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Electrical birefringence in solutions of rigid-chain polymers

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Abstract. Experimental and theoretical aspects of the application of steady and transient electrical birefringence methods to dilute solutions of rigid-chain polymers are examined. The prospects of using the Kerr effect to study the conformational and the structural characteristics of macromolecular chains are analysed. The effect of the polarity of the medium on the electro-optical properties of polymeric molecules is discussed. The bibliography includes 117 references.

I. Introduction

The wide interest which studies of the molecular properties of rigid-chain polymers have attracted is due partly to the extensive industrial applications of materials based on these polymers and partly to the increasing need for general concepts concerning the structure and the physical properties of macromolecular compounds.

Latterly we have witnessed an increasing interest in studies of rigid-chain polymers able to undergo thermotropic and lyotropic mesomorphism, such as aromatic polyesters and polyamides, and also cellulose esters. This interest has been stimulated by the applications of substances of this type in various electronic devices and by improvements in the technology of polymer processing.

The structure and the conformation of the molecules of rigid-chain polymers, which are responsible for the unique properties of the materials prepared from these polymers, are determined by studying the behaviour of their macromolecules in very dilute solutions, in which the intermolecular interaction of the polymer chains is negligibly small. The measurement of electrical birefringence (EBR, the Kerr effect) is one of the most important methods of studying the conformational and the kinetic characteristics of rigid-chain polymers in dilute solutions, since it provides information on the structural and the dynamic properties of rigid-chain macromolecules which is needed in order to identify the interrelationship between the molecular structure and the physical properties of the polymers. This information is an essential first step in the creation of new materials having prescribed properties.

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II. Theoretical aspects and experimental procedure

1. Theory of the steady Kerr effect for rigid molecules

In 1875 Kerr established[1] that a transparent isotropic substance exposed to an electric field acquires the optical properties of a uniaxial crystal with its axis parallel to the field. In the case of weak DC fields the optical anisotropy generated in the substance is proportional to the square of the field intensity (Kerr's law):

$$\frac{\Delta n}{n} \equiv \frac{n_p - n_s}{n} = K_e E^2 . \quad (1)$$

Here $\Delta n = n_p - n_s$ is the difference between the refractive indices (extraordinary n_p and ordinary n_s) for two light rays with electric vectors oscillating in directions parallel and perpendicular to the electric field respectively; E is the intensity of the electric field, directed at right angles to the light rays; n is the average refractive index of the substance; K_e is the Kerr constant.

The electro-optical properties of substances are often described in terms of the specific Kerr constant K_ρ defined as

$$K_\rho = \frac{\Delta n}{\rho E^2} , \quad (2)$$

where ρ is the density of the liquid.

In the case of a solution the EBR caused by the presence of the solute can be characterised by the Kerr constant of the latter, defined by the expression

$$K = \lim_{E \to 0,\, c \to 0} \frac{\Delta n}{cE^2} , \quad (3)$$

where Δn is the excess difference in refractive indices, due to the solute, and c is the concentration of solute (g cm^{-3}).

The molar Kerr constant ${}_mK$, defined (according to Debye[2]) by the expression

$${}_mK = \frac{6K_\rho Mn}{[(n^2+2)(\varepsilon+2)]^2} , \quad (4)$$

is sometimes used to characterise the molecular properties of liquids. Here M is the molecular weight of the liquid and ε is its dielectric permittivity.

The molar Kerr constant ${}_mK_{12}$ of a two-component solution is an additive quantity, expressed in terms of the molar Kerr constants of the solvent ${}_mK_1$ and of the solute ${}_mK_2$ (see Stuart[3]):

$$ {}_mK_{12} = (1-f_2){}_mK_1 + f_2\,{}_mK_2 , \tag{5}$$

where f_2 is the mole fraction of the solute.

It follows from Eqns (3)–(5) that the molar constant of the solute extrapolated to zero concentration (${}_mK_{c\to 0}$) is given by

$$ ({}_mK)_{c\to 0} = \frac{6KnM}{[(n^2+2)(\varepsilon+2)]^2} . \tag{6}$$

Here n and ε are the refractive index and the dielectric permittivity of the solvent respectively.

