

Annealing and Melting of Polyoxymethylene Crystals Polymerized Within Irradiated Trioxane Crystals

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Annealing and Melting of Polyoxymethylene Crystals Polymerized Within Irradiated Trioxane Crystals

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Morphological changes produced by the annealing and melting of the polyoxymethylene crystals that polymerize inside irradiated trioxane crystals were observed. The crystals in which the polyoxymethylene chains were oriented parallel to the threefold axis of the trioxane underwent major reorganization when held at 184°C for 30 sec. The polyoxymethylene crystals in which the chain axis was inclined at a large angle with respect to the threefold axis of the trioxane transformed and melted at temperatures approximately 5°C lower.

I. INTRODUCTION

In a previous paper¹ the present authors showed that three kinds of polyoxymethylene (POM) crystals grew inside irradiated trioxane (TOX) crystals. In all three types of POM crystals, the long axis of the polymer crystal was parallel to the threefold axis of the parent TOX crystal. The three types of POM crystals were labeled *Z*, *W*, and *T* crystals.

In *Z* crystals the chain axis was parallel to the threefold axis of the TOX. The *Z* crystals usually had a hexagonal cross section and the chains were parallel to the long axis. About one-half of the polymer produced in a typical irradiated TOX crystal was in the form of *Z* crystals.

In *W* crystals the chain axis was inclined at an angle of 76.1° with respect to the long axis. The *W* crystals produced the so-called¹ "twin" spots observed in typical x-ray diffraction patterns such as those reported by Carrazzolo, Leghissa, and Mammi² or Chatani, Uchida, Tadokoro, Hayashi, Nishii, and Okamura.³ The *W* crystals were flat blade-shaped crystals in which the chains were oriented nearly perpendicular to the broad faces of the crystal. The polymer chains in the *W* crystals were either folded, or less likely, of low molecular weight. Slightly less than half the POM produced in a typical irradiated TOX crystal was in the form of *W* crystals.

The *T* crystals were, in fact, bicrystals with a twin boundary between the two parts. One part of the bicrystal was exactly like a *Z* crystal. The

other part of the bicrystal was a thin bladelike crystal in which the chains were nearly normal to the broad faces of the crystal. The bladelike part of the *T* crystals was similar in appearance to the *W* crystals. The *W* and *T* crystals were distinguished by different values for the angle between an \vec{a} axis and the long axis of the crystal. Only a small part of the POM in a typical sample was present in the form of *T* crystals.

This paper reports the morphological changes that were produced by annealing and melting samples that were composed of *Z* crystals and *W* or *T* crystals. The *W* and *T* crystals were not distinguished from each other in this work.

Studies of the annealing and melting behavior of POM crystals were published by Geil,^{4,5} Garber and Geil,⁶ O'Leary and Geil,⁷ Hirai, Tokumori, Katayama, Fujita, and Yamashita,⁸ Carter and Baer,⁹ Jaffe and Wunderlich,¹⁰ and Amano, Fischer and Hinrichsen.¹¹ In all but the last two of these papers the lamellar, folded-chain morphology that POM adopted when crystallized from dilute solution or from the melt, was correlated with observations such as differential thermal analysis, electron microscopy, x-ray diffraction, and density. Jaffe *et al.*¹⁰ studied the polymer produced in solid TOX after chemical initiation. Such material has since been shown¹² to have a morphology similar to the polymer produced by initiation with radiation. Amano *et al.*¹¹ concentrated their attention on thermal properties and changes in morphology produced by heating of POM produced inside irradiated TOX crystals.

II. EXPERIMENTAL

The samples of POM crystals were prepared on thin graphite-coated mica sheets as described previously.¹ The area of the TOX crystals was made about 4 cm² and each sample was divided so that several annealing experiments were done on each preparation.

It was found desirable to anneal the TOX crystals (which grew very rapidly after the mica sheet was placed on the molten drop of TOX) at 58 °C for about 30 min before irradiation in order to increase the perfection of the TOX crystals. The sample was irradiated with α particles from an americium-241 α -particle source. The α particles passed through the graphite-coated mica sheet into the TOX crystals. A typical dose was 10 α/μ^2 .

After irradiation, the sample was heated to 58 °C in an atmosphere of air saturated with TOX vapor for periods of 16 to 48 h. During this time POM crystals grew inside the TOX crystals. The unreacted TOX was then sublimed in a refrigerator to minimize the disarrangement of the POM crystals by the surface tension of the TOX. The yield of polymer was low, perhaps 10%, so that the individual polymer crystals were separated enough

to be observed individually. The mica bearing the POM crystals was then cut into several pieces for annealing at different temperatures and different times.

