Morphology of nascent polyoxymethylene obtained by polymerization of trioxane in nitrobenzene solution

M. Mihailov, E. Nedkov and L. Terlemezyan
Central Laboratory for Polymers, Bulgarian Academy of Sciences, Sofia 1113, Bulgaria

The morphology of the crystal structure of nascent polyoxymethylene (POM) obtained by cationic polymerization of trioxane in nitrobenzene was investigated by optical and electron microscopy. It was found that the morphology depends on temperature and conversion of polymerization at constant initial monomeric concentration (1.5 mol/l). Morphological changes were observed near the equilibrium concentration of trioxane in nitrobenzene (1.5 mol/l, 35°C). At lower temperatures (10–30°C), thin lamellar crystallites, organized in spherulites, are formed by successive polymerization and crystallization. At higher temperatures (40–90°C), thick crystallites organized in oval structures are formed by simultaneous polymerizaton and crystallization. Peculiarities of crystal formation of POM, obtained by simultaneous and successive polymerization and crystallization, are discussed.

Cationic polymerization of trioxane is a reversible process. Depolymerization of the polyoxymethylene (POM) chains formed with formation of formaldehyde, trioxane, tetraoxane and higher cyclic formaldehyde oligomers takes place within the polymerizing system. An equilibrium concentration of trioxane corresponds to the equilibrium between trioxane and dissolved POM chains or segments. The value of the equilibrium concentration depends on the solvent type and on the temperature, but is independent on the catalyst type and concentration[1,2]. By means of electron microscopy Enikolopyan and coworkers[1,2] showed that the structure formed by the trioxane polymerization in solution depends on the concentration of the monomer. When the polymerization is carried out at initial monomer concentrations lower than equilibrium, single crystals with large hexagonal lamellae with well defined planes are obtained. At concentrations higher than the critical one, crystal formations, often of indefinite form, are obtained. Mateva, Wegner and Lieser[3,4] investigated the morphology of crystal structures, obtained by trioxane polymerization in nitrobenzene at 35°C and prolonged time of polymerization (up to 9 h). The initial monomer concentration – 1.8 mol/l is close to, but somewhat higher than the equilibrium one at this temperature. It is distinguished by the fact that crystals of great thickness are formed and a mechanism for their thickening was proposed.

In our previous papers[5–7] the conformational structure of crystalline nascent polyoxymethylene, obtained by cationic polymerization of trioxane in nitrobenzene was studied. The purpose of the present work is the investigation of the influence of polymerization temperature and duration on the morphology of the crystal structure of the same samples of nascent polyoxymethylene. Peculiarities of crystal formation are discussed in the light of the existing hypotheses for simultaneous and successive polymerization and crystallization.

MATERIALS AND METHODS

The trioxane was purified as described previously[8]. Nitrobenzene was dried with phosphoric anhydride and distilled under vacuum (b.p. 93°C/20 mm). The catalyst $BF_3O(C_2H_5)_2$ was distilled under vacuum (b.p. 42–43°C/15 mm). It was added as a nitrobenzene solution. The polymerization was carried out by stirring under argon atmosphere over the temperature range from 10° to 90°C, where the initial monomer concentration in the solution was 1.5 mol/l and the catalyst

