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Dynamical Birefringence of Polymethylmethacrylate Solutions with Various Solvents and the Form of the Macromolecules

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An investigation was conducted of the dynamical birefringence of two fractions ($M = 3.5 \times 10^5$ and $M = 4.2 \times 10^6$) of polymethylmethacrylate in various solvents. The results obtained are compared with theories based on a molecular model of anisotropic ellipsoidal complexes, and on the model of elastic-viscous spheres. The experimental data are in better agreement with the model of anisotropic complexes.

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1. INTRODUCTION

BIREFRINGENCE in the flow of a solution of a polymer is determined by the optical anisotropy of its molecules. As was shown earlier[1,2], the optical anisotropy of a macromolecule in solution may be due to asymmetry of its form (anisotropy of form) and to internal anisotropy (anisotropy of the substance of the molecular complex). Both anisotropy of form and internal anisotropy depend on the hydrodynamic forces acting on the molecular complex in a laminar flow. These forces deform the molecular complex, increasing the asymmetry of its form and evoking the photoelastic effect in the macromolecule, i.e., the appearance of optical anisotropy in its substance on account of the stresses arising there.

Experiments conducted over a broad range of flow velocity gradients[1] have shown that in the observed birefringence the role of the effect due to deformation of the macromolecules with an increase of velocity gradient. Thus, dynamical birefringence in a solution of a polymer observed in the region of large flow velocity gradients, is to a considerable extent a deformation effect, and in the case of equal indices of refraction of the polymer and the solvent, a photoelastic effect.

The nature of the effect observed in solutions of polymers at small flow velocity gradients g (under the conditions $g \to 0$) is an open question at the present time.

2. THEORY OF BIREFRINGENCE OF SOLUTIONS OF A POLYMER IN A WEAK FLOW

According to the statistical theory of Kuhn[3], the most probable form of a linear chain macromolecule in solution is the form of a coiled complex, the length of which is 2-3 times its transverse dimensions.

As an optical model of such a complex, we proposed[1] a particle of ellipsoidal form, thoroughly saturated with solvent, and having a mean index of refraction n_ω, differing from the index of refraction of the solvent n_s by the quantity $n_\omega - n_s$:

$$n_\omega^2 - n_s^2 = \omega^{-1}(n_k^2 - n_s^2). \tag{1}$$

Here n_k is the index of refraction of the dry polymer, ω is its "volume" in solution determined by the relation

$$\omega = \rho V / m = V \rho N_A / M, \tag{2}$$

where ρ is the density of the polymer, M its molecular weight, m the mass of the macromolecule, V the volume of the molecular ellipsoid (particle) in the solution, and N_A Avogadro's number.

According to the statistical theory[4], a molecular complex in the absence of external deforming forces has internal anisotropy; moreover, the difference between the indices of refraction of its substance under stresses parallel to the major and minor geometrical axes is

$$n_1^2 - n_2^2 = \left(\frac{n_s^2 + 2}{3}\right)^2 \frac{4\pi}{V} \frac{3}{5} (\alpha_1 - \alpha_2), \tag{3}$$

where α_1 and α_2 are the principal polarizabilities of the segment in vacuum.

The anisotropy of form of an ellipsoidal molecular complex can be calculated by the application of the laws of colloidal optics[5-7], with the use of a molecular model[1] based on Eqs. (1) and (2). The total difference, obtained in this way, of the two principal polarizabilities of the molecular ellipsoid in solution, taking account of Eq. (3), is[2]

$$\gamma_1 - \gamma_2 = \frac{n_1^2 - n_2^2}{4\pi} V + \frac{(n_k^2 - n_s^2)^2}{16\pi^2 n_s^2 \omega^2} V (L_2 - L_1) \tag{4}$$

$$= \left(\frac{n_s^2 + 2}{3}\right)^2 \frac{3}{5} (\alpha_1 - \alpha_2) + \left(\frac{n_k^2 - n_s^2}{4\pi n_s \rho N_A}\right)^2 \frac{M^2}{V} (L_2 - L_1),$$

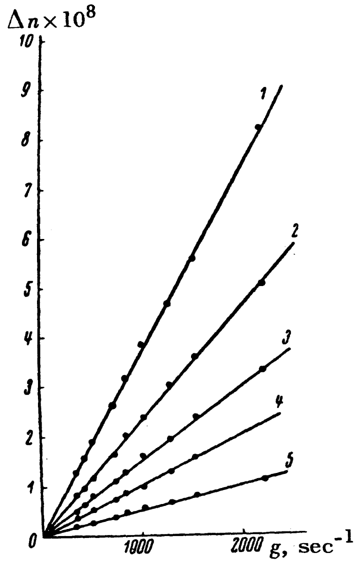

FIG. 1. Dependence of the magnitude of birefringence on the velocity gradient in solutions of polymethylmethacrylate in acetone. $M = 4.2 \times 10^6$: 1-$c = 0.5$; 2-$c = 0.4$; 3-$c \doteq 0.3$; 4-$c = 0.2$; 5-$c = 0.1$ (gm/100 cm^3).

where L_1 and L_2 are constants, depending on p, the ratio of the semiaxes of the ellipsoid.

Recently, Kopik[7] calculated the quantity $\gamma_1 - \gamma_2$, expressing it as a function of the distance h between the ends of the molecular chain. His result agrees precisely with ours, if we set $p = 2$ and $V = 0.3\,h^3$ in Eq. (4).