The theories of Langevin[4] and Born,[5] developed for gases, relate the constant ${}_mK$ of a substance to the principal components of the tensor of the optical (γ_1, γ_2, γ_3) and the dielectric polarisabilities (δ_1, δ_2, δ_3) of the molecule and to the corresponding components (μ_1, μ_2, μ_3) of its dipole moment by the expression

$$ {}_mK = \frac{2\pi N_A}{405kT}\left[\sum_{i,j=1}^{3}(\gamma_i-\gamma_j)(\delta_i-\delta_j) + \frac{1}{kT}\sum_{i,j=1}^{3}(\gamma_i-\gamma_j)(\mu_i^2-\mu_j^2)\right] , \tag{7}$$

where N_A is Avogadro's number.

It should be noted that Eqn (7) does not contain terms explicitly dependent on the state of aggregation of the substance. This explains the many reported attempts to use the equation in descriptions of the electro-optic properties not only of gases but also of liquids and solutions. Experiments have shown[3] that Eqn (7) adequately describes those properties in the case of polar molecules and of nonpolar substances not only in the gas phase but also in their solutions in nonpolar solvents, but in the case of polar (conducting) liquids and of solutions in polar solvents the equation is unacceptable.

For substances in dilute solutions and consisting of molecules having axially symmetrical optical and dielectric properties the constant K in Eqns (6) and (7) is given by

$$ K = \frac{2\pi N_A}{135kTn}\left[\frac{(n^2+2)(\varepsilon+2)}{3}\right]^2 \frac{\gamma_1-\gamma_2}{M} \times\left[\delta_1-\delta_2+\frac{\mu^2}{kT}\,\frac{3\cos^2\theta-1}{2}\right] , \tag{8}$$

where θ is the angle defined by the dipole μ and the axis of symmetry of the optical and of the dielectric polarisability (γ_1 and δ_1).

Eqn (8) shows that the sign of K depends on the magnitude and direction (angle θ) of the dipole moment of the molecule. Thus for nonpolar molecules ($\mu = 0$) the Kerr constant is always positive, because the signs of $(\gamma_1-\gamma_2)$ and $(\delta_1-\delta_2)$ are the same. For strongly polar molecules, in which the term $\delta_1-\delta_2$ can be ignored, the Kerr effect is positive for $\theta < 54.72°$ and negative for $\theta > 54.72°$.

We should stress the fact that the Langevin–Born theory, which leads to Eqns (7) and (8), relies on the assumption that the potential energy of the molecules associated with their rotation in an electric field is small in comparison with the energy of the thermal motion, $\mu\epsilon/kT \ll 1$ and $(\delta_1-\delta_2)\epsilon^2/kT \ll 1$, where ϵ is the field acting on the molecule [according to Lorentz $\epsilon = E(e+2)/3$]. In the opposite case the dependence of Δn on E^2 reaches saturation (see Kuhn et al.[6] and O'Konski et al.[7]).

2. Transient electrical birefringence

The study of the electro-optical properties of molecules under the influence of electrical pulses of various forms yields valuable information on their rotational mobility and justifies a number of conclusions on the nature of the EBR under study (is it due mainly to the presence of a constant dipole moment in the molecule, or to the anisotropy of its dielectric polarisability, or even to a combination of these factors).

These possibilities arise because the reorientation of the molecules under the influence of the electric field is not instantaneous, but requires a certain time, depending both on the rotational diffusion coefficient of the particles D_r and on the nature of the observed effect. Experiments of this type are difficult when the samples under study are low-molecular substances, because the molecular reorientation times are very short in these materials (10^{-11}–10^{-9} s). However, in solutions containing supermolecular species or rigid macromolecules the reorientation times are significantly longer, and they can be measured electrooptically.

Rectangular-pulse and sinusoidal periodic fields are the types of field most often used in studies of the relaxation processes. The pulsed field method was proposed independently by Russian[8] and by French physicists.[9,10]

The disappearance of the EBR in a monodispersed system of rigid particles or molecules with an axial symmetry of form and of optical properties following the instantaneous switching off of the field is determined only by their spontaneous disorientation as a result of thermal rotation, is independent of the electrical properties of the species, and is described by the expression[9,10]

$$ \Delta n = \Delta n_0\, e^{-t/\tau_0} , \tag{9}$$

where Δn_0 is the initial EBR of the system in a steady field, t is the time, and τ_0 is the relaxation time,

$$ \tau_0 = \tfrac{1}{6}D_r . \tag{10}$$

Here D_r is the diffusion coefficient of the particles rotating round their short axis (normal to the axis of symmetry). The rate of the establishment of the EBR by switching on the electric field is determined not only by the thermal motion of the particles but also by the electrical properties of the molecules.