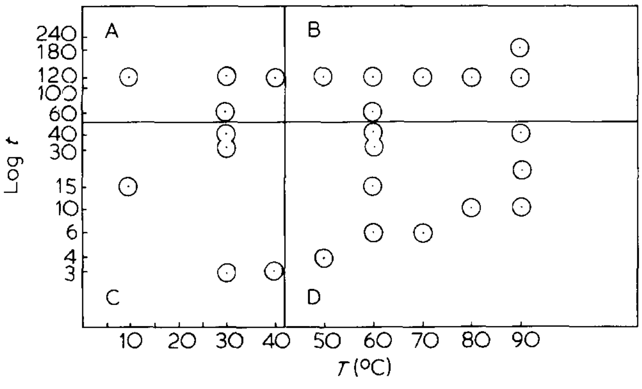

Figure 1 Diagram of samples used and the dependence of type and dimensions of supermolecular structures of nascent polyoxymethylene studied by light and electron microscopy on polymerization temperature and time. A; aggregates (30 μm) from spherulites (2.5 μm), formed by thick structures (l = 2500 Å; d = 2.5 μm) with globules on the surface (0.15 μm). B; aggregates (50 μm) from ovals (12 μm) formed by thick structure (l = 3000 Å; d = 2.5 μm) with lamellae on the surface (0.15–1 μm). C; spherulities (2 μm) formed by lamellar blocks (l̄ = 500 Å; d = 0.5 μm) and lamellae (l̄ = 100 Å; d = 0.4 μm). D; ovals (10 μm) formed by lamellar blocks (l̄ = 900 Å; d = 1.2 μm) and lamellae (l̄ = 110 Å; d = 0.5 μm) with roughnesses on the surface (0.07 μm)