If birefringence in the flow of a solution of a polymer under the conditions $g \to 0$ is regarded as the result of the orientation of molecular complexes of asymmetric form, then the simple application of orientation theory for rigid ellipsoidal particles[8], with the use of Eq. (4), leads to the following expression for the dynamo-optical constant[2]:

$$[n] = \lim_{\substack{g\to 0\\ c\to 0}} \left(\frac{\Delta n}{gc\eta_0}\right) \tag{5}$$
$$= \frac{2\pi}{225}\,\frac{bN_A}{\eta_0 DM}\,\frac{(n_s^2+2)^2}{n_s}(\alpha_1-\alpha_2) + \frac{bM}{120\pi\eta_0 DV\rho^2 N_A}\,\frac{(n_k^2-n_s^2)^2}{n_s^3}(L_2-L_1)$$
$$= [n]_e + [n]_f.$$

Here η_0 is the viscosity of the solvent, Δn is the observed birefringence in the solution, c is the concentration in g/cm^3, D is the coefficient of rotational diffusion of the macromolecule, $b = (p^2 - 1)/(p^2 + 1)$; $[n]_e$ and $[n]_f$ are the parts of the dynamic-optical constant characterizing, respectively, the effect of internal anisotropy and the effect of the form of the macromolecule.

Another point of view concerning the nature of the Maxwell effect in a solution of a polymer under the conditions $g \to 0$ is developed by Cerf[9,10]. The model applied by us in the form of a colloidal particle whose mean index of refraction n_ω is determined by Eq. (1), is used in his theory for the characteristics of the optical properties of the molecule. However, in contrast to Kuhn, it is proposed in this theory that the statistically most probable form of a free macromolecule is a spherical complex of radius a_0, characterized by the internal

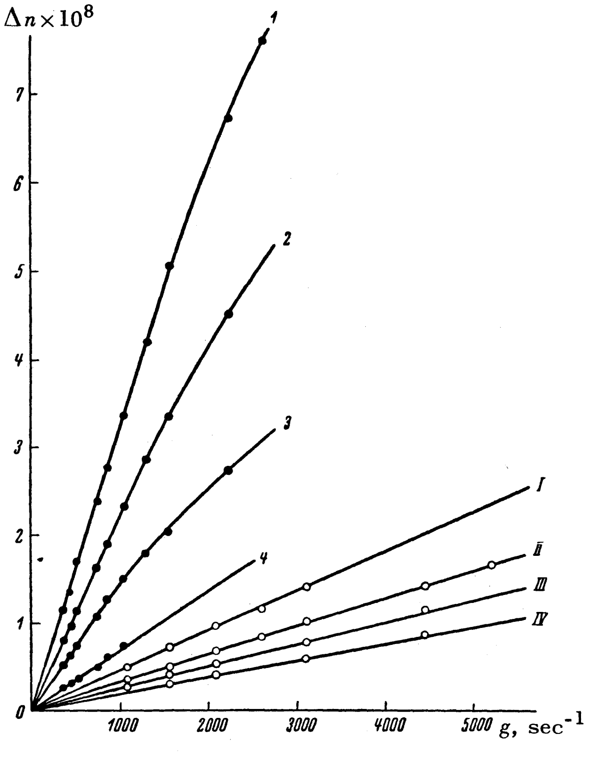

FIG. 2. Dependence of the magnitude of birefringence on the velocity gradient in solutions of polymethylmethacrylate in ethyl acetate. $M = 4.2 \times 10^6$: 1-$c = 0.4$; 2-$c = 0.3$; 3-$c = 0.2$; 4-$c = 0.1$ (gm/100 cm^3). $M = 3.5 \times 10^5$: I-$c = 1.5$; II-$c = 1.2$; III-$c = 1.0$; IV-$c = 0.8$ (gm/100 cm^3).

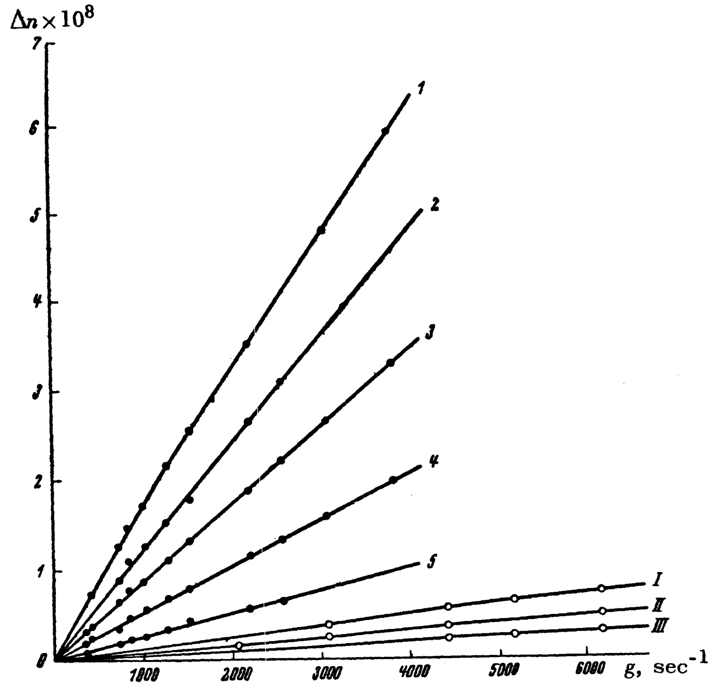

FIG. 3. Dependence of the magnitude of birefringence on the velocity gradient in solutions of polymethylmethacrylate in chloroform. $M = 4.2 \times 10^6$: *1*-$c = 0.5$; *2*-$c = 0.4$; *3*-$c = 0.3$; *4*-$c = 0.2$; *5*-$c = 0.1$ (gm/100 cm^3). $M = 3.5 \times 10^5$: *I*-$c = 1.2$; *II*-$c = 1.0$; *III*-$c = 0.8$ (gm/100 cm^3).

viscosity η_i and the shear modulus of elasticity μ. Thermal motion may deform the molecular complex, transforming it into a spheroid, the major semiaxis of which is

$$a = a_0 (1 + \delta). \tag{6}$$

Here δ denites the coefficient of deformation. The mean squared magnitude of Brownian deformation δ_0 is

$$\delta_0 = (kT/3V\mu)^{1/2}, \tag{7}$$

where T is the temperature and k is Boltzmann's constant.

