Generation of orthorhombic polyoxymethylene in a cationic polymerization system of trioxane

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Orthorhombic polyoxymethylene, which was originally found two decades ago in Italy in a polymerization system of aqueous formaldehyde, has been rediscovered in a cationic polymerization system of trioxane designed to grow needle-like polyoxymethylene single crystals. Besides the single crystals obtained in the liquid phase, it has been known that a thin film bearing a number of particles, up to ~1 mm diameter, is formed as a by-product on the inner wall in contact with the gaseous phase. X-ray analysis has now revealed that the particles consist essentially of the orthorhombic crystalline form. The morphology has been investigated and the growth mechanism briefly discussed.

Keywords Orthorhombic polyoxymethylene; polyoxymethylene crystals; cationic polymerization of trioxane

INTRODUCTION

Previously, infra-red (i.r.) spectra of various polyoxymethylene crystals were studied in our laboratory in comparison with needle-like single crystals and it was established that the spectrum of polyoxymethylene was rather strongly dependent on the origin of the specimens, reflecting conformational disorder or distortion of the molecular helix[1]. In an extensive collaborative study on vibrational spectroscopy carried out at Osaka University[2], a special case was encountered in that one sample, obtained in a cationic polymerization system of trioxane as needle-like crystals, showed unusual absorption bands in both far-i.r. and Raman spectra in addition to those expected for the normal hexagonal crystal form. These extra bands were not considered to be related to molecular distortion but appeared to agree with the bands of another possible modification of polyoxymethylene, the orthorhombic modification consisting of 2/1 molecular helices instead of the normal 9/5 (or 29/16) helices.

In the X-ray diffraction diagram, the sample in question showed reflections from the orthorhombic crystals (unit cell) overlapped with the normal reflections. That a very small amount of orthorhombic portion might be formed and contained on rare occasions in needle-like samples had been suspected before from the trace of X-ray measurements made at Hokkaido University[3], but the extra reflections from the present sample were strong and could not be neglected. Morphologically, the sample contained, besides the usual needles, a significant amount of a new type of 'moth-shaped' crystals which were revealed to be orthorhombic by a detailed micro-focus Raman measurement[2].

Originally, the orthorhombic polyoxymethylene was discovered two decades ago by an Italian group[4], in powders obtained from a polymerization system of aqueous formaldehyde in which the supersaturation and the alkalinity were strictly controlled. Although X-ray[5,6] and spectroscopic[7] analyses were published for the new crystal structure and molecular conformation, no detail was reported on the morphological and physical aspects of the material by the same group or any other. In fact, the formation of orthorhombic crystals is not common and has been referred to thereafter only in the solid-state polymerization of hexoxane[8] as a fraction in the normal hexagonal form. It has now become evident that the cationic polymerization of trioxane is another system which may generate the orthorhombic crystals.

This paper is a progress report on the search for orthorhombic polyoxymethylene and describes polymer particles grown on the inner surface of the reaction vessel and identified as the orthorhombic crystals.

