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OPTICAL ANISOTROPY OF CERTAIN CHAIN MOLECULES CONTAINING BENZENE RINGS

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As is known, the study of birefringence in the flow of a polymer solution is the most direct method for determining the optical anisotropy of its molecules.

If a polymer consisting of chainlike linear molecules is dissolved in a solvent whose refractive index coincides with that of the polymer, i.e., if the so-called “form effect” is absent ($^{1\ 2}$), then statistical theory (^{3}) leads to the following relation between the intrinsic viscosity $[\eta]$ of the solution and its dynamo-optical constant $[n]$

$$[n] = \lim_{\substack{c\to 0\\ g\to 0}} \left(\frac{\Delta n}{gc\eta}\right) : \frac{[n]}{[\eta]} = 0.195\,\frac{(n^2+2)^2}{nkT}\,(\alpha_1-\alpha_2). \tag{1}$$

Here n is the refractive index of the solvent, η is its viscosity, k is the Boltzmann constant, T is the absolute temperature, c is the concentration, and Δn is the difference between the two principal refractive indices of the solution, observed in laminar flow with velocity gradient g; $\alpha_1-\alpha_2$ is the difference between the two principal polarizabilities (in the direction of the chain and in the direction perpendicular to it) of a chain segment, i.e., of such a portion of it whose length is sufficiently great that the direction of this portion does not depend on the directions of the two segments adjacent to it.

Thus, measurement of the quantities $[n]$ and $[\eta]$ in solution makes it possible to determine the anisotropy of the segment, $\alpha_1-\alpha_2$.

On the other hand, the anisotropy of the segment is determined by the chemical structure of the polymer chain. In those cases where this structure is sufficiently well known (both in the sense of the stereochemistry of the monomer unit and with respect to rotation about the valence bonds of the chain), theory (^{4}) makes it possible to calculate the difference of the segment polarizabilities from the known polarizabilities of the bonds of the monomer unit.

Much more often one has to deal with polymer chains of complex structure, the details of which are little known. Under such conditions it is not possible to give

Figure 1 and Figure 2: Dependence of birefringence on velocity gradient.

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a quantitative relation between the anisotropy of the segment and the anisotropy of the monomer unit. However, even in these cases, using the experimentally found value of $\alpha_1 - \alpha_2$, it is sometimes possible to draw a qualitative conclusion about the structure of the monomer unit of the polymer chain under study. Thus, for example, experience shows that the difference of the polarizabilities of the monomer unit (in the direction of the chain of principal valences and in the direction perpendicular to it) has the same sign as the anisotropy of the segment.

In the present work this circumstance is used for a comparative study of the structure of polymer chains containing benzene rings.

The following four polymers were investigated: 1) polystyrene (P_1), 2) poly-*p*-tert-butylphenyl methacrylate (P_2), 3) poly-1,4-diisopropenyl-

benzene (P_3) and 4) poly-4,4′-diisopropenyldiphenylethane (P_4). The second substance was obtained by M. M. Koton, T. V. Sheremet' eva, and M. G. Zhenevskaya (^{5}), and the third and fourth by Yu. V. Mitin and N. A. Glukhov (^{6}). All four polymers were unfractionated. Their weight-average molecular weights, determined from light scattering by V. G. Aldoshin, are given in Table 1.

To find the difference $\alpha_1 - \alpha_2$ from equation (1), dynamo-optical and viscometric measurements of the polymers were carried out in solvents in which the shape effect is excluded. For P_2, chlorobenzene was used; for the other three, bromoform. The values of the intrinsic viscosity, determined in an ordinary Ostwald viscometer, are placed in the third column of the table.

Fig. 1. Dependence of birefringence on the velocity gradient. Poly-1,4-diisopropenylbenzene: 1 $-C = 7.70$; 2 $-C = 5.80$; 3 $-C = 4.20$; 4 $-C = 2.60$; 5 $-C = 2.10$. Polystyrene: 6 $-C = 0.22$; 7 $-C = 0.28$; 8 $-C = 0.42$; 9 $-C = 0.51$; 10 $-C = 0.65$; 11 $-C = 0.79$.

Fig. 2. Dependence of birefringence on the velocity gradient. Poly-4,4′-diisopropenyldiphenylethane: 1 $-C = 1.00$; 2 $-C = 0.80$; 3 $-C = 0.48$; 4 $-C = 0.35$; 5 $-C = 0.22$. Poly-*p*-tert-butylphenyl methacrylate: 6 $-C = 0.52$; 7 $-C = 0.69$; 8 $-C = 1.15$; 9 $-C = 1.48$; 10 $-C = 2.03$; 11 $-C = 2.50$. The concentrations C in Figs. 1 and 2 are given in g/100 ml.

Dynamic birefringence was investigated in a dynamo-optical meter with an internal rotor. The rotor length was 3 cm, the gap width 0.26 mm; the critical gradient $g_k = 4.9 \cdot 10^5 \frac{\eta}{\rho}$ (η is the viscosity, ρ the density of the solvent) was nowhere exceeded. Birefringence was measured with an elliptical compensator with an additional shadow device. The compensator path difference was $\delta = 0.027\lambda$, where $\lambda = 5.5 \cdot 10^{-5}$ cm.

