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Polymorphosis of Poly(oxymethylene) Crystals Grown in a Cationic Polymerization System of 1,3,5-Trioxane in Solution

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SUMMARY:

The morphology of poly(oxymethylene) appearing in the polymerization system of 1,3,5-trioxane in cyclohexane using BF_3 [or $\text{BF}_3\text{O}(\text{C}_2\text{H}_5)_2$] and water catalysis was studied in parallel with the kinetic behaviour of the reaction. Feather-shaped crystals, whose poor reproducibility was a problem, were found to be formed in a limited range of catalytic conditions. As a function of the mole ratio $\text{H}_2\text{O}/\text{BF}_3$, the change of morphology was ordered as follows: needle-like crystals ($\text{H}_2\text{O}/\text{BF}_3 < 0,05$), heterogeneous products ($\text{H}_2\text{O}/\text{BF}_3 = 0,05$ to 3), feather-shaped crystals ($\text{H}_2\text{O}/\text{BF}_3 = 3$ to 10), and amorphous products ($\text{H}_2\text{O}/\text{BF}_3 > 10$). A new type of single-crystal, tapered hexagonal rod, was found in the same catalytic region where feathershaped crystals were formed. The results of older preliminary work in a polar solvent, where a hexagonal, plate-like crystal had been obtained, are also briefly reconsidered in the discussion.

ZUSAMMENFASSUNG:

Es wurden sowohl die Morphologie von Poly(oxymethylen), das bei der Polymerisation von 1,3,5-Trioxan in Cyclohexan mit BF_3 [bzw. $\text{BF}_3\text{O}(\text{C}_2\text{H}_5)_2$] und H_2O als Katalysatorsystem entsteht, als auch das kinetische Verhalten dieser Reaktion untersucht. Federförmige Kristalle, deren schlechte Reproduzierbarkeit ein Problem darstellte, wurden nur in einem begrenzten Bereich katalytischer Verhältnisse gefunden. Die Änderung der Morphologie läßt sich als Funktion des Molverhältnisses $\text{H}_2\text{O}/\text{BF}_3$ wie folgt darstellen: Nadelförmige Kristalle ($\text{H}_2\text{O}/\text{BF}_3 < 0,05$), heterogene Produkte ($\text{H}_2\text{O}/\text{BF}_3 = 0,05$ bis 3), federförmige Kristalle ($\text{H}_2\text{O}/\text{BF}_3 = 3$ bis 10) und amorphe Produkte ($\text{H}_2\text{O}/\text{BF}_3 > 10$). Im selben Bereich wie die federförmigen Kristalle wurde auch ein neuer Typ von Einkristallen – abgeflachte hexagonale Stäbchen – gefunden. Die Ergebnisse von älteren, vorläufigen Arbeiten, bei denen hexagonale, plättchenförmige Kristalle gefunden worden waren, werden ebenfalls kurz diskutiert.

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Introduction

In quest of a theoretical mechanism of forming extended-chain polymer single-crystals, directly from monomeric units, in the course of polymerization, the authors^{1,2)} have long been interested in the structure of polymers precipitating from various polymerization systems and several years ago obtained a feather-shaped, plate-like single(twin)-crystal³⁾ of poly(oxymethylene) in a cyclohexane solution of 1,3,5-trioxane using boron trifluoride diethyletherate [$\text{BF}_3\text{O}(\text{C}_2\text{H}_5)_2$] as catalyst. The process of the crystal growth was clearly shown in a series of runs and a reasonable interpretation was available for the growth mechanism, but a potential problem remained in the lack of reproducibility. The kinetic behaviour of the reaction (i.e. the appearance of precipitation, the conversion etc.) varied from run to run and feather-shaped crystals were reproduced on rather rare occasions, while irregularly shaped products resulted more often. The needle-like crystal was another characteristic feature found incidentally.

The role of a very small amount of water⁴⁾, left unremoved from the system and acting as a co-catalyst, was discovered, and when the refinement of the experimental method (viz. the drying of the system) was extended, reproducible conditions were established first for the growth of needle-like crystals⁵⁻⁷⁾. Although this had no direct bearing on the original problem (i.e. poor reproducibility for feather-shaped crystals), it was encouraging that a particular morphology was obtained under a more reliable condition involving less water. It was previously⁶⁾ concluded that "the growth of needle-like crystals was favoured by large $\text{BF}_3/\text{H}_2\text{O}$ ratios".