The annealing of the POM was done with the sample, on the graphite-coated mica, held loosely between sheets of glass in a microscope hot stage. Optical changes in the POM crystals were used to monitor the annealing process. A heating rate of 10 °C/min was used to approach the annealing temperature. The samples were held at the annealing temperature for times ranging from 15 sec to 5 min. At the end of the anneal the sample was cooled at approximately 30 °C/min.

The annealed POM crystals were shadowed with evaporated platinum-palladium alloy at an angle of approximately 45°. Electron micrographs and selected-area electron-diffraction patterns were made with 8-sec exposures at beam doses of up to 10⁶ electrons/ μm^2 (0.16 C/m²) at the sample. Higher beam-current densities produced severe damage to the polymer crystals.¹

III. OBSERVATIONS

Figure 1 shows the temperatures and times at

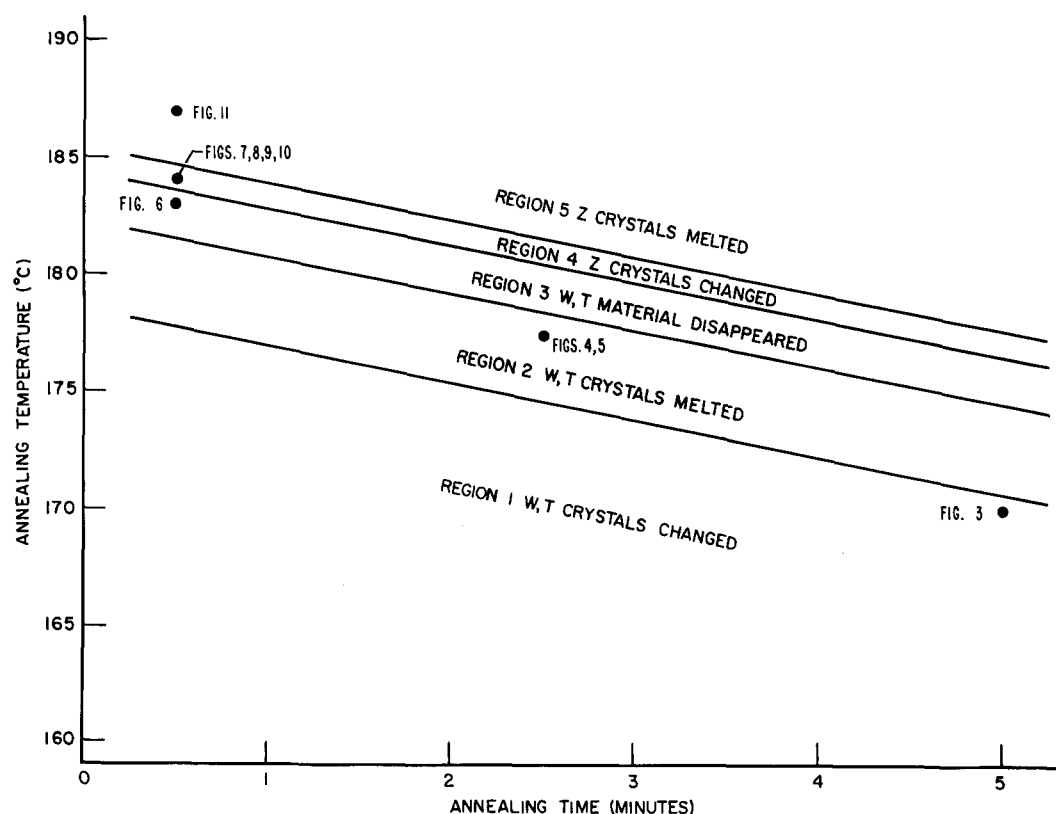


FIG. 1. Graph showing the time and temperature range investigated. The labeled points indicate the conditions to which each of the samples shown in the following figures were subjected. The regions in which the different kinds of crystals underwent various transformations are indicated.



FIG. 2. Polyoxymethylene crystals as prepared by heating α -particle-irradiated trioxane crystals.

which the POM crystals were annealed. Annealing for long times at lower temperatures produced the same general effect as annealing for short times at high temperatures.¹¹ The figures that follow are arranged in order of increasing effect of the annealing procedure.

