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Abstract

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NEW DATA ON THE ORIENTATION OF BIREFRINGENCE IN THE FLOW OF POLYMER SOLUTIONS

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The study of dynamic birefringence in polymer solutions has shown that a number of experimental data ($^{1-5}$) cannot be explained if the difference of the principal polarizabilities of the macromolecule $\gamma_1 - \gamma_2$ is characterized only by its intrinsic anisotropy (^{6}). The optical behavior of the solution is described much better if the macromolecule in solution is represented as an ellipsoidal particle saturated with solvent, and if it is assigned a refractive index different from the refractive index of the polymer (^{1}). Proceeding from such ideas, an expression was obtained for $\gamma_1 - \gamma_2$ (^{7,5}), which contains two terms and combines the conclusions of statistical theory (^{6,8}) and the laws of colloid optics (^{9,10}). The term determined by intrinsic anisotropy may be positive or negative, while the term determined by the asymmetry of the macromolecular ellipsoid is always positive, and its role increases with increasing molecular weight and with the difference between the refractive indices of the polymer and the solvent. Let us note that, upon deformation of the macromolecule in the field of the velocity gradient g, the intrinsic anisotropy increases more rapidly than the anisotropy of shape (^{4,5}). Thus the magnitude of the birefringence Δn, proportional to the difference of the principal polarizabilities of the macromolecule, also contains two terms, one of which, Δn_i, represents birefringence due to intrinsic anisotropy, and the other, Δn_f, the birefringence of shape.

The role of the birefringence of shape is manifested especially clearly in the case of negative intrinsic anisotropy of the macromolecule. In this case, for one and the same polymer-solvent system, one can obtain different signs of birefringence for different molecular weights, for one molecular weight at different velocity gradients, and even for different concentrations of the solution. Such results were obtained for solutions of polystyrene fractions in dioxane (^{4,5}). All these results are explained by the different roles of $-\Delta n_f$ and $+\Delta n_f$ in different cases (^{7,5,11,12}).

Of particular interest is the unusual dependence, set forth in the present work, of the orientation angle α on the velocity gradient g, obtained for the indicated polymer-solvent system.

The magnitude and orientation of the birefringence of solutions of a polystyrene fraction ($M = 3.4 \cdot 10^6$) in dioxane were studied in an apparatus with an external rotor, whose working length was $l = 10$ cm and gap $\Delta r = 0.005$ cm. The optical setup used by us was described earlier (^{2,13}). A mica plate of 0.024λ

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($\lambda = 5461$ Å) served as the compensator.

Figure 1 presents the dependence of Δn on g for different concentrations C of the solution. In the region of small concentrations and velocity gradients, Δn is positive and increases with increasing C. A further increase in concentration leads to a decrease in the positive birefringence and to a change in its sign. In the region of large velocity gradients, the positive

the birefringence changes sign, and this change occurs at the larger g, the lower the concentration of the solution.

As was indicated, the change in the sign of Δn with increasing g is explained by the unequal dependence of the intrinsic anisotropy and the shape anisotropy on the deformation of the molecule.

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At small g, the shape anisotropy plays the greater role; at large g, the intrinsic anisotropy does. At a certain value of g, the roles of both quantities are the same and $\Delta n = 0$. The decrease in the positive value of Δn with the concentration of the solution is explained by the fact that, with increasing C, the optical inhomogeneity of the solution decreases and the hydrodynamic force deforming the molecule increases (the viscosity of the solution increases) (5).

The dependence of the orientation angle α on the velocity gradient g is shown in Fig. 2*. For those concentrations for which a positive value of Δn is retained over a sufficiently large region of d, the dependence of α on g initially has the normal form: as $g \to 0$, $\alpha \to 45^\circ$, and as g increases, α decreases. In the region of gradients where the positive birefringence tends to zero, the orientation angle becomes negative, tending to the value -45°; then it changes sign again and the dependence on g again acquires the normal form. Of course, the values $+45^\circ$ and -45° are equivalent. It is interesting to note that $\alpha = \pm 45^\circ$ at that value of g for which $\Delta n = 0$. Usually, as $g \to 0$, $\Delta n \to 0$ and $\alpha \to 45^\circ$. In the present case, g is different from 0 and, nevertheless, as $\Delta n \to 0$, $\alpha \to 45^\circ$.

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Negative angles α may be replaced by positive ones greater than 45°.

* The dependences of α on g for $C = 0.05$ and 0.5 g/100 cm^3 are not given, since Δn for these solutions is very small and the values of α are estimated only roughly.

If the "anomalous" points are assigned a positive sign, then Δn is negative for them. The choice of the sign of α was determined by the choice of the sign of Δn.

Until recently, the orientation of birefringence in flow was associated only with the hydrodynamic behavior of the solution. Experiment shows that the magnitude α also depends on the optical properties of the solution. As the velocity gradient increases, the geometrical orientation of the macromolecules always increases. The optical orientation increases with increasing g in the region where $\Delta n > 0$ or $\Delta n < 0$, i.e., at such values of the velocity gradient for which the anisotropy of form is greater or less than the intrinsic anisotropy. In the region where the indicated quantities are approximately equal to one another, the optical orientation decreases, and $\alpha = 45^\circ$ at that value of g for which the intrinsic anisotropy is equal to the anisotropy of form ($\Delta n = 0$).

Since, with increasing concentration, the anisotropy of form decreases, the value of g at which α changes sign is shifted toward smaller values. For a solution with $C = 0.6$ g/100 cm^3, the intrinsic anisotropy is equal to the anisotropy of form at very small velocity gradients.

If the optical properties of the macromolecule are characterized by an ellipsoid of polarizabilities, then such an ellipsoid will be deformed in the field of the gradient. The axis of greatest polarizability at small g becomes the axis of least polarizability at large g. This, apparently, is what determines such a complex dependence of α on g.

The possibility that the orientation angle depends on the ratio of the intrinsic anisotropy to the anisotropy of form was pointed out in the work of Čopič. However, such a dependence has been obtained only for rigid molecules. Therefore the "anomaly" may be observed upon going from one solvent to another.

For a quantitative interpretation of our results, a theory is needed that would take into account the dependence of α on the change in the ratio of the intrinsic anisotropy to the anisotropy of form with changes in the velocity gradient and concentration.

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