EXPERIMENTAL

Polymerization

Briefly, the crucial points for obtaining needle-like crystals in the cationic polymerization system of trioxane are the preparation of pure and dry monomer solution, the procedure of adding catalyst (boron trifluoride) and co-catalyst (water) and the storage of the solution at rest, in addition to the selection of solvent, monomer concentration, temperature, etc.[9,10] The conventional apparatus[11] used in our laboratory consists mainly of a monomer solution reservoir, a plunger pump, a drying column and a glassware reactor bottle, linked airtight with miniature valves and fittings (e.g. 'Omnifit' from Biolab). The whole system is placed in an air thermostat. In the standard procedure, the monomer solution (0.4 mol trioxane in a litre of cyclohexane) is passed through the drying column (filled with anhydrous calcium sulphate) to a water content well below 1 ppm and received in the reaction bottle through one of the three valves. Gaseous
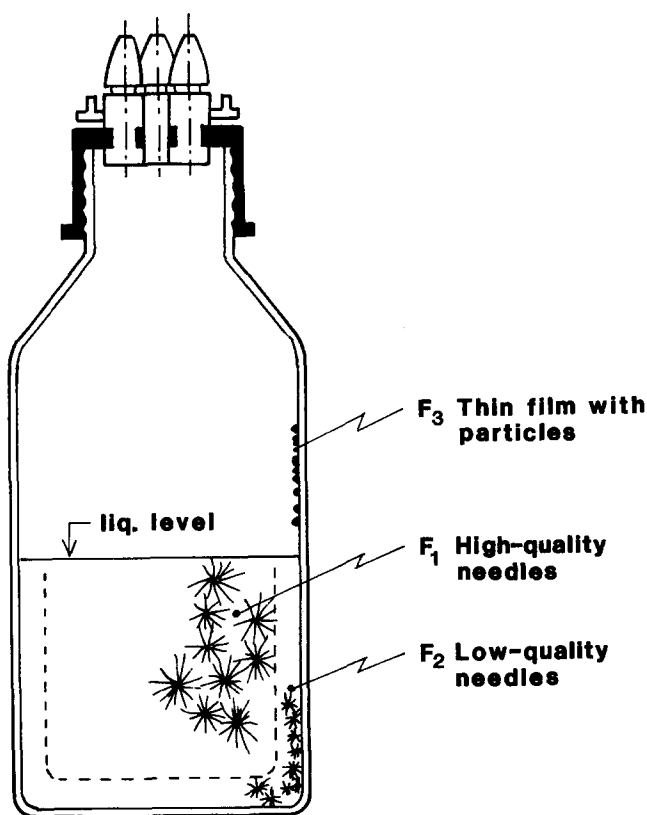
Figure 1 Schematic illustration of polyoxymethylene formed in the reaction vessel. (The crystals are exaggerated in size)

boron trifluoride ($50 \, cm^3$ or $\sim 2 \times 10^{-3}$) followed by moist air ($10 \, cm^3$, equivalent to $\sim 1 \times 10^{-5} \, mol \, H_2O$) is added from syringes through a septum equipped with the second valve and the bottle is shaken for mixing on each addition. To obtain good needles, the activated solution is transferred, by means of argon pressure, to another bottle through a micropore filter ($0.46–5 \, \mu m$) to exclude coarse nuclei formed in the very initial stage. All of these operations are made in an air bath of $50°C$ where the bottle is left for 1–3 days. The reaction is then terminated by adding alcoholic triethylamine, washed and dried. For the present purpose of searching for the generation of orthorhombic crystals, the polymerization was carried out in conditions deviating from the standard procedure just described.

X-ray diffraction

X-ray diffraction was carried out by the transmission powder method. For this purpose, samples were placed without selective orientation in a hole made in a lead plate, $\sim 0.6 \, mm$ thick. The apparatus used was a Gei-gerflex WGC20, of Rigaku Denki Co., equipped with a Philips tube. The Cu radiation was filtered by Ni. The slit system selected was $0.05/0.15/0.5°$ and the scanning was made stepwise by $0.05°$ (2θ) intervals.

Observations and other measurements

Methods for observations and other measurements are not special and are described below wherever necessary.

RESULTS AND DISCUSSION

The polymerization is a kind of heterogeneous reaction, in which monomer molecules are slowly transported and react on the growing crystals, carried out under gravity in a limited system. Thus, in general, high-quality needles are formed in the middle part of the liquid phase and the needles formed around the bottom and the side wall of the bottle are of low quality (see *Figure 1*). Of course, there is no sharp boundary between the two fractions and the term 'quality' which described the length and the appearance is not closely defined. The quality fluctuates also with the quality of the material, the monomer and catalyst concentrations and other experimental conditions in addition to whether or not the activated solution has been filtered prior to being left standing. Besides these polymers formed in the liquid phase, it has been known that a thin film is formed all over the inner wall, in contact with both the liquid and gaseous phases; and on the wall not in contact with the liquid, one observes the deposition of small particles up to $\sim 1 \, mm$ diameter.

