OPTICAL ANISOTROPY OF SEMIRIGID CHAIN MOLECULES

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Abstract

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OPTICAL ANISOTROPY OF SEMIRIGID CHAIN MOLECULES

AND FLOW BIREFRINGENCE IN THEIR SOLUTIONS

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The optical anisotropy of chain molecules is an essential characteristic of their equilibrium flexibility. The study of the dependence of the anisotropy of semirigid molecules (^{1}) (nucleic acids, helical polypeptides) on molecular weight can serve as a method for determining their "persistent" length a (^{2}).

In work (^{1}) the equilibrium optical anisotropy of a persistent chain was calculated in the coordinate axes of its first element, and it was shown how the difference of the principal polarizabilities $\gamma_1 - \gamma_2$ of a semirigid molecule increases with increasing parameter $x = L/a$, where L is the contour length of the chain (see curve $1'$, Fig. 1). The expression for $\gamma_1 - \gamma_2$ was subsequently (^{3}) used to calculate the magnitude of flow birefringence in a solution of semirigid molecules in the region of small x, where birefringence is an orientational effect (curve $2'$, Fig. 1). In the present work the quantity $\gamma_1 - \gamma_2$, as a function of x, is calculated in the molecular coordinate system whose axis of symmetry coincides with the vector n—the distance between the ends of the molecular chain. In addition, an expression is obtained for the flow birefringence in a solution of chain molecules, valid in the region of sufficiently large x ($x \geq 15$). Both results follow from the basic formulas of the statistics of "Langevin" chains, developed by W. Kuhn et al. (^{4,5}). According to Kuhn and Grün (^{4}), the difference of the principal polarizabilities of a flexible chain molecule, consisting of a large number $N = L/2a$ of freely jointed segments and stretched to a distance h between its ends, is equal to (^{4})

$$\gamma_1 - \gamma_2 = \beta L \left[1 - \frac{3h}{L} \Big/ \mathcal{L}^*\left(\frac{h}{L}\right)\right]. \tag{1}$$

Here βL is the anisotropy of a completely straightened chain; β is the anisotropy of a unit of its length; $\mathcal{L}^*(h/L)$ is the "inverse" Langevin function, defined by

Fig. 1

Figure 1: Fig. 1

the series:

$$\mathcal{L}^*(h/L) = 3h/L + {}^{9}/_{5}(h/L)^3 + {}^{297}/_{175}(h/L)^5 + {}^{1539}/_{875}(h/L)^7 + ...$$

$$= 3(h/L)\{1 + {}^{3}/_{5}(h/L)^2[1 + 0.943(h/L)^2 + 0.978(h/L)^4 + ...]\}. \qquad (2)$$

Expression (1) is valid for all values $0 \leq h \leq L$, i.e., it is applicable to chain molecules at any degree of their coiling h/L. Although in the derivation of (1) the model considered was that of a flexible chain stretched by an external force, and therefore the classical statistical methods of a large ensemble of N freely jointed segments were used, in its final form expression (1) contains no quantity N and is determined only by the total contour anisotropy βL and the degree of coiling of the chain h/L. Therefore we are entitled to assume that expression (1) is also applicable to semirigid, persistent chains, for which the small degree —

the degree of coiling (at small x) is determined not by an external stretching force, but by the "natural," skeletal rigidity of the chain.

According to Porod [2], the degree of coiling of a persistent chain is determined by the equality

$$\left(\frac{h}{L}\right)^2 = \frac{2}{x}\left[1 - \frac{1}{x}\left(1 - e^{-x}\right)\right]. \qquad (3)$$

The set of relations (1)–(3) makes it possible to calculate the equilibrium anisotropy of the chain $\gamma_1 - \gamma_2$ as a function of x. As a first approximation, replacing in (2) the coefficients 0.943 and 0.978 by 1, substituting (2) and (3) into (1), and

Fig. 1. $1 - (\gamma_1 - \gamma_2)/(\gamma_1 - \gamma_2)_{x\to\infty} \equiv Z(x)$ according to formula (4); $1'$—the same according to theory [1]; 2—$\dfrac{\Delta n}{\Delta \tau}/B(\alpha_1 - \alpha_2) \equiv y(x)$, orientational birefringence of kinetically rigid chains according to formulas (4) and (5); $2'$—the same according to theory [3]; 3—$y(x)$ according to formulas (6)–(8), orientational-deformational birefringence of kinetically flexible chains

taking into account that $\beta L = \frac{1}{2}(\alpha_1 - \alpha_2)x$, where $\alpha_1 - \alpha_2$ is the segmental anisotropy of the chain, we obtain

$$\gamma_1 - \gamma_2 = \frac{3}{5}(\alpha_1 - \alpha_2)\left[1 - \frac{1}{x}\left(1 - e^{-x}\right)\right] \Big/ \left\{1 - \frac{4}{5}\frac{1}{x}\left[1 - \frac{1}{x}\left(1 - e^{-x}\right)\right]\right\}. \qquad (4)$$