0032–3861/80/010066–05$02.00

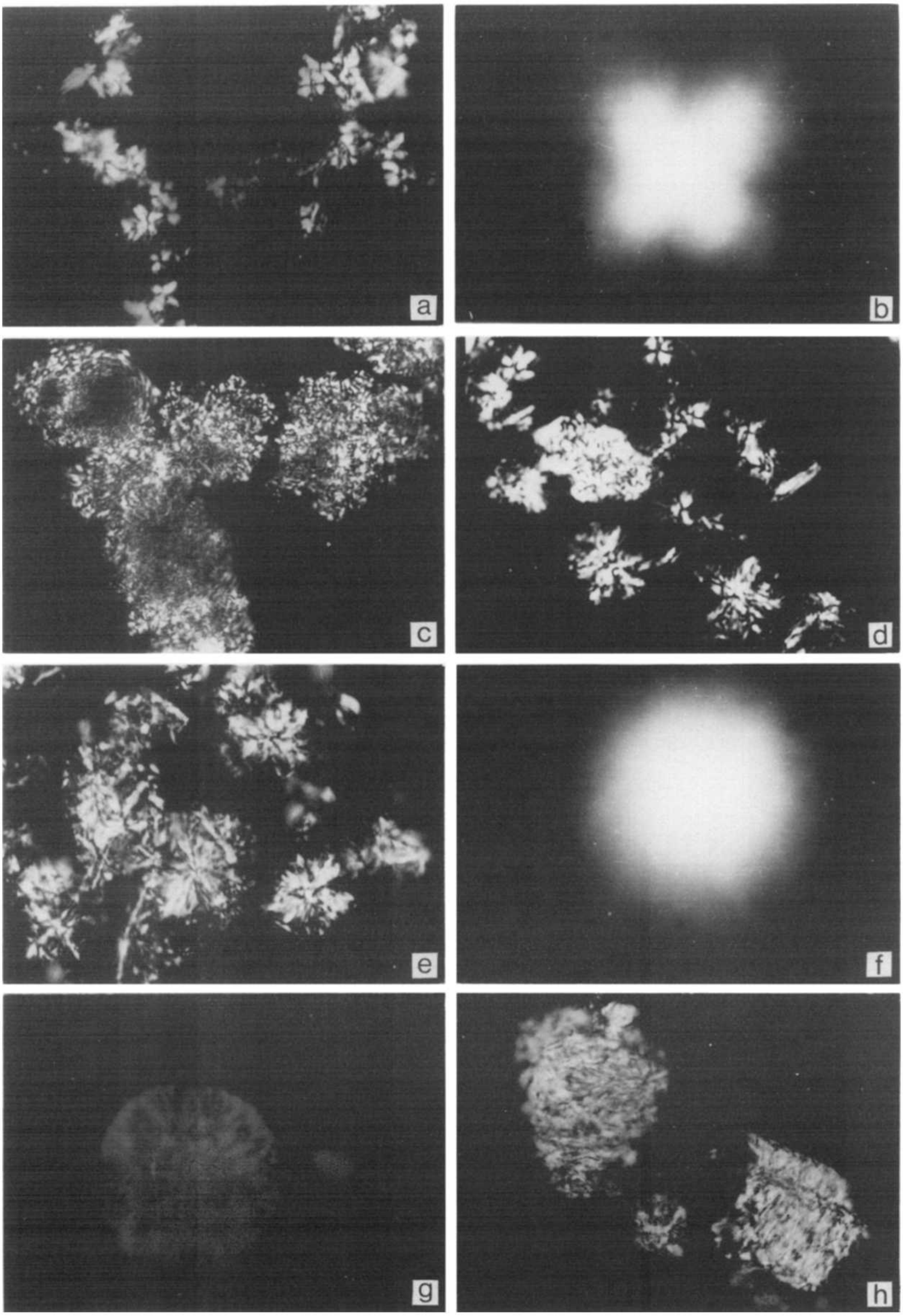

Figure 2 Optical micrographs of structures of nascent polyoxymethylene; (a) spherulites, T_p = 30°C (temperature of polymerization), t_p = 40 min (time of polymerization), 800x, 90° polaroids; (b) H_v spherulitic scattering pattern with central reflex obtained from the structures on *Figure 2a,* 504x, Bertran lenz; (c) aggregates of spherulites, T_p = 30°C, t_p = 120 min, 504x, 90° polaroids; (d) after prolonged polymerization the spherulites change into non-spherulitic structures, T_p = 30°C, t_p = 120 min, 504x, 90° polaroids; (e) ovals, T_p = 50°C, t_p = 3 min, 504x, 90° polaroids; (f) H_v circular scattering pattern of the structures in *Figures 2e,* 504x; (g) oval, T_p = 90° C, t_p = 180 min, 504x, 90° polaroids; (h) structures grown from primary nuclei placed near one to another on line, T_p = 90°C, t_p = 130 min, 504x, 90° polaroids

