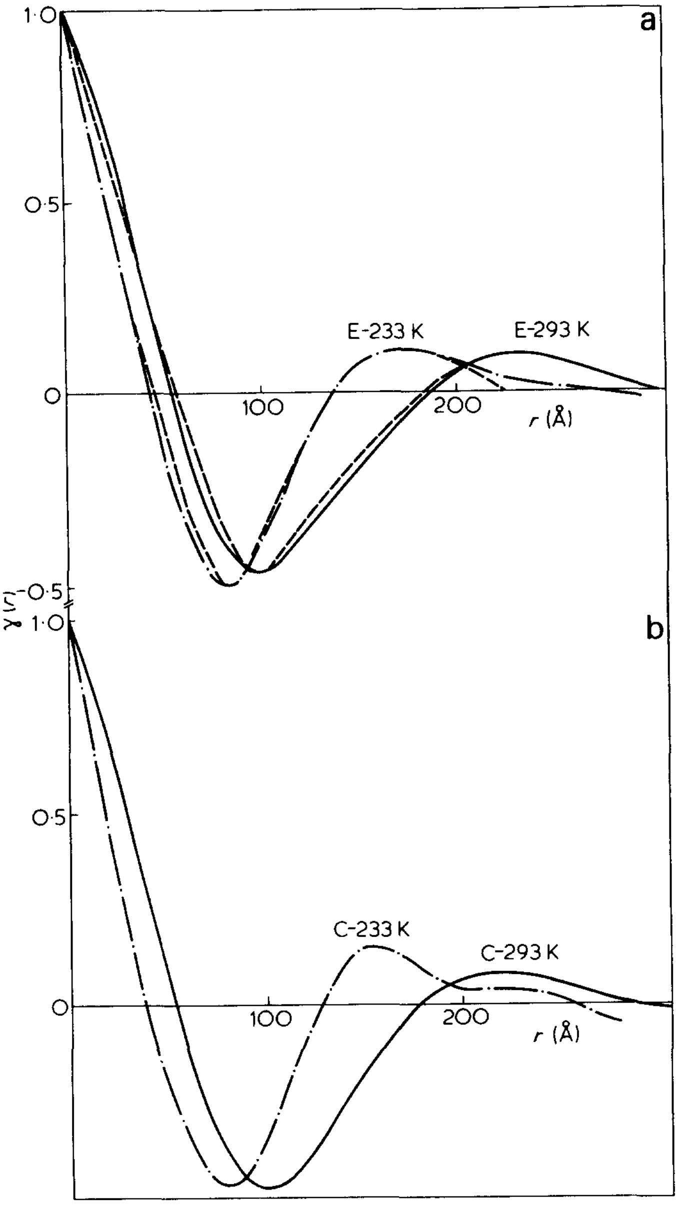

Figure 3 (a) Experimental correlation functions (——) and best fit theoretical correlation functions (– – – –) for samples E (293 K) and E (233 K). (b) Experimental correlation functions for samples C (293 K) and C (233 K)

reduced on cooling and that the amorphous phase has a significantly reduced average thickness with a narrower thickness distribution. Assuming average values of C and A from the correlation function analysis it can be shown that the crystalline thickness (induced at low temperatures) between lamellae is 64 Å with crystallization occurring in 40% of the original amorphous regions. Although the assumption of average values of C and A in the calculation may not be wholly correct, as it would be expected that the new lamellae would crystallize in the larger amorphous regions, nevertheless the calculation should yield at least an approximate value of the new crystal size. From d.s.c. and SAXS measurements it was found that the inter-lamellar crystalline material could be melted off and re-crystallized independently of the more stable original material.

The large quantity of amorphous material (>50%) in isothermally crystallized PTMO that is unable to crystallize (apart from slight lamellar thickening[4]) without a decrease in temperature, precludes a diffusion controlled mechanism of crystallization. Since thick amorphous regions are known to be present in isothermally crystallized PTMO, growth of new lamellae must normally be prevented by constraints imposed by the existing lamellar structure. Applying general ideas of surface nucleation, the shortest stable lamellar thickness C^* is given by:

$$C^* = 2\sigma_e T_m^\circ / \Delta H_f \Delta T$$

where σ_e is the end surface free energy, T_m° is the melting point of an infinitely thick crystal of the same perfection and ΔT is the supercooling below T_m°. In the strained amorphous region, the surface energy of any new lamellae will be raised and, if less perfect lamellae are formed ΔH_f will be lowered with respect to the original lamellae. Thus growth will only occur at a high supercooling (ΔT) which yields a small enough C^* to fit the available space. On cooling, it is expected that crystallization will occur first in the thicker amorphous regions and that these lamellae would melt at a higher temperature than those formed at lower temperatures, thereby creating a broad spectrum of melting points. The extreme breadth of the melting curve can be explained in terms of a range of lamellar thickness down to ~30 Å. In addition a simultaneous increase in σ_e and/or decrease in ΔH would have the effect of reducing melting points beyond those expected for a given C^*. An increase in σ_e could be interpreted in terms of the formation of new lamellae with higher surface energies or by a loop tightening process on the loose-looped surface of existing lamellae analogous to the opposite of surface melting. However, as the small-angle scattering data support the formation of new lamellae, it is doubtful whether surface crystallinity effects on the original lamellae are important in terms of the overall picture.