In laminar flow, hydrodynamic forces also deform the macromolecule, transforming it into an ellipsoid with a ratio of semiaxes

$$p = 1 + (2{,}5/\mu)\,\eta_0\, g. \tag{8}$$

Deformation of the elastic-viscous sphere evokes in it the appearance of optical anisotropy, leading to a form effect and to a photoelastic effect in the substance of the macromolecule.

Thus, the theory of the elastic-viscous sphere regards the Maxwell effect in a solution of a polymer, under the conditions $g \to 0$, as a composite phenomenon, evoked by the orientation of spheroids (coefficient of asymmetry of form δ_0) and their deformation in the flow. The relative role of these two effects depends on the relation between the viscosity of the solvent η_0 and the internal viscosity of the macromolecule η_i. For $\eta_i \gg \eta_0$ the effect is basically orientational; for $\eta_i \ll \eta_0$, it is deformational.

Cerf's theory leads to the following value of the dynamo-optical constant of the solution:

$$\Delta = \left(\frac{\Delta n}{g\eta_0\,\Omega n_s}\right)_{\substack{g\to 0\\ c\to 0}} \tag{9}$$

$$= 5\,\frac{\varepsilon}{\mu}\,\theta + \frac{2}{\mu}\left(\frac{n_\omega - n_s}{n_\omega}\right)^2 \theta = \Delta_e + \Delta_f;$$

$$\theta = [(\eta_0/\eta_i) + {}^4/_5\,\delta_0^2]/[(\eta_0/\eta_i) + {}^4/_3\,\delta_0^2], \tag{9'}$$

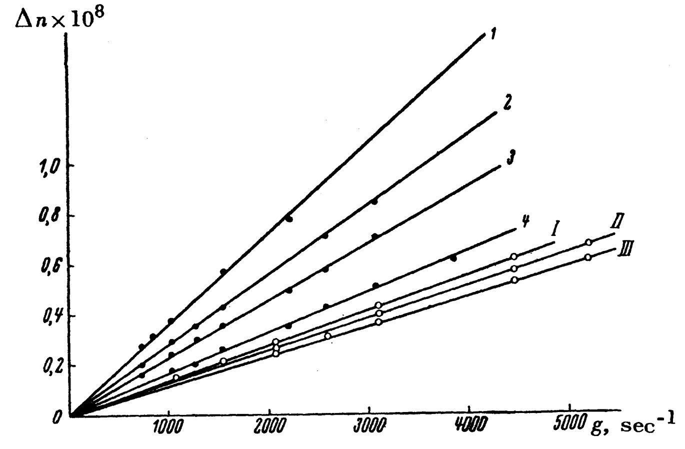

FIG. 4. Dependence of the magnitude of birefringence on the velocity gradient in solutions of polymethylmethacrylate in toluene. $M = 4.2 \times 10^6$: *1*-$c = 0.5$; *2*-$c = 0.4$; *3*-$c = 0.3$; *4*-$c = 0.2$ (gm/100 cm^3). $M = 3.5 \times 10^5$: *I*-$c = 1.7$; *II*-$c = 1.5$; *III*-$c = 1.2$ (gm/100 cm^3).

where Δ_e and Δ_f are the parts of the dynamo-optical constant due, respectively, to internal anisotropy and anisotropy of form of the macromolecule, Ω is the portion of the volume occupied by the particles in the solution, ϵ is the photoelastic coefficient of the substance of the macromolecule, determined from the relation

$$\frac{n_1-n_2}{n_\omega} = \frac{5}{2}\varepsilon\frac{\eta_0}{\mu}g, \tag{10}$$

where $n_1 - n_2$ is the difference between the principal indices of refraction of the substance of the

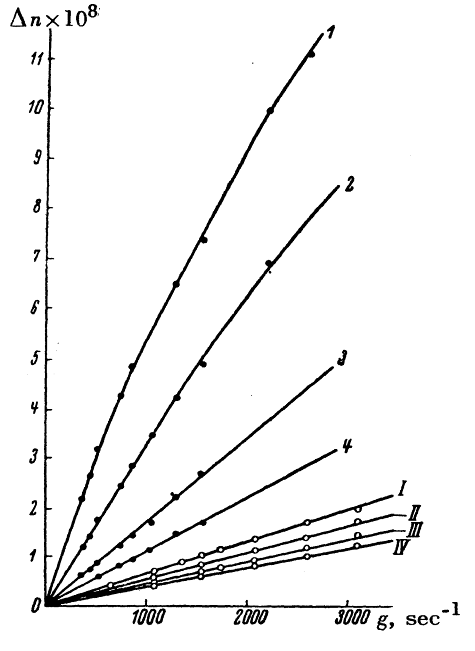

FIG. 5. Dependence of the magnitude of birefringence on the velocity gradient in solutions of polymethylmethacrylate in bromoform. $M = 4.2 \times 10^6$: *1*-$c = 0.4$; *2*-$c = 0.288$; *3*-$c = 0.147$; *4*-$c = 0.1$ (gm/100 cm^3). $M = 3.5 \times 10^5$: *I*-$c = 1.2$; *II*-$c = 1.0$; *III*-$c = 0.8$; *IV*-$c = 0.6$ (gm/100 cm^3).

