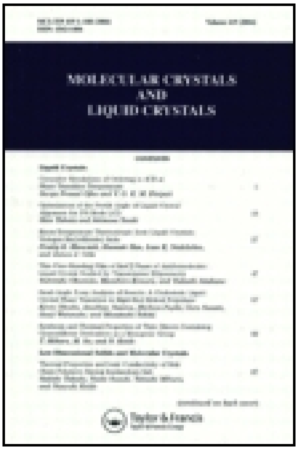

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Optical Anisotropy of Mesogenic Macromolecules with a Spacer in the Side Chain

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Optical Anisotropy of Mesogenic Macromolecules with a Spacer in the Side Chain

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Methods of translational diffusion, sedimentation, viscometry and flow and electric birefringence were used in the study of conformational properties of a number of comb-like polymers containing mesogenic side groups in dilute solution. Quantitative data on the degree of equilibrium rigidity of the main chain of these polymers were obtained by using modern theoretical concepts and hydrodynamic data. The value of optical anisotropy and the equilibrium and relaxation electro-optical properties of comb-like thermotropic macromolecules indicate that these macromolecules exhibit high intramolecular orientational and dipolar order. It is shown experimentally that in a comb-like molecule the increase in the distance between the mesogenic group and the main chain is accompanied by a sharp decrease in this intramolecular order.

INTRODUCTION

The study of the optical and electro-optical properties of comb-like macromolecules containing mesogenic chain side groups has revealed the existence of high intramolecular and dipolar orientational order.[1] As the experiments show,[1,2] the degree of this order at a molecular level depends on the chemical structure and length of the side chains.

The present paper considers the hydrodynamic, optical and electro-optical properties of a number of comb-like polymer molecules differing in the length of the aliphatic part of the side group substituent and in the character of the attachment of the mesogenic group (aromatic rings) to the main chain in dilute solution.

EXPERIMENTAL

Quantitative data on the conformation and intramolecular order of the macromolecules investigated were obtained by the methods of translational diffusion, sedimentation, viscometry and flow and electric birefringence.

For fractions of some comb-like macromolecules, the chemical formulae of which are listed in Tables I and II, the coefficients of translational diffusion D, sedimentation S and intrinsic viscosity $[\eta]$ were measured as a function of molecular weight M.

Diffusion coefficients D were determined for all the polymers studied with a polarizing diffusometer,[3] which made it possible to carry out measurements in the range of limiting low concentrations c of polymers and to obtain diffusion coefficients S_o extrapolated to zero concentration.

High-speed sedimentation of solutions of polymer fractions was investigated with an MOM (Hungary) analytical ultracentrifuge with a polarizing-interferometric attachment.[3] This instrument also made it possible to obtain sedimentation coefficients S_o at limiting low solution concentrations (i.e. $c \to 0$).

The molecular weights of fractions and samples of all the polymers investigated were determined, by using Svedberg's equation, from the experimental values of the diffusion, and sedimentation coefficients, D_o and S_o,

$$M = \frac{S_oRT}{D_o(1 - \bar{v}\rho)}$$

where R is the universal gas constant, T is the absolute temperature, ρ is the density of the solvent used and $\bar{v}$ is the partial specific volume of the polymer determined piconometrically for each polymer.

Table I gives the chemical formulae of the comb-like polymers investigated and the Mark-Kuhn equation relating the molecular weights M to intrinsic viscosities $[\eta]$. The values of $[\eta]$ are determined in capillary viscometers in the same solvents in which M was measured and at the same temperatures.

Flow birefringence for the polymers investigated here was measured with a visual instrument[4] in 3 cm dynamo-optimeters with inner rotors. The width of the rotor-stator gap in various instruments did not exceed $0.03\ 10^{-4}$ m. This fact permitted the operation in a laminar flow up to flow rate gradients $g \leqslant 10000$ s.$^{-1}$ in the solvents used.

RESULTS

Figure 1 shows a typical plot of the dependence of the birefringence Δn on flow shear stress $g\ (\eta - \eta_o)$, (η and η_o are the viscosities of the solution and the solvent, respectively) for polymer 2 in Table I in tetrachloromethane. The points with various symbols correspond to the experimental values of Δn obtained for fractions of different molecular weights. The slope of the dependence $\Delta n = f[g(\eta - \eta_o)]$ shown in Figure 1 yields the value of the optical shear coefficient $\Delta n/\Delta\tau$:

$$\frac{\Delta n}{\Delta\tau} \equiv \left[\frac{\Delta n}{g(\eta - \eta_0)}\right]_{\substack{g\to 0\\ c\to 0}} = \frac{[n]}{[\eta]} \quad \text{and} \quad [n] \equiv \lim_{\substack{g\to 0\\ c\to 0}} \frac{\Delta n}{gc\eta_0}.$$

The optical shear coefficients for the polymers investigated are given in Tables I and II.

Flow birefringence in an electric field was measured by a visual method.[4] Brace compensators with a path length difference not exceeding 0.03 of a wavelength of light (550 nm) were used. Kerr glass cells with titanium electrodes having the gaps of less than $0.5\ 10^{-2}$ m. and electrode length along the light beam path of $3\ 10^{-2}$ m. The measurements were carried out in the steady-state and sinusoidal electric fields in the frequency range of 20 Hz – 700 kHz and up to 3kV potential difference were applied to the samples. The concentrations of the solutions investigated ranged from 12.0 to 1.5 kg/m^3.

