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On the Morphology of Rod-like Trigonal Polyoxymethylene Single Crystals

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Abstract

A new type of single crystals of trigonal polyoxymethylene was found in a cationic polymerization system of trioxane designed to grow needle-like polyoxymethylene single crystals (polymer whisker). A number of small particles of polyoxymethylene (Figure 2) were observed on the thin film of t-POM formed over the inner wall of the reaction vessel. The particle samples were comprising a lots of small rod-like transparent crystalline units packed at random. It has been clarified that the particles consist of the trigonal crystalline form of polyoxymethylene, moreover these rod-like single crystals consist of the extended chain structures from the infrared spectra.

Introduction

Polyoxymethylene, $(\text{CH}_2\text{O})_n$ (abbreviated as POM) crystallizes into two modifications, trigonal polyoxymethylene (t-POM) consisting of 9/5 (or 29/16) helical conformation^{1,2,3} and orthorhombic polyoxymethylene (o-POM) consisting of 2/1 helical molecules⁴. The former is exclusively obtained through the ordinary crystallization process from the melt or dilute solutions of polyoxymethylene resins. The single crystals of t-POM have been obtained in dilute solution, which show the typical hexagonal morphology consisting of folded chains. Feather-shaped platelets and needle-like (polymer whisker) single crystals consisting of extended chains having other crystal morphology were obtained in a cationic polymerization system of trioxane using boron trifluoride and water as catalyst^{5,6}, respectively.

On the other hand, o-POM was originally discovered about three decades ago by

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Italian scientists in a polymerization system of alkaline aqueous formaldehyde⁴). Moth-shaped platelets and rod-like o-POM single crystals consisting of extended chains^{7,8}) were obtained as a by-product^{9,10}) in a cationic polymerization system of trioxane designed to grow needle-like t-POM single crystals. Kobayashi *et al.* succeeded to measure polarized Raman spectra on the moth-shaped single crystals by means of the Raman microprobe technique, and then based on the polarization data and the result of normal mode analysis, the orientation of the crystal axes in the moth-shaped single crystal was investigated^{11,12,13}). It was determined that c axis is parallel to the striations on the plate surface of the moth-shaped single crystals and a axis perpendicular to c axis within the plate surface.

The authors clarified that the metastable o-POM single crystals transformed irreversibly to the stable t-POM single crystals at 69°C with an endotherm 0.6 kJ/mol per CH₂O unit on heating, when the morphology, the fiber axis orientation, and the extended-chain structure of the starting orthorhombic crystals remained unchanged throughout the thermal transition¹⁴). Moreover, on the morphology of POM crystals pressure-induced solid-state phase transition from t-POM to o-POM phase was investigated by means of infrared and Raman spectroscopy. It was clarified that the morphology of the starting t-POM samples (extended-chain and folded-chain crystals) was kept unaltered on the pressure-induced phase transition to o-POM phase^{7,8}). Thus, it became evident that the morphology of the crystalline structure was preserved through the solid-state phase transition between two modifications of POM.

The present authors found that a new type of single crystals of t-POM were obtained in the course of investigating the relationship among the crystalline morphology of POM. In the present study, it is reported to the preparation of rod-like single crystals of t-POM and morphological structures of these single crystals, we make an interim report of this study.

Experimental

Preparation of trioxane (HCHO)₃: Paraformaldehyde (S.P. grade) and silicotungstic acid (guaranteed reagent) were used the article on the market without purifying.

A sample of trioxane was prepared on a reaction by heating of formaldehyde which produced from paraformaldehyde and water in the presence of silicotungstic acid as catalyst¹⁵). A charge of 15.0g of paraformaldehyde, 25.0g of silicotungstic acid and 10.0ml of water was placed into a 200ml flask fitted with a condenser, the

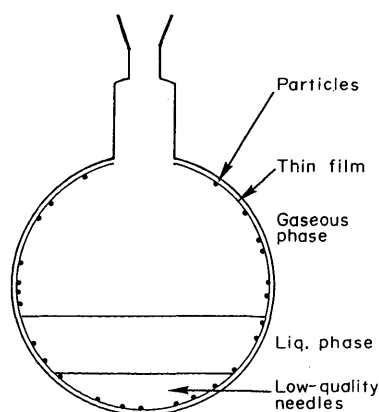


Figure 1. Schematic illustration of t-POM formed in the reaction vessel

mixture was heated under a reflux in the temperature range, 90~100°C. Then, distillation of trioxane was carried out, and 3.2g of trioxane (b.p. 64°C) were obtained.