X-ray examination has been made on polymers obtained under various experimental conditions and, in conclusion, it has been found that the particles consist essentially of the orthorhombic crystals (form). *Figure 2* shows parts of expanded X-ray diffraction diagrams ($2\theta = 21–24°$) covering the (100) reflection of the hexagonal and the (110) and (020) of the orthorhombic crystallographic planes. As seen in *Figure 2a–d*, the crystalline form of the needle-like specimens (as well as the feather-shaped specimen which had been obtained under a different condition[10,12]) is hexagonal, as has been well established, except that contamination by a small amount of the orthorhombic portion has been revealed in the low-quality needle, and by a trace amount in the high-quality needle, by this very careful measurement. However, the film with particles (*Figure 2e*) has been found to contain a considerable amount of orthorhombic portion and the removal of the substrate film from particles, by fragmentation of the former by ultrasonic irradiation, has given rise to a typical orthorhombic diffraction pattern (*Figure 2g*), proving that the particles have the different crystalline modification. A small shoulder of the hexagonal (100) peak observed on the orthorhombic (020) reflection is regarded as being due to incomplete fragmentation of the film. The film itself is hexagonal as seen in *Figure 2f*.

According to the Italian literature[4–7], the orthorhombic samples obtained by the polymerization of aqueous formaldehyde were 100% crystalline. This is true also for the present orthorhombic particles and no amorphous background has been observed, which, if present, would have a broad maximum at around $2\theta = 20°$. It is also noted in the present diffraction diagram that the peak profiles from the particles are as narrow as those from the needles, although the data have not been analysed quantitatively. That the crystalline perfection of needles is extremely high has been proved by the careful analysis of X-ray profiles and supported by spectroscopic and other measurements. In the literature[4–7], it was mentioned that the orthorhombic crystalline form was unstable above $60°C$ where it is transformed into the hexagonal form. It is clear from *Figure 2h* that the orthorhombic reflections have disappeared after heat treatment ($105°C$, 30 min), giving rise to the hexagonal reflections instead. These hexagonal reflections are rather broad in comparison to the original orthorhombic reflections as well as the reflections from the needles, suggesting that the transformation is accompanied by some crystalline disordering.

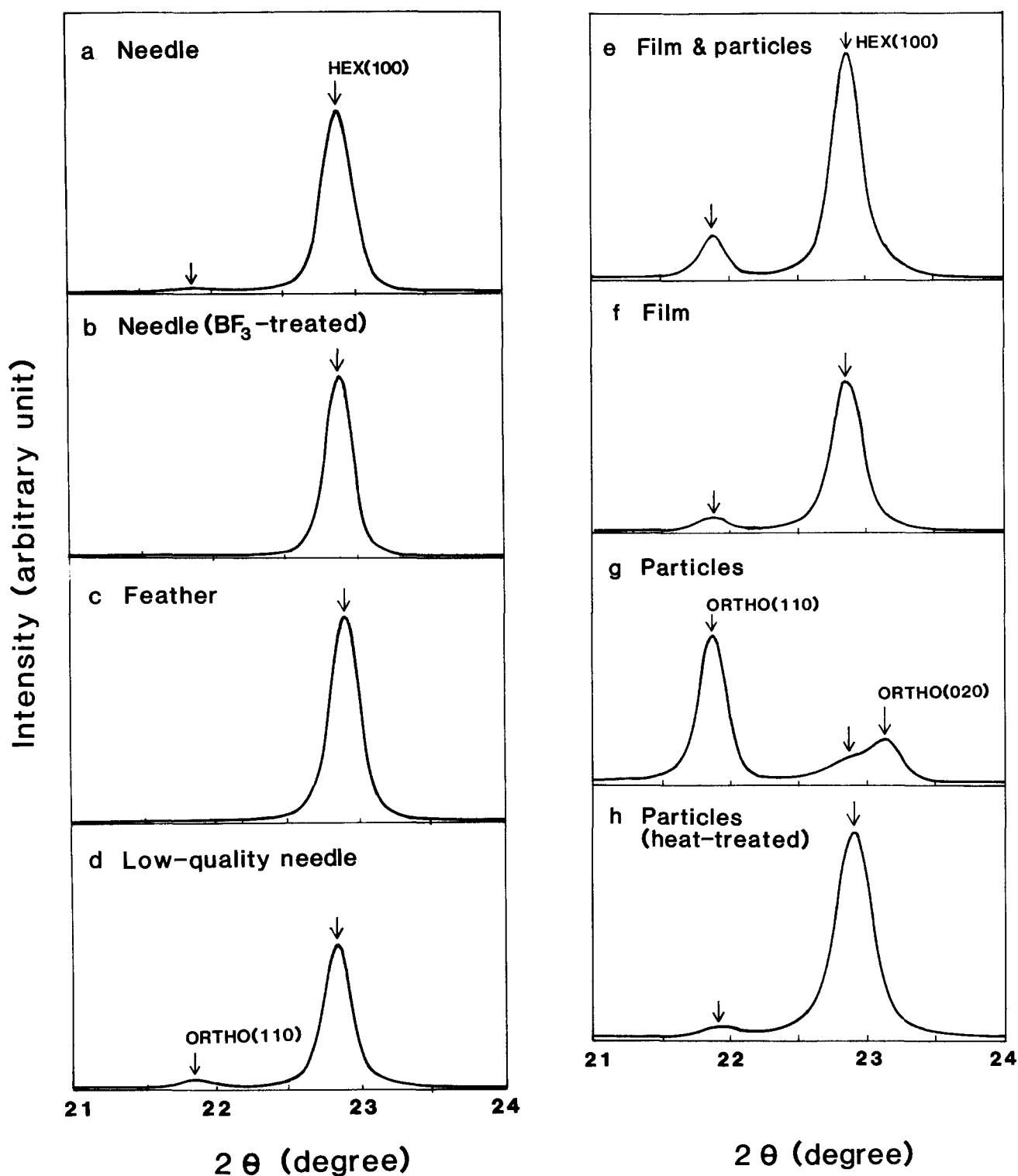The transformation has been examined by differential