For axially symmetric particles, in which the vector or the dipole moment μ is parallel to the axis of symmetry, the dependence of Δn on t when the field has been switched on ($\mu\epsilon/kT \ll 1$) is described by the expression[9,10]

$$ \frac{\Delta n}{\Delta n_0} = 1 - 3\frac{\alpha^2}{\beta}\left(\frac{2\alpha^2}{\beta}+4\right)^{-1} e^{-t/\tau} + \left(\frac{2\alpha^2}{\beta}+4\right)^{-1}\left(\frac{\alpha^2}{\beta}-4\right)e^{-t/\tau_0} , \tag{11}$$

where

$$ \tau = \tfrac{1}{2}D_r ; \quad \alpha = \frac{\mu\epsilon}{kT} ; \quad \beta = \frac{(\delta_1-\delta_2)\epsilon^2}{2kT} . \tag{12}$$

If the particle has no dipole moment ($\alpha = 0$) and the EBR is determined exclusively by the anisotropy of its polarisability ($\delta_1-\delta_2$), Eqn (11) becomes

$$ \Delta n = \Delta n_0(1 - e^{-t/\tau_0}) . \tag{13}$$

In this case the growth of Δn on switching on the field (curve *1* of Fig. 1) corresponds exactly to its decay (curve *3*). If the molecules are oriented by the field E only because of the dipole moment μ we find from (11)

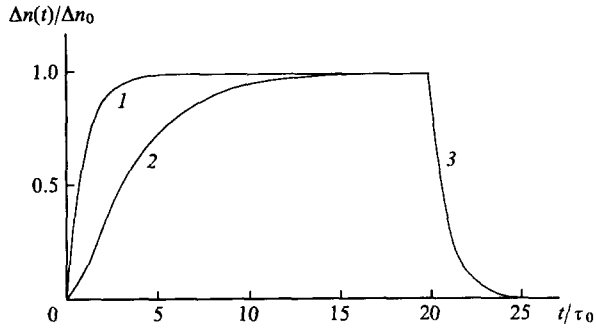


Figure 1. Dependence of the relative value of the EBR on the relative time for instantaneous switching the electric field on (*1*, *2*) and off (*3*): (*1*) and (*3*) nondipolar ($\alpha = 0$) and electrically anisotropic particles, (*2*) and (3) dipolar and electrically isotropic particles ($\beta = 0$).

$$\frac{\Delta n}{\Delta n_0} = 1 - \frac{3}{2}e^{-t/\tau} + \frac{1}{2}e^{-t/\tau_0} . \tag{14}$$

In this case Δn increases more slowly than in the case of inductive orientation, and the $\Delta n(t)$ dependence (curve *2* of Fig. 1) is tangential to the t axis for $t = 0$.

In the more general case, Δn increases more slowly when the steady dipole of the particles plays a dominant role in the EBR.

In a sinusoidal electric field of voltage $E = E_0 \cos \omega t$ the orientation distribution function of dielectrically anisotropic and polar particles should be time-dependent. Accordingly, the observed excess birefringence Δn stimulated by the dissolved substance is also time-dependent.

For dielectrically isotropic particles the instantaneous value of the excess EBR of the solution $[\Delta n(t)]$ and the corresponding instantaneous value of the Kerr constant $[K(t)]$ are defined by the expressions[11]

$$K(t) = \frac{2\Delta n(t)}{cE^2} = K\left\{1 + \left[\frac{\cos(2\omega\tau - \varphi)}{(1+\omega^2\tau_0^2)^{1/2}}\right]\right\} , \tag{15}$$

$$\tan\varphi = 2\omega\tau_0 ,$$

where ω and E_0 are the angular frequency and the amplitude of the electric field.

