T. V. SHAMRAEVSKAYA, N. A. SHCHEGOLEVSKAYA, S. I. SOKOLOV

1963

SovietRxiv

Figure 1

Figure 1: Figure 1

Figure 2

Figure 2: Figure 2

Abstract

Full Text

PHYSICAL CHEMISTRY

T. V. SHAMRAEVSKAYA, N. A. SHCHEGOLEVSKAYA, S. I. SOKOLOV

ON THE CHANGE IN SIGN OF DOUBLE REFRACTION UNDER DEFORMATIONS IN GLASSY POLYMERS

(Presented by Academician P. A. Rehbinder, January 26, 1963)

The double refraction of polymers is used as a method for studying the distribution of stresses under deformation and for investigating changes in the structure of a material. The phenomenon has been studied in detail under flow conditions —in solutions and melts ($^{1-3}$)—and in the highly elastic state.

A statistical theory of double refraction has been developed on the basis of a simplified model and with allowance for the anisotropy of the polarizability of the links and segments of the chain ($^{4-7}$). Under conditions of the glassy state, the phenomenon has been insufficiently studied. The effect of double refraction is the result of the superposition of several effects characterized by different dependences on external factors and on the structure of the material.

Fig. 1. Dependence of the optical coefficient $C_\sigma \cdot 10^{-7}$ (cm^2/kg) on time for the copolymer MMA : ST : BMA = 1 : 1 : 1.
1—$t = 15°$; 2—$t = 39°$; 3—$t = 65°$; 4—$t = 80°$.

To clarify the general picture of the behavior of polymers in the glassy state, the case in which, under the influence of external factors and also in connection with a change in composition, a change in the sign of double refraction and passage through a zero value are observed is of particular interest. Pure and copolymers of three vinyl monomers were investigated: methyl methacrylate (MMA), styrene (ST), and benzyl methacrylate (BMA). The influence of the following factors was studied: time, magnitude of the load, temperature, and composition.

Fig. 3

Figure 3: Fig. 3

Fig. 4

Figure 4: Fig. 4

Fig. 2. Dependence of the optical coefficient $C \cdot 10^{-7}$ (cm^2/kg) on the stress σ (kg/cm^2) for the copolymer MMA : ST : BMA = 1 : 1 : 1.

Typical dependences of birefringence on time are shown in Fig. 1. In the glassy state (curve 1), because of the long relaxation times, and in the highly elastic state (curve 4), because of the short relaxation times, no appreciable time dependences are observed.

Time effects are observed in the region of transition from the glassy state to the highly elastic state (curve 3) and at temperatures where the optical coefficient changes sign (curve 2). The optical coefficient corresponding to equilibrium may, under certain conditions, show a dependence on load (Fig. 2). In our example, at a temperature of 38° a dependence on stress was observed, and even a passage through zero with a change of sign.

Fig. 3. Temperature dependence of the optical coefficient $C_\sigma \cdot 10^{-7}$ (cm^2/kg) of the copolymer MMA : ST : BMA = 1 : 1 : 1

As a function of temperature, a considerable change in the optical coefficient is observed (Fig. 3), especially in the region of transition from the glassy state to the highly elastic state; in this case, too, a change of sign may occur. With all the above-mentioned factors kept constant, the magnitude of the optical coefficient depends on composition in the case of copolymers. Fig. 4 gives a ternary system of vinyl monomers MMA, ST, and BMA. For a number of compositions in this system the copolymers have zero optical sensitivity.

Fig. 4. "Composition—property" diagram for the optical coefficient $C_\sigma \cdot 10^{-7}$ (cm^2/kg) for polymerization products in the ternary system of vinyl monomers: MMA, ST, and BMA

The complex behavior of polymers with respect to birefringence can be explained only on the basis of ideas about orientation. In the glassy state, in the region of small deformations, orientation of atomic groupings that are part both of the main chain skeleton and of side groups—characterized by a considerable anisotropy of polarizability—is possible, apparently only through rotations by small angles within the potential wells between two barriers of rotation. Changes in interatomic distances and distortion of valence angles belong to the so-called atomic effect, which gives a positive sign upon stretching and is devoid of time dependences.

The results obtained may be of definite interest in solving the problem of creating optically insensitive materials, -

suitable for use in the practice of the polarization-optical method.

Moscow Institute
of Chemical Machine Building

Received
24 I 1963

REFERENCES

[1] H. Kuhn, F. Moning, W. Kuhn, *Helv. chim. acta*, **36**, 731 (1953).
[2] V. N. Tsvetkov, *Vestn. Leningr. univ.*, No. 1, 51 (1947).
[3] V. N. Tsvetkov, E. V. Frisman, *DAN*, **97**, No. 4, 647 (1954).
[4] W. Kuhn, F. Grün, *Kolloid-Zs.*, **101**, 248 (1942).
[5] L. R. G. Treloar, *Trans. Farad. Soc.*, **43**, 277, 289 (1947).
[6] M. V. Vol' kenshtein, *Configurational Statistics of Polymer Chains*, Moscow—Leningrad, 1959.
[7] Yu. Ya. Gotlib, *Uch. zap. Leningr. gos. ped. inst. im. A. I. Herzen*, **141**, 121 (1958).

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

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.