Figure 2 X-ray diffraction diagrams of various polyoxymethylene samples around the main reflection peaks from hexagonal and orthombic unit cells

scanning calorimetry (d.s.c.) and a trace is shown in *Figure 3*. The curve is endothermic above 70°C but it is very complex in shape. The shape itself seems to be reproducible for the same sample but no explanation is possible at this moment. The temperature of the melting peak observed at around 190°C is similar to those of needle-like crystals and much higher than those of typical folded-chain crystals[13], suggesting that the molecular chains in

the specimen, and accordingly in the original orthorhombic specimen, may be of the extended form.

The morphology of the crystal was observed by various means. From the macro-photograph of *Figure 4*, the particles appear to be of spherical form, truncated at the bottom, comprising a number of small transparent crystalline units packed rather at random. Loose aggregates of crystalline units also observed on the substrate film are
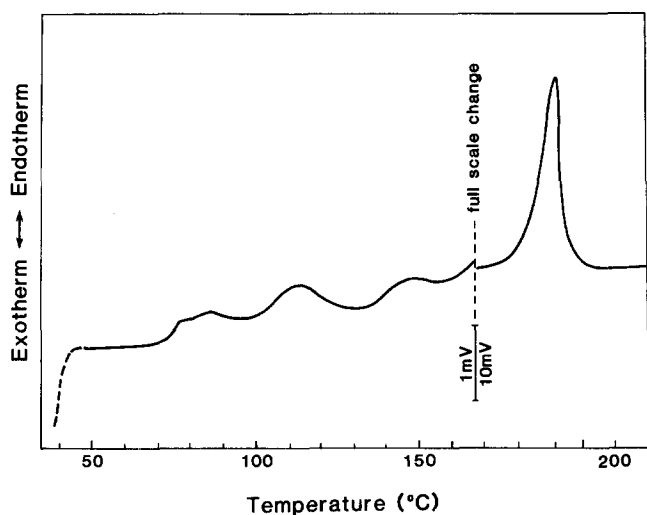
Figure 3 A differential scanning calorimetry curve of orthorhombic polyoxymethylene particles. (Apparatus, Perkin–Elmer DSC-II; heating rate, 10°C min⁻¹; sample weight, 4.26 mg)
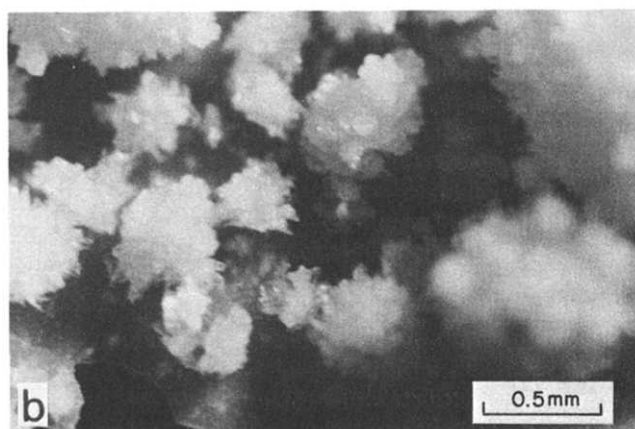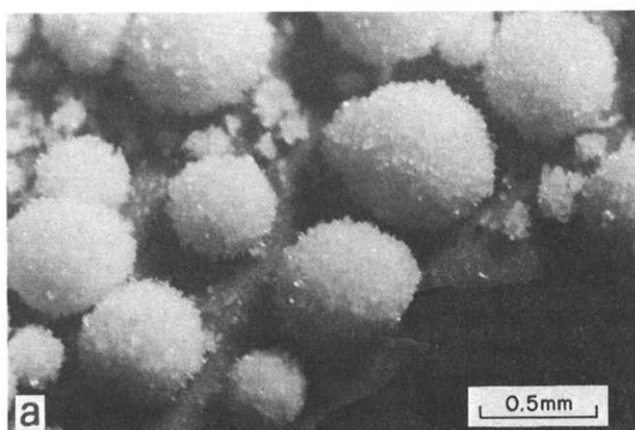

Figure 4 Macro-photograph of particles formed on substrate film: (a) mature and (b) immature

considered to be a precursor form of the spheres. An optical micrograph in *Figure 5* focused on the edge of the particles shows that the crystalline units are not homogeneous in shape. The scanning electron micrographs in *Figure 6* show the details more clearly, the typical shapes of the units being a thin scale and a pseudo-hexagonal rod (as seen in *Figure 6a*). Frequently on the substrate, a moth-shaped morphology (in *Figure 6b*) is found. In fact, this is

the morphology initially observed in the sample concerned, and may be the basic form of the scales which comprise a part of the spheres. It would be reasonable to assume that these crystalline units are grown by a surface reaction and, to form the spherical shape, secondary nucleation (or branching) and impingement have occurred repeatedly. The molecular orientation in these crystalline units has not been proved by diffraction but it is at least evident, from the birefringence, that the molecular axis lies parallel with the striation on the moth-shaped units and with the longitudinal axis of the pseudo-hexagonal rods. (At a glance, the moth-shaped morphology looks similar to that of 'feather-shaped' crystals[10,12], but the crystallographic difference is evident from the results of X-ray diffraction (*Figure 2*).)