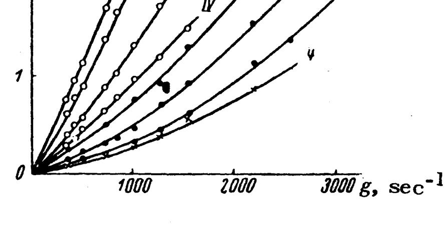

FIG. 6. Dependence of the magnitude of birefringence on the velocity gradient in solutions of polymethylmethacrylate ($M = 4.2 \times 10^6$) in two solvents. Bromobenzene: *I*-$c = 0.5$; *II*-$c = 0.4$; *III*-$c = 0.3$; *IV*-$c = 0.2$ (gm/100 cm^3). Chlorobenzene: *1*-$c = 0.5$; *2*-$c = 0.4$; *3*-$c = 0.3$; *4*-$c = 0.2$ (gm/100 cm^3).

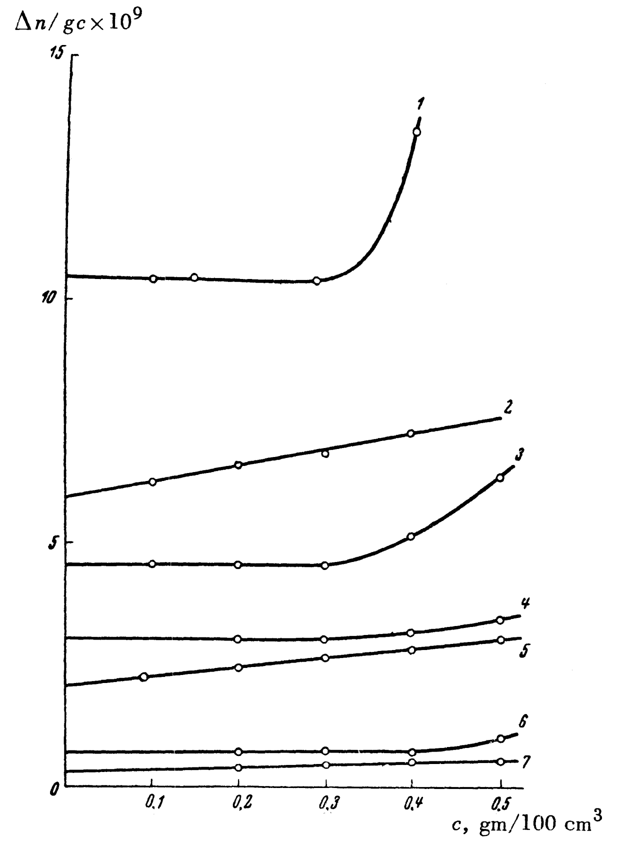

FIG. 7. Dependence of $\Delta n/gc$ on concentration for a fraction of polymethylmethacrylate ($M = 4.2 \times 10^6$) in various solvents: *1*-bromoform, *2*-ethyl acetate, *3*-acetone, *4*-bromobenzene, *5*-chloroform, *6*-chlorobenzene, *7*-toluene.

particle, arising in a mechanical field of gradient g.

As is shown by Eqs. (9) and (9′), the magnitude of the dynamo-optical constant Δ in the theory of the elastic-viscous sphere differs only by a factor of 3/5 for the two extreme conceivable cases of pure orientation ($\eta_0/\eta_i \ll \delta_0^2$) and pure deformation ($\eta_0/\eta_i \gg \delta_0^2$), and is determined by the quantities ϵ, μ, n_ω and n_s. Therefore, the measurement of Δ may not serve for a qualitative comparison of the roles of the orientational and deformational effects in the observed birefringence. The experimental determination of the quantities Δ_e and Δ_f separately leads to more instructive conclusions as will be shown below.

3. METHOD AND RESULTS OF THE INVESTIGATION

In conformance with previous results[1,11,12] in order to separate the effect of form from the effect of internal anisotropy, an investigation was conducted, in the present work, of birefringence in the flow of solutions of two fractions of polymethylmethacrylate in various solvents. The molecular weights of the fractions were determined by the magnitude of their characteristic viscosity $[\eta]$ in benzene, according to the formula[13]

$$[\eta] = 0.468 \times 10^{-4} M^{0.77}.$$

The optical setup used by us has been described earlier[14,15]. For the measurement of the magnitude of birefringence of solutions of the first fraction ($M = 4.2 \times 10^6$), a mica plate 0.04 λ served as a compensator. For the investigation of the second fraction ($M = 3.5 \times 10^5$), where the magnitude of birefringence is very small, a mica plate (0.019 λ) was used as a compensator (λ = 5461 Å). The phase difference arising in a solution with a given velocity gradient was calculated according to the formula

$$\delta = \sin \delta_0 \sin 2(\beta - \beta_0),$$

where β and β_0 are the extinction azimuths of the compensator in the presence and in the absence of a velocity gradient in the solution investigated, and δ_0 is the phase difference created by the compensator.

A universal dynamo-optimeter similar to those described in other works[14,15] was used for the measurements. The measurements were performed in a gap with an external rotor. The length of the layer of liquid worked was $l = 6$ cm. A rotor forming a gap $\Delta R = 0.86$ mm was used for the study of high-molecular fractions. The low-molecular fractions were investigated in a gap $\Delta R = 0.36$ mm. Laminar flow was maintained for all the solutions over the interval of velocity gradients investigated. All the measurements were made at the temperature $t = 21°$.