A typical low-magnification electron micrograph of POM crystals as prepared is shown in Fig. 2. The crystals were in the form of slender needles or fibers a fraction of a μm wide and several μm long. Examination of areas such as this at higher magnification showed that *Z*, *W*, and *T* crystals were all present. There were rows of polymer particles¹³ with irregular shapes near the blunt end (bottom end in Fig. 2) of some of these crystals. The surface tension of the subliming TOX and handling of the sample bent some of the crystals, broke others, and caused bundles of crystals to cross over each other. Some crystals were bent elastically while others were kinked by these forces.

The crystals shown in Fig. 3 were annealed for 5 min at 170 °C. Morphological changes at the ends of the *Z* crystals and throughout *W* and *T* crystals were produced. The darker, straight-edged crystals in Fig. 3 were *Z* crystals. The rows of irregular material at the ends of the *Z* crystals disappeared leaving only tiny rounded droplets. The central or axial part of the re-

maining ends of the *Z* crystals also disappeared, leaving a thin incomplete shell. As will be shown, this shell also disappeared when the crystals were annealed at longer times or higher temperatures. The middle parts of *Z* crystals, that is, the parts away from the ends, remained smooth and straight edged.

The thinner, rough-edged crystals and the discontinuous rows of material were the remains of *W* and *T* crystals. A characteristic early change in *W* and *T* crystals was a roughening of the edges, which in many areas showed small facets and a multilayer structure. Bend contours¹⁴ were present in many of the remaining crystals. Small irregular liquid or greaselike droplets were left in areas where parts of crystals disappeared.

At temperatures a few degrees higher the *W* and *T* crystals melted completely. Figure 4 shows a sample that was annealed for 2.5 min at 177.5 °C. Some of the material of which the *W* and *T* crystals were composed degraded and disappeared.

A faint odor of formaldehyde was noted as this sample was annealed. The liquid material that did not degrade resolidified into droplets with an imperfect spherulitic appearance. The droplets lay in rows along the axis of the POM crystal from which they were derived. A smooth-edged *Z* crystal is shown lying diagonally across the upper part of Fig. 4.



FIG. 3. *Z* crystals and *W* or *T* crystals of POM annealed at 170 °C for 5 min.

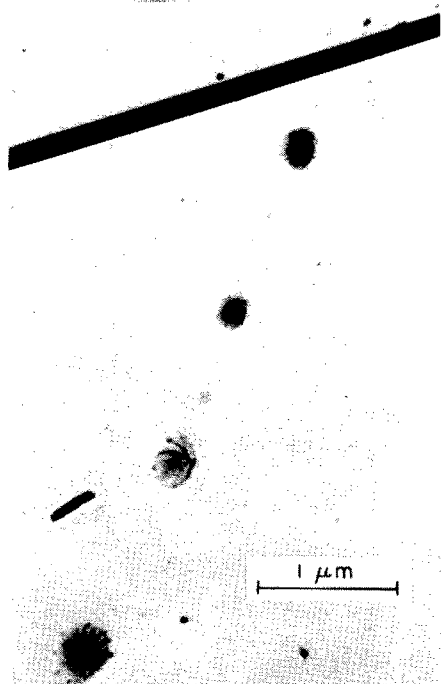


FIG. 4. Refrozen POM spherulites from melted *W* or *T* crystals. The dark line at the top is part of the *Z* crystal which was unaffected by the anneal at 177.5 °C for 2 min.

Figure 5 shows a different area of the same sample shown in Fig. 4. In this area some of the molten material refroze into a terraced hexagonal crystal. This hexagonal crystal contained moiré fringes

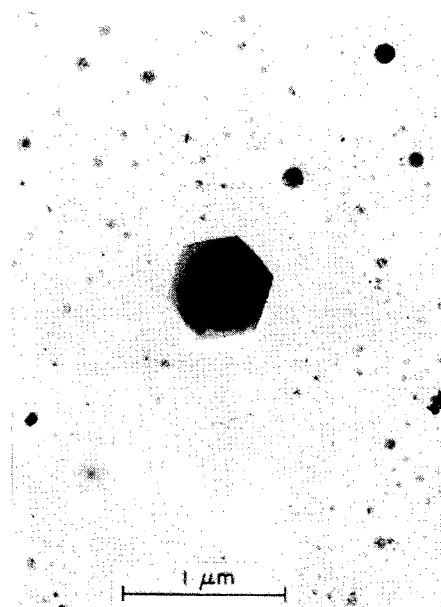


FIG. 5. A hexagonal POM crystal grown from molten POM in the same sample as Fig. 4.