DISCUSSION OF RESULTS

Hydrodynamic properties

The dependence of the intrinsic viscosities $[\eta]$, the diffusion coefficients D_o and the sedimentation coefficients S_o on molecular weight M are listed in Table I and the following relations hold,

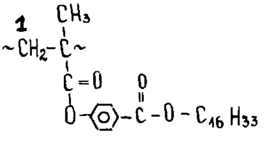
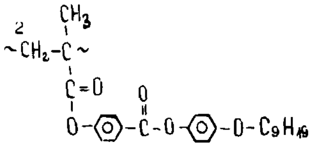
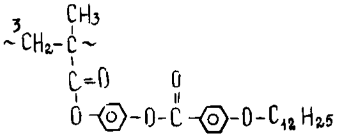
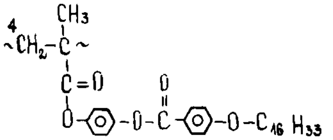
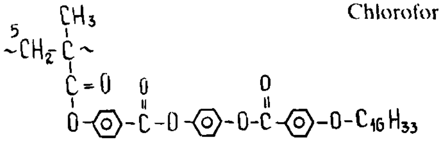
$$[\eta] = K_\eta M^a, \tag{1}$$

$$D_o = K_D M^{-b}, \quad \text{and} \tag{2}$$

$$S_o = K_S M^{1-b}. \tag{3}$$

TABLE I

Hydrodynamic, optical and electro-optical characteristics of comb-like

N	Monomer unit	Solvent	Range of $M \times 10^6$	$[\eta] = K_\eta M^a$ $D_0 = K_D M^{-b}$ $S_0 = K_s M^{1-b}$
1		Tetrachloromethane	(0.02 – 0.5)	$K_\eta = 3.73\ 10^{-3}$ $a = 0.8$ $K_d = 3.3\ 10^{-4}$ $b = +0.6$ $K_s = 8.1\ 10^{-15}$ $1 - b = 0.4$
2		Tetrachloromethane	(0.1 – 1.7)	$K_\eta = 4.4\ 10^{-2}$ $a = 0.5$ $K_D = 1.33\ 10^{-4}$ $b = +0.5$ $K_s = 2.1\ 10^{-15}$ $1 - b = 0.5$
3		Tetrachloromethane	(0.05 – 1.6)	$K_\eta = 1.6\ 10^{-2}$ $a = 0.5$ $K_D = 1.8\ 10^{-4}$ $b = 0.5$ $K_s = 2.83\ 10^{-15}$ $1 - b = 0.5$
4		Tetrachloromethane	(0.5 – 20)	$K_\eta = 3.3\ 10^{-2}$ $a = 0.5$ $K_D = 0.62\ 10^{-4}$ $b = +0.5$ $K_S = 2.54\ 10^{-15}$ $1 - b = 0.5$
5		Chloroform	(0.01 – 1.3)	$K_\eta = 1\ 10^{-1}$ $a = 0.5$ $K_D = 1.97\ 10^{-4}$ $b = +0.5$
		Benzene		$K_\eta = 2.04\ 10^{-2}$ $a = 0.5$

The character of each dependence ($a = 0.5$ and $b = 0.5$) for polymers 2-5 in Table I agrees with the constancy of experimental values of the hydrodynamic constant A_o for various fractions.[5]

The general characteristic feature of comb-like polymers with mesogenic groups listed in Table I (2-5) is the equality of the exponents macromolecules containing mesogenic side groups in dilute solution

$A \times 10^8$	$d \times 10^8$	$[n]/[\eta] \times 10^{10}$	$(\alpha_1 - \alpha_2) \times 10^{25}$	$\Delta\alpha_m \cdot 10^{25}$	$K \times 10^{10}$
64 ± 10	22 ± 2	−35	−445	−18	−0.5
40 ± 5	22-18	−220	−2700		−(3.1 to 8)
42 ± 5	15 ± 2	−190			
55 ± 5	19 ± 2	−220	−2700	−110	−(4 to 20)
125 ± 5	43 ± 2	−390	−4900	−100	
50 ± 5	18 ± 2	−245	−3000	−150	

in the Mark-Kuhn equation, $a = 0.5$. This equality indicates that the molecules of these polymers are non-draining and that volume effects in the molecular weight range investigated are virtually absent. Hence, it is possible to find the length of the statistical Kuhn segment A, the degree of equilibrium rigidity of the main chain, from the values of