If follows from this expression that in a sinusoidal field $\Delta n(t)$ and $K(t)$ oscillate symmetrically with respect to the mean value of K with a doubled frequency, and that their sign at any instant is the same as that of K. The amplitude of these oscillations falls to zero as the frequency ω increases. When the time-average value of Δn is the monitored quantity the measured EBR is independent of the frequency of the field, and remains equal to its equilibrium value in a steady field of amplitude $E = E_0/\sqrt{2}$.

If particles having constant dipoles are exposed to a sinusoidal electric field the expression for their Kerr constant takes the form

$$K(t) = \frac{2\Delta n(t)}{cE^2}$$

$$= K\left[\frac{1}{1+\omega^2\tau^2} + \frac{\cos(2\omega t - \varphi)}{(1+4\omega^2\tau_0^2)^{1/2}(1-\omega^2\tau^2)^{1/2}}\right] , \tag{16}$$

$$\tan\varphi = \frac{5\omega\tau}{3 - 2\omega^2\tau^2} .$$

The first term in Eqn (16) is time-independent. It is a time-averaged value of the Kerr constant for a fixed field frequency ν:

$$K_\nu = \frac{K}{(1+\omega^2\tau^2)} . \tag{17}$$

This average value of K_ν decreases with increasing frequency of the field, and vanishes at high frequencies because of the relaxation of the rotational motion of the dipolar particles. According to Eqn (17) τ can be determined from the dispersion curve by using the condition

$$\tau = \frac{1}{\omega_m} , \tag{18}$$

where ω_m is the angular frequency for which $\Delta n_\nu = (\Delta n_0 + \Delta n_\infty)/2$ (Δn_0 and Δn_∞ are the values of Δn for $\omega = 0$ and $\omega = \infty$ respectively).

If a particle (or a rigid molecule) has both a steady dipole and dielectric anisotropy the time-dependent value of $K(t)$ is determined by the sum of the expressions (15) and (16) with appropriate weighting coefficients. If the quantity monitored in the experiment is the time-averaged value of the EBR as a function of the frequency of the external field the plot of K has the form shown in Fig. 2:

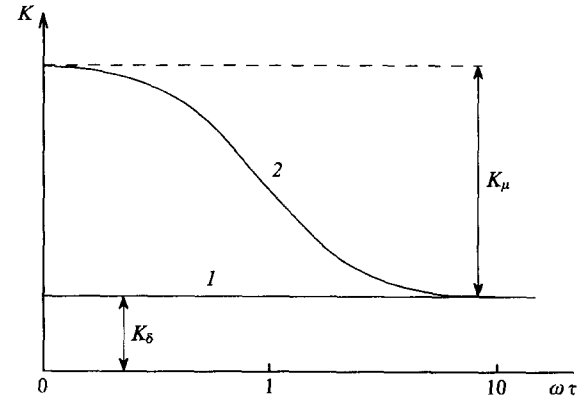


Figure 2. Frequency dependence of the mean Kerr constant for a solution of dielectrically anisotropic dipolar particles: (*1*) K_δ, the anisotropic part of the Kerr constant, (*2*) overall effect $K = K_\delta + K_\mu$ (K_μ is the dipolar part of the Kerr constant).

However, it should not be forgotten that the expressions (9)–(18) are valid only for monodispersed systems of particles or of rigid molecules. Substances studied experimentally are usually polydispersed in relaxation time. In this case the total value of $\Delta n(t)$ is a superposition of the $\Delta n_i(t)$ values (where i is the number of the group of molecules having identical relaxation times, allowing for their mass fractions in the sample). For rigid polar molecules Eqns (9) and (14) can be re-written

$$\frac{\Delta n(t)}{\Delta n_0} = \int_0^\infty \varphi(\tau) f(t,\tau)\, d\tau , \tag{19}$$

where $f(t,\tau) = e^{-3t/\tau}$ for the decay and $f(t,\tau) = 1 - (3/2)e^{-t/\tau} + (1/2)e^{-3t/\tau}$ for the growth of $\Delta n(t)$, and the function $\varphi(\tau)$ allows for the contribution to the EBR from molecules having relaxation times between τ and $\tau + d\tau$. The areas delinated by the growth and decay curves are, respectively,

$$Q_g = \int_0^\infty \left(1 - \frac{\Delta n(t)}{\Delta n_0}\right) dt \quad \text{and} \quad Q_d = \int_0^\infty \frac{\Delta n(t)}{\Delta n_0} dt .$$

Starting from Eqns (13) and (14) for monodispersed rigid particles or molecules we obtain

$$Q_d = \tfrac{1}{3}\tau = \tau_0 ,$$

for the decay curve and

$$Q_g = \tfrac{4}{3}\tau = 4Q_d$$

for the growth curve. In this case Q_d is the 'free relaxation' time.