Preparation of polyoxymethylene: Commercial boron trifluoride ether complex (47% contained BF_3) was purified by fractional distillation before use.

POM crystals were grown in a cationic polymerization system of trioxane under the similar conditions to the generation of needle-like single crystals^{16,17}. Points to which special attention should be paid are omitted as much as water in this synthetic system of POM. 3.2g of trioxane were dissolved in 100ml of cyclohexane (S.P. grade), and the solution was refluxed with sodium metal to complete drying at around 100°C for a day in an atmosphere of dry Ar. Then, the solution was distilled together with the solvent, 50ml of distilled trioxane solution was stored still in the constant temperature oven controlled at 50°C. The distilled boron trifluoride ether complex (about 0.02ml) was added to the trioxane solution by use of a syringe into reaction vessel through the silicon-rubber stopper, and the solution was immediately well-shaken. Continuously, little of water (rather moisture) was added to the solution and vigorously shaken, too. The solution was set aside to polymerize in the constant temperature oven of 55°C for 3 days. Then, the polymerization was terminated by adding of a charge of 2.5ml of triethylamine and 10ml of ethanol as a reaction stop reagent. POM crystals having a different of morphology were produced in the bottom and the side wall of the reaction vessel.

Raman scattering spectrum: Raman spectra of the particle samples of t-POM were measured with a JASCO R-500 double monochromator using the 488.0 nm line from an Ar^+ laser as the excitation source.

Infrared absorption spectrum: The absorption spectrum in the finger-region was measured with a SHIMADZU IR-450 spectrometer, and the measurement was taken by the Nujol-mull methods. The far infrared absorption spectra were measured with HITACHI model FIS-3 spectrometer. Powder samples were mixed with paraffin wax, and sandwiched between two silicon plates, and subjected to measurement.

Results and Discussion

Figure 1 shows the schematic illustration of POM formed into the reaction vessel. A thin film was formed in all inner wall of the vessel for reaction, and a number of small particles (Figure 2) up to ~1mm diame-

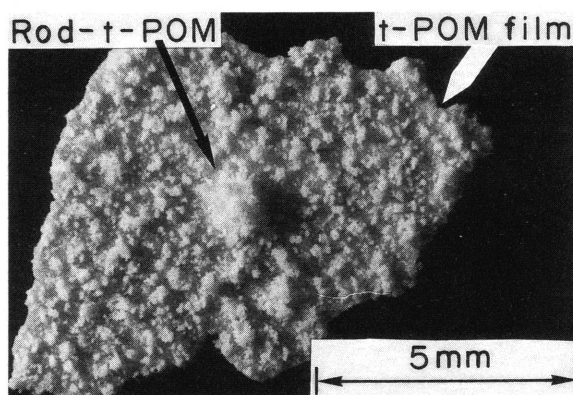


Figure 2. Macro-photograph of t-POM particles formed on t-POM film

ter were observed on the thin film in the liquid and gaseous phases. On the other hand, in the liquid phase a lot of low-quality needle crystals³⁾ (Figure 3) were formed around the bottom of the reaction vessel.

For the thin film and low-quality needle crystals, it has been already reported that these specimens obtained in the similar synthesis method were of t-POM from X-ray diffraction by Iguchi³⁾. In the present work, it has been confirmed that both specimens are of t-POM by means of Raman scattering, too.

On the particle specimen obtained, Iguchi³⁾ has reported that these samples were formed on the thin film of t-POM in contact with gaseous phase into the reaction vessel at 50°C and consisted essentially of orthorhombic form. While in the present work, particle samples (Figure 2) are formed on the t-POM film in contact with gaseous and liquid phases. The obtained particles are consisted of a number of rod-like crystalline units packed at random under the observation by a light microscope. An optical micrograph in Figure 4 focused on the edge of the particles shows that the crystalline unit are not homogeneous in shape. Each rod-like crystalline is optically active under crossed nicols (i.e. having a birefringence). Therefore, it is clear that each crystalline shows characteristic of a single crystals.