A condition for feather-shaped growth was finally determined by adjusting the amount of water. When the catalytic condition, i.e. the amount of BF_3 and water, was changed in a wide range, the morphology and the behaviour of the progress of the reaction changed in various ways. Among the products, a quite new type of single-crystal was found, a long conical rod with a hexagonal cross section (diameter: ca. $10\mu\text{m}$ (at the bottom ca. $50\mu\text{m}$)), which is also thought to consist of fully extended-chain molecules. In summary, the variety of morphologies was put in an order as a function of the ratio of the two catalytic components (i.e. $\text{H}_2\text{O}/\text{BF}_3$).

To present and discuss these results obtained from cyclohexane solutions is the principal aim of this paper, though the results of older preliminary work with a polar solvent⁸⁾ will be briefly reconsidered on the basis of present knowledge. A crucial evidence for the view that each needle-like

crystal consists of a single-crystal, obtained recently from the study of a replica, will be included.

Experimental Part

Cyclohexane: In the early experiments, commercial cyclohexane (of G. R. grade) was used after purifying by the usual method including nitration of possible olefins, drying, and fractional dist. However, sufficiently good purity was often not attainable, depending on the quality of the supply. Spectroscopy-grade solvents (e.g. 'Uvasol' from E. G. Merck Ltd.) were preferred and used in most of the later experiments after refluxing over sodium-potassium alloy, and distilling fractionally in an atmosphere of dry argon (H_2O in the gas <5 ppm).

1,3,5-Trioxane: Commercial 1,3,5-trioxane (E. P.) was refluxed in pure cyclohexane in the presence of sodium wire and was then recrystallized. The purified material was dried i. vac. and stored over potassium hydroxide pellets.

Catalyst: $BF_3O(C_2H_5)_2$ (E. P., purity $>99,7\%$) was dist. immediately before use. Gaseous BF_3 , supplied in a cylinder (purity $>99,7\%$), was used without purification.

Preparation of monomer solution: The method was as described previously⁹⁻¹¹. All glass-ware, sulfuric acid-potassium permanganate cleaned, was heated in an oven at temps. $>120^\circ C$. While hot, it was set up for dist. (as well as for polymerization), evacuated and filled with dry argon. 7,2 g (0,08 mol) 1,3,5-trioxane, dissolved in 250 ml cyclohexane, was refluxed with sodium-potassium alloy to complete drying, and was then directly dist. together with a 200 ml portion of the solvent. During the distillation, 1,3,5-trioxane was efficiently transferred in the early stages.

Polymerization: For a series of runs, several 20 ml portions of the solution were distributed by use of a syringe into reaction tubes (30 ml test tubes) in the stream of dry argon and sealed with silicone-rubber stoppers. Polymerization was conducted at $50^\circ C$ by adding, from two separate syringes, water (occasionally moisture) followed by gaseous BF_3 or freshly dist. $BF_3O(C_2H_5)_2$, and maintaining the system unstirred for 20 h. The amount of applied BF_3 [or $BF_3O(C_2H_5)_2$] and water ranged from $1,34$ to $7,9 \times 10^{-5}$ and 5×10^{-7} to $5,5 \times 10^{-4}$ mol, resp., each batch containing ca. 0,008 mol 1,3,5-trioxane. The monomer solution, initially transparent, turned turbid (very soon or slowly depending on the amount of the two catalytic components), and precipitated white polymer.

Results

Because feather-shaped crystals were produced only occasionally during the repetition of the original procedure³ using not well-dried monomer solution and $BF_3O(C_2H_5)_2$, not only the effect of residual water, but also those of such components as diethyl ether (liberated by water from $BF_3O(C_2H_5)_2$) and unknown impurities were suspected, but tested for in vain. The situation