In the presence of polydisperseness with respect to the molecular mass M or to the relaxation time τ the areas Q_g and Q_d are altered (in this case $Q_d = \langle\tau_0\rangle$ is the mean free relaxation time), but according to Eqn (19) their ratio stays the same: $Q_g/Q_d = 4$, irrespective of the form of the function $\varphi(\tau)$.

Often the experimental dispersion curves are wider than predicted by Eqn (17), suggesting polydisperseness of the ensemble of molecules with respect to the relaxation times. These dispersion curves can be described by replacing Eqn (17) by

$$\frac{\Delta n_\nu}{\Delta n_0} = \int_0^\infty \varphi(\tau)(1+\omega^2\tau^2)^{-1}\,d\tau. \tag{20}$$

3. Relationship between the relaxation times and the hydrodynamic and the structural properties of the molecules

Studies of the dynamics of the Kerr effect yield information on the rotational mobility of particles or of rigid molecules, and therefore on their size and shape, thus allowing meaningful conclusions on the nature of the observed EBR to be made. The same is true of studies of the time-dependent EBR in dilute solutions of polymers, but in this case the possibilities offered by the method are much wider: it can evaluate both the structural (equilibrium) and the kinetic rigidity of the macromolecules. The term kinetically rigid denotes a polymeric molecule whose orientation time (τ_{or}) under the stimulus of an external field is smaller than the time needed for its deformation (τ_{def}) in the same field. This definition suggests that a given macromolecule can behave both as kinetically rigid and kinetically flexible, depending on the nature of the forces acting on it. The length of the Kuhn segment (A)[12,13] can be used as a measure of the equilibrium rigidity ($\langle \boldsymbol{h}^2\rangle$). If the beginning and the end of a real polymeric molecule are super-imposed on the beginning and the end of a model, freely coupled Kuhn chain having the same contour line L the equilibrium rigidity can be evaluated by the equation[12-14]

$$\langle \boldsymbol{h}^2\rangle = LA\,; \quad L = NA\,, \tag{21}$$

where $\boldsymbol{h}$ is a vector connecting the end-points of the chain, and N is the number of Kuhn segments in the chain. The angle brackets in Eqn (21) denote averaging over all the conformations of the macromolecule.

Depending on their A value all polymers are usually classified into two groups: rigid-chain polymers (with a large A) and flexible-chain polymers (with a small A). Experimental data[13] show that macromolecules having a high equilibrium rigidity also show kinetic rigidity, and are oriented in externally applied fields by a mechanism involving the large-scale rotation of the molecule as a whole. Conversely, the molecules of flexible-chain polymers have a small kinetic rigidity,[13] and therefore their orientation in an electric field takes place by the deformation mechanism.

The study of the dependence of the relaxation time of the EBR on the molecular weight of the polymer is of fundamental importance for determining the character of the motion of the molecules in an electric field. This dependence can be described approximately by the following empirical expression, which is valid over a reasonably narrow range of molecular masses:

$$D = K_{D_r} M^{-b}\,, \tag{22}$$

where D is the rotational diffusion coefficient, K_{D_r} is a constant [$D_r = 1/2\tau$]; b lies between 3 (for infinitely thin kinetically rigid rods) and 1.5 (for kinetically rigid nonpercolating Gaussian tangles).

A more general expression relates the relaxation time τ of a kinetically rigid molecule to its molecular mass and to its characteristic viscosity $[\eta]$ in solution:[13]

$$\tau = \frac{M[\eta]\eta_0}{2FRT}\,, \tag{23}$$

where η_0 is the viscosity of the solvent and $R = kN_A$. The coefficient F depends on the hydrodynamic properties of the particles used as models of the molecules: its limiting values are 2/15 for thin rods and 5/12 for spherical tangles.