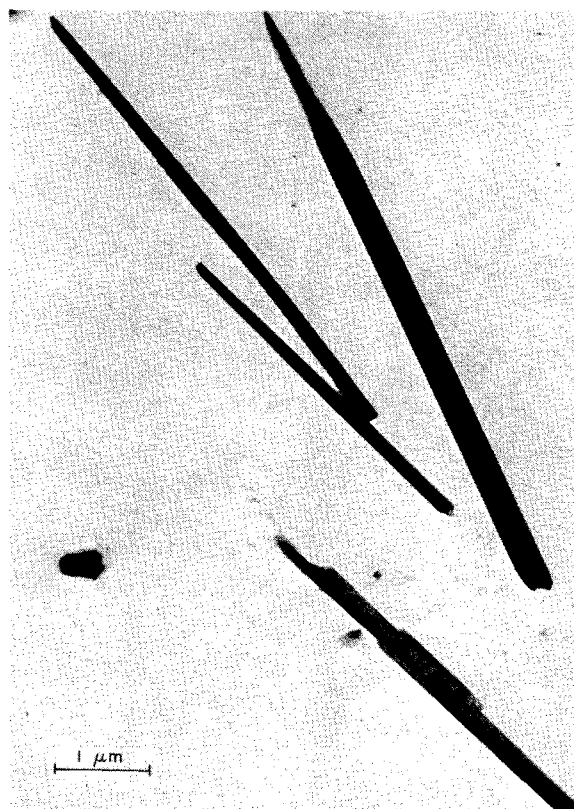


FIG. 6. *Z* crystals of POM that survived an anneal at 183 °C for 30 sec. Only traces of the *W* and *T* crystals and the irregular material near the ends of the *Z* crystals remained.

indicating that the crystal was composed of several misaligned layers. Many objects with degrees of perfection intermediate between the hexagonal crystal shown in Fig. 5 and the spherulites shown in Fig. 4 were present in this sample.

Figure 6 shows a group of *Z* crystals that survived an anneal at 183 °C for 30 sec. It is interesting to note that the ends that developed on the *Z* crystals annealed under these conditions were distinguishable. One end was characteristically indented while the other end had a rounded tip. Previous observations¹ showed that *W* and *T* crystals had distinguishable ends. This is the most definite indication yet observed that *Z* crystals also have a direction or polarity.

A *Z* crystal from a sample annealed at 184 °C for 30 sec is shown in Fig. 7 along with the electron-diffraction pattern obtained from it. The diffraction spots are all of the type $\{1, 1, 2, l\}$. This indicates that the flat faces of the crystal were of the type $\{1, 0, 1, 0\}$ if it is assumed that the crystal was lying flat on the carbon substrate.

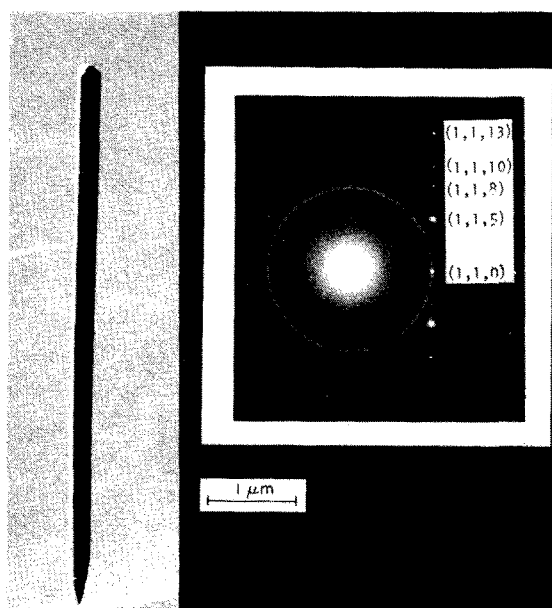


FIG. 7. Selected-area electron-diffraction pattern from a Z crystal after an anneal at 184 °C for 30 sec. The rings were produced by the Pt/Pd used for shadowing.