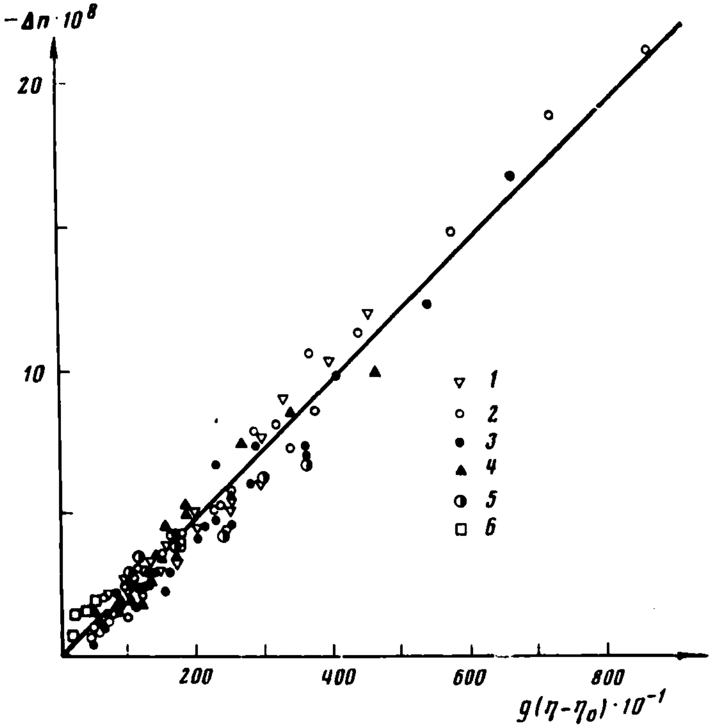


FIGURE 1 Value of flow birefringence Δn vs shear stress g $(\eta - \eta_o)$ for polymer 2 in Table I in tetrachloromethane. The points corresponds to molecular weights 1) $M = 1.7 \times 10^6$; 2) $M = 0.91 \times 10^6$, 3) $M = 0.85 \times 10^6$, 4) $M = 0.8 \times 10^6$, 5) $M = 0.46 \times 10^6$ and 6) $M = 0.12 \times 10^6$ daltons.

pre-exponential factors in eqs. (1)–(3) from the data of both the measurements of translational diffusion (or sedimentation) i.e.

$$K_D = \frac{RT}{\bar{\upsilon}\rho - 1}, \qquad K_S = \frac{k_B T}{P_o \eta_o} \cdot \left(\frac{M_o}{A\lambda}\right)^{1/2} \tag{4}$$

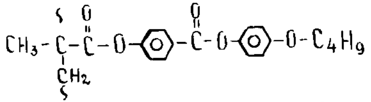
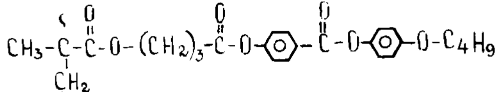
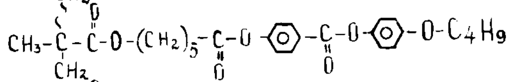
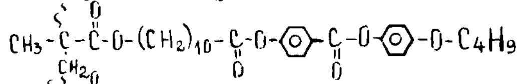
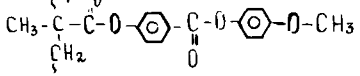
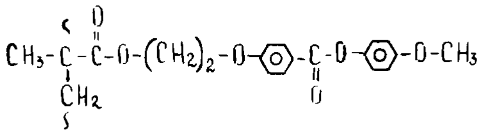
and for the viscometric data i.e.

$$K_\eta = \Phi_o \left(\frac{A\lambda}{M_o}\right)^{3/2}. \tag{5}$$

In Eqs. (4) and (5) k_B is Boltzmann's constant, Φ_o is Flory's constant, P_o is the hydrodynamic constant of translational friction,[5] M_o is the molecular weight of the monomer unit of the molecule and λ is the length of the projection of the monomer unit on the direction of the main chain. For the polymers listed in Table I λ is 2.5 Å.

TABLE II

Optical and electrooptical characteristics of comb-like macromolecules containing mesogenic side groups in dilute solution

N	Monomer unit	Solvent	Range of M × 10^6	$\frac{[n]}{[\eta]} \times 10^{10}$	K × 10^{10}
1		Dioxane	(0.25 to 2.5)	−(22 to 28)	
2		Dioxane	(0.46 to 2)	−7	
3		Dioxane	(0.38)	−(23 to 25)	
4		Dioxane	(0.06 to 1.5)	−8.5	−0.8
5		Tetrachloroethane	0.42	−40	
6		Tetrachloroethane	0.042	−10	

The values of the Kuhn segments are determined from the data of intrinsic viscosity by using the theoretical values of Flory's constant $\Phi_o = 2.87\ 10^{23}$ and eq. (5). Table I gives the average values of A for a number of comb-like polymers.

The data in Table I show that, just as for previously studied comb-like macromolecules,[1] for those of thermotropic polymers containing mesogenic fragments in the side chains, the rigidity of the main chain increases with the length of the substituent side chain. The observed equilibrium rigidity exceeds that of flexible polymer molecules by three or four times and increases with the length of the aliphatic chain upon passing from polymers 2, 3 and 4 to polymer 5. (Table I). This increase in the rigidity of the main chain of comb-like macromolecules is due to an increase in the intramolecular interaction between the mesogenic side chains.

Figure 2 shows the dependence of intrinsic viscosity $[\eta]$ on the square root of the degree of polymerization of the molecule Z. The increase in the slope of the straight line $[\eta] = f(Z^{1/2})$ reflects an increase in the segment length of the molecule with increasing length of the side group.

In accordance with the hydrodynamic theories for non-draining Gaussian coils without volume effects,[6,7] the connection between the values of hydrodynamic diameter, d, and equilibrium rigidity, A, of the chain obeys the relation $\ln A/d = Q$ where $Q = 1.43$ [6] and $Q = 1.056$.[7] The values of hydrodynamic diameters calculated according to ref. 7 are given in column 7 of Table I. These high values of the diameter of the molecule d, lying in the (15–40) Å range, reflect the characteristic increase in the diameter of comb-like macromolecules with these very long side branches and are in reasonable agreement with the geometric length of the side groups.

Optical properties

Flow birefringence observed for the comb-like polymers listed in Tables I and II and characterized by the value of shear optical coefficient $[n]/[\eta]$ is negative in sign. The negative sign of this value implies that long side groups exhibit high positive optical anisotropy in a system of its own axes, i.e., the optical polarizability of the monomer unit is higher in the direction perpendicular to the polymer backbone. This property is characteristic of all comb-like macromolecules[1] and is an experimental confirmation of the comb-like structure of the molecule rather than of its possible branching.

