Chemistry

Academician V. A. KARGIN, A. A. EFENDIEV, Z. Ya. BERESTNEVA

1964

SovietRxiv

Abstract

Full Text

Chemistry

Academician V. A. KARGIN, A. A. EFENDIEV, Z. Ya. BERESTNEVA

SPONTANEOUS FORMATION OF LARGE ORIENTED STRUCTURES IN AN IRREGULAR COPOLYMER OF DIETHYL VINYLPHOSPHINIC ACID ESTER AND ACRYLIC ACID

We have already begun to become accustomed to the fact that polymers, even in the amorphous state, are well-ordered structures and that they are built either of globules or of bundles of extended chains, which can form geometrically regular shapes.

The works of Kargin and Bakeev (^1, ^2) have shown that the emergence of regular shapes in amorphous polymers is the result of an ordered arrangement of molecules due to intense intermolecular interaction. A similar picture was also observed in irregular copolymers (^3). However, the spontaneous formation of well-ordered large structures has not been observed in amorphous irregular polymers and copolymers.

In a previous communication (^4) we described an electron-microscopic study of the structure of a copolymer of diethyl vinylphosphinic acid ester and acrylic acid, obtained by two of us by radical polymerization with initiation of the reaction by cumene hydroperoxide and ultraviolet light (^5). It was shown that at pH equal to 1.1, oriented formations, consisting of fibrils, arise spontaneously. When the pH of the copolymer solution is increased to 3, the regular structure is disrupted and the copolymer structure assumes a globular form, retaining it up to a pH value close to the neutral region (6–8). A further increase in pH leads to the fact that, owing to the formation of a well-dissociating salt of the copolymer, fibrillar structures again arise as a result of electrostatic repulsion of charged groups. At the same time, as the data of electron-diffraction analysis showed, the copolymer is in the amorphous state in the pH interval from 1.1 to 10.5 (Fig. 1a, see insert, p. 117).

In the present work a further study of the structure of the copolymer by optical microscopy and X-ray structural analysis is described. The samples for study were prepared as described by us in the previous work. Cover glass and a collodion film were used as substrates. Copolymer solutions (at pH 1.1, 6–8, and 10.5), both alcoholic (a good solvent) and aqueous (a poor solvent), were applied to the substrate, and the solvent was evaporated at room temperature. The studies were carried out in transmitted light on an MIN-8 microscope equipped

with a "Start" camera.

Figure 2 shows the structure of the copolymer at pH 1.1. It is evident from the figure that, both in alcoholic and in aqueous medium, dendritic formations are present, built in a very regular manner. These dendritic regular structures are not observed in crossed nicols (Fig. 2v), which confirms the data of electron-diffraction analysis on their amorphous structure. The amorphous structure of these oriented structures arising in the copolymer at pH 1.1 was also confirmed by an X-ray pattern of the copolymer under the same conditions (Fig. 1b).

In a neutral medium this regularity is disrupted, and structures of globular form arise in both solvents (Fig. 3*a*).

With a further increase in the pH of the copolymer solution to 10.5, fibrillar formations of amorphous structure again appear (Fig. 3*b*), exhibiting no birefringence. Thus, the spontaneous formation of large oriented structures occurs in an irregular copolymer obtained by ordinary radical copolymerization, although the copolymer thereby retains an amorphous structure.

Thus, we observe the strange phenomenon of the appearance of large (hundreds of microns), geometrically regular formations without any external directed influences during the separation of a substance from solutions. These formations are amorphous in the usual sense of the word, i.e., they show no diffraction phenomena either in an electron beam or in X-rays. Optically, they are also isotropic and show no birefringence within the resolution limits of an ordinary polarizing microscope. It is possible that more subtle methods may reveal a small optical anisotropy. But the very formation of sharply asymmetric shapes already testifies to the presence of certain elements of anisotropy, leading to a sharp difference in growth rates in different directions. The formations themselves are so large that the possibility of a fluctuation nature for the regular forms that arise is completely excluded.

In a subsequent communication we shall consider specifically the question of the thermodynamic nature of such formations.

Physicochemical Institute
named after L. Ya. Karpov

Received
24 II 1964

REFERENCES

1. V. A. Kargin, G. L. Slonimskii, *Brief Essays on the Physical Chemistry of Polymers*, Moscow, 1960.

2. V. A. Kargin, N. F. Bakeev, *Colloid Journal*, **19**, 133 (1957).

3. V. A. Kargin, N. F. Bakeev, Kh. Vergin, *Doklady Akademii Nauk*, **122**, No. 1, 97 (1958).

4. V. A. Kargin, A. A. Efendiev, Z. Ya. Berestneva, *Doklady Akademii Nauk*, **155**, No. 6 (1964).

5. A. A. Efendiev, E. P. Cherneva et al., *Azerbaijan Chemical Journal*, No. 5, 73 (1963).

Note: Figure translations are in progress. See original paper for figures.