The Z crystals in a sample annealed at 184 °C for 30 sec were more dramatically affected by the anneal. The crystal shown in Fig. 8(a) had transverse striations which extended from the edge of the crystal about one-third of the way across. The crystal had a featherlike appearance. The striations are shown at higher magnification in Fig. 8(b). Selected-area diffraction showed that the chains in the striated areas were oriented nearly parallel to the long axis of the object. The striations were about 100 Å (10 nm) wide and appeared to be chain-folded lamellae viewed edge on. Figure 8(c) shows the tip of



FIG. 9. Z crystal which melted near the tip and developed striations in its midsection as a consequence of an anneal at 184 °C for 30 sec.

another Z crystal which was only 5 μm from the crystal shown in Fig. 8(a). The crystal shown in Fig. 8(c) had coarser striations that did not extend very far into the crystal. Subtle differences between Z crystals were revealed by this experiment.

Figure 9 shows another Z crystal from the same sample as Fig. 8. The tip of the crystal shown in Fig. 9 melted completely so that memory of

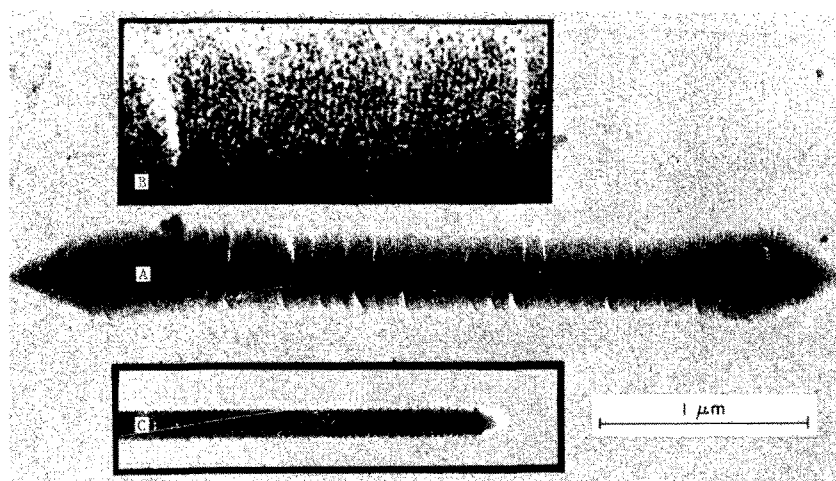


FIG. 8. (a) Z crystal that developed a featherlike appearance after annealing at 184 °C for 30 sec. (b) Magnified region of (a) showing the striations. The period of the striations is nearly 100 Å (10 nm). (c) Z crystal less dramatically changed by the anneal which was lying only 5 μm from the crystal shown in (a). The scale applies to parts (a) and (c).

the original chain orientation was lost. The dark lines in the area near the tip are bend contours associated with reflections from $\{1, 0, 1, 0\}$ planes. The middle part of the crystal was striated in the same way as the crystal in Fig. 8(a).

The area near the boundary between a featherlike annealed Z crystal and the melted and refrozen region near the tip of the same crystal is shown in Fig. 9. The sample from which Fig. 9 was obtained was annealed at 184°C for 30 sec. The diffraction pattern showed the $\{1, 0, \bar{1}, 0\}$ reflections associated with the bend contours in the refrozen part of the crystal as well as faint arcs corresponding to $\{1, 0, 1, 5\}$ reflections from the featherlike part of the object. The relative orientation of the POM chains on the two sides of the boundary shown in Fig. 10 was similar to, but less perfect than, the relative orientation of the chains on the two sides of the twin boundary in T -twin crystals.¹

The crystal shown in Fig. 11 was heated to 187°C for 30 sec. At that temperature all the crystals melted in less than 30 sec. The molten material flowed with low viscosity in response to surface tension forces which were particularly evident in regions where the polymer wet both the mica substrate and the glass cover slip. In other regions, such as shown in Fig. 11, the polymer from a crystal remained as a thin line while molten and then refroze into a relatively complicated lamellar form. The edges of the lamellae are shown in the magnified insets of Fig. 11. The electron-diffraction pattern shows $\{1, 0, \bar{1}, 0\}$ spots with arcing that indicates a randomization of the azimuthal orientation of the lamellae.

