

Growth of Needle-like Crystals of Polyoxymethylene During Polymerisation

Masatoshi Iguchi

Research Institute for Polymers and Textiles, 4 Sawatari, Kanagawa-ku, Yokohama, Japan

(Paper received and accepted 7 May 1973)

Needle-like crystals of polyoxymethylene, 5 to 20 μm long, have been obtained in the course of the polymerisation of trioxane in cyclohexane. It has been found that such crystal growth is favoured at large $\text{BF}_3 \cdot \text{OEt}_2 / \text{H}_2\text{O}$ or $\text{BF}_3 / \text{H}_2\text{O}$ ratios, when the nucleation takes place fast. The needle is considered to consist of fully extended chains oriented parallel with the direction of the length. The mechanism of the needle-type growth is briefly discussed with reference to the plate-like growth previously found.

1. Introduction

The author is reporting on a new type of polymer crystal, a needle-like crystal of polyoxymethylene which is grown in a polymerisation system and expected to be a 'whisker' consisting of extended polymer chains. The polymerisation of trioxane, with respect to the structure of the precipitate formed, has long been of interest to the author and co-workers^{1,2} and, in cyclohexane using boron trifluoride etherate ($\text{BF}_3 \cdot \text{OEt}_2$) as catalyst, a feather-shaped, plate-like single crystal growth was once found.¹ Although the process of the crystal growth was clearly arrested in a series of runs and the mechanism of the growth was reasonably understood from the structural and other evidences, it was recognised that the reproducibility was not necessarily satisfactory, both kinetically and morphologically, between runs carried out at different times with monomer and catalyst solutions prepared on each occasion. A very small amount of water which might be left unremoved from the system was a serious concern of the author and believed to play a role not only on the chemical mechanisms but also on the metamorphoses of the product, the needle-like feature being one of those. The refinement of the experiment has been extended and the nature of the crystals investigated.

2. Experimental

The effort was continued to exclude water from the system, namely from the monomer solution, more vigorously than before. Although the details are to be described elsewhere, a sound purification was performed by refluxing the solution over sodium wire, preferably followed by a direct distillation. When the drying was thus good enough,

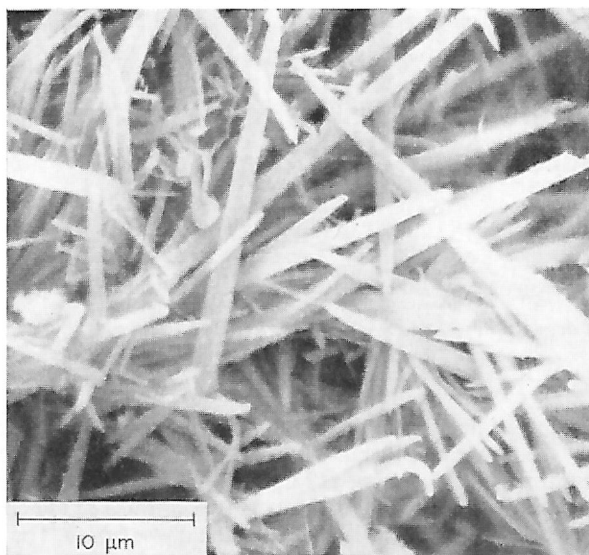


Figure 1. A scanning-type electron micrograph of needle-like polyoxymethylene crystals grown during the polymerisation of trioxane in cyclohexane with $\text{BF}_3/\text{H}_2\text{O}$ catalysis.

it was found that the addition of a small amount of $\text{BF}_3\cdot\text{OEt}_2$ ($c. 3 \times 10^{-6}$ mol to 20 ml of 0.4 mol/l monomer solution) gave essentially no initiation and the system remained to be transparent: it was true even when a relatively large amount of the catalyst (a droplet, $c. 3 \times 10^{-5}$ mol) was added further. When a very small amount of water ($c. 1 \times 10^{-6}$ mol, actually one millilitre of moist air) was added subsequently, however, a dramatic change happened to the system: the system instantaneously became turbid, indicating the initiation of the reaction. The precipitate, observed under a microscope, was a loose aggregate of needle-like crystals.

3. Results and Discussion

This experiment was of dual importance: first, the role of water, which was not quite clearly pointed out before,¹ was proved to be very significant indeed and second, the growth of the needle-like crystal was favoured at large catalyst/water ratios where clouding appeared fast. In fact, it was found that the similar result, i.e. the formation of needle-like crystal, was obtained smoothly by using gaseous boron trifluoride, in place of the etherate, and water.

Figure 1 shows a scanning-type electron micrograph of the needle-like crystals, where it is seen that the whole aggregate consists of a same type of needles, 5 to 20 μm long. (The reaction for this sample was carried out at 50 °C in a flask equipped with a silicon-rubber stopper with 7.2 g (0.08 mol) trioxane dissolved in $c. 200$ ml cyclohexane, introducing 10 ml (4.1×10^{-4} mol) gaseous BF_3 and 10 ml moisture-saturated air ($c. 1 \times 10^{-5}$ mol water) through use of syringes and standing for 20 h. Conversion: 65%.) The feature seems, at first sight, to be similar to that of not well grown feather-