For considering the growth mechanism, careful observation on film and particles formed on the internal wall of the vessel may be helpful. Upon introduction of the catalyst and the co-catalyst, the film is formed within a relatively short period, up to half an hour, and does not seem to thicken as judged by the opacity seen through the glass wall. Then, particles begin to appear and the number as well as the diameter increase with time. This phenomenon is quite reproducible under a wide range of reaction conditions whether or not the polymer formed in the liquid phase consists of good needles. However, the area of the particle deposition is not distributed all over the film but located in some part, due perhaps to the minor temperature distribution in and around the reaction vessel. In order to follow the growth of particles, a series of photographs such as shown in *Figure 7* have been taken by fixing a camera in front of the reaction vessel. The change in diameter is plotted against time in *Figure 8* for several particles of different sizes. The diameter increase is smooth and rather linear in the initial period and then tends to be very slow after 48 h. It is noted that the rates for different particles are almost the same at any particular reaction time irrespective of whether they have been nucleated earlier or later. This suggests that monomer supply to the gas phase is very slow and its diffusion to the reactive site and consumption is fast. Otherwise, the rate should have been determined by the reaction itself. Although no kinetical datum has been available for the polymerization in the liquid phase, the slowing-down of the growth rate corresponds to the consumption of monomer in the liquid phase.
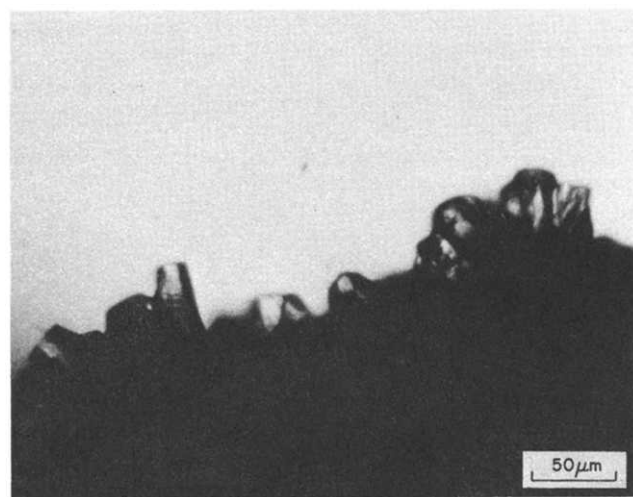

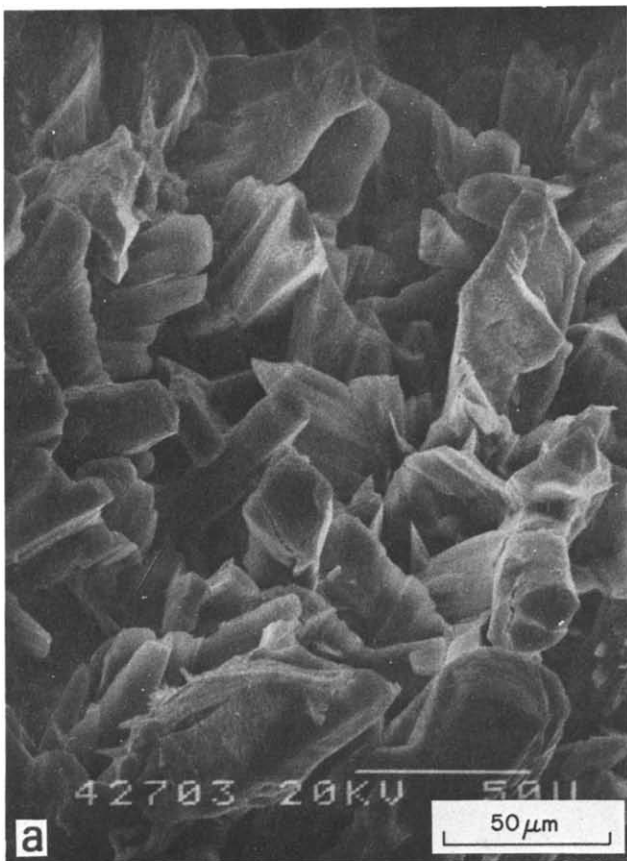Figure 5 An optical micrograph focused on the edge of an orthorhombic polyoxymethylene particle