IV. SUMMARY

A characteristic series of changes was observed with increased annealing temperature and annealing time for samples of POM produced by the solid-state polymerization of TOX. The regions on a time-temperature plot at which the various effects were observed are indicated in Fig. 1. Region 1—The W and T crystals showed a roughening of edges, development of small facets, and development of a multilayer structure. Region 2—The W and T crystals melted. Some of the polymer degraded and evaporated. Irregular material at the ends of Z crystals melted and disappeared. Upon cooling, the molten material resolidified in a spherulitic or hexagonal habit. Region 3—Most of the W and T crystals and the irregular material disappeared leaving smooth-edged Z crystals with one end rounded and the other indented in a characteristic way. Region 4—The Z crystals started to change. Transverse striations appeared after cooling. The striations

resulted in a featherlike appearance. The tips of some Z crystals melted and refroze in a lamellar habit when cooled. Region 5—All the remaining polymer in the sample melted and refroze into a complicated lamellar object when cooled.

V. DISCUSSION

A number of the interesting but puzzling results reported in the various investigations of melting

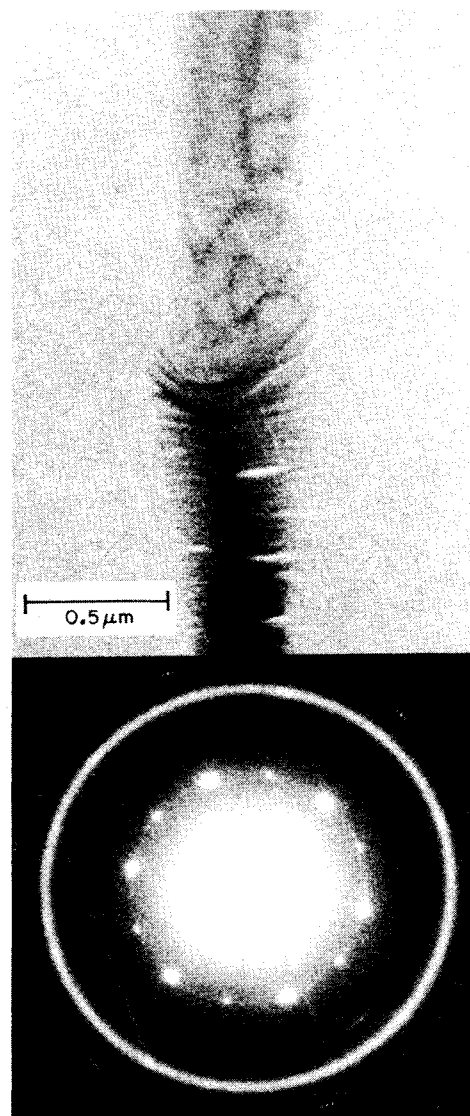


FIG. 10. Selected-area electron-diffraction pattern from the boundary region of a partly melted and refrozen Z crystal in the same sample as Fig. 9. The prominent spots were $\{1, 0, 1, 0\}$ reflections associated with the bend contours in the upper part of the object. Weak $\{1, 0, 1, 5\}$ spots from the striated part of the crystal were evident on the original film. The continuous rings are from the Pt/Pd used for shadowing.