The dependence $\Delta n = f(g)$, obtained for the solutions studied, are presented graphically in Figs. 1-6. The figures show that for all the solutions of low-molecular fraction, the dependence $\Delta n = f(g)$ has the form of a straight line over the entire range of velocity gradients investigated. Similar behavior of solutions of high-molecular fraction depends on the solvent used.

In all cases, the experimental points permit a sufficiently trustworthy determination of the quantity $(\Delta n/g)_{g\to 0}$ of the solution. In the region of concentrations of interest to us, solutions of

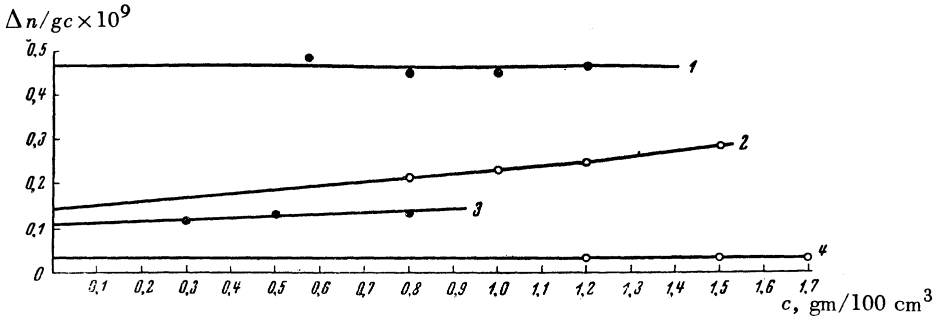

FIG. 8. Dependence of $\Delta n/gc_{g \to 0}$ on concentration for a fraction of polymethylmethacrylate ($M = 3.5 \times 10^5$) in various solvents: *1*-bromoform, *2*-ethyl acetate, *3*-chloroform, *4*-toluene.

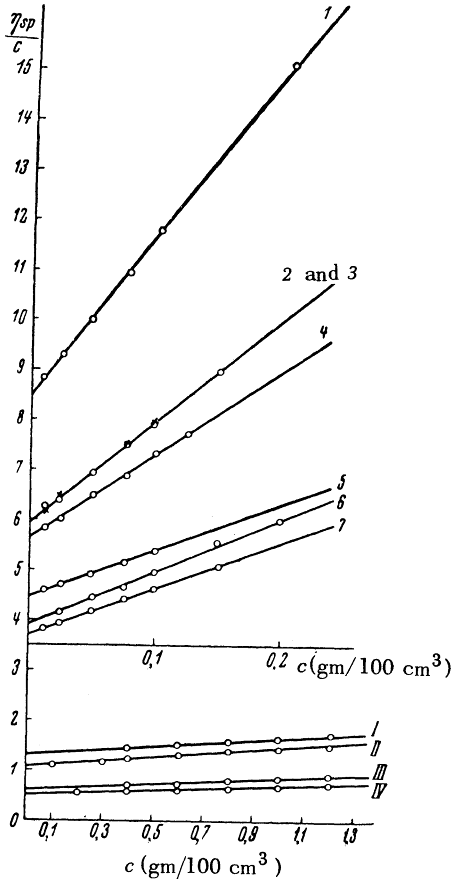

FIG. 9. Dependence of η_{sp}/c on concentration for fractions of polymethylmethacrylate in various solvents. $M = 4.2 \times 10^6$: *1*-chloroform, *2*-chlorobenzene, *3*-bromoform, *4*-bromobenzene, *5*-ethyl acetate, *6*-toluene, *7*-acetone. $M = 3.5 \times 10^5$: *I*-chloroform, *II*-bromoform, *III*-ethyl acetate, *IV*-toluene.

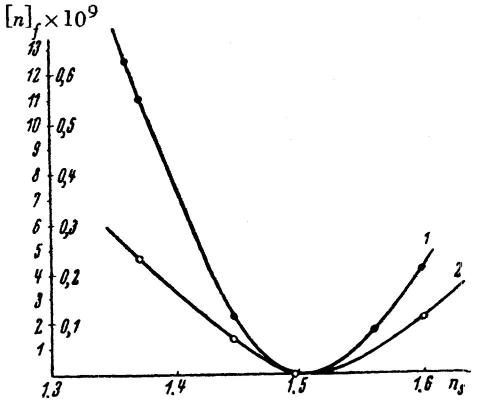

FIG. 10. Dependence of the part of the dynamo-optical constant $[n]_f$ due to the effect of form, on the index of refraction of the solvent n_s : 1-$M = 4.2 \times 10^6$, 2-$M = 3.5 \times 10^5$.

polymethylmethacrylate have a comparatively small magnitude of dynamical birefringence, which makes it necessary to take into account the role of its solvent. This was carried out by assuming additivity of the magnitude of birefringence of the solute and of the solvent. From the value of $(\Delta n/g)_{g\to 0}$ obtained for the solution, the value of $(\Delta n/g)_s$ corresponding to the solvent was calculated, which was measured in all cases when the role of the latter was clearly manifested. The value of $(\Delta n/g)_s$ for the solvents investigated are given in Table I.

The dynamic-optical constants $[n] = \lim\limits_{c\to 0} \times (\Delta n/g\eta_0 c)_{g\to 0}$ of the fractions were found from curves of the concentration dependence of the quantity $c^{-1}(\Delta n/g)_{g\to 0} - c^{-1}(\Delta n/g)_s$ by the extrapolation of this quantity to zero concentration. These curves are shown in Figs. 7 and 8. The vlaues of $[n]$ obtained by this means for both fractions are given in columns 6 and 12 of Table I. Concentration measurements of relative viscosity (Fig. 9) permitted the determination of the characteristic viscosity of both fractions of polymethylmethacrylate in various solvents, the values of which are given in columns 5 and 11 of Table I.