On one of the particle samples Raman spectrum was measured, and re-

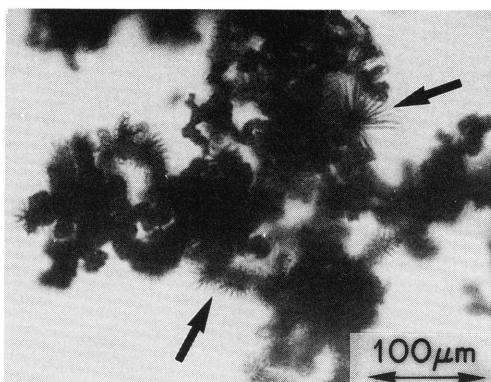


Figure 3. An optical micro-photograph of low-quality needles of t-POM

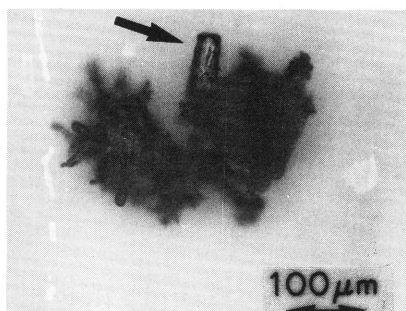


Figure 4. An optical micro-photograph of Rod-like single crystals of t-POM

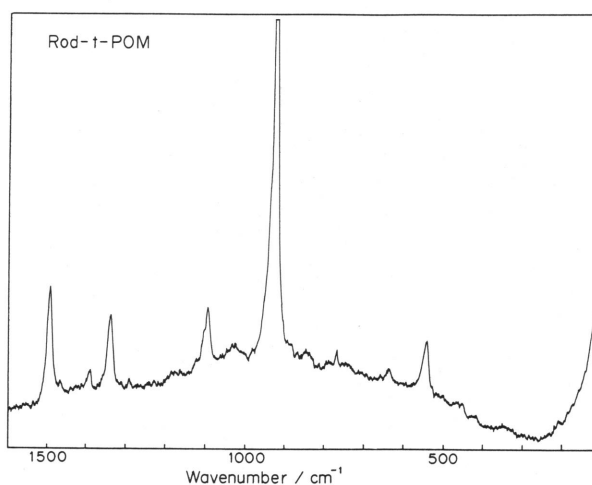


Figure 5. Raman spectra of a particle sample of t-POM

produced in Figure 5. The spectral characteristic of the particle samples gave the spectrum consisting exclusively of the band to assign the trigonal form. Therefore, it became evident that these rod-like crystals were not orthorhombic form, but were single crystals of the trigonal form of POM.

The infrared absorption spectrum of t-POM is strongly affected by the crystal morphology of the samples as it has been reported in previous papers^{18,19,20}. The infrared and Raman bands of needle-like single crystals having a fully extended chain structures of t-POM are in good accord with the results of the normal mode calculations^{18,21}, while on the folded chain crystals of t-POM, only the infrared bands due to the A_2 symmetry species having the transition dipole along the chain axis shift toward high-frequency side from the position of the corresponding A_2 bands in extended chain crystals^{18,19}. Figure 6 shows far infrared spectra of various specimens of t-POM. The CO torsional mode $A_2(5)$ of various specimens appears at around 230 cm^{-1} at room temperature and liquid N_2 temperature, respectively. The wavenumber shift of $A_2(5)$ among different specimens of t-POM in the morphology is clearly indicated. It is remarked that the peak position of the specimen of the typical extended