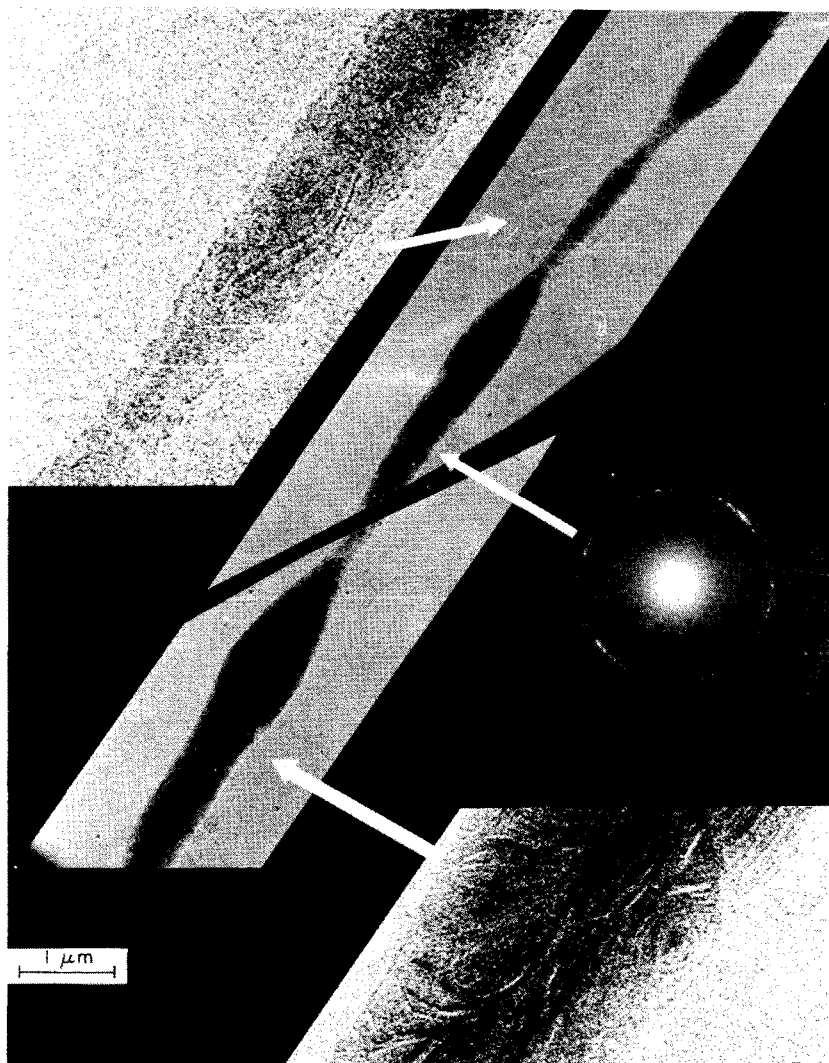


FIG. 11. Refrozen POM from a *Z* crystal that melted during heat treatment at 187°C for 30 sec. Enlarged portions show the edges of lamellae similar to those observed in the crystallization of commercial POM from the melt. The electron-diffraction pattern indicates that the chains had a preferred orientation perpendicular to the plane of the figure, but a nearly random azimuthal orientation.

phenomena in POM crystals are illuminated by the observations reported above, but it is not presently possible to make detailed correlations.

Amano *et al.*¹¹ reported three types of melting phenomena. Their type-I and type-II crystals had melting temperatures that corresponded reasonably well with our *W* or *T* crystals and our *Z* crystals, respectively. However, they did not observe a type-I melting peak unless the sample had been annealed under conditions that would cause the x-ray diffraction spots associated with *W* and *T* ("twin") crystals to disappear. We did not see any morphological evidence of material that could be identified with their type-III material which gave a melting temperature of around 200°C but was only observed at heating rates much higher than we used.

Molecular weight variations from sample to sample and from laboratory to laboratory probably

account for some of the apparent discrepancies. Molecular weight measurements are beset with difficulties that arise from a tendency for POM to degrade rapidly when heated to dissolve it for a molecular weight measurement. The quantities of material in the samples we prepared were too small to permit molecular weight measurements to be made so we relied on reports in the literature summarized by Moinard¹⁵ that in general the polymer produced by the solid-state polymerization of TOX is of reasonably high molecular weight. The moiré lines on the original micrograph of the crystal shown in Fig. 9 were examined carefully to see if the effects due to fold planes reported by Bassett¹⁶ were present. If such effects were present they could be used as an indication of a minimum molecular weight large enough to produce chain folding. Unfortunately, the number of lines that crossed a possible fold domain boundary was too small to say whether or not these effects were present.

Vogl, Ivansons, Miller, and Williams¹⁷ reported thermal degradation spectra of paraform, experimental uncapped POM, and acetate-capped high molecular weight POM. The paraform and uncapped POM lost weight rapidly in the temperature range between 150 and 250 °C. The temperature of maximum rate of weight loss appeared to be a function of molecular weight. A moderately low molecular weight component in some of the samples studied by differential thermal analysis (DTA) might confuse the results both by melting and degrading.

Another source of uncharacterized variability in the samples studied in the various laboratories is the amount and form of POM in the primary Z-crystal form and the amount in various other crystal habits. The experiments reported here showed that it was possible to observe the morphological changes produced in each type of crystal separately. No experiment to study separately the thermal properties of each of the various kinds of POM crystals has yet been reported. Only the later annealing studies¹¹ indicate the amount of W crystals ("twin") in the samples studied. Reports of amount of "twin" material were based on estimates of the intensities of x-ray diffraction patterns and are not exact.

Since the W and T crystals in the samples studied are believed to consist of folded-chain crystals, it is of interest to compare our results with previous observations of morphological changes produced in lamellar POM crystals that were grown from dilute solution. Garber and Geil⁶ showed marked differences in the annealing behavior of crystals on different substrates. Their experiments were performed at lower temperatures (up to 167 °C) and longer times (up to 30 min). At 167 °C all their samples had melted. Our annealing experiments were performed on a graphite surface. Unfortunately, graphite was not included in the surfaces reported by Garber and Geil.