4. DISCUSSION OF RESULTS

The experimental results obtained by us should be compared with the basic equations: with Eq. (5) of the theory of anisotropic complexes and with Eq. (9) of the theory of elasto-viscous spheres.

As is shown by Eq. (5), the value of $[n]_f$ may be determined, if the measured values of $[n]$, the dynamo-optical constant and $[n]_e$, the part of it determined by internal anisotropy of the complex, are known.

The hydrodynamical theories of solutions of macromolecules yield the general relation

$$D = RT / B\eta_0 [\eta] M, \tag{11}$$

where B is a numerical coefficient depending on the particular hydrodynamic model of the molecule. Thus, for the statistics of a coiled complex, theory gives[16,17] $B = 4$, for an extended ellipsoid[18] $B = 6/F(p)$, where $F(p)$ is a form factor. With $p = 3$, $F(p) = 3/2$ and the result for the ellipsoid agrees with the formula for the complex.

Combining Eqs. (5) and (11), and setting $B = 4$, we get

$$[n]_e = 0.11\,[\eta]\,(b/kT)\,[(n_s^2 + 2)^2/n_s]\,(\alpha_1 - \alpha_2). \tag{12}$$

It cannot be asserted *a priori* that the difference between the polarizabilities of the segment $\alpha_1 - \alpha_2$ in the solvent does not depend on the index of refraction of the latter. At the present time there are not sufficient data for a duscussion of this question. However, it seems probable to us that the effect of a change in $\alpha_1 - \alpha_2$ with a change in n_s will play a considerably smaller role than the effect of the form of the complex. Therefore, as a first approximation, we neglect these changes, and will consider the anisotropy of the segment to be the same in all of the solvents, and to coincide with the quantity $\alpha_1 - \alpha_2$ entering into Eq. (12).

With the use of a solvent whose index of refraction n_s coincides with the index of refraction n_k of the substance, the second term on the right hand side of Eq. (5) becomes zero, so that $[n] = [n]_e$. In our case, toluene satisfies the condition $n_k = n_s$. Thus, the dynamo-optical constant obtained for solutions in toluene, makes it possible to determine $(\alpha_1 - \alpha_2)$. Applying Eq. (12) to toluene, we get

$$\alpha_1 - \alpha_2 = \frac{[n]_t}{[\eta]_t}\,\frac{kT}{0{,}11b}\,\frac{n_t}{(n_t^2 + 2)^2}. \tag{13}$$

The subscript t indicates that the solvent is toluene. Substituting Eq. (13) for $\alpha_1 - \alpha_2$ into Eq. (12), we obtain for the quantity $[n]_e$ in any solvent

TABLE I

Solvent				$M = 4.2 \times 10^6$			
Substance	$\left(\frac{\Delta n}{g}\right)_s \cdot 10^{12}$	$\eta_s \cdot 10^2$ poise	n_s	$[\eta]$, gm/100 cm^3	$[n] \cdot 10^7$	$[n]_e \cdot 10^7$	$[n]_f \cdot 10^7$
1	2	3	4	5	6	7	8
Chlorobenzene .	1.35	0,800	1,523	5.95	0.866	0.752	0.114
Toluene. . . .	0.79	0,589	1,498	3.87	0.480	0.480	0.000
Chloroform . .	0.13	0,592	1,446	8.45	3.340	1.015	2.325
Ethyl Acetate .	0.20	0,510	1.372	4.45	11,500	0.500	11.000
Bromoform . .	1.04	2.080	1.598	5.92	5.000	0.784	4.216
Bromobenzene .	2.20	1.167	1.560	5,65	2,545	0.737	1,808
Acetone	—	0.347	1.359	3.70	12,967	0.417	12.550

$$[n]_e = [n]_t \frac{[\eta]}{[\eta)_t} \frac{n_t}{n_s} \frac{\left(n_s^2+2\right)^2}{\left(n_t^2+2\right)^2}. \qquad (12')$$

The expression for $[n]_f$ entering into Eq. (5), may be transformed by the substitution in it of the coefficient of rotational diffusion from the relation

$$D = kT / \eta_0 V f_0, \qquad (11')$$

where f_0 is a form factor determined by Eq. (16). The use of (11′) and (12′) in Eq. (5) gives

$$[n]_f = \frac{M}{120\,\pi\rho^2 RT} \{(L_2 - L_1)\, b f_0\} \frac{\left(n_k^2 - n_s^2\right)^2}{n_s^3} \qquad (14)$$

$$= [n] - [n]_t \frac{[\eta]}{[\eta]_t} \frac{n_t}{n_s} \frac{\left(n_s^2+2\right)^2}{\left(n_t^2+2\right)^2}.$$

All of the quantities entering into the right hand side of Eq. (14) are obtained from the experiments. The values of $[n]_e$, obtained from the experimental data through Eq. (12′), are presented in Table I for all the solvents investigated. Also tabulated is the quantity $[n]_f$, calculated as the difference between $[n]$ and $[n]_e$.

The dependence $[n]_f = f(n_s)$ is shown in Fig. 10 for the two fractions of polymethylmethacrylate. The ordinate has a scale corresponding to each molecular weight. It is evident from the graph that in both cases the points lie on parabolic curves, in agreement with Eq. (14).