Figure 6 Scanning electron micrographs of orthorhombic polyoxymethylene, showing (a) scale-like and rod-like morphologies and (b) moth-shaped morphology
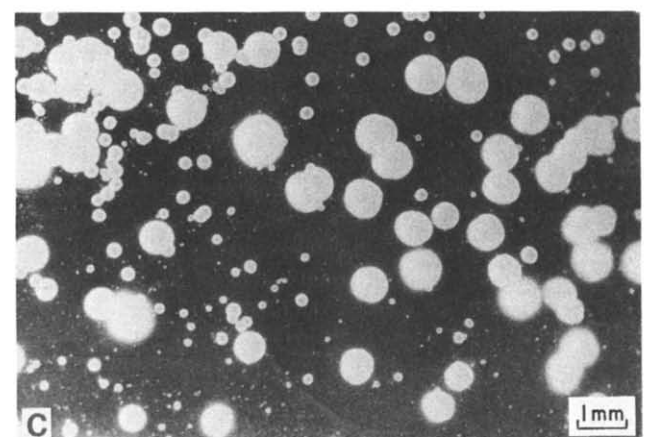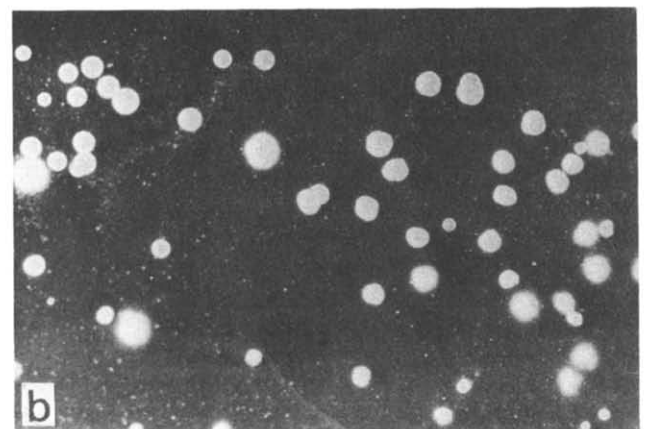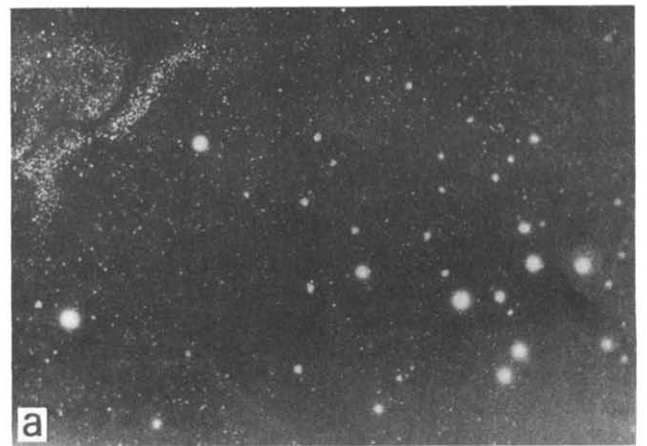

Figure 7 A series of photographs of particles growing on the internal wall of the reaction vessel: (a) 14.20, (b) 27.35 and (c) 45.05 h

CONCLUSIONS

To conclude briefly, two points have not been made clear. First, the orthorhombic crystals which triggered this search were the moth-shaped ones grown as independent pieces, presumably having come off the wall, and found together with needle-like crystals. The reproduction of such conditions has not been successful, although some needle-like samples have contained some orthorhombic fraction as shown by X-ray diffraction. For the preparation of the original sample, there has been no special record in our notebook. Secondly, the monomeric species forming the orthorhombic crystals has not been de-
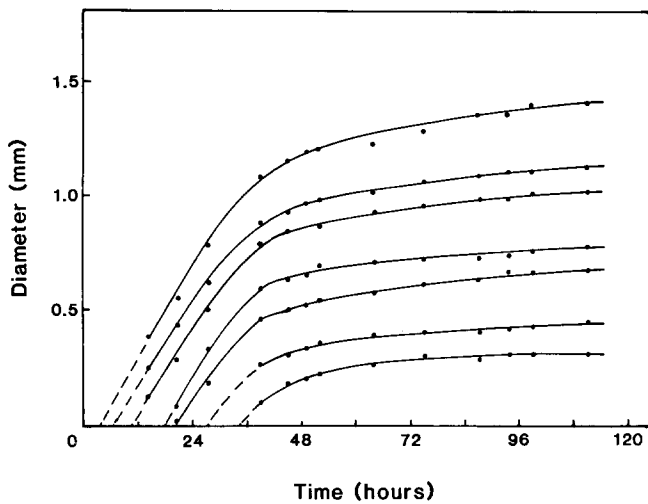
Figure 8 Diameter of particles with various induction times plotted as a function of the reaction time

termined. Although the monomer charge in the system was trioxane, formaldehyde generated secondarily is conceivably the monomer for crystal growth. Even for the growth of needle-like crystals, the direct addition of trioxane has been thought rather unlikely[10].

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