Hirai *et al.*⁸ studied the annealing of folded-chain lamellar crystals of POM and reported thickening of the crystals at annealing temperatures up to 172 °C. O'Leary and Geil⁷ reported a similar thickening of lamellae in POM crystallized from the melt but concentrated their attention on a reversible change in angle and intensity of x rays diffracted from the lamellae at low angles. More recently, Burmester and Geil¹⁸ looked for morphological changes associated with the reversible thickening of POM lamellae. The principle morphological change produced was an approximate doubling of the number of lamella edges apparent on the free surface of a POM sample crystallized from the melt and subsequently annealed. This is

probably related to our observation that W or T crystals develop a multilamellar structure when annealed at temperatures around 160 to 165 °C for periods of a few minutes.

The serration and development of a featherlike appearance in annealed Z crystals is similar to the row nucleation phenomena described by Keller and Machin.¹⁹ It appears that an unmelted central core of the Z crystal served as the nucleus for the oriented recrystallization of the molten outer region of the crystal.

ACKNOWLEDGMENTS

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Strain-Induced Crystallization of Isotactic Polystyrene from the Glassy and "Rubbery" States

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In a continuing effort to extend our understanding of the strain-induced crystallization mechanism we have examined the morphology of oriented isotactic polystyrene (IPS) crystallized from the glassy and "rubbery" states under a variety of experimental conditions (elongation, annealing temperature and time, and sample geometry) by means of a wide variety of experimental techniques using Au decorations, solvent etching, electron diffraction, and bright- and dark-field electron microscopy. The oriented morphology is found to be strongly dependent on the original strained state and other experimental variables; it can be either lamellar, fibrillar, or a combination of the two. A fine texture is found to exist in both the lamellar and fibrillar crystals. Extended-chain line nuclei were also sought. Our results, including dark-field studies of highly stretched samples and samples which have been Au decorated or elutriated with solvent, do not reveal any crystallites of length greater than about 100 Å along the stretch direction, thus essentially ruling out their presence in IPS crystallized under strain. The observations are in complete agreement with the strain-induced crystallization mechanism suggested by Yeh and can also account for such phenomena as stress decay and melting temperature increase.

I. INTRODUCTION

Polymer fibers and films are important commercial products. The major contribution to their commercial importance is the strength of these materials which is a result of their oriented crystal morphology that is brought about by the stretching and the subsequent (and/or concurrent) crystallization processes. Traditionally, the oriented crystallites in fibers or films were thought to be due to a two-step process involving first, a parallel alignment of chain segments due to the stretching process and second, an additional parallel-chain alignment in the stretch direction during the subsequent crystallization, resulting in a bundle or fringed-micellar-type morphology. This traditional view of nucleation and growth of crystallites in the oriented state was used in Flory's theory¹ to account for phenomena such as the stress decay as a function of crystallization time and for the increase in melting temperature of the resulting oriented crystallites. Gent's observations of stress decay and melting-point rise in crosslinked cis-1, 4-polyisoprene,² trans-polychloroprene,³ and trans-1, 4-polyisoprene⁴ were interpreted as proof for this traditional view of bundlelike crystallization in oriented polymers.

However, numerous morphological studies showed

that the dominant morphology of polymers, including crosslinked polyethylene⁵ and natural rubber,^{6,7} when crystallized under strain consists of rows of perpendicularly oriented chain-folded lamellas. The chain folding would predict a stress rise rather than the often observed stress decay during oriented crystallization. A stress rise has been reported by Gent⁴ to occur during oriented crystallization of trans-1, 4-polyisoprene (balata) for extensions less than about 100% and this has been attributed by him to be evidence for the formation of chain-folded crystals at these low extensions. We have observed well-defined lamellas and obtained a small-angle meridional periodicity from trans-1, 4-polyisoprene after crystallization in the stretched state at elongations well above 100% and up to 400–500%.⁸ This would predict a stress rise during the oriented crystallization, but experimental studies by Gent showed otherwise.

Keller and Machin proposed a two-step mechanism for formation of row-oriented lamellas.⁵ It involved the formation of fibrillar crystals which they suggested consisted essentially of extended chains resulting from the stretching process, and followed subsequently during the growth step by the formation of chain-folded lamellas onto the fibrillar nuclei. They further suggested that the