A quantitative description of the equilibrium conformational properties of polymeric molecules can be based on the theory of the rotational friction of kinetically rigid vermiform chains.

In the first variant, developed by Hearst[15] for the vermiform necklace model, the theoretical expressions were reduced to the form

$$\tau = \tau_r f(x)\,, \tag{24}$$

$$\tau_r = \frac{(6kT)^{-1}\pi\eta_0 L^3}{\ln(L/d) - 0.877 + 7[(1/\ln(2L/d)) - 0.28]^2}\,.$$

Here τ_r is the rotational relaxation time of the rod-like molecule[16] whose length L and diameter d are equal (respectively) to the contour line and to the hydrodynamic diameter of the molecule; $f(x)$ is a function which allows for the equilibrium flexibility of the chain, and $x = 2L/A$.

In Hearst's theory[15] the function $f(x)$ is a linear correction (with respect to x) applied to the τ_r value of a rod-like molecule and valid only for $x \ll 1$, which seriously limits the prospects of using this variant in conjunction with experimental data.

Hearst's theory was subsequently developed by Hagerman and Zimm,[17] who used it in conjunction with the Monte Carlo method to express the function $f(x)$ as a power series in x, thus markedly extending its region of validity to $0.1 \leqslant x \leqslant 5$:

$$f(x) = (1.0120 - 0.24813x + 0.033703x^2 - 0.0019177x^3) \times (1 - 0.06469x + 0.01153x^2 - 0.0009893x^3)\,. \tag{25}$$

By varying the parameters d and A we can construct a theoretical curve offering the best description of the experimental data [$\tau = \tau(M)$], and thus determine the equilibrium rigidity and the hydrodynamic diameter of the molecule. This calculation was carried out[18,19] for a group of DNA samples, and gave results satisfactorily consistent with data obtained by translational diffusion methods.

4. The Kerr effect in solutions of vermiform chains

As was pointed out above, macromolecules of rigid-chain polymers behave as kinetically rigid chains in an electric field. Furthermore, it was found that the EBR and the flow birefringence (FBR) had the same sign for solutions of this class of polymer in the Gaussian region. This shows that the character of the orientation of their molecules in electrical and in mechanical (shear) fields is the same, and involves a large-scale rotation mechanism. Therefore the use of data obtained by the FBR method for interpreting EBR results is fully justified. The equilibrium electro-optical properties of solutions of rigid-chain polymers can be described by starting from the theory of the Kerr effect for rigid dipolar particles with axially symmetrical optical and dielectric polarisabilities, using the $\boldsymbol{h}$ axis (which connects the ends of the chain) as a symmetry vector. The latter postulate is consistent with the basic conformational characteristics of polymer chains discussed in the original papers by Kuhn et al.[20-22]

Thus Eqn (8) becomes the starting expression for the Kerr constant of a rigid-chain polymer. However, in order to establish the quantitative dependence of K on the conformation and structure of the macromolecule we need a specific molecular model to describe its electro-optical properties. A large volume of experimental and theoretical information[13] confirms that the most universal model of the conformational, hydrodynamic, and dynamic-optical properties of rigid-chain polymeric molecules is the vermiform chain model, and that this model can reasonably be used also to describe the electro-optical properties of these molecules.

The theory of the equilibrium Kerr effect in dilute solutions of vermiform chains has been fully developed.[23,24] Since in the ensemble of unfolded vermiform polymer molecules the dipolar, the optical, and the dielectric terms which appear in Eqn (8) are statistical quantities, averaged over all the conformations of the macromolecules, a similar averaging is needed also for Eqn (8). In this case the difference between the two principal optical polarisabilities of the vermiform molecule (along the $\boldsymbol{h}$ axis and at right angles to it) is given by the expression[25]

$$\langle \gamma_1 - \gamma_2 \rangle = \frac{3}{5} \frac{\Delta a S x f_1(x)}{f_2(x)} , \tag{26}$$

where Δa is the optical anisotropy of the monomer unit of the chain, and S is the number of monomer units in the Kuhn segment. Throughout this review angle brackets will be used to denote quantities averaged over conformations. The functions $f_1(x)$ and $f_2(x)$ take the form

$$f_1(x) = x - 1 + e^{-x} ; \quad f_2(x) = x^2 - 0.8 f_1(x) . \tag{27}$$

The difference between the two principal dielectric polarisabilities $\langle \delta_1 - \delta_2 \rangle$ of a vermiform chain is also given by formula (26) when Δa is replaced by Δb (where Δb is the dielectric anisotropy of the monomer unit).

