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Crystallinity of POM films cast from solution
I. Microscopic and scanning electron microscopic studies

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SUMMARY

The process of crystallization and the structure of poly/oxymethylene/ (POM) films cast from hexafluoroacetone sesquihydrate solutions were studied. The supermolecular structure of thin POM films was studied by the use of polarization microscope. It has been found to consist mainly of spherulites, the size of which are essentially independent of the initial concentration of the solution. Similarly to the findings reported for thin films made of melts, ovoids and spiral ovodis were also found in minor amounts. Two additional formations indicating more complex structure were also detected. Further details of the structures formed could be recognized applying scanning electron microscopy.

INTRODUCTION

The process of crystallization and the structure of POM samples made of melts are thoroughly studied (1-3) and reviewed e.g. (4) but little is known about the structure of POM films made from solution.

The aim of this work was to get information about the process of crystallization of POM cast from hexafluoroacetone sesquihydrate solution and also the supermolecular structure of POM films.

EXPERIMENTAL

Sample preparation

For the preparation of samples, Delrin 150 type POM, M_n = 50 000 was used. Hexafluoroacetone sesquihydrate was applied as solvent since HFA dissolves POM even at room temperature (5). Solution concentration ranged between 1 and 6 wt%. Complete dissolution required 20 to 30 h. Aliquot of the solution was dropped on a microscopic slide, evaporation of HFA was proceeded either in room atmosphere or under airconditioning at 22-23 °C, 60-70 % relative humidity. The thin layer formed was studied microscopically by a Zeiss AMPLIVAL Pol.U. type polarization microscope. The optical character of the spherulites was determined by the aim of a gypsum-plate. Scanning electron micrographs were taken by a Stereoscan SH-10 type electron microscope.

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The course of crystallization

Crossed Nicols were tested for studying the course of crystallization. In this case the patterns were found to be of poor intensity requiring too long exposition times relatively to the rate of spherulite formation. Therefore, the crystal growth was examined without polarizers. The first signs of crystallization could be observed at the flanges of the samples at about 10 minutes after dropping of the solution. As a rule, spherulite formation could not be observed in this region. The growth of spherulites started from the crystal nuclei located in the inner regions. These nuclei were generally not fixed, but freely moving in the solution. The process is illustrated by microphotographs (Fig.1a-1c) taken successively in a short period.

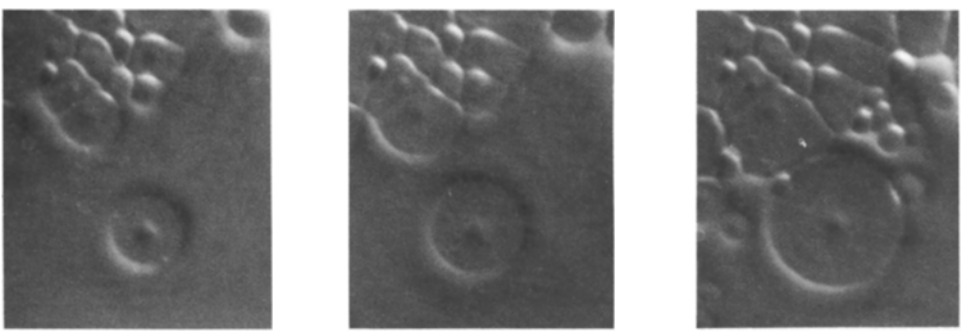

Fig.1(a-c): Photomicrographs of POM in hexafluoroacetone sesquihydrate taken successively in a few min (M: 78x) $c_0 = 2.2$ %.

The supermolecular structure of thin films

A photomicrograph (Fig.2) shows a "honeycomb" structure involving superstructure with central symmetry. The structure of this species alters with the distance from the nucleus. The inner region presumedly a spiral ovoidal formation, while the outer one consists of radially directed fibrils.

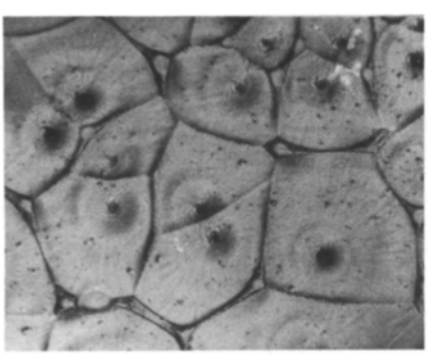

Fig.2: Honeycomb-like structure on photomicrograph of thin POM film cast from HFA solution.

Contrary to the quite uniform image obtained in unpolarized light, different crystal forms can be distinguished by applying crossed Nicols. Predominants are spherulites of Maltese cross type with negative optical sign (Fig.3a,3b), but ovoidic and spiral ovoidic structures also appeare (see 3c and 3d, resp.).

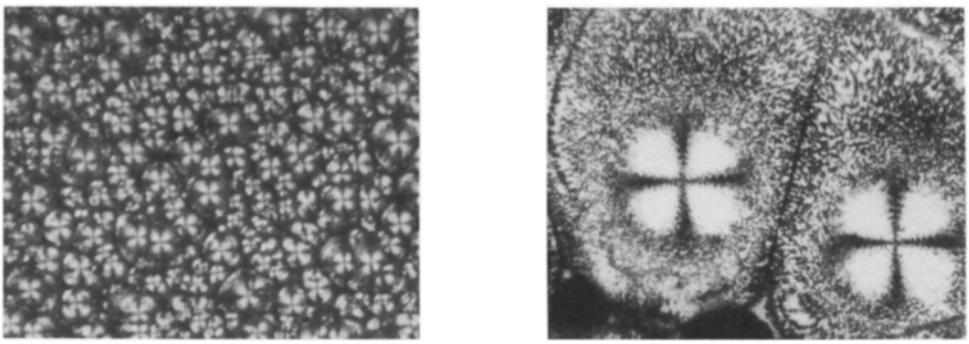

Fig.3(a-b): Photomicrographs of POM films between crossed Nicols, magnification: a) 50x, b) 157x.