The dependence $Z \equiv (\gamma_1 - \gamma_2)/\frac{3}{5}(\alpha_1 - \alpha_2) = Z(x)$ is shown by curve 1 on two scales in Fig. 1. It practically does not differ from the corresponding dependence of the anisotropy calculated in the axes of the first chain element (curve $1'$) [1]. The birefringence Δn in the flow of a solution of semirigid molecules in the region of small x is an orientational effect and can be calculated by formula [3]

$$\frac{[n]}{[\eta]} = \left(\frac{\Delta n}{\Delta \tau}\right)_{\Delta\tau \to 0} = \frac{3}{5} B(\alpha_1 - \alpha_2) Z(x) F(x). \tag{5}$$

Here $[n]$ and $[\eta]$ are characteristic quantities of birefringence and viscosity; $\Delta\tau$ is the shear stress in the solution, n is the refractive index of the solution, $B = 4\pi(n^2+2)^2/45kTn$; $F(x)$ is the hydrodynamic factor, calculated in [3] and taking into account the change in the geometrical asymmetry of the molecule with increasing x. Using (4) and (5), we obtain the dependence $y \equiv \dfrac{\Delta n}{\Delta \tau}/B(\alpha_1 - \alpha_2)$ on x in the region $x < 3$ (orientational effect), shown by curve 2 on two scales in Fig. 1. This dependence practically coincides with that obtained earlier [3] and shown by curve $2'$. It is in good quantitative agreement with the results of an experimental study of the birefringence of a fraction of poly-γ-benzyl-L-glutamate [6], where the observed effect has an orientational nature. A characteristic feature of the curves of molecular anisotropy 1 and the orientational part of birefringence 2 is that they attain values close to the limiting value already in the region $x \approx 3$. Meanwhile, the birefringence observed

observed experimentally in solutions of semiflexible molecules (^{7}) and flexible chain oligomers (^{8}), continues to increase for $x > 3$, reaching "saturation" only at considerably larger values of x. This fact is explained by the circumstance that for sufficiently long chain molecules (at large x) the flow birefringence, even at small velocity gradients, is caused not only by the orientation of molecular coils that are asymmetric in shape, but also by their deformation under the action of the shear stress $\Delta\tau$ of the flow. For a solution of ideally flexible Gaussian chains ($x \to \infty, h/L \to 0$), flow birefringence is equivalent to the phenomenon of photoelasticity of a labile (^{10}) swollen Gaussian network (^{12}), whose links undergo stretching and orientation under the action of the tensile stress $\Delta p = 2\Delta\tau$. For this case, at small $\Delta\tau$, the theory (^{9}-^{11}) leads to an expression differing from (5) by the absence of the factors $Z(x)^{3/5}$ and $F(x)$, and in good agreement with experimental data for flexible chain polymers of high molecular weight (x several hundreds and more). In the intermediate range of mean values of x, the phenomenon of birefringence is complicated by the influence of at least two factors: 1) the non-Gaussian character of the chains (the finiteness of the quantities x and h/L); 2) the increase in the kinetic rigidity of the molecule with decreasing x, and, as a consequence, the transformation of birefringence from orientation-deformation to purely orientational. A quantitative account of the influence of the second factor requires a molecular theory of the kinetic rigidity of chain molecules and is not discussed here. The influence of the non-Gaussian character of chains in the phenomenon of photoelasticity of a swollen polymer network was considered in (5) on the basis of the statistics of Langevin chains. The results of that work can be used for flow birefringence. In the range $x > 15$, in the "Langevin" approximation, with an accuracy up to $\left(q^{2/3}/x\right)^2$, the expression for birefringence can be written in the form