The isothermal secondary crystallization at 293 K has a marked effect on the amount of low temperature crystallization possible and also on the peak melting point of low temperature crystallized material, as is shown in *Table 3*. During secondary crystallization lamellar thickening occurs preferentially in the thicker amorphous regions[4], thereby reducing the thickness available for interlamellar material. This explains the decrease both in melting point and the quantity of interlamellar material as secondary crystallization proceeds. During secondary crystallization from 1 to 49 days at 293 K, the volume fraction crystallinity (φ) increases by 0.032 whilst the interlamellar material decreases by 0.041, the latter value being calculated from a simple area comparison of the d.s.c. curves. This should be considered to be a low

Table 2 Structural parameters derived from SAXS before and after low temperature crystallization. (Sample E)

Sample temperature (K)	ϕ	β_C	β_A	$(C+A)$ (Å)	C (Å)	A (Å)	ΔC (Å)	ΔA (Å)
293	0.42	0.027	0.36	218	92	126	14	185
233	0.48	0.04	0.35	169	81	88	16	140

Table 3 The effect of isothermal secondary crystallization on low temperature melting material

Crystallization time at 293 K (days)	1	2	5	14	27	49
T_{max} (K ± 2) (for A_1)	286.9	287.1	285.2	284.5	283.9	282.2
Area ratio A_1/A_2 (±.02)	0.18	0.17	0.13	0.11	0.09	0.08

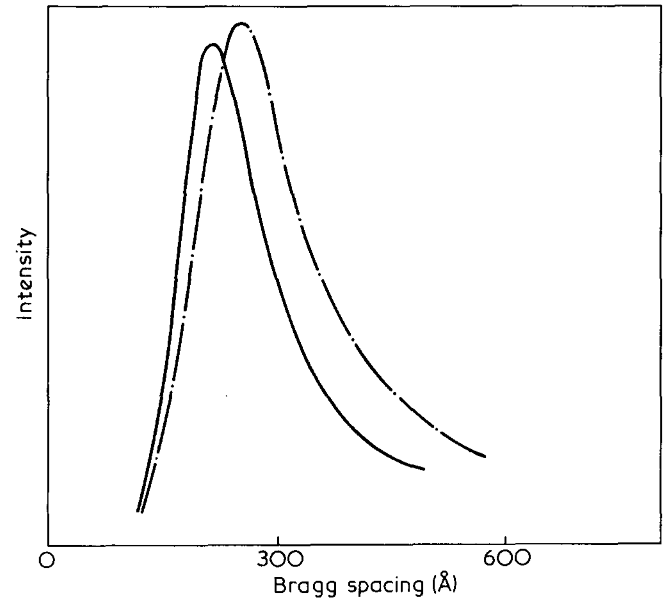

Figure 4 Desmeared and Lorentz corrected SAXS data for PTHF crystallized at 293 K for 112 days (—·—·—·—·—) and same sample after X radiation damage at 293 (———)

Table 4 Structural parameters of radiation damaged material

Sample	ϕ	C (Å)	A (Å)	ΔC (Å)	ΔA (Å)
Crystallized at 293 K for 112 days	0.47	105	118	20	179
Radiation damaged	0.57	110	83	36	132

estimate since ΔH_f will be lower for the more imperfect crystallinity expected at low temperatures. The difference between the two values may give support to a mechanism of either preferential lamellar thickening adjacent to wide amorphous regions or to an increasing surface constraint during secondary crystallization.

Although the growth of new lamellae at low temperatures will undoubtedly depend on the available amorphous material, it has been possible to examine the effect of constraints on chains in the amorphous regions by a simple radiation damage experiment. Isothermally crystallized PTMO was exposed to a total X-ray dose of 500 Gy (0.05 M rad) on six occasions spread over a period of 84 days at 293 K. G.p.c. molecular weight analyses showed the molecular weight of the damaged polymer ranged from 2 800 to 130 000 compared with the original value of $M_n = 2.3 \times 10^5$. Permanent chain scission by the radiation has occurred and this is more likely to have happened in the amorphous regions at points of strain (where recombination processes are unlikely). *Figure 4* compares the SAXS pattern of the radiation damaged sample without cooling, with the original material isothermally crystallized at 293 K for 112 days. In common with the cooled undamaged polymer, the radiation damaged sample showed a distinct reduction in long period in addition to a reduced probability of finding very large (>400 Å) repeat periods. *Table 4* shows parameters derived from matching the experimental and theoretical correlation functions. It can be seen that there is a considerable increase in volume fraction crystallinity (φ) and a reduction in the average value of the amorphous thickness. It may be inferred that isothermal crystallization between existing lamellae has occurred also with a small amount of lamellar thickening. This process is allowed to occur isothermally by the release of amorphous phase constraints after chain scission.

CONCLUSIONS

Further lamellar crystallization of the amorphous component in previously isothermally crystallized high molecular weight PTMO has been detected by d.s.c. and SAXS. This crystallinity may be induced by lowering the crystallization temperature or by isothermal radiation damaging the previously crystallized material. The only possible interpretation of the data is that induced crystallinity is occurring in new lamellae growing between the original lamellae preferentially in the larger amorphous regions. This type of crystallization is not observed during the isothermal secondary crystallization of the polymer even though large amorphous regions are available. It is thought that the constraints applied by the existing lamellae are sufficiently strong to prevent new lamellar growth. Increasing the super-cooling allows the growth of smaller crystals or alternatively the strains can be relieved by chain scission in the amorphous regions by X-radiation. The melting temperature of the new lamellae is considerably below that of the original material owing to their smaller lamellar thickness, higher surface energy and the poorer state of crystal perfection. The amount of low temperature crystallinity decreases with isothermal crystallization time. The results are consistent with an increasing surface energy and the already proposed[4] preferential lamellar thickening of lamellae bounded by thick amorphous regions during secondary crystallization.

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