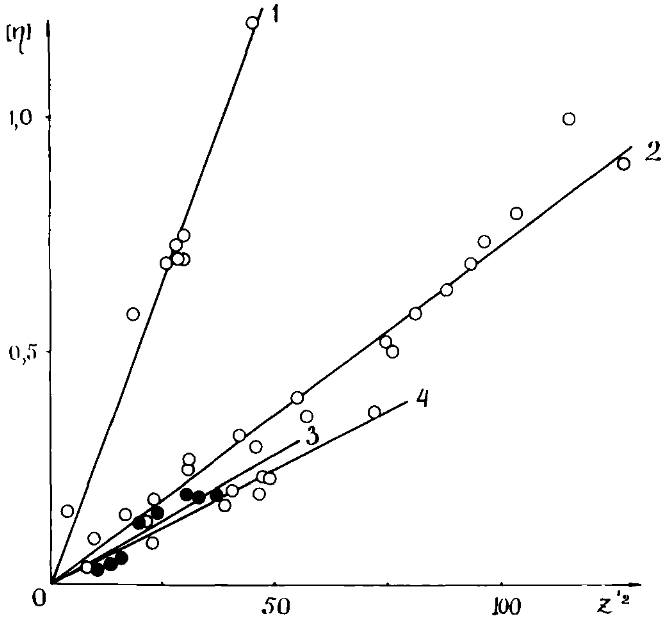


FIGURE 2 Intrinsic viscosity [η] of fractions of comb-like polymers vs degree of polymerization of the polymer $Z^{1/2}$. Numbers on curves are: 1—polymer 5; 2—polymer 4, 3—polymer 3; 4—polymer 2 all in Table I.

In the molecular weight range investigated the observed birefringence, as a function of the optical anisotropy of the segment,[3] $\alpha_1 - \alpha_2$, is virtually independent of molecular weight. This feature is characteristic of polymers exhibiting a relatively high flexibility of the main chain and quantitatively characterised on the basis of hydrodynamic data. This implies that the increase in the equilibrium rigidity of the main chain observed for comb-like macromolecules is not sufficient for the appearance of the dependence of the optical anisotropy or $[n]/[\eta]$ on the molecular weight[4] which is characteristic of rigid-chain macromolecules.

In accordance with the theory of optical anisotropy of Gaussian chains[4] it is possible to determine the optical anisotropy of the segment, $\alpha_1 - \alpha_2$, from the experimental value of the shear optical coefficient, $[n]/[\eta]$, according to Kuhn's equation:[8]

$$\frac{[n]}{[\eta]} = \frac{4\pi(n_s^2 + 2)^2}{45nk_BT} \cdot (\alpha_1 - \alpha_2) \tag{6}$$

where n_s is the refractive index of the solvent used.

The values of $\alpha_1 - \alpha_2$ calculated from eq. (6) are given in Tables I and II. For comparison Table I lists a comb-like polymer (I) the side chains of which contain no mesogenic fragments: a polymer of cetyl ester of n-methacryloyloxybenzoic acid.

The optical anisotropy of the molecule (values of $[n]/[\eta]$ and $\alpha_1 - \alpha_2$) is determined by the chemical structure of the molecule which gives use to $\Delta\alpha_m$ (where $\Delta\alpha_m$ is the optical anisotropy of the monomer unit) and by the degree of its intramolecular order. The value of A or S (S is the number of monomer units in a segment, $S = A/\lambda$) i. e. $\alpha_1 - \alpha_2 = \Delta\alpha_m \cdot S$.

The experimentally observed values of $[n]/[\eta]$ and $\alpha_1 - \alpha_2$ for thermotropic polymers (with the order of magnitude close to that of the corresponding characteristics of rigid-chain polymer molecules[4]) are not due to the high values of S but are determined by the high values of the anisotropy of the monomer unit, $\Delta\alpha_m$. This exceeds by almost one order of magnitude those values for both the comb-like polymer listed in Table I, for comparison, and those for rigid-chain polymers. This fact reflects the high intramolecular orientational order. The generation of this order and the ability of the molecules of the thermotropic polymers investigated to form ordered structures in dilute solutions is due to the interaction between mesogenic side groups. The study of copolymers based on phenylmethacrylic esters of cetyloxybenzoic acid (polymer 4 in Table I) and cetyl methacrylate has made it possible to establish quantitatively[2] that the value of the optical anisotropy of molecules containing mesogenic groups is caused not only by the anisotropy of side groups themselves but also by their ordered arrangement with respect to the main chain.

The investigation of the optical anisotropy of macromolecules of polymers listed in Table II shows that intramolecular order strongly depends not only on the structure of the mesogenic side group of the molecule but also on the character of inclusion of the mesogenic fragment into the side chain.

The data in Table II indicate that on passing from polymer 1 to polymers 2, 3 and 4 and from polymer 5 to polymer 6 (the comparison was carried out in the same solvent) the shear optical coefficient (and, correspondingly, the optical anisotropy) decreases several times. Hence, the contribution provided by the anisotropy of side group to the optical anisotropy of the molecule as a whole decreases, although the length of this group increases. This decrease is due to a higher freedom of rotation of the mesogenic group, which leads to a decrease in the optical anisotropy of the molecule. Similar experimental facts have been observed in the investigation of a number of flexible chain polymers containing optically anisotropic side groups.[3]

For polymers 2, 3, 4 and 6 in Table II this increase in the distance between the mesogenic group and the main chain and the increase in its freedom of rotation are accompanied by a decrease in the interaction between the mesogenic fragments and the disappearance of high intramolecular orientational order.