$$\left(\frac{\Delta n}{\Delta \tau}\right)_{\Delta\tau\to 0} = B(\alpha_1 - \alpha_2)\left[1 - \frac{6}{5}\left(\frac{q^{2/3}}{x}\right)\left(1 - \frac{14}{5}\frac{1}{x}\right) - \frac{84}{25}\left(\frac{q^{2/3}}{x}\right)^2\left(1 - \frac{6}{x}\right)\right], \tag{6}$$

where q is the maximum (equilibrium) degree of volume swelling of the polymer network in the solvent. The quantity x characterizes the mean length $L = ax$ of a branch of the labile network modeling the solution, for which L may be taken equal to the contour length of the dissolved molecules. Formula (6) shows that in the region of sufficiently large x, with decreasing molecular weight (i.e., x), the quantity $\Delta n/\Delta\tau$ must decrease. In fact, this phenomenon was observed in the study of the photoelasticity of swollen films of atactic polystyrene (13). If in the "Gaussian" approximation the volume of a molecular coil is taken to be $v = 0.36\,(\overline{h^2})^{3/2}$, then the degree of swelling q of a chain molecule in solution can be determined from the expression

$$q = 2.16 \cdot 10^{23}\rho[\eta]/\Phi \approx \rho[\eta], \tag{7}$$

where ρ is the density of the dry polymer, and Φ is the Flory constant.

In a number of polymer homologs, q can also be determined from the equation of the theory of swelling (5, 14)

$$M/M_m = (q^{5/3} - q)/(q_m^{5/3} - q_m), \tag{8}$$

where M_m is the molecular weight of the sample for which $[\eta]_m$ is known and, consequently, q_m is determined by formula (7).

In Fig. 1, curve 3 represents the dependence $y(x)$ in the range $x > 15$, calculated from formulas (6)-(8) for a solution of a chain polymer characterized by the parameters: molecular weight of the monomer $M_0 = 100$, number of monomer units in a segment $s = 8$, with $M_m = 1.1 \cdot 10^5$, $[\eta]_m = 50$. These conditions correspond, for example, to solutions of polymethyl methacrylate in chloroform (15). Formulas (6)-(8) also make it possible to satisfactorily explain the available experimental data on the depend-

dependence of $\Delta n/\Delta\tau$ on M for a number of low-molecular-weight polymers of styrene and methylstyrene [8], as well as oligomers of styrene and oxypropylene glycol. Extrapolation of curve 3 in Fig. 1 to the region of small x (the dotted part of the curve) joins it to segment 2, corresponding to the orientational effect. At the same time, it should be borne in mind that curve 3, describing the orientation-deformation birefringence even of non-Gaussian but kinetically flexible chain molecules, cannot be universal for all polymers, since relation (6) does not take into account the role of the kinetic rigidity of the chain, which increases as x decreases.

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CITED LITERATURE

[1] V. N. Tsvetkov, *Vysokomolekulyarn. soed.*, **4**, 894 (1962).
[2] G. Porod, *Monatsh.*, **80**, 251 (1949).
[3] V. N. Tsvetkov, *Vysokomolekulyarn. soed.*, **7**, No. 8 (1965).
[4] W. Kuhn, F. Grün, *Koll. Zs.*, **101**, 248 (1942).
[5] W. Kuhn, R. Pasternak, H. Kuhn, *Velv. chim. acta*, **30**, 1705 (1948).
[6] V. N. Tsvetkov, I. N. Shcheglikova et al., *Vysokomolekulyarn. soed.*, **7**, No. 6 (1965).
[7] V. N. Tsvetkov, L. N. Andreeva, L. N. Kvitchenko, *Vysokomolekulyarn. soed.*, **7**, No. 11 (1965).
[8] E. V. Frisman, M. A. Sibileva, *Vysokomolekulyarn. soed.*, **3**, 1284 (1961).
[9] W. Kuhn, H. Kuhn, P. Buchner, *Ergebn. exakt. Naturwiss.*, **25**, 1 (1951).
[10] A. S. Lodge, *Nature*, **176**, 838 (1955).
[11] A. S. Lodge, *Koll. Zs.*, **171**, 46 (1960).
[12] L. Treloar, *The Physics of Rubber Elasticity*, IL, 1953.
[13] V. N. Tsvetkov, A. E. Grishchenko, E. P. Vorob' eva, *Vysokomolekulyarn. soed., Carbohydrate Compounds*, 1963, p. 198.
[14] P. J. Flory, J. Rehner, *J. Chem. Phys.*, **11**, 521 (1943).
[15] V. N. Tsvetkov, S. I. Klenin, *ZhTF*, **28**, 1019 (1958).

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