# Academician V. A. Kargin, M. Azori, N. A. Plate,

S. I. Banduryan

1964

SovietRxiv

## Abstract

## Full Text

## Physical Chemistry

Academician V. A. Kargin, M. Azori, N. A. Plate,
S. I. Banduryan

# Direct Electron-Microscopic Observation of the Polymerization Processes of Crystalline Monomers

In studying polymerization processes in the solid phase, methods well developed for liquid-phase polymerization often prove unsuitable, and the criteria determining the reaction mechanism are ambiguous. Therefore, much attention has come to be devoted to the search for new methods of investigation that would better correspond to the nature of these phenomena. Among these methods, the following have proved fruitful: X-ray diffraction ([1–5]), optical microscopy ([6,7]), and electron microscopy ([8–10]). In the last case, the technique used was that of taking replicas from the surface of previously partially polymerized samples.

To study the polymerization of crystalline monomers we applied a direct electron-microscopic method of observation. Polymerization was carried out directly in the column of a JEM-5U microscope, using the electron beam (at 80 kV) also to initiate the process. Owing to heating of the samples under the action of the electron beam and to the high vacuum in the microscope column, the monomers must have a sufficiently high melting point and low vapor pressure. In this connection, attempts to use acrylamide and methacrylamide proved unsuccessful, and therefore the following were chosen as monomers: *N*-phenylmethacrylamide (m.p. 89°), *n*-biphenylmethacrylamide (m.p. 161°), and sodium acrylate (not melting up to 350°).

***N*-Phenylmethacrylamide (PMA).** A freshly prepared suspension of small PMA crystals rapidly precipitated (from an alcoholic solution by water) was deposited on a copper grid with a collodion support and dried in air at 50°. When these samples were introduced into the electron microscope, globular and fibrous formations immediately appeared on the crystals, arranged in parallel rows along the length of the crystal. The entire process took place over several seconds. The polymer structures formed were visible owing to the continuous sublimation of the monomer without its melting, and by the end of the process unchanged polyphenylmethacrylamide remained on the support. Figure 1 (see insert, p. 1192) shows a photograph of PMA crystals after polymerization in the electron microscope. When these crystals are examined in an optical microscope, it is seen that they are needle-like formations with distinct faces.

As is evident from the microphotograph presented, the polymerization process is facilitated on the edges of the crystals; in particular, more fully formed fibrils were produced at the edges of the crystals. In the case where the surface of the crystals is defective and transverse cracks are present on them (visible in the optical microscope), the growth of structures proceeds in the direction of these cracks and the fibers formed are arranged perpendicular to the length of the crystal (Fig. 2, see insert, p. 1192). In the case where the cracks do not penetrate deeply into the crystal and are not situated along its entire length, both types of structure-formation processes are observed. Similar structures for already prepared polymers have been detected with the aid of the electron microscope in the case of rubbers ([11]) and polyacrylamide ([8,9]).

The electron diffraction pattern of bulk single crystals that retained their shape very rapidly changed into a diffraction pattern typical of amorphous substances.

**N-(_n_-biphenyl)-methacrylamide.** Crystals of biphenylmethacrylamide (BPMA), obtained from a saturated alcohol solution, had an irregular hexagonal shape, with dimensions of several microns. During the first seconds of irradiation, rapid motion of waves from the corners and edges was observed on the crystals in the electron microscope, resembling the process of "annealing" of defects and dislocations (Fig. 3, see insert, p. 1192). In contrast to PMA, these crystals did not noticeably change their external appearance even under longer irradiation (10–20 min). BPMA crystals gave a single-crystal electron diffraction pattern, which disappeared within 10–15 sec. Over approximately the same period of time the passage of "waves" was observed; therefore one may assume that this phenomenon represents propagation of the polymerization front by a dislocation mechanism. Morawetz also pointed out the formal similarity between the kinetics of post-polymerization and the processes of "annealing" of irradiation defects in the solid phase (^10).

Observing the change in the electron diffraction pattern of one crystal with time, we found that the reflections fade nonuniformly and, after some time, diffuse rings appear against the background of point reflections as a result of superposition of the diffraction patterns of the amorphous and crystalline phases, which indicates the heterogeneity of the polymerization process (^2, ^5). After 15 sec the initial pattern is completely transformed into an amorphous diagram.

From these observations it follows that biphenylmethacrylamide is capable of polymerization in the solid phase (polymerization of this monomer in the melt was described earlier (^12)). Owing to the phenomenon of pseudomorphosis, also observed in other cases (^7), the crystals retain their external shape during polymerization.

**Sodium acrylate.** The samples for investigation were obtained by precipitation from a saturated solution of sodium acrylate in methanol with carbon tetrachloride and benzene. The crystals had a rhombic shape, which also did not change upon irradiation (10–15 sec), as in the case of BPMA. In this case, motion of the fronts of "waves" was also detected. The disappearance of the crystalline diffraction of the monomer is, without doubt, associated here with polymerization of the crystals, since the melting point of sodium acrylate lies above its decomposition temperature.

To reveal the microstructure of the sodium polyacrylate formed during the polymerization process, the method of differential dissolution was applied. For this purpose, crystals irradiated for 2-3 sec were treated with *n*-propyl alcohol, which dissolves the monomer but does not dissolve the polymer. In Fig. 4a (see insert, p. 1192) one can see a system of fibers arranged in one direction of a thin crystal, and between the fibers there are randomly arranged globular and short threadlike formations. In the case of thick (opaque) and more defective crystals, densely arranged fibrils in one direction are visible (Fig. 4b). After dissolution of the monomer, the outline of the samples appears blurred. A different picture is observed in Fig. 4c; here the outline of the crystal has been well preserved, as in the case of the more perfect PMA crystals (Fig. 1), when polymerization proceeded along an edge. On the surface of the former crystal, the polymer particles formed are visible, of globular and elongated shape (with transverse dimensions of 100-300 Å). The latter are bent at certain angles and very much resemble bundles of polysalvarsan molecules (⁀13). The disorder in the arrangement of these structural elements can be explained by the randomness of the formation of defects caused by irradiation.

On the basis of the results obtained, it may be concluded that the direct electron-microscopic method makes it possible to observe polymerization processes occurring in the solid phase and to study the polymer structures formed in the process.

The authors consider it their pleasant duty to express their gratitude to T. A. Sokolova for providing the monomer *n*-biphenyl methacrylamide, and to N. F. Bakeev for valuable advice during the work and for participation in the discussion.

Moscow State University
named after M. V. Lomonosov

Received
14 IX 1963

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