Electro-optical properties

A combination of the relatively low equilibrium rigidity of the main chain and the presence of long side chains containing mesogenic fragments leads to unique electro-optical properties of comb-like macromolecules.

In the steady-state using low-frequency sinusoidal electric fields on solutions of polymers 1, 2 and 4 (Table I) the birefringence Δn was negative in sign and proportional to the square of the field strength E^2 for all of the solutions investigated in accordance with the Kerr law (Figure 3).

Specific Kerr constants $K = \Delta n/cE^2$ were determined from the slopes of the straight lines plotted in Figure 3 for each concentration c of polymer 2 (Table I). The concentration dependence of K in the concentration range studied K was virtually independent of concentration (Figure 4). The values of K (Table I) exceed by two orders of magnitude those for flexible-chain polymers and exhibit a dependence on the molecular-weight of fractions characteristic of polymers with a high equilibrium chain rigidity. In accordance with this, the analysis of experimental data is carried out with the aid of the theory of electric birefringence for rigid-chain polymers exhibiting the orientational polarization mechanism.[4] According to this theory, the Kerr constant K depending on the reduced chain length, $x = 2M/M_oS$, is given by:

$$K = \mathbf{B}K_\infty[1 - 0.6\tan^2\vartheta\mathbf{A}]\cdot\frac{3}{5}\cdot\frac{\langle h^4\rangle}{\langle h^2\rangle^2} \tag{7}$$

where

$$\mathbf{A} = \frac{x - 1 + e^{-x}}{x^2 - 0.8(x - 1 + e^{-x})}; \qquad \mathbf{B} = \frac{(x - 1 + e^{-x})^2}{x^2 - 0.8\,(x - 1 + e^{-x})}$$

and $\langle h^2\rangle$ and $\langle h^4\rangle$ are the second and the fourth moments of Gaussian distribution of the end-to-end distances h of an assembly of wormlike chains. The value of K_∞ is the limiting value attained by K in the Gaussian range and expressed by the equation:

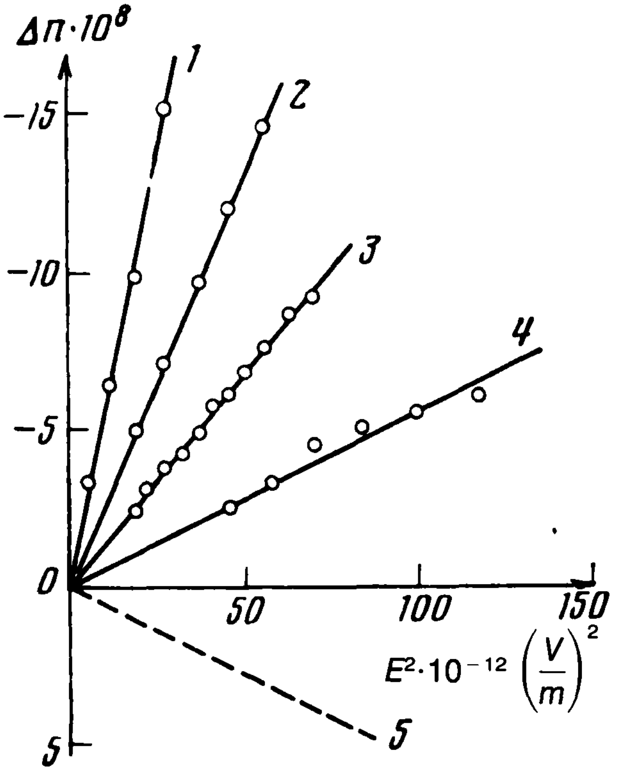


FIGURE 3 Value of the electric birefringence Δn vs square of electric field strength $E^2\left(\frac{V}{m}\right)^2$ for solutions of fractions of polymer 2 (Table I) in tetrachloromethane at the following concentrations: 1) $C = 8.64$, 2) $c = 4.94$, 3) $C = 2.74$, 4) $C = 1.62$ kg/m^3. Broken line 5 refers to pure tetrachloromethane.

$$K_\infty = \frac{2\pi \mathcal{N}_A (n^2 + 2)^2 (\epsilon + 2)^2 (\alpha_1 - \alpha_2) \mu_o S^2 \cos^2 \vartheta}{1215 n (k_B T)^2 M_o} \tag{8}$$

where μ_o is the dipole moment of the monomer unit, ϑ is the angle formed by the direction of the dipole moment μ_o and the chain direction, M_o is the molecular weight of the monomer unit, ϵ and n are the dielectric constant and the refractive index of the solvent and $\mathcal{N}_A$ is Avogadro's number. This plot is shown for polymer 2 (in Table I) in Figure 5.