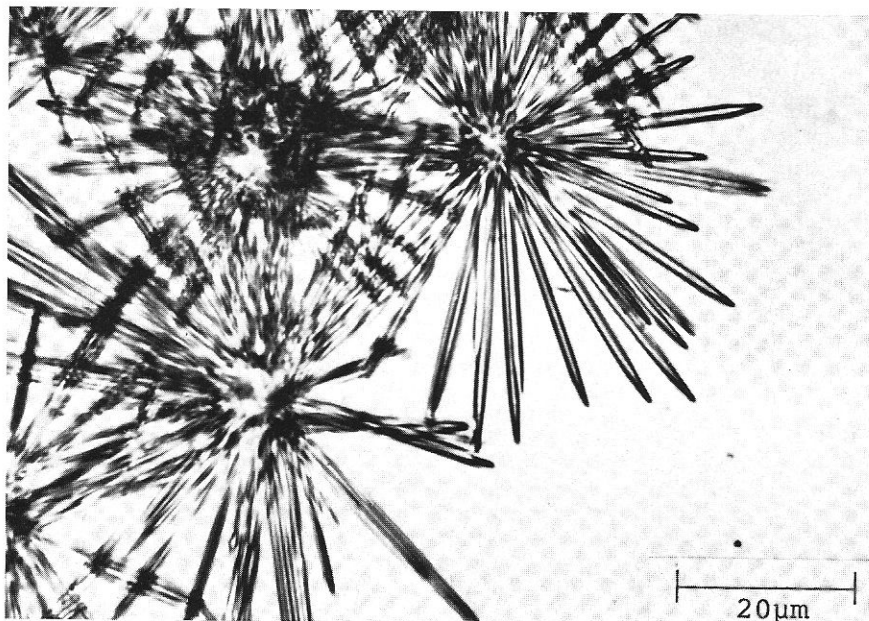


Fig. 1a

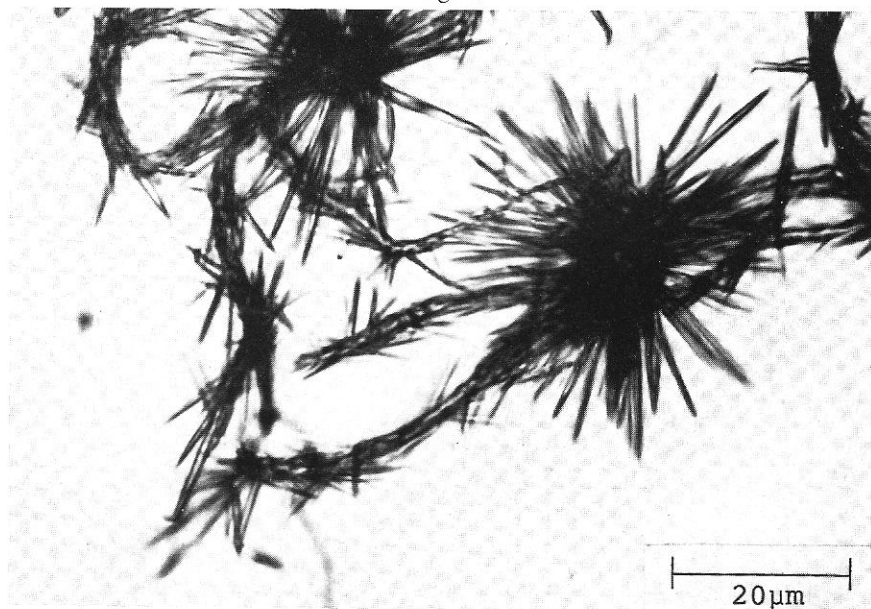


Fig. 1b

Fig. 1. Needle-like crystals of poly(oxymethylene), neat (Fig. 1a) and branched (Fig. 1b), grown in a cyclohexane solution of 1,3,5-trioxane at a small $\text{H}_2\text{O}/\text{BF}_3$ mole ratio (<0.05). Optical micrograph. Figs. were taken from specially prepared batches outside the series of runs: to 200 ml of 0.4 mol/l monomer solution, $4 \cdot 10^{-4}$ mol BF_3 and then 10^{-5} mol H_2O were added⁽¹⁰⁾

was simplified, however, when feather-shaped crystals turned out in a screening run: monomer solution, prepared by the improved technique, was deliberately wetted, prior to the addition of BF_3 , with a small quantity of water (roughly with 5 times of the amount of BF_3).

It became apparent that the components, effective for the reaction, were BF_3 and water as in the case of the formation of needle-like crystals⁴⁾, the substantial difference being the use of a large amount of water. This difference could well be influential in the chemical mechanism and hence to the nucleation and the growth of the crystals. The order of the addition of the two species also seemed to be significant. The addition of water first and then of BF_3 gave better results for the growth of feather-shaped crystals. This seems not only to be a matter of mixing, but also to be related to the mechanism of initiation.

Morphology as well as the behaviour of the reaction was studied systematically at various catalyst conditions. The addition of water and BF_3 was fixed as in this order. Typical examples of various morphologies are shown in Figs. 1–5.