In addition to the geometric segment A, the electrical (dipolar) segment has been used to describe the properties of a freely coupled Kuhn chain: it consists of a rigid linear combination of uniformly oriented dipole moments μ_0 of the monomer units of the chain,[26] in which the 'dipolar' and the 'geometric' rigidities are assumed to be equal. However, allowance was made for the difference in the vector sum of the segment dipoles μ_s parallel to the axis of the geometric segment ($\mu_{s\parallel}$) and of the dipoles perpendicular to that axis ($\mu_{s\perp}$). In the former, the dipole moment of the molecule is parallel to the vector $\boldsymbol{h}$, and its mean square value is given by the expression

$$\langle \mu_\parallel^2 \rangle = N \mu_{s\parallel}^2 . \tag{28}$$

Eqn (28) reflects the 'accumulation' of the longitudinal components of the dipoles of the monomer units, resulting in an increase of the macromolecular dipole with increasing length of the polymer chain. In the latter case the overall dipole of the molecule is no longer parallel to $\boldsymbol{h}$, but has a longitudinal (parallel to $\boldsymbol{h}$) and a perpendicular component, whose mean square values are given by

$$\langle \mu_\parallel^2 \rangle = N \mu_{s\perp}^2 \left(\frac{h}{L}\right) \alpha^*\left(\frac{h}{L}\right) ;$$

$$\langle \mu_\perp^2 \rangle = N \mu_{s\perp}^2 \left[1 - \left(\frac{h}{L}\right) \Big/ \alpha^*\left(\frac{h}{L}\right)\right] , \tag{29}$$

where $\alpha^*(h/L)$ is the inverse Langevin function of the convolution parameter (h/L) of the chain.[22]

These ideas have been applied[23,24] to vermiform chains by considering the general case of the dipole moment μ_0 of the monomer unit at an angle ϑ to the tangent to the contour of the chain. It has also been pointed out[24] that the dipolar and the geometric rigidity of the chain can differ for reasons not allowed for in Kuhn's theory. The equality of the geometric and of the longitudinal (dipole) rigidity (characterised by the number $S_\parallel = S$ of longitudinal components $\mu_{0\parallel}$ of monomeric dipoles in the electrical segment) is beyond doubt. However, this hypothesis may not be applicable to many rigid-chain molecules met in practice: for example, *para* aromatic polyamides and polyethers. The high geometric rigidity of the chains of these polymers is due to their 'crankshaft' conformation,[27] one of whose features is a substantial freedom to undergo intramolecular rotations round the *para* aromatic axes. Allowance for the possible differences between the longitudinal and the transverse dipole rigidity can be made by introducing the parameter $\alpha \geqslant 1$;

$$S_\parallel = \alpha S_\perp = S ; \quad \mu_{s\parallel} = S_\parallel \mu_{0\parallel} = S_\parallel \mu_0 \cos\vartheta ; \tag{30}$$

$$\mu_{s\perp} = S_\perp \mu_{0\perp} = S_\perp \mu_0 \sin\vartheta .$$

Furthermore, noting that

$$\left\langle \mu^2 \frac{3\cos^2\vartheta - 1}{2} \right\rangle = \left\langle \mu_\parallel^2 - \frac{\mu_\perp^2}{2} \right\rangle , \tag{31}$$

using Eqn (30), and inserting into (29) $\langle h^2 \rangle / L$ for a vermiform chain, we obtain

$$\left\langle \mu^2 \frac{3\cos^2\vartheta - 1}{2} \right\rangle = \frac{M S \mu_0^2}{M_0} \frac{f_1(x)}{x} \left[\cos^2\vartheta \frac{3 f_1^2(\alpha x) \sin^2\vartheta}{5\alpha f_2(\alpha x) f_1(x)}\right] , \tag{32}$$

where M_0 is the molecular weight of the monomer unit in the polymer.

