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V. G. BARANOV, T. I. VOLKOV, S. Ya. FRENKEL

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Abstract

Full Text

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PHYSICAL CHEMISTRY

V. G. BARANOV, T. I. VOLKOV, S. Ya. FRENKEL

POLARIZATION-DIFFRACTOMETRIC STUDY OF THE FORMATION OF SUPRAMOLEC- ULAR STRUCTURE IN A SOLUTION OF A HELICAL POLYPEPTIDE

(Presented by Academician V. A. Kargin, 24 XI 1964)

One of the central problems of modern physical chemistry of polymers, with implications both for technology and for biology, is the detailed study of structure-formation processes in the liquid phase (solution, melt) or directly during the process of polymerization. Experiments of this kind using polarization and electron-microscopic observation techniques have recently been described in the works of V. A. Kargin and co-workers (1, 2). For studying the detailed kinetics of such processes it is important to observe two principles: first, "noninterference" in the system, while allowing rapid recording of the phenomena occurring in it, and second, quantitative interpretation of the measurements (in terms of the sizes of structural elements, magnitudes of periods, etc.). These principles are satisfied to the greatest degree by the technique of small-angle scattering of polarized light by polymer systems in which processes of supramolecular ordering are taking place. This technique stands in approximately the same relation to polarization microscopy as X-ray or electron diffraction does to electron microscopy. It makes it possible to describe supramolecular order in terms of averaged parameters and permits the recording of fine details inaccessible to the polarization microscope. Naturally, what has been said does not preclude parallel microscopic control. The application of this method to films of crystalline polymers has been described in a series of works by R. Stein (3), and a modified experimental arrangement for studying structure-formation processes in polymer solutions—by us (4). To determine the capabilities of this method and to provide its "qualitative calibration" (identification of various types of supramolecular order from the character of the scattering photodiagrams), we used a system with well-studied optically active (5) and final (6) states—a solution of the synthetic polypeptide poly- γ -benzyl-L-glutamate (PBG) in dioxane.

K. Robinson described the emergence of a cholesteric-type liquid-crystalline structure in concentrated solutions of two helical polypeptides, PBG and poly- γ -methyl-L-glutamate (6); however, the intermediate states of the system were not recorded in those works. Below we present the results of a study of the structure-formation process of PBG as a function of concentration and time.

PBG with $M = 10^5$, synthesized in our institute,* was used, together with chemically pure dioxane. The solution was placed in a sealed flat cuvette with a 1 mm gap, located between polarizers perpendicular to the light beam ($\lambda = 546 \text{ m}$). The scattering patterns (diffractograms) were recorded photographically; at the same time, with the aid of a detachable device (4), microphotographs were taken.

* We express our sincere gratitude to Yu. V. Mitin for providing this sample.

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Fig. 1. Spherulitic phase of structure formation. Polarizers crossed. $c = 12\%$. *a* –microphotograph, *b* –scattering photograph, *c* –large spherulite

Fig. 2. Collapsed spherulites. Polarizers crossed. $c = 12\%$. *a* –microphotograph, *b* –scattering photograph

Fig. 3. Initial stage of formation of the liquid-crystalline phase. Polarizers crossed. $c = 12\%$. *a* –microphotograph, *b* –scattering photograph

Fig. 4. Final stage of formation of the liquid-crystalline phase. Polarizers crossed. $c = 12\%$. *a* –microphotograph, *b* –scattering photograph from the undisturbed solution, *c* –scattering photograph from the stirred solution

All experiments were carried out at room temperature. The results are presented in Figs. 1-4 (see the insert to p. 825). In a 6% solution, in any case over the course of 70 days, no registrable supramolecular structure arises. In a 12% solution, already after 3-4 hours there appears a multitude of small anisotropic spherical elements (Fig. 1a), whose optical behavior permits them to be regarded as liquid spherulites.

