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Abstract

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Dependence of the Sign of Flow Birefringence on the Concentration of a Polymer Solution

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The birefringence in the flow of polymer solutions is determined by the difference of the principal polarizabilities of the macromolecule in solution. Numerous experiments ([1–3]) have made it possible to suppose that a macromolecule in solution may be regarded as an ellipsoidal particle saturated with solvent, whose refractive index differs from the refractive index of the polymer.

Proceeding from these notions, an expression was obtained ([4]) for the difference of the polarizabilities of the macromolecule, which combines the conclusions of statistical theory ([5,6]) and the laws of colloid optics ([7–9]):

$$\gamma_1 - \gamma_2 = \left(\frac{n_s^2+2}{3}\right)^2 \frac{3}{5}(\alpha_1-\alpha_2)\frac{\overline{h^2}}{h_0^2} + \left(\frac{n_k^2-n_s^2}{4\pi\rho n_s^2 N_A}\right)^2 \frac{M^2}{v}(L_2-L_1). \quad (1)$$

Here $\alpha_1 - \alpha_2$ is the difference of the polarizabilities of the statistical element in vacuum; n_s and n_k are the refractive indices, respectively, of the solvent and the polymer; h_0^2 and $\overline{h^2}$ are the mean-square distances between the ends of the molecular chain in the unperturbed and perturbed states, respectively; ρ is the density of the polymer; M is its molecular weight; V is the volume of the molecular ellipsoid; N_A is Avogadro' s number; $L_2 - L_1$ is a factor depending on the ratio of the semiaxes of the ellipsoid. In equation (1) the first term is determined by the intrinsic anisotropy of the macromolecule, the second by the anisotropy of shape, which plays a role only in the case $n_k \neq n_s$. Depending on the structure of the molecule, the intrinsic anisotropy may have a positive or negative value, whereas the anisotropy of shape is always positive.

Thus, for a macromolecule whose anisotropy is negative, the sign of the resulting difference of polarizabilities depends on the contribution made by the separate terms of equation (1).

It is easy to see that, in the presence of laminar flow in the solution, the contribution of the separate terms depends differently on the hydrodynamic force applied to the macromolecule (and hence on the velocity gradient g). Indeed, the first term of equation (1) increases in proportion to $\overline{h^2}/h_0^2$, the second in

Figure 1

Figure 1: Figure 1

proportion to $\sqrt{\overline{h^2}/h_0^2}$ (for it can be shown that $L_2 - L_1 \sim \sqrt{\overline{h^2}/h_0^2}$, assuming constancy of volume). Thus, with a change in g, the sign of $\gamma_1 - \gamma_2$ may change (for given M^2/v and $(n_k - n_s)$).

At a small value of the hydrodynamic force ($g \to 0$), one may take $\overline{h^2}/h_0^2 \approx 1$ and $L_2 - L_1$ as a constant quantity. Then the sign of $\gamma_1 - \gamma_2$ depends only on M^2/v and $(n_k - n_s)$.

It follows from what has been said that, under the conditions $g \to 0$, one may expect a change in the sign of the optical anisotropy with a change in molecular weight in one and the same solvent ($n_k \neq n_s$).

This phenomenon was found [10] in the study of solutions of two fractions ($M = 3 \cdot 10^5$ and $M = 100 \cdot 10^5$) of polystyrene in dioxane. Solutions of the low-molecular fraction possess negative birefringence over a wide range of concentrations and velocity gradients. Solutions of the high-molecular fraction showed positive birefringence Δn, but only in the region of small velocity gradients g. With increasing g, the positive birefringence decreases, then passes through zero and assumes a large negative value. The latter is explained by the fact that, with increasing velocity gradient, the first term of equation (1) increases faster than the second.

Fig. 1. Dependence $\Delta n = f(g)$ for solutions of polystyrene ($M = 1.5 \cdot 10^6$) in dioxane.
1, 2 –$C = 0.1$ g/100 cm^3 and $C = 0.2$ g/100 cm^3 (drawn on an enlarged scale); 3 –$C = 0.3$ g/100 cm^3; 4 –$C = 0.5$ g/100 cm^3; 5 –$C = 0.6$ g/100 cm^3; 6 – $C = 0.8$ g/100 cm^3.

It should be supposed that the value of g at which $\Delta n = 0$ corresponds to the case $\gamma_1 - \gamma_2 = 0$, i.e. to the equal role of the two terms of equation (1) (valid for a monodisperse system), which makes it possible to estimate the extension of the macromolecule under these conditions.

The experiment described makes it possible to elucidate the dependence on g of the value of Δn, due to intrinsic anisotropy, and of Δn, due to shape [13]. Let us note that the value of g at which Δn changes sign decreases with increasing concentration [10]. This makes it possible to understand the new phenomenon set forth in the present work, discovered in the study of solutions of a polystyrene fraction ($M = 1.5 \cdot 10^6$) in dioxane.

The magnitude and orientation of the birefringence were measured in an apparatus with an external rotor [2,10–12], the working length of which was $l = 10$ cm and the gap $\Delta r = 0.085$ cm. The optical scheme used by us was described earlier [2,3,11].

Fig. 2

Figure 2: Fig. 2

The dependence of the magnitude of the birefringence Δn on the velocity gradient g for solutions of different concentration is shown in Fig. 1. In accordance with previous results [10], in the region of large g the quantity Δn changes sign; namely, for the solution $C = 0.3$ g/100 cm^3, at a value of g close to 5000. For solutions of lower concentration, the positive value of Δn is retained in the investigated region of velocity gradients, while more concentrated solutions ($C = 0.5$ g/100 cm^3 and above) exhibit negative birefringence, beginning with the very smallest values of g.

From Fig. 2 it is seen that for the concentration $C = 0.4$ g/100 cm^3, $\Delta n = 0$. In view of the fact that the hydrodynamic force in the flow depends on the viscosity of the solution, it could have been thought that, with increasing concentration, the deformational birefringence increases, as a result of which the resultant value Δn becomes negative. However, since in a series of solutions Δn

negative as $g \to 0$, then the observed phenomenon cannot be explained by this circumstance alone.

It must be supposed that here the optical behavior of the solution depends on the concentration. In a dilute solution, where each macromolecule is surrounded by solvent molecules, the refractive index of the region in which the macromolecule is located differs from the refractive index of the surrounding medium. As the concentration increases, the macromolecules come into contact. A further increase in concentration causes mutual interpenetration of individual parts of the macromolecules; the medium becomes optically more homogeneous, which decreases the form birefringence. An estimate of h^3 from the viscosity according to Flory and of the volume according to Kuhn shows that, in a solution with $C = 0.5$ g/100 cm^3 (for the given M), interlacing of macromolecules already takes place, which causes a decrease in the positive component Δn.

We believe that at sufficiently high concentrations, when the macromolecules are strongly entangled, the birefringence should be determined only by the intrinsic anisotropy.

Fig. 2. Dependence

$$\frac{\Delta n}{g}\Big|_{g\to 0} = f(C)$$

for solutions of polystyrene ($M = 1.5 \cdot 10^6$) in dioxane

The observed effect of the change of sign of Δn with concentration is also connected with a change in the hydrodynamic behavior of the macromolecule in solution when the concentration changes [14,15]. However, for a quantitative interpretation, more extensive experimental material and further development

of the theory are required. In any case, it may be noted that the experiment confirms the point of view developed by us, according to which the form birefringence is determined by a geometrically asymmetric macromolecular ellipsoid.

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