Using the value of equilibrium rigidity S obtained from hydrodynamic data and selecting the limiting value of the Kerr constant $K_\infty = 9\ 10^{-10}$ cm^{5}g^{-1}(stat volt)$^{-2}$, it is possible to superpose the exper-

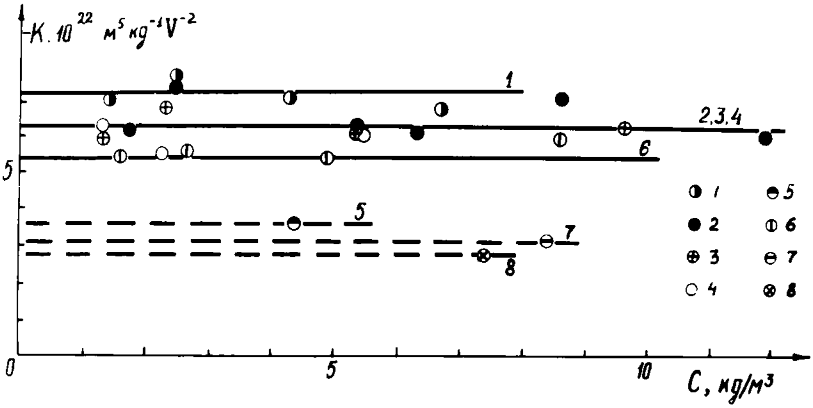


FIGURE 4 Specific Kerr constant K for fractions of polymer 2 in Table I vs solution concentration c in tetrachloromethane.

imental dependence $K = K(x)$ and the theoretical curve over the range of angles $\vartheta = 75 - 80°$ (Figure 5). A considerable deviation of angle ϑ from 0° is an experimental confirmation of the fact that polar side groups of the polymer chain provide a considerable contribution to the dipole moment of the monomer unit. Using the value of $\alpha_1 - \alpha_2 = 2700\ 10^{-25}\text{cm}^3$ (according to flow birefringence data) and the experimentally determined angle $\vartheta = (77 \pm 3)°$, we find according to Eq. (8) the values of $\mu_o = (1.6 \pm 0.3)\ D$ and $\mu_{o\parallel} =$

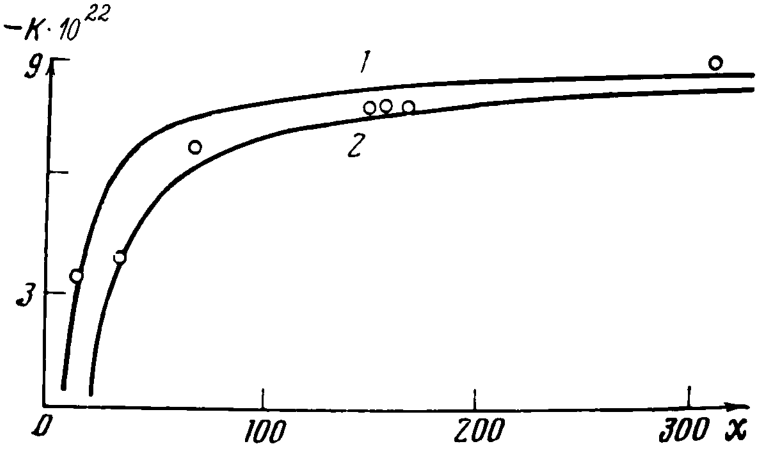


FIGURE 5 Value of K vs x (points) for solutions of fractions of polymer 2 in Table I. Curves 1 and 2 are plotted according to Tsvetkov's theory of electric birefringence[4] for kinetically rigid wormlike chains at the values of $\vartheta = 75°$ and 80°, respectively.

$\mu_0 \cdot \cos\vartheta \simeq (0.4 - 0.1)\,D$ ($1D = 1 \times 10^{-18}$ cgs). These values are in reasonable agreement with the structure of the monomer unit of polymer 2 (Table I) and close to the corresponding values found for other comb-like molecules with mesogenic side chains.[1,2]

Hence, in the investigation of solutions of polymers 2 and 4 (Table I), the following equilibrium electro-optical properties are established: (i) a high negative value of the Kerr constant characteristic of rigid-chain polymers, (ii) the coincidence of the signs of the Kerr and Maxwell effects in the investigation of the polymer in the same solvent and (iii) the experimental dependence of the specific Kerr constant on molecular weight which may be adequately interpreted in terms of the theory of electric birefringence for rigid-chain polymers. All these experimental data indicate that the orientation of polar groups of these polymers in the electric field occurs by the mechanism of large-scale intramolecular motion characteristic of rigid-chain polymers. This conclusion is confirmed by the non-equilibrium electrooptical properties considered below.

Figure 6 demonstrates the existence of a low-frequency dispersion in solutions of fractions of polymer 2 (Table I). The values of the specific Kerr constant K determined from the slopes of straight lines

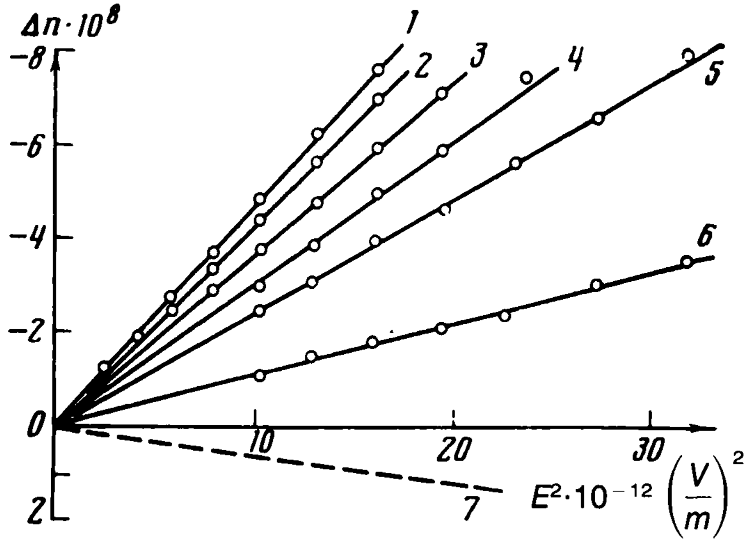


FIGURE 6 Value of the electric birefringence Δn vs square of electric field strength $E^2\left(\frac{V}{m}\right)^2$ for solutions of a fraction ($M = 3.6\ 10^5$) of polymer 2 in Table I in tetrachloromethane at a concentration of 9.7 kg/m^3 and frequencies 1) 0.2, 2) 5, 3) 10, 4) 15, 5) 40 and 6) 700kHz. Broken line 7 refers to pure tetrachloromethane.