Similar formations were observed by K. Robinson, while Flory (7) suggested that they are disordered spherical aggregates of rigid anisotropic elements. Judging, however, from the fact that the scattering pattern (Fig. 1b) from such a system is identical to that observed by Stein for scattering from crystalline films containing spherulites, the liquid spherulites must possess a certain internal order. With increasing size of the liquid spherulites, apparently because of thermal fluctuations, their order decreases (Fig. 1c). In the course of further structuring of the system, the number of liquid spherulites becomes so large that practically no volume not occupied by them remains in the system. Since the spherulites are liquid, with their further growth or multiplication close packing cannot be

achieved, and they begin to collapse. This occurs at approximately the 10th-12th hour. The corresponding characteristics are shown in Fig. 2.

The scattering pattern (Fig. 2b) indicates an absolutely disordered orientation of the anisotropic scattering elements. Then self-ordering of the system begins. As is known, it is due to the fact that parallel packing of anisodiametric particles (in the present case, helical molecules or their multihelical aggregates) is energetically more favorable than chaotic packing⁽⁸⁾. Figure 3a shows the formation of a liquid-crystalline phase in the solution 30 hours after the beginning of the experiment. From the corresponding scattering pattern (Fig. 3b), one can estimate the magnitude of two periods characterizing this system: 10 and 30 μ .

Let us note that the distance between the bands in Fig. 3a is also 10 μ . Therefore the period of 10 μ should be ascribed to the distance between layers of identically oriented anisodiametric particles forming a cholesteric system.

Interpretation of the second period is still difficult. In general, as follows from calculations (which are omitted here), the scattering pattern is characteristic of a system of rhombohedral or cylindrical incoherent scattering elements.

In a more concentrated solution (20-30%), self-ordering occurs more rapidly and, apparently, to a higher degree, characterized by the emergence of correlation between the orientations of neighboring scattering elements and, accordingly, of longer-range order. The diffractograms thereby acquire the usual form of X-ray patterns from oriented crystalline polymers (Fig. 4a, b). The order is stable, since stirring the solution leads not to disappearance of the diffractogram, but only to broadening of the reflections, with some tendency toward transformation into a "Debye pattern" (Fig. 4b). Estimation of the interplanar spacings from the diffractograms shows that in the more concentrated solution they have decreased to 3 μ , which agrees with the period determined from the microphotograph (Fig. 4a).

Thus, by the method of small-angle scattering of polarized light, we were able to observe the successive appearance of various levels of supramolecular order in a true molecular solution of PBG in dioxane and to characterize the corresponding structures. By analogy with block polymers, structuring begins with the spherulitic phase, whose mechanical instability facilitates the spontaneous emergence of a new, liquid-crystalline phase, subsequently transforming into a system with long-range orientational order.

At this final stage of structuring, the diffractogram from the solution is analogous to X-ray diffraction patterns from oriented crystalline polymers.

Institute of High-Molecular-Weight Compounds
Academy of Sciences of the USSR

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REFERENCES

- ¹ V. I. Selikhov, G. S. Markova, V. A. Kargin, *Vysokomolek. soed.*, **6**, 1132 (1964); **6**, 1136 (1964).
- ² P. V. Kozlov, N. F. Bakeev et al., *Biofizika*, **7**, 266 (1962).
- ³ R. S. Stein, M. B. Rhodes, *J. Appl. Phys.*, **31**, 1873 (1960); M. B. Rhodes, R. S. Stein, *J. Appl. Phys.*, **32**, 2344 (1961); M. B. Rhodes, R. S. Stein, *J. Polym. Sci.*, **1**, 663 (1963).
- ⁴ T. I. Volkov, V. G. Baranov, S. Ya. Frenkel, Abstracts of reports at the Interuniversity Scientific Conference “Optical Studies of Molecular Motion and Intermolecular Interactions in Liquids and Solutions,” Samarkand, 1964, p. 12.
- ⁵ C. H. Bamford, A. Elliot, W. E. Hanby, *Synthetic Polypeptides*, N.-Y., 1956.
- ⁶ C. Robinson, J. C. Ward, R. B. Beevers, *Disc. Farad. Soc.*, **25**, 29 (1958).
- ⁷ P. Flory, *J. Proc. Roy. Soc. (London)*, **A234**, 73 (1956).
- ⁸ P. Flory, *J. Polym. Sci.*, **49**, 105 (1961).

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