The results of measurements of the dependence of birefringence on the velocity gradient are shown in Fig. 1 for polymers P_3 and P_1, and in Fig. 2 for

P_4 and P_2. In Fig. 3 the concentration extrapolation of the quantities $\frac{\Delta n}{gc\eta}$ is given, and the values of the dynamo-optical constant are determined; these are presented in the fourth column of the table. In all calculations the birefringence values of the solvents were respectively added or subtracted; for both bromoform and chlorobenzene these are equal to $\frac{\Delta n}{g} = 1 \cdot 10^{-12}$.

The fifth column of Table 1 contains the values of the optical anisotropy of the statistical segment $\alpha_1 - \alpha_2$, calculated from equation (1).

As is seen from the data given, the difference in polarizabilities of the statistical segment is a large positive quantity for P_3 and P_4, while for P_1 and P_2 $(\alpha_1 - \alpha_2)$ is a large negative quantity.

In interpreting the results obtained, one should first of all bear in mind that the optical anisotropy of the molecular chains under study must, to a considerable extent, be determined by the arrangement in them of phenyl groups, whose polarizability in the plane of the ring is considerably greater than in the direction normal to the ring. Therefore one should expect positive

Fig. 3. Dependence of the quantity $\frac{\Delta n}{gc\eta}$ on concentration.

a —poly-4,4′-diisopropenylphenylethane, *b* —poly-1,4-diisopropenylbenzene $\left(\frac{\Delta n}{gc\eta} \cdot 10\right)$, *v* —poly-*p*-tert-butylphenyl methacrylate, *g* —polystyrene

Table 1

Polymer	$M \cdot 10^{-4}$	$[\eta]$	$[n] \cdot 10^{10}$	$(\alpha_1 - \alpha_2) \cdot 10^{25}$	$(\beta_1 - \beta_2) \cdot 10^{25}$
Polystyrene (P_1)	27	0.82	−9.7	−190	−26
Poly-*p*-tert-butylphenyl methacrylate (P_2)	37	0.85	−4.5	−90	−15
Poly-1,4-diisopropenylbenzene (P_3)	0.7	0.066	0.32	78	30
Poly-1,4′-diisopropenyldiphenylethane (P_4)	78	0.70	6.20	142	24

Fig. 4. Scheme of polymer structures.

Figure 2: Fig. 4. Scheme of polymer structures.

values of $[n]/[\eta]$ and, correspondingly, $\alpha_1 - \alpha_2$ for polymers containing benzene rings in the chain of the main valences, and negative values of the same quantities for chains in which the phenyl nuclei are included in side groups. Consequently, the results presented in Table 1 show that P_3 and P_4 belong to polymers of the first type, and P_1 and P_2 to the second type. Indeed, in polymers P_1 and P_2, whose structure is fairly well known and is shown in Fig. 4 *v*, *g*, the phenyl nuclei are radicals of side groups.

The structure of the new polymers P_3 and P_4 has not yet been sufficiently studied. However, proceeding from the scheme of the polymerization reaction proposed by its authors (6), the arrangement of the benzene rings in the chains of P_1 and P_2 can be represented in the form shown in Fig. 4 *a*, *b*.

Using the scheme of structures shown in Fig. 4, one can calculate the anisotropy of the monomer unit in the polymers studied. The results are placed in the last column of Table 1, where the values of the difference of polarizabilities $\beta_1 - \beta_2$ are given in the direction of the chain of the principal valences and perpendicular to it, per one C–C bond of the chain about which rotation is possible. These quantities were calculated according to the scheme of additivity of bond polarizabilities, the numerical values of the polarizabilities and of the valence angles being taken from Stuart’ s book (7). The calculations for Π_1

Fig. 4. Scheme of polymer structures.
a –poly-1,4-diisopropenylbenzene, *b* –poly-4,4′-diisopropenyldiphenylethane, *c* –polystyrene, *d* –poly-*p*-tert-butylphenyl methacrylate

were made under the assumption of a planar arrangement of the benzene rings, normal to the chain of the principal valences. The value $\beta_1 - \beta_2$ given for Π_2 refers to the case of a rigid planar configuration of the side chain, but with complete freedom of rotation of the plane of the benzene ring about its bond $C_{\text{aliph.}}$—$C_{\text{arom.}}$ and O—$C_{\text{arom.}}$. The values $\beta_1 - \beta_2$ given for Π_3 and Π_4 are approximate estimates. In them only the anisotropy of the benzene rings and of those C–C bonds that can give an appreciable difference of polarizabilities in the directions along and across the chain has been taken into account.

We see that the differences of polarizabilities of the chain units, $\beta_1 - \beta_2$, found in this way in all cases agree in sign with the experimental values $\alpha_1 - \alpha_2$ and have quite admissible absolute magnitudes, several times smaller than the values of $\alpha_1 - \alpha_2$.

Thus, the results obtained from measurements of the dynamo-optical constants of all the polymers studied are in good agreement with their structural formulas shown in Fig. 4 and, consequently, confirm the correctness of the latter.

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