Among others, both ovoids and spiral ovoids were earlier detected in thin POM films made from melt (2). The radially oriented, slightly twisting fibrils setting up the spherulites can clearly

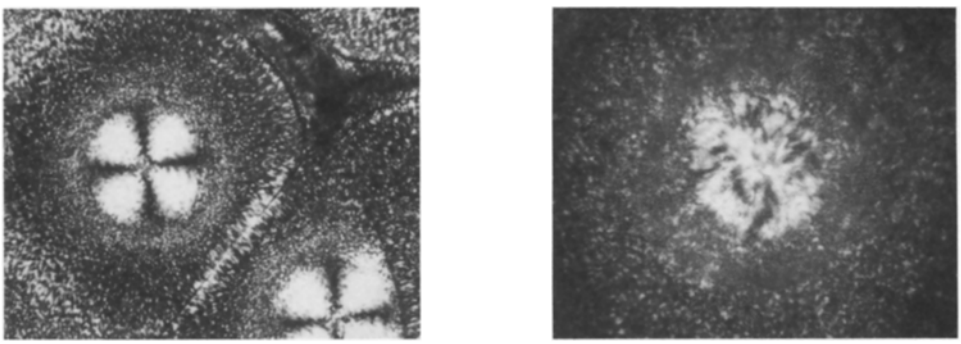

Fig.3(c-d): Photomicrographs of POM films between crossed Nicols, magnification: c) 157x, d) 400x.

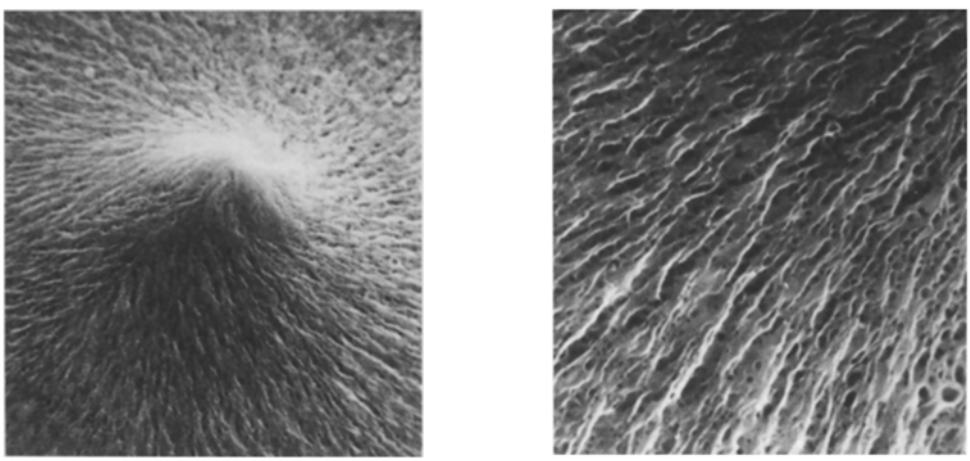

Fig.4(a,b): Scanning electron micrographs of POM films cast from HFA solution. (Magnification: a) 5 µm , b) 2 µm).

be seen in scanning electron micrographs (Fig.4a). As it is shown in Fig.4b, a porous spongelike structure becomes discernible at higher magnification.

Two additional images referring to the formation of more complex superstructures are shown in Figs.5a and 5b. These are presumably due to the embedding of spherulites. Similar formation was detected in poly/1,3-dioxolane/ films (6). Although, it should be noted, that the formation of crystallites rotating helically along the radial axis might give similar image (7).

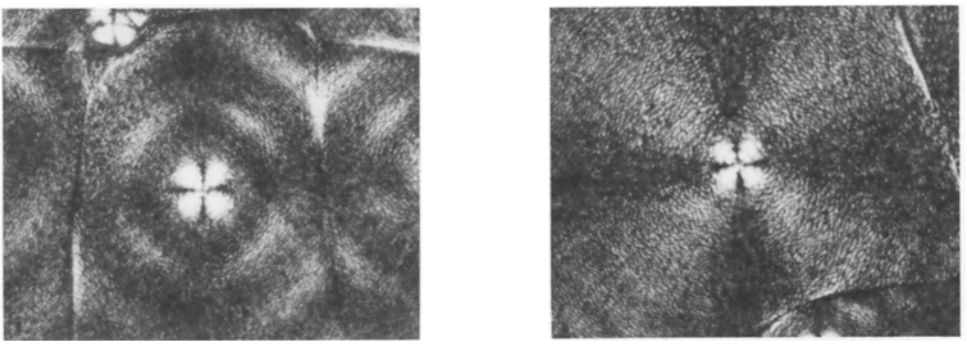

Fig.5(a-b): Photomicrographs of POM between crossed Nicols. M: 160x.

The size of spherulites in films obtained from solutions of different concentrations did not differ considerably.

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