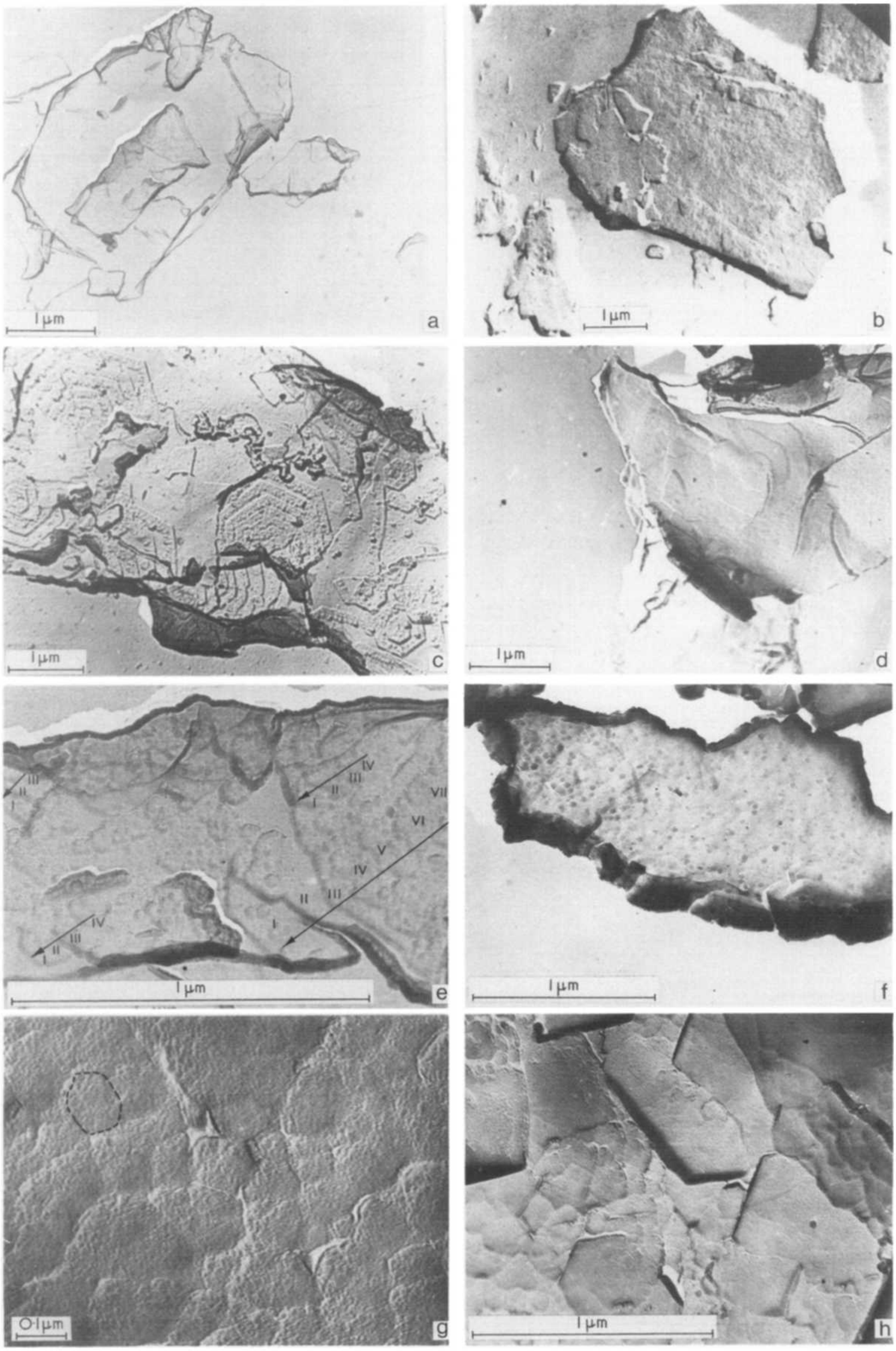

Figure 3 Electron micrographs of nascent polyoxymethylene; (a) single lamellae appear onto lamellar blocks. In the middle there is a lamella which thickens by the screw-dislocation mechanism, T_p = 60°C, t_p = 3 min; (b) lamellar blocks; lamellae growing by screw-dislocation are not observable on their surface, T_p = 50°C, t_p = 3 min; (c) pyramidal crystals, T_p = 60°C, t_p = 3 min; (d) lamella, growing by screw dislocation, T_p = 60°C, t_p = 3 min; (e) a big amount of lamellae, growing by screw dislocations, T_p = 60°C, t_p = 3 min; (f) a thick flat structure with fine grains on the surface, T_p = 30°C, t_p = 120 min; (g) the surface of thick structures (T_p = 50°C) consists of rounded lamellae, t_p = 120 min; (h) the surface of the thick blocks consists of thick hexagonal lamellae, T_p = 50°C, t_p = 120 min

concentration was 10 mmol/l. Samples were taken from the reaction mixture at definite time intervals. They were investigated by means of a polarization microscope without removing the solvent after the polymerization had been stopped with triethylamine. The polymer was filtered and dried for the electron microscope preparations. Replicas were prepared in the standard way from aqueous suspension (shadowed under 45° with Pt–C).

RESULTS AND DISCUSSION

The samples obtained at different polymerization temperatures and times are shown in the diagram in *Figure 1*. In each sector of the diagram the type and the dimensions of the crystals, typical for the conditions used, are shown.

At polymerization temperatures below 40°C negative spherulites with dimensions 2–3 μm (*Figure 2a, b*) are formed in the initial steps of the process. In the later stages of polymerization the spherulites form large aggregates (*Figure 2c*). The spherulites which remain free in the suspension become larger and lose their spherulitic character (*Figure 2d*).

At temperatures above 40°C ovals are formed (10–15 μm). They do not exhibit the typical spherulitic extinction Maltese cross (*Figure 2e*) and their low angle light scattering pattern is circular (*Figure 2f*). The dimensions of the ovals are greater than those of the spherulites (*Figures 2a* and *2c*). The dimensions of the ovals are nearly constant in the range $40 \leqslant T_p \leqslant 70$°C and thereafter they increase (*Figure 2e* and *2g*). The lamellar block and lamellae of the ovals also have larger dimensions in comparison with the spherulites (*Figure 1*).