Using the obtained values of $[n]_f$, the factor $(L_2 - L_1)bf_0$ of Eq. (14) may be calculated. The results for both fractions investigated are given in columns 9 and 15 of Table I. The factor $(L_2 - L_1)bf_0$ is a single-valued function of the ratio p of the axes of the macromolecule, and makes it possible to determine p through the use of the well-known relations[5-7]:

$$L_2 - L_1 \qquad (15)$$

$$= \frac{\pi}{p^2-1}\left(2p^2 + 4 - \frac{3p}{\sqrt{p^2-1}} \ln \frac{p+\sqrt{p^2-1}}{p-\sqrt{p^2-1}}\right);$$

$$\overline{f_0} \qquad (16)$$

$$= \frac{p^2}{4\left(p^4-1\right)}\left(-1 + \frac{2p^2-1}{2p\sqrt{p^2-1}} \ln \frac{p+\sqrt{p^2-1}}{p-\sqrt{p^2-1}}\right).$$

The values of p obtained in this way are given in columns 10 and 16 of Table I. Within the limits of experimental error, these quantities appear to be constants for a given fraction, independent of the solvent, and close to one-another for the two fractions investigated. The somewhat low value of p found for the low-molecular fraction is explained, possibly, by the large relative error in the determination of $[n]_e$ for this fraction. In any case, the experimental values of p, lying in a range from 2 to 3, may be considered to be in good agreement with the theoretical values predicted by the statistical theory of Kuhn[3].

The experimental data of Table I allow one comparison to be made with the results of orientation theory. Using Eqs. (12), (14), (11) and (11′), it is not difficult to obtain the relation

TABLE I

Substance	$M=4.2\times10^6$		$M = 3.5\times10^5$					
	$(L_2-L_1)bf_0$	$p=\frac{A}{B}$	$[\eta]$,(gm/100 cm^3)	$[n]\cdot10^7$	$[n]_e\cdot10^7$	$[n]_f\cdot10^7$	$(L_2=L_1)bf_0$	$p=\frac{A}{B}$
	9	10	11	12	13	14	15	16
Chlorobenzene .	24.4	2.32						
Toluene	—	—	0.58	0.058	0.058	0.000	—	—
Chloroform . . .	60.6	3.30	1.28	0,189	0.118	0.071	22.1	2.20
Ethyl Acetate . .	44.5	2.92	0.51	0.277	0.045	0.232	11.3	1,80
Bromoform . . .	40.8	2.82	1.06	0.224	0.111	0.113	13.2	1,85
Bromobenzene .	44,4	2.92						
Acetone	43.2	2.90						

$$\frac{[n]}{[\eta]}=\frac{[n]_e}{[\eta]}+\frac{[n]_f}{[\eta]}=0,11\,\frac{b}{kT}\frac{\left(n_s^2+2\right)^2}{n_s}\left(\alpha_1-\alpha_2\right) \tag{17}$$

$$+\frac{1}{30\pi\rho^2 N_A RT}\frac{\left(n_k^2-n_s^2\right)^2}{n_s^3}\left(L_2-L_1\right)b\,\frac{M^2}{V}$$

$$=\frac{[n]_t}{[\eta]_t}\frac{n_t}{n_s}\frac{\left(n_s^2+2\right)^2}{\left(n_t^2+2\right)^2}$$

$$+\frac{M}{[\eta]}\frac{\left(n_k^2-n_s^2\right)^2}{n_s^3}\{(L_2-L_1)\,bf_0\}\frac{1}{120\,\pi\rho^2 RT},$$

which indicates that in one and the same solvent, in the presence of the effect of form ($n_k \neq n_s$), the quantity $[n]/[\eta]$ must depend on the molecular weight of the fraction. Actually, experiments with fractions of polystyrene in butanone ($n_k - n_s = 0.21$) showed a sharp increase of $[n]/[\eta]$ with an increase in the molecular weight of the fractions[15]. On the contrary, for fractions of polybutadiene[19] and polystyrene[15] in solvents with indices of refraction close to the index of refraction of the polymer ($n_k - n_s \approx 0$), the experiments disclosed the constancy of $[n]/[\eta]$ with a change in M, which is in full agreement with Eq. (17).

A comparison of the magnitudes of $[n]/[\eta]$ for the two fractions of polymethylmethacrylate investigated in the present work, in four solvents, is made in Table II. In the last column of the Table, the ratio X is given, of the magnitudes of $[n]/[\eta]$ corresponding to the fractions $M = 4.2\times10^6$ and $M = 3.5\times10^5$ in one and the same solvent. The value of X increases with an increase in $n_k - n_s$, in accordance with Eq. (17). For toluene ($n_k = n_s$) one would expect $X = 1$. The too-high value $X = 1.24$, found in the experiment, is apparently associated with the fact that in the calculation of the quantity $[n]/[\eta]$, the extrapolation of $[\eta]$ to $g \to 0$ was not made, which for the high-molecular fraction may introduce a noticeable error in a direction to increase the values of $[n]/[\eta]$.

We compared the experimental results with Eq. (5) of the theory of anisotropic complexes. A similar comparison can be made with Eq. (9) of the theory of elasto-viscous spheres. For this,

TABLE II. Comparison of the magnitudes of $[n]/[\eta]$ for two fractions of polymethylmethacrylate in various solvents.

Solvent	$n_k - n_s$	$[n]/[\eta]\cdot10^{10}$		$X=\left\{\left(\frac{[n]}{[\eta]}\right)_2 \Big/ \left(\frac{[n]}{[\eta]}\right)_3\right\}$
		$M=4.2\times10^6$	$M=3.5\times10^5$	
Toluene	0.002	1.24	1.00	1.24
Chloroform	0.054	3.95	1.48	2.66
Bromoform	0.098	8.44	2.11	4.00
Ethyl Acetate	0.128	25.80	5.45	4.75

TABLE III. Characteristic constants of macromolecules of poymethylmethacrylate according to the theory of elasto-viscous spheres.