Inserting (26) and (32) into (8) gives an expression for the Kerr constant of the vermiform chain:

$$\frac{K}{K_\infty} = \frac{3\langle h^4 \rangle f_1^2(x)}{5\langle h^2 \rangle^2 f_2(x)} \times \left[1 - \frac{3 f_1^2(\alpha x)}{5\alpha^2 f_1(x) f_2(\alpha x)} \tan^2\vartheta + \frac{6 k T x \Delta b}{5\mu_{0\parallel}^2 S f_2(x) \cos^2\vartheta}\right] . \tag{33}$$

Here K_∞ is the limiting value of the Kerr constant in the region of $x \to \infty$:

$$K_\infty = \left(\frac{B \Delta a}{M_0 k T}\right) \mu_0^2 S^2 \cos^2\vartheta . \tag{34}$$

Using the Lorentz internal field multiplier gives the following expression for the coefficient B:

$$B = \left(\frac{2\pi N_A}{1215 k T n}\right) (n^2 + 2)^2 (\varepsilon + 2)^2 . \tag{35}$$

Eqn (33) contains the term

$$\frac{\langle h^4 \rangle}{\langle h^2 \rangle^2} = \frac{11}{3} x^2 - (2x + 8) f_1(x) + \frac{2}{27} \frac{f_1(3x)}{f_1^2(x)} , \tag{36}$$

introduced in order to allow for the polydisperseness with respect to conformations in the ensemble of vermiform chains; it varies from 1 to 5/3 as x is varied from 0 to ∞.

It follows from Eqn (34) that the sign of K_∞ is the same as the sign of Δa, since in a solution of kinetically rigid vermiform chains the signs of the EBR and of the FBR should coincide in the Gaussian region. We should stress that in order to achieve a quantitative characterisation of the dipole structure of macromolecules the parameter Δa must be known. For polymers Δa can be found by the FBR method, starting from the experimentally

determined value of the optical shift coefficient in the Gaussian region.

$$\left(\frac{\Delta n}{\Delta \tau}\right)_{\infty} = \frac{4\pi(n^2+2)^2}{45kTn}\Delta a S ,$$

where $\Delta\tau$ is the shear stress in the flow.

Fig. 3*a* shows plots of the relative Kerr constant $K/K_{\infty,\vartheta=0}$ against x for $\alpha = 1$ in the case of kinetically rigid vermiform chains. The curves differ not only in their asymptotic value (which is proportional to $\cos^2\vartheta$) but also in their shape. If the dipole is perpendicular to the direction of the chain ($\vartheta = 90°$) the Kerr effect is opposite in sign to Δa for all values of x, and decreases to zero (in absolute value) as x is increased. This is because the correlation in direction between the dipole moment of the chain molecule (obtained by summing all the perpendicular components of the dipole moments of the monomer units) and the direction of $\boldsymbol{h}$ decreases as x is increased, and disappears in the Gaussian region.

An entirely different situation is observed on summing the longitudinal components of the dipole moments of the monomer units, since in this case the dipole of the molecule is parallel to $\boldsymbol{h}$ and increases with x. These effects produce a sign inversion (at $90° > \vartheta > 54.74°$) in the plots of the relative Kerr constant against x (see Fig. 3*a*).

Possible effects of the difference between the longitudinal and the transverse dipole rigidity on the Kerr constant are illustrated in Fig. 3*b*, which shows plots of the ratio K/K_{∞} for fixed angles $\vartheta = 0°$ and 70° and different values of α.

The most widely used methods of measuring the EBR rely on monitoring changes in the light flow.[28-30] The methods therefore cannot be applied when the light flow undergoes time changes unrelated to the effect of interest. In these circumstances EBR measurements are possible only by the null method, in which an elliptical compensator is used to identify the effect due to birefringence.

Most of the rigid-chain polymers are soluble only in strongly polar, conducting solvents, and therefore their EBR can be studied only by using pulsed electric fields. The most widely used fields consist of rectangular pulses. However, in order to identify unambiguously the nature of the EBR we must use electric fields of varying sign: in this case sinusoidal-pulse fields are the most convenient.

The apparatus for measuring EBR in sinusoidal-pulse and in rectangular-pulse fields is shown diagrammatically in Fig. 4. The operating principle of its electrical part has