It is known that the spherulites are formed mainly by two-dimensional secondary nucleation[9] on small defects on the lamellar surface already formed[10] and therefore they have a better defined centre of symmetry. The hedritic sturctures grow mainly through a screw dislocation mechanism[9,10] and that is why they have a better defined axis of symmetry. In this type of growth the rate of the two dimensional secondary nucleation is much lower[9]. The morphological results described above show that the increase of both the polymerization temperature and the conversion diminish the rate of two-dimensional secondary nucleation.

Investigation of the morphology of the crystals by electron microscopy shows that their type and dimensions depend on the duration of polymerization (that is, monomer concentration) rather than on the temperature (*Figure 1*). At short polymerization times lamellae and pyramidal crystals are formed (*Figure 3a, b, c*) and a screw dislocation thickening of the lamellae occurs (*Figure 3a, d, e*). At prolonged polymerization times, thick flat formations are obtained (*Figure 3f*) with rough surfaces built from small lamellae and lamellar blocks with rounded ends (*Figure 3g*). At higher crystallization temperatures thick lamellae shaped as regular hexagons are also formed (*Figure 3h*).

Similar results were obtained by Wegner and coworkers by polymerization of trioxane at concentrations near to equilibrium (1.8 mol/l, 35°C). At conversion up to 20%, lamellae with thickness 50–100 Å were obtained. In this case only the lateral dimensions of the lamellae increase. Above 20% conversion a thickening of the lamellae was observed[3,4,11].

The POM crystallites obtained from Enikolopyan and coworkers by trioxane polymerization in nitrobenzene with monomer concentrations 1.5 mol/l at 30°C for 20–30 min have defective planes, small dimensions (0.1–0.5 μm) and lower X-ray crystallinity. However, the polyoxymethylene obtained at monomer concentrations lower than the equilibrium, shows large hexagonal lamellae with well shaped planes, which are packed in multilayer crystals and have higher degree of crystallinity[12]

According to Berlin and Enikolopyan[13] at monomer concentrations below that for equilibrium, the chain growth proceeds on the surface of the simultaneously formed crystallites and at concentrations above that for equilibrium, the growth proceeds on the active centres in solution.

Based on the literature data described, our morphological results can be explained by two different mechanisms of polymerization and crystallization[14] as follows.

(1) At polymerization temperatures below 40°C in the initial stages of polymerization the trioxane concentration is above or near equilibrium[1]. The polymerization proceeds mainly at active centres in the solution[13] (*Figure 4a*). Polymerization and crystallization occur in succession[14]. Lamellae with constant thickness and increasing dimensions are formed[3,12] (*Figure 4a*). It might be supposed that the long segments with active centres, facing on the lamellar surface in solution could serve as secondary two-dimensional nuclei (*Figure 4a*). Their large number causes a statistically regular radial position of the secondary and tertiary lamellae growing onto them[9]. The suggestion that the dissolved active centres also serve as secondary crystallization nuclei is supported well by the small lamellar dimensions observed, i.e. the high rate of seconary nucleation. This is a main requirement for spherulite formation, which is actually observed in the present case. As conversion increases the mechanism of successive polymerization and crystallization changes into a mechanism where polymerization and crystallization occur simultaneously. In this case the polymerization proceeds mainly at active centres on the lamellar surface. The lamellae thicken according to the mechanism of Mateva, Wegner and Lieser (*Figure 4b*)[3,4]. Then we observe the growth of the