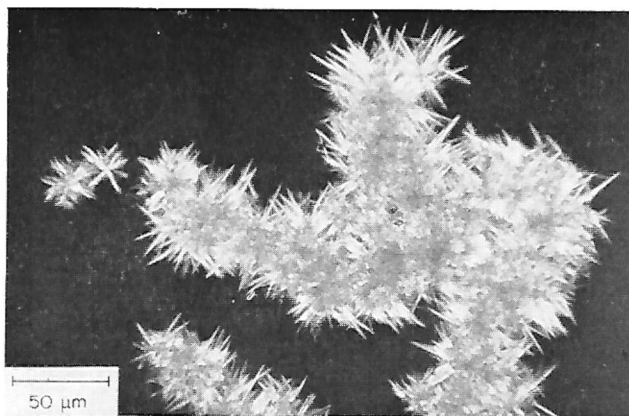


Figure 2. A polarised micrograph of the needle-like crystals.

shaped crystals (Figure 4 of reference 1). Under polarised microscope, however, the needles showed a strong molecular orientation which was assigned, using 530 nm compensator, to be parallel with the direction of the length (Figure 2). Thermal analysis (by DSC-II, heating rate: 10 deg. C/min) showed a sharp melting between 181 and 198 °C, the peak temperature being at 191.5 °C which was much higher than those of folded-chain type crystals and higher yet than that of the extended-chain type, feather-shaped crystal.¹ The base line of the thermogram was quite neat and straight throughout. This observation could be implicit evidence for the view that the crystal consists of really extended chains of not low molecular weight. Accurate measurement of the molecular weight is most desirable, but a reliable method has not been developed for this type of as-polymerised polyoxymethylene. Quite stable in its as-polymerised form though, the polymer tends to decompose seriously, if the original crystalline state is once destroyed by dissolution as well as by melting. When heated in *p*-chlorophenol containing 2% α -pinene, the needle-like crystal did not dissolve or even swell up to *c.* 150 °C and thereafter dissolved abruptly accompanying an apparent decomposition, whereas the stabilised polymer, commercial Delrin, dissolved easily below 120 °C. In hexafluoroacetone sesquihydrate with 2% triethylamine at 30 °C, η_{sp}/c (*c:* 0.4%) measured as high as 3.65 just after the preparation of the solution (which took about 10 min) but the value decreased steeply with time, indicating decomposition. The molecular length of polyoxymethylene, say 10 μ m, roughly corresponds to the molecular weight, a million. To attain this order of length would not be difficult for this type of polymerisation, when the reaction, forming extended-chain crystal, proceeded successively and 'livingly'.

Another piece of evidence that the needle consists of extended chains of high molecular weight is the fact that the needle is very hard to break up mechanically, particularly normal to the direction of the length. Figure 3 shows a fracture surface of hardened cyanoacrylate-resin (Alon Alpha, from Tōa Chem. Co.) in which the needles have been embedded. The adhesion between them would not be expected to be too bad, while the tips of the needles are seen to have slipped out from the matrix rather than to have torn off. The result was similar when an epoxide-resin was used.

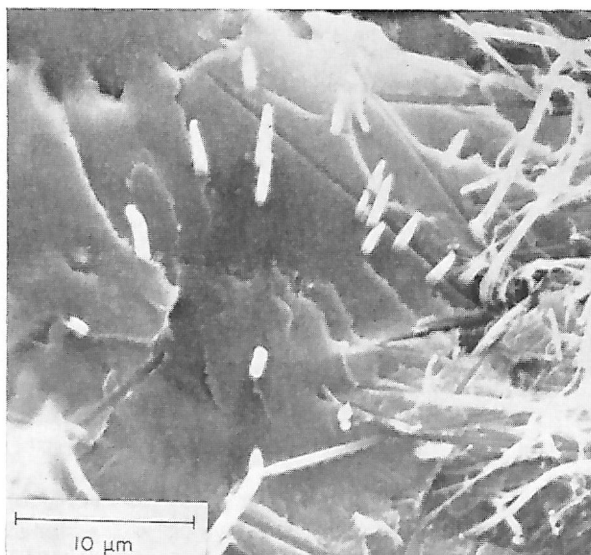


Figure 3. A scanning-type electron micrograph of a fracture surface of cyanoacrylate-resin in which needle-like crystals had been embedded.

The growth habit is unchanged with time. The crystals obtained for shorter polymerisation time were similar needles, only the average length being short, e.g. 2 to 5 μm at 2 h. As for the mechanism of the growth, that for the whisker-growth from atoms or simple substances³ could be envisaged. However, an additional condition is required for the present case: the 'chemical' reaction should occur at the dislocation front, when the polymerising unit, whether CH_2O or $[(\text{CH}_2\text{O})_3]$ has not been clear, is approached.

The difference between the plate-like and the needle-like growth may be traced to the difference of the nucleation. It can be said, at least qualitatively, that fast nucleation with 'active species', generated at the beginning of the reaction, is favourable to the needle-type growth, while slow nucleation is considered to be essential for the plate-type growth. In fact, the plate-like crystal has been obtained with the etherified catalyst, not in a large excess against water. (When water is present in a large excess, whether BF_3 is etherified or not, the system precipitates only amorphous particles, in the initial stage, which are apparently inactive.) Certainly, the nuclei for the needle-like growth are very small in size and large in number, while that for the plate-like growth is a long, triangular one.¹

Similar needle-like crystal has been obtained also in another solvent, *n*-hexane.

References

1. Iguchi, M.; Kanetsuna, H.; Kawai, T. *Makromolekul. Chem.* 1969, **128**, 63.
2. Iguchi, M.; Kanetsuna, H.; Kawai, T. *Br. Polym. J.* 1971, **3**, 177.
3. Frank, F. C. e.g. In *Introduction to Solid State Physics* (Kittel, C. ed.). John Wiley & Sons, Inc., New York, London, Sydney, Toronto. 1971, 4th Edn, p. 689.