in Figure 6 decrease markedly with increasing field frequency ν. In this case the dispersion range of the Kerr effect depends on molecular weight. The relaxation of the relative value of the Kerr constant K_ν/K is shown in Figure 7 for all fractions. The dependence shown in Figure 7, i.e. $K_\nu/K = f(\log \nu)$, was used for the determination of the frequencies $\nu_{0.5}$ at which the value of the Kerr constant decreased by a factor of two (i.e. $K_\nu/K = 0.5$). Here K and K_ν are the specific Kerr constants in the plateau region and that in the dispersion at the $\nu_{0.5}$ frequency, respectively.

Strictly speaking, the relaxation curves obtained are described by a spectrum of relaxation times, which may be related both to the molecular weight polydispersity and to the manifestation of intramolecular motions on various scales. However, for comparison of the dispersion curves obtained for the various fractions each curve may be characterized by the average times of dipole relaxation[9] i.e. $\bar{\tau} = 1/2\ \pi\nu$ using the frequency values $\nu_{0.5}$ extrapolated to zero concentrations c. The $\bar{\tau}$ values obtained by this procedure increase with molecular weight.

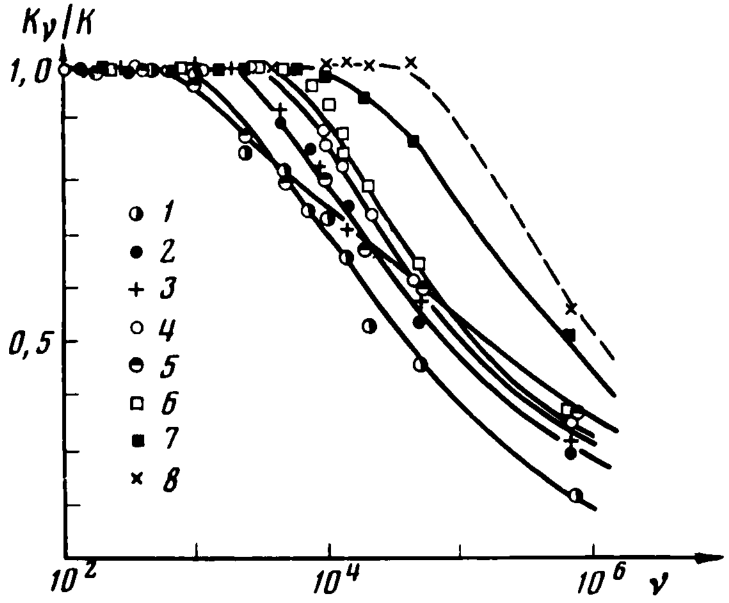


FIGURE 7 Relative value of the Kerr constant K_ν/K vs ν, the frequency of the electric field for solutions of fractions of polymer 2 in Table I in tetrachloromethane. Numbers are numbers of fractions with M: $-1-M = 17 \cdot 10^5$, $2-M = 9.1 \cdot 10^5$, $3-M = 8.5 \cdot 10^5$, $4-M = 8.4 \cdot 10^5$, $5-M = 4.6 \cdot 10^5$, $6-M = 3.6 \cdot 10^5$, $7-M = 1.8 \cdot 10^5$ and $8-M = 1.2 \cdot 10^5$.

The coefficient G, the value of which depends on the type of motion of the polymer chain in the electric field, was calculated by using the experimental values of τ, M and $[\eta]$ according to the equation:

$$\tau = G\frac{M[\eta]\eta_o}{RT} \tag{9}$$

The experimental values of G decrease with increasing M (Figure 8), which indicates that increasingly higher modes of intramolecular motion[9] are successively included in this motion (with increasing M). In accordance with the determination of the kinetic segment,[9] it may be assumed that in the molecular-weight range investigated the macromolecules of polymer 2 (Table I) contain from one to three of such segments. These kinetic segments which cover a considerable part of the main chain are probably formed as a result of specific interactions between mesogenic side groups of a comb-like molecule. As a result, with increasing molecular weight the properties of the molecule vary from those of a kinetically rigid coil to those of a kinetically flexible coil.

This is also confirmed by Figure 9 which shows the Kuhn-Hirst plot[8,10] constructed according to Eq. (10) and valid for molecules rotating as a whole in a frozen conformation of a rigid Gaussian coil

$$\frac{\eta_o D_r M^2}{K_B T} = 0.72\left[\left(\frac{M_o}{\lambda^2 S}\right)^{3/2} M^{1/2} + \left(\frac{M_o}{\lambda}\right)^2 \frac{1}{\lambda S} 0.884\left(\ln\frac{\lambda S}{d} - 1.43\right)\right] \tag{10}$$

The points in Figure 9 represent the experimental molecular weight dependence of the value of $\eta_o D_r M^2/k_B T$ where $D_r = 1/2\bar{\tau}$ is the rotational diffusion coefficient of the macromolecule determined by the time of dipole-orientational relaxation $\bar{\tau}$ of the Kerr effect.[11] Figure 9 shows that the experimental dependence at low M values may be represented by a straight line passing through the origin. This implies that in this range the rotational diffusion coefficient increases proportionally to $M^{1.5}$ with increasing molecular weight, which corresponds to the properties of a rigid non-draining Gaussian coil.[9] The deviation of experimental points upwards from the theoretical straight line at high M indicates that the motion of the molecule in the electric field in this molecular-weight range cannot take place by the mechanism of rotation as a whole but should include segmental motion the significance of which increases with M.