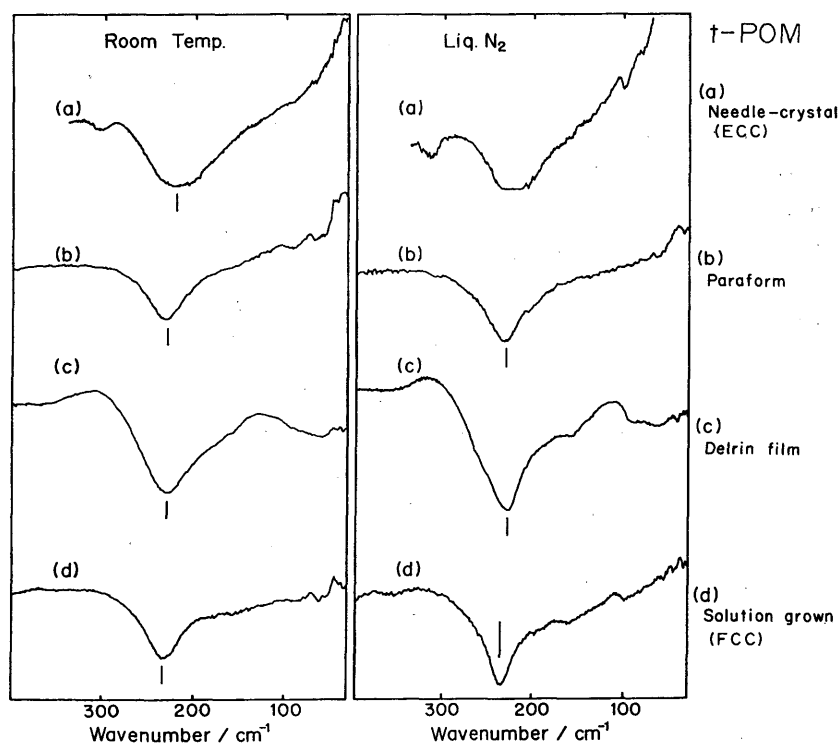


Figure 6. Far infrared spectra of various polyoxymethylene specimens measured at room temperature (left) and liquid N_2 temperature (right).

chain crystals having the highest crystalline perfection, i.e. needle-like single crystal, is measured at 220 cm^{-1} , whereas the peak position of typical folded chain crystals, i.e. solution grown crystal, is measured at 236 cm^{-1} at room temperature. Thus, it has been revealed that the band positions of A_2 modes in the infrared spectrum can be utilized for the characterization of morphological structures of t-POM^{18,19,20}.

For infrared measurement, these particle samples (Rod-t-POM) were mullied with nujol and sandwiched between two KBr plates as a window. Infrared spectrum in the $1300\text{--}400\text{ cm}^{-1}$ of these particle samples is reproduced in Figure 7. In this infrared spectrum, the spectral pattern is similar to the spectral pattern of needle-like single crystals consist of extended chain structures (refer

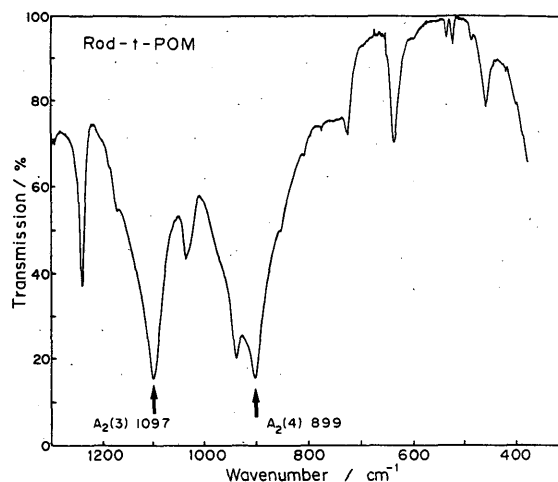


Figure 7. Infrared spectrum in the finger region of Rod-t-POM particle samples measured by Nujol mull method. The A_2 bands indicated by the arrow are due to the morphology of extended chain crystals.

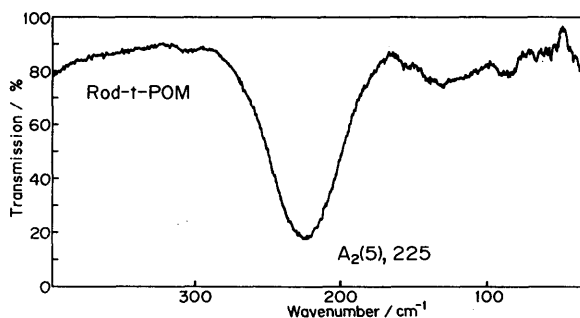


Figure 8. Far infrared spectra of Rod-t-POM

to Figure 4 of ref. 20). That is, the observed wavenumber of the infrared absorption bands of A_2 modes which are reflected in the crystal morphology of t-POM agree with the A_2 bands of needle-like crystal, $A_2(3)$ 1097 cm^{-1} and $A_2(4)$ 899 cm^{-1} . Figure 8 shows the far infrared spectrum in the $400\text{--}30\text{ cm}^{-1}$ of these particle samples. The $A_2(5)$ band is measured at 225 cm^{-1} , and this peak position is closely with the needle-like crystal of t-POM. From these experimental results, we could conclude that the rod-like single crystals obtained are consisted of extended chain structures as crystal morphology of t-POM.

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