Solvent	$M = 4.2\times10^6$			$M = 3.5\times10^5$		
	δ_0	p according to Eq. (22)	$\mu\cdot10^{-2}$	δ_0	p according to Eq. (22)	$\mu\cdot10^{-4}$
Bromoform	0.34	1.55	0,72	0.20	1.3	1,50
Chloroform	0.43	1.70	0,31	0.26	1.4	0.67
Ethyl Acetate	0.38	1.61	0,75	0.20	1.3	3.10
Chlorobenzene	0.27	1.41	1,17	—	—	—
	0.36	1.57	0,68	—	—	—
Acetone	0.38	1.61	0,93	—	—	—

the dynamo-optical constant Δ of Eq. (9) is transformed into the characteristic value $[n]$ of Eq. (5), by converting from the volume concentrations Ω to weight concentrations g /cm^3. Taking into account that in Eq. (9), $\Omega = VcN_A/M$, we obtain in place of (9),

$$[n] = \lim\left(\frac{\Delta n}{g\eta_0 c}\right)_{\substack{g\to0\\c\to0}} = \frac{5\varepsilon}{\mu}\theta\frac{n_s VN_A}{M} + \frac{2}{\mu}\left(\frac{n_\omega - n_s}{n_\omega}\right)^2\theta\frac{n_s VN_A}{M}, \tag{18}$$

and using Eqs. (1) and (2), we will have

$$[n]_e = 5n_s N_A\theta\frac{\varepsilon V}{\mu M}; \tag{19}$$

$$[n]_f = \frac{2}{\mu}\theta\frac{M}{V\rho^2 N_A}\frac{(n_k - n_s)^2}{n_s}.$$

It is convenient to modify expressions (19) somewhat, using in the formulas for $[n]_e$, the Einstein equation, appearing in the combination of (11) and (11′) for suspended spherical particles:

$$VN_A/M = [\eta]/2.5 \tag{20}$$

and introducing into the expression for $[n]_f$, the quantity δ_0 from Eq. (7) of the theory of elasto-viscous spheres. Then in place of Eq. (19) we obtain

$$[n]_e = 2n_s\theta[\eta]\varepsilon/\mu; \tag{21}$$

$$[n]_f = \frac{6M}{RT\rho^2}\frac{(n_k - n_s)^2}{n_s}\theta\delta_0^2.$$

Equations (21) apparently may be used for an approximate determination of the quantities ϵ/μ and δ_0 from the experimental data since variations of the unknown factor θ are insignificant ($1 \geq \theta \geq 3/5$). The quantity $[n]_e$ is obtained from measurements in toluene. According to the data in Table II, $[n]/[\eta]$ is close to 1×10^{-10} for both fractions in toluene. Therefore, assuming $n_s = 1.5$ and $\theta = 3/5$, we obtain $\epsilon/\mu = 5.5\times10^{-11}$ for both of the fractions investigated. Hence, taking Eq. (10) into account, it follows that $(n_1 - n_2)/n_\omega = 1.4\times10^{-10}\eta_0 g$. This means that the magnitude of the relative difference between the indices of refraction of the equivalent elasto-viscous sphere is determined by the magnitude of the shearing stress in the flow, and does not depend on the molecular weight (at least with a change of the latter from 3.5×10^5 to 4.2×10^6).

Expression (21) for $[n]_f$ is completely analogous in form to Eq. (14) and, therefore, conforms as well as Eq. (14), to the parabolic dependence $[n]_f = f(n_s)$ obtained experimentally. Values of δ_0 are given in Table III, calculated by Eq. (21) with the use of the experimental magnitudes of $[n]_f$ in Table I. Here, we have used $\theta = 3/5$, which corresponds to the case of pure orientation. In the case of pure deformation, $\theta = 1$, and the values of δ_0 become 1.3 times smaller than those given in Table III.

The ratios of the axes of the deformed sphere p may be calculated from the values of δ_0 according to the formula

$$p = (1 + \delta_0)^{3/2}. \tag{22}$$

The values thus obtained are represented in Table III. Combining Eq. (20) and the expression for $[n]_f$ in the form (19) yields

$$\mu = \frac{5\theta}{\rho^2[\eta][n]_f}\frac{(n_k - n_s)^2}{n_s}. \tag{23}$$

Relation (23) may be used for the determination of μ. The values of μ thus obtained are given in the last column of Table III. These values have the same order of magnitude in the various solvents and decrease with an increase of M, which is found fo be in agreement with the predictions of the theory of elasto-viscous spheres.

The coefficients of asymmetry δ_0 and p found by Eqs. (21) and (22) are practically the same for the various solvents and molecular weights. They are smaller in absolute value than the magnitudes of p calculated by Eq. (14), although of the same order of magnitude. However, the latter circumstance apparently is associated with peculiarities of the calculation of the optical effect of form in the theory of elasto-viscous spheres, because in principal, for the case of pure orientation ($\theta=3/5$), Eq. (21) could coincide exactly with Eq. (14) of the orientation theory. In any case, the values of p (or δ_0) from Eq. (14) as well as from Eq. (21) are sufficiently large. Therefore, even from the point of view of the theory of elastic spheres[10], it is not possible to neglect the effect of orientation in the region $g \to 0$ for the polymer $M = 4.2 \times 10^6$. However, the most serious difficulty in the interpretation of our results from the point of view of the model of elasto-viscous spheres is the fact that, for this model, δ_0 should decrease with an increase of the molecular weight of the sample, while the experimental data lead to the conclusion that δ_0 practically does not change with a change of more than a factor of ten in M.

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