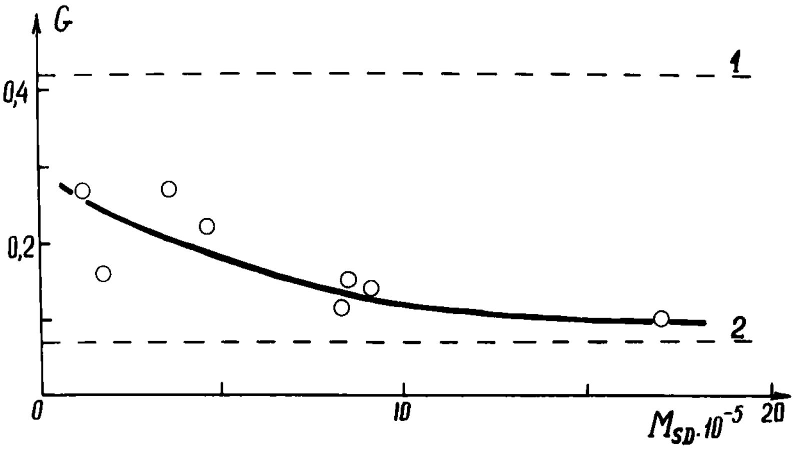


FIGURE 8 Coefficient G vs molecular weight of fractions of polymer 2 in Table I in tetrachloromethane.

According to Eq. (10), the initial slope of the curve at low molecular weights is 0.72 $(M_o/\lambda^2 S)^{3/2}$ and enables us to establish the value of equilibrium chain rigidity $S = 26$ at $M_o = 424$ and $\lambda = 2.5\ 10^{-10}$ m. This value, $S = 26$, corresponds to that obtained from the experimental data on the translational friction of this polymer.

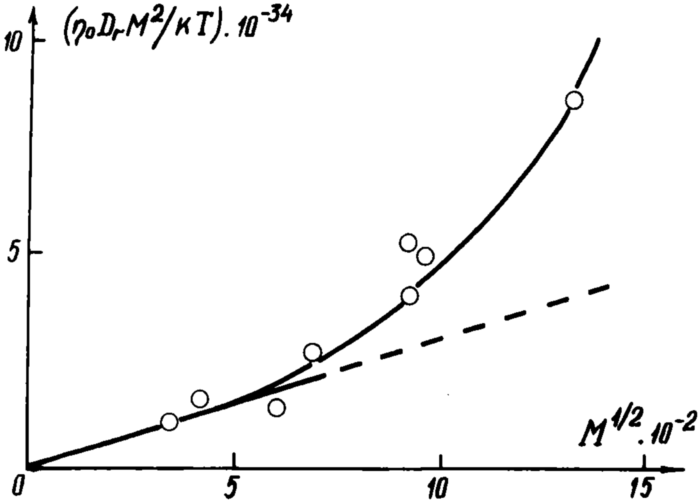


FIGURE 9 Value of $\eta_0 D_r M^2/k_B T$ vs $M^{1/2}$ for fractions of polymer 2 in Table I in tetrachloromethane. The straight line is plotted according to the theory in ref. 10 at $S = 26$.

Similar experimental electro-optical investigations were carried out for a comb-like polymer (polymer 4 in Table II) the mesogenic portion of the side group of which is separated from the main chain by a flexible spacer $(CH_2)_{10}$. They showed that the specific Kerr constant for this polymer in dioxane is also negative in sign but it's absolute value is lower by almost one order of magnitude in comparison with that for polymers 2 and 4 in Table I. Just as for polymers in Table I, the negative sign of the Kerr constant indicates that in the electric field the side groups of polymer 4 in Table II are oriented with their longitudinal axis normal to the field and, hence, this orientation correlates with the direction of the main chain. However, no dispersion in the radio-frequency range was detected. This fact implies that the molecules of polymer 4 in Table II behave as kinetically flexible chains in which the Kerr effect is determined by intramolecular small-scale motion, moreover, the size of kinetic units is much smaller and their mobility is much higher than for polymers 2 and 4 in Table I. A markedly low value of the specific Kerr constant is also an indication of this.

Using the results of dynamo-optical investigations of polymer 4 in Table II $(\alpha_1 - \alpha_2)$, it is possible to determine from Eq. (8) at $M_o = 523$ and $S = 26$ the component of the dipole moment of the monomer unit $\mu_{o\parallel} = 0.4$ D correlating with the chain direction L and responsible for the Kerr effect in the Gaussian range of M values. The value of $\mu_{o\parallel}$ found here is close to the corresponding value obtained for polymers without a spacer (polymer 2 in Table), which is in reasonable agreement with the structure of monomer units of the polymers investigated.

Hence, a comparison of electro-optical properties of polymers 2 and 4 in Table I and of polymer 4 in Table II showed that the separation of the mesogenic part of the side group from the main chain by the introduction of a flexible polymethylene spacer between them leads to a sharp decrease in the correlation between the orientation of the side groups and of the main chain and as a result, to decrease in intramolecular order.

At the same time the weakening of orientational correlation between the main chain and the mesogenic side part of the mesogenic molecule in the bulk of the polymer favours the generation of orientational order between the side groups of different molecules and thus facilitates the formation of the mesomorphic structure in the polymer.[12]

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