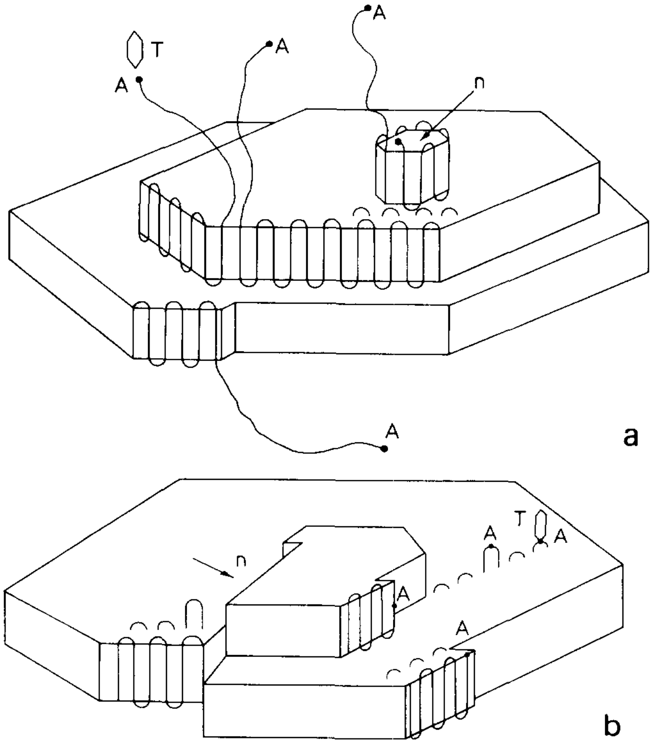

Figure 4 (a) Diagram of crystal nucleation and growth in the case of successive polymerization and crystallization of POM; A, active centre; T, trioxane; n, secondary nucleus. (b) Diagram od crystal nucleation, growth and thickening in the case of simultaneous polymerization and crystallization of POM.

existing lamellae and new secondary nuclei into larger lamellae proceeding simultaneously with their thickening, (*Figure 4b*) which requires formation of structures with better defined axes of symmetry.

(2) At polymerization temperatures above 40°C simultaneous polymerization and crystallization will occur in the initial stage of polymerization (*Figure 4b*). The secondary nucleation will proceed mainly onto large defects on existing primary lamella. So the formation of pyramidal crystals and the screw-dislocation growth will be the main mechanism of crystal growth. At a later stage these structures will thicken (*Figure 4b*)[3,4]. All this will cause the appearance of oval structures. At 80°C and 90°C the primary and secondary nucleations proceed at a very low rate and this leads to formation of large ovals and bands of them (*Figure 2g, h*) similar to those observed by crystallization from the melt with very little supercooling.

REFERENCES

1 Berlin, A. A., Kravchuk, I. P., Rakova, G. V., Rosenberg, B. A. and Enikolopyan, N. S. *Vysokomol. Soedin. (A)* (1973), **15**, 554

2 Vorobeva, G. A., Trofimova, G. M., Berlin, A. A., Enikolopyan, N. S. *Vysokomol. Soedin (A)* 1974, **16**, 1493

3 Mateva, R., Wegner, G., Lieser, G. *J. Polym. Sci. (B)* 1973, **11**, 369

4 Wegner, G., Fischer, E. W., Munoz-Escalona, A. *Makromol. Chem.* 1975, Suppl. *1*, 521

5 Mihailov, M., Terlemezyan, L. *Compt. Rend., Acad. Bulg. Sci.* 1975, **28**, (5), 643

6 Terlemezyan, L., Mihailov, M., Schmidt, P., Schneider, B. *Makromol. Chem.* 1978, **179**, 807

7 Terlemezyan, L., Mihailov, M., Schmidt, P., Schneider, B. *Makromol. Chem.* 1978, **179**, 2315

8 Mihailov, M., Terlemezyan, L. *Makromol. Chem.* 1969, **129** 267

9 Geil, P. H. Polymer single crystals (Ed. Himia) 1968, p 342 and 192

10 Mihailov, M., Nedkov, E., Goshev, I. *J. Macromol. Sci. (B)* 1978, **15**, 313

11 Wegner, G. *Symp. 'Polymers'*, Varna, Bulgaria 1973, **2**, 5

12 Karuhina, A. K., Berlin, A. A., Enikolopyan, N. S. *Dokl. ANUSSR*, 1970, **195**, 1147

13 Berlin, A. A., Enikolopyan, N. S. *Vysokomol. Soedin (A)* 1969, **11**, 2671

14 Wunderlich, B. *Adv. Polym. Sci.* 1968, **5**, 568