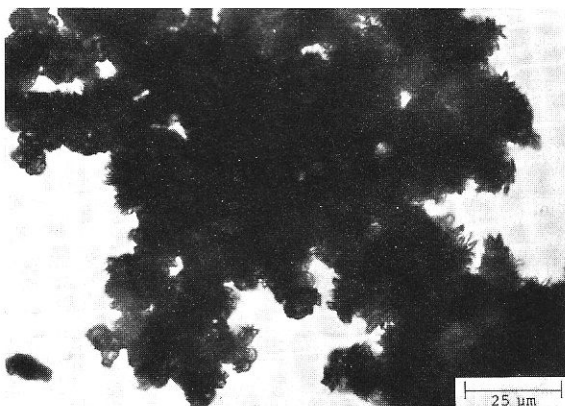


Fig. 2. 'Heterogeneous' poly(oxymethylene) aggregate produced at a $\text{H}_2\text{O}/\text{BF}_3$ mole ratio of ca. 0.05–3 (s. text). Optical micrograph

When the results from different groups of runs were summarized as a function of the $\text{H}_2\text{O}/\text{BF}_3$ mole ratio, a consistent pattern was found for the change of habit, as shown in Fig. 6. (In three groups of runs out of six, $\text{BF}_3\text{O}(\text{C}_2\text{H}_5)_2$ was used in place of BF_3 , but no significant difference was seen, supporting the view that diethyl ether is without effect in the system.) Four regions can be distinguished as follows.

When the $\text{H}_2\text{O}/\text{BF}_3$ ratio was roughly less than 0.05, the system was favorable for the formation of needle-like crystals (Fig. 1a), as had been

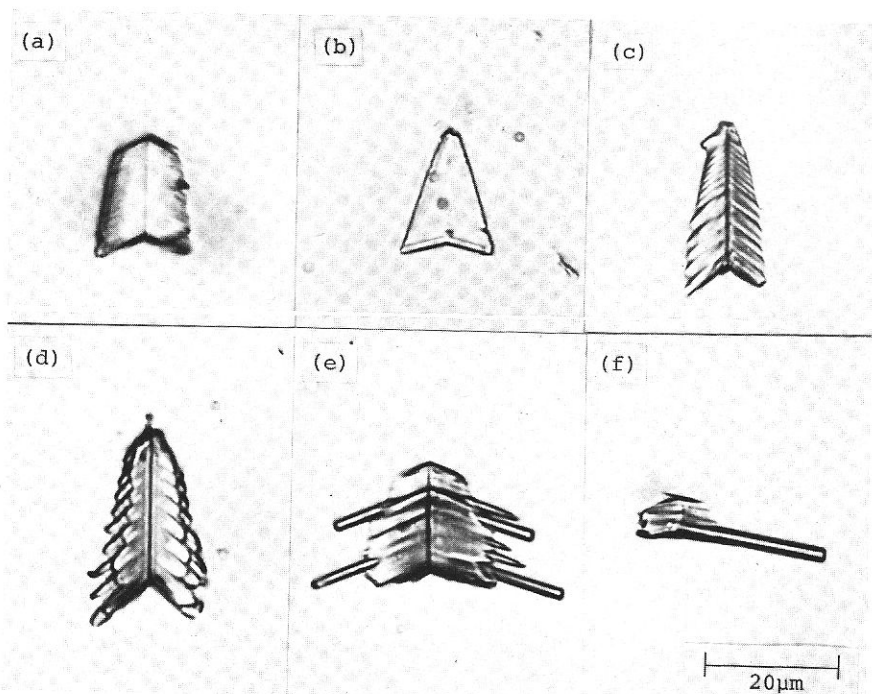


Fig. 3. Feather-shaped poly(oxyethylene) crystals, typical (a) and modified (b)–(f) forms, grown at a $\text{H}_2\text{O}/\text{BF}_3$ mole ratio of ca. 3–10 (s. text). Optical micrograph

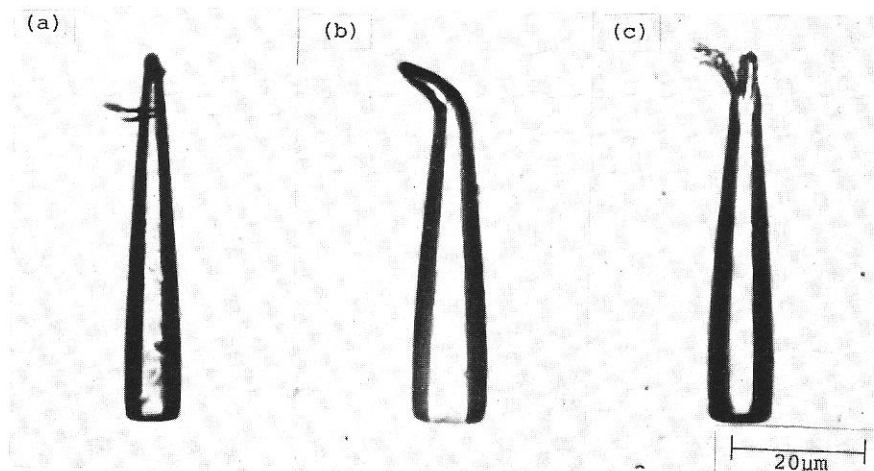


Fig. 4. Hexagonal, rod-like poly(oxyethylene) crystals, normal (a), bent (b), and fibrillized (c), newly found at the same $\text{H}_2\text{O}/\text{BF}_3$ mole ratios (ca. 3–10) at which feather-shaped crystals were formed (s. text). Optical micrograph

Fig. 5. 'Amorphous' poly-(oxymethylene) (of low molecular-weight) precipitated at $\text{H}_2\text{O}/\text{BF}_3$ mole ratios > 10 (s. text). Optical micrograph

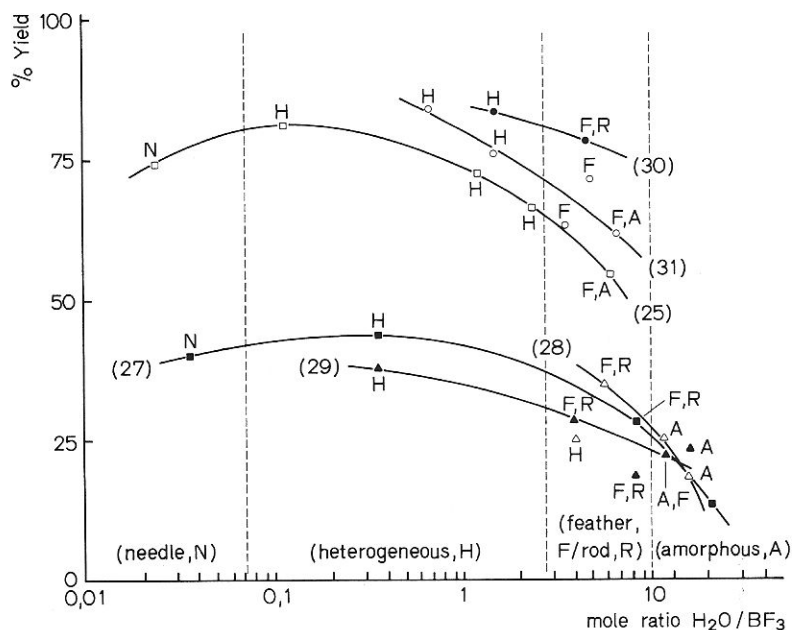
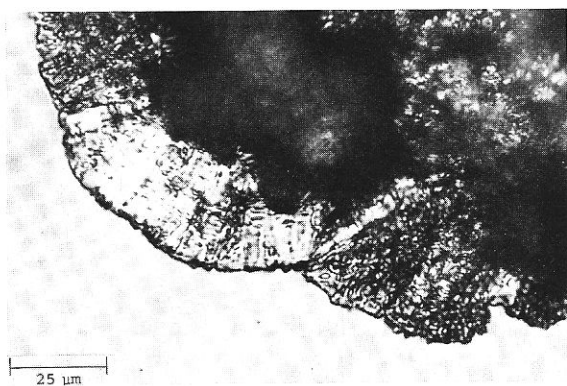


Fig. 6. Yield of poly(oxymethylene) (reaction time: 20 h) and morphology, plotted against the mole ratio $\text{H}_2\text{O}/\text{BF}_3$. N, H, F, R and A denote needle-like, heterogeneous, feather-shaped, rod like, and amorphous, resp. (s. Figs. 1–5). The figures in the brackets indicate series of runs: the amount of BF_3 (or $\text{BF}_3\text{O}(\text{C}_2\text{H}_5)_2$) applied was: $7.9 \cdot 10^{-5}$ mol $\text{BF}_3\text{O}(\text{C}_2\text{H}_5)_2$ [(30) and (31)], $4.5 \cdot 10^{-5}$ mol BF_3 (25), $1.34 \cdot 10^{-5}$ mol BF_3 [(27) and (28)], and $1.34 \cdot 10^{-5}$ mol $\text{BF}_3\text{O}(\text{C}_2\text{H}_5)_2$ (29)

already established^{5–7}). The appearance of clouding, an indication of the initiation of the reaction, was instantaneous and followed by a steady increase

in the mass of the precipitate. The yield of polymer was modest. Needle-like crystals obtained by this way of adding catalyst (i.e. water first and then BF_3) were generally not as homogeneous and pretty as for the reverse order.

The view that each needle comprises a single crystal, which had been supported so far through many structural and physical investigations^{5-7,9-13}, is confirmed. Electron microscopic observation with a special replication method (Fig. 7)^{*} revealed a hexagonal outline, obvious enlargement of (100) facet of the unit cell structure, being maintained throughout the length towards the narrowed tip. The surface looks rather smooth and no large step, as is expected by the screw-dislocation mechanism¹⁴, is observed within the limit of the resolution (ca. 25 Å). The origin of the quasi-parabolic shape of the tip could be explained alternatively with reference to the diffusion-control mechanism proposed by Papapetrou¹⁵.

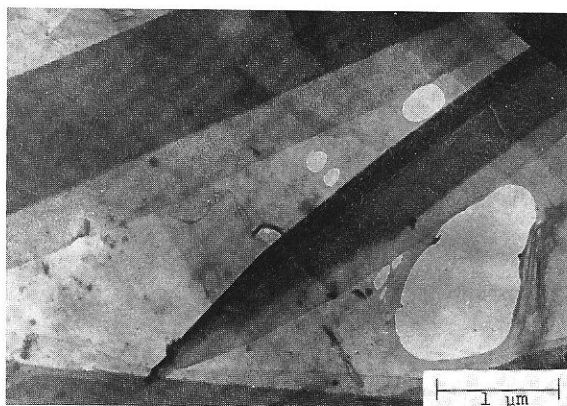


Fig. 7. An electronmicrograph of surface replica of needle-like poly(oxymethylene) crystals

On a few occasions (though not in these series of experiments), needle-like crystals grew with dense branchings as seen in Fig. 1b). This tended to happen, when the stopper was not properly inserted, in the upper part of the precipitate (i.e. near the surface of the liquid layer); therefore, the effect of moisture penetrating from the atmosphere into the system was suspected. It is considered that the branching was nucleated by a secondary deposit of catalytic species activated after a delay on the surface of growing needles: a splitting of the original needle is hard to imagine from the growth mechanism

^{*}) Fig. 7 was made by the courtesy of Dr. Kōmoto, Tokyo Institute of Technology.

and, in fact, division into halves of the original diameter at branching points did not occur.

As the water content increases, the needle-like feature tended to be blurred and, in the $\text{H}_2\text{O}/\text{BF}_3$ range 0.05–3, the morphology was dominated by such heterogeneous products as seen in Fig. 2. In detail, they seemed to indicate some premature signs of needle formation and other crystalline habits, the latter appearing at larger water content (s. the next paragraph). The products as a whole, however, did not seem to have grown with any regular habit. In this region, the apparent rate of polymerization as well as the clouding was quickest and the conversion attained its maximum. In addition to the presence of large amount of catalytic species ($\text{H}^+\text{BF}_3\text{OH}^-$), the result may also occur because propagation proceeded at high rate at chain-ends which were not well-organized upon a crystalline surface. Leaving morphology aside, it may be said that polymerization was most successful in this range of catalytic composition.

Feather-shaped crystals were found to be produced in the range of catalytic ratio between 3 and 10. Although clouding was observed soon after the addition of BF_3 , the increase of the polymer precipitate was rather slow and steady, the conversion staying at relatively low level. Feather-shaped crystals were thus reproduced, but conditions to produce them selectively upon the precipitate have yet to be defined. This problem seems partly related to the inevitable inhomogeneity on mixing catalyst with monomer solution. The crystals were more or less concurrent with heterogeneous polymer mentioned in the previous section (Fig. 2). Besides the morphology shown in Fig. 3a, the authentic form of what was called³⁾ 'feather-shaped' crystals grown out in such abnormal fashions as seen in Fig. 3c–f were frequently observed. (This type of transformation was pointed out originally³⁾.)

In addition to these, quite a new type of crystal, a long conical rod with a hexagonal cross-section (Fig. 4) was also found in the products of the same catalytic region. Although, details have not been studied, the crystal is certainly a single-crystal judging from the morphology as well as from a preliminary X-ray test which showed a typical single-crystal pattern. Bending and fibrillization (Fig. 4b and c) suggested it to consist of extended-chain molecules.

When the amount of water increased beyond the catalytic ratio (i.e. $\text{H}_2\text{O}/\text{BF}_3 > 10$), the system tended to give crystalline particles of indefinite shapes (Fig. 5), at low yield. The product is brittle and fragile and considered to consist of oligomeric or low molecular weight chain homologues.

$$\begin{array}{c}
 \text{BF}_3 \xrightarrow{(\text{CH}_2\text{O})_3} \begin{array}{c} \text{O}-\text{CH}_2 \\ | \quad | \\ \text{H}_2\text{C} \quad \text{O} : \text{BF}_3 \\ | \quad | \\ \text{O}-\text{CH}_2 \end{array} \\
 \downarrow \text{H}_2\text{O} \qquad \qquad \downarrow \text{H}_2\text{O} \\
 \text{H}^+ \text{BF}_3\text{OH}^- \xrightarrow{-\text{CH}_2\text{O}-} \text{HO} \sim \text{CH}_2^+ \text{BF}_3\text{OH}^- \xrightarrow{-\text{CH}_2\text{O}-} \text{HO} \sim \text{CH}_2\text{OCH}_2^+ \text{BF}_3\text{OH}^- \xrightarrow{-\text{CH}_2\text{O}-} \\
 \updownarrow \text{H}_2\text{O} \qquad \qquad \updownarrow \text{H}_2\text{O} \qquad \qquad \updownarrow \text{H}_2\text{O} \\
 \text{H}_3\text{O}^+ \text{BF}_3\text{OH}^- \qquad \text{HO} \sim \text{CH}_2\text{OH} \qquad \text{HO} \sim \text{CH}_2\text{OCH}_2\text{OH} \\
 \qquad \qquad \qquad + \qquad \qquad \qquad + \\
 \qquad \qquad \qquad \text{H}^+ \text{BF}_3\text{OH}^- \qquad \qquad \qquad \text{H}^+ \text{BF}_3\text{OH}^-
 \end{array}$$

When the amount of water was very small relative to BF_3 and needle-like crystals resulted, water would have been used up rapidly for the initiation only, whatever the mechanism of the initiation. From the instantaneous appear-

ance of the clouding, it was suggested that the initial product would promptly coagulate in the form of fine clusters, before many formaldehyde units were added, thus furnishing the centres of nucleation for the radial growth of needles. (For growing needles, the initiation mechanism of formation of BF_3 -trioxane complex, followed by the attack of water, may perhaps be inferred because adding BF_3 first and then water was in favour of obtaining good needle-like crystals.) The nucleation may be classified as 'predetermined', using a general term of crystal growth theory.

With the increase of water, side reactions with excess water would no longer be negligible. The reaction between BF_3 and water will go, through the monohydrate, forward to the dihydrate (or even further), the concentration or supply of monohydrate being controlled by the equilibrium. The active end-groups generated after the addition of $-\text{CH}_2\text{O}-$ units may also be affected, transferring to water and giving rise to oligomers with hydroxy groups. This reaction, however, regenerates monohydrate. Perhaps this is the important process for the consumption of an excess of water which could eventually lead the system to a living condition.

When water presented at a level such that feather-shaped or rod-like crystals were obtained, living species would slowly increase through this mechanism and removed from the solution to build up active nuclei. By adding the experimental observation that crystals formed were dispersed independently over the precipitate, the nucleation is considered to be 'sporadic'.

The nuclei for feather-shaped crystals are considered³⁾ to be long (triangular) plates, with reactive surfaces on both sides, composed of short reactive molecules aligned at an angle nearly perpendicular to the direction of the length. Why then are the two growth fronts not parallel? A mechanism was suggested (by the courtesy of Dr. Small, of I. C. I. Ltd.) that the start of lateral growth (i.e. the addition of monomer to the growth-surface) will soon follow after the piling-up of reactive molecules which proceeds along the symmetry axis from the bottom (notch) to the top of the crystal. Thus, two growth fronts are merging at the top and retain a sharp angle (Fig. 3b), because nucleation persists to the end of the reaction, whereas early exhaustion of the nucleator would give an obtuse-angled top (Fig. 3a). The origin of the anomalous growth, the protrusion of narrow hexagonal rods having either a sharp or flat end and other habits (Fig. 3c-f), is not certain: they could be caused by the poisoning by foreign molecules as is common with ordinary crystal growth. The nucleus for the large rod-like crystal is supposed to be a hexagonal platelet or cone.

For growth of single-crystals, discrete occurrence of nucleation is desirable as for all types of crystals. In the intermediate region ($\text{H}_2\text{O}/\text{BF}_3$, ca. 0.1–3), where heterogeneous polymer developed, nucleation and growth were perhaps competitive without permitting formation of clear nuclei and led to rather random deposit of growing chains. The case that only brittle products of oligomeric substance were obtained at low yield (at a $\text{H}_2\text{O}/\text{BF}_3$ mole ratio > 10) is interpreted to be the result of easy chain-transfer reaction to water. The propagation would have been depressed seriously, the precipitate being formed with inactivated oligomers.

In the early stage of this research, the morphology was studied also for the polymer precipitating from polar solvents, viz. nitrobenzene⁸⁾. The result is to be reconsidered on the basis of present knowledge. In early runs, hexagonal crystals were grown with $\text{BF}_3\text{O}(\text{C}_2\text{H}_5)_2$ as catalyst (on one occasion to such a large size as 2–3 μm thick and 150–200 μm across, shown in Fig. 8). When dryness of the system was improved, however, it was found that growth with such a habit was limited to the very early stage of the reaction, or to the induction period. During the progress of the reaction, such forms became obscured, being covered by subsequent deposit of polymer until it turned into a heterogeneous crystalline mass. From kinetic studies, it was pointed out by Higashimura et al.¹⁶⁾ that the course of polymerization of a similar system is approximated by a second order law with respect to the residual monomer concentration. An interpretation for this anomaly offered by one of us¹⁷⁾ was based upon the assumption that reactive chain ends are immobilized, as they are embedded in the mass, so that diffusion of monomer to the sites becomes difficult.

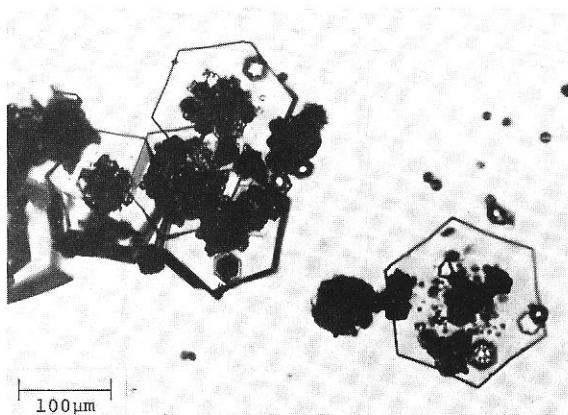


Fig. 8. Large hexagonal crystals of poly(oxymethylene) formed in a previous study⁸⁾ in nitrobenzene solution of 1,3,5-trioxane (not well-dried) using $\text{BF}_3\text{O}(\text{C}_2\text{H}_5)_2$ as catalyst. Optical micrograph

Whether $\text{BF}_3\text{O}(\text{C}_2\text{H}_5)_2$ (used as catalyst) can directly effect polymerization in polar solvents, or whether water is necessary as co-catalyst, is not certain, but that these complexes are soluble is important. The solvent has larger affinity to oligomeric chain molecules, so that the precipitation may be impeded until they grow large. It is considered that hexagonal crystals were composed of short chains precipitated from the system, but in the condition that propagation was controlled by transfer to water. Concerning the structure, there was no evidence to regard the crystal as the 'extended-chain' type: the occurrence of chain folding was not established either.

The random deposit of polymer would have resulted either from the lack of nuclei with ordered active surface or from the fact that propagation itself in such a polar environment was too fast to allow a steady growth on the surface, or both.

Growth of similar hexagonal crystals in the polymerization system of 1,3,5-trioxane in solution has been reported, e.g. in methylene dichloride by *Leese* and *Baumber*¹⁸⁾ and more recently by *Mateva* et al.¹⁹⁾, but more information from studies on the chemical mechanism seems to be desirable before details of the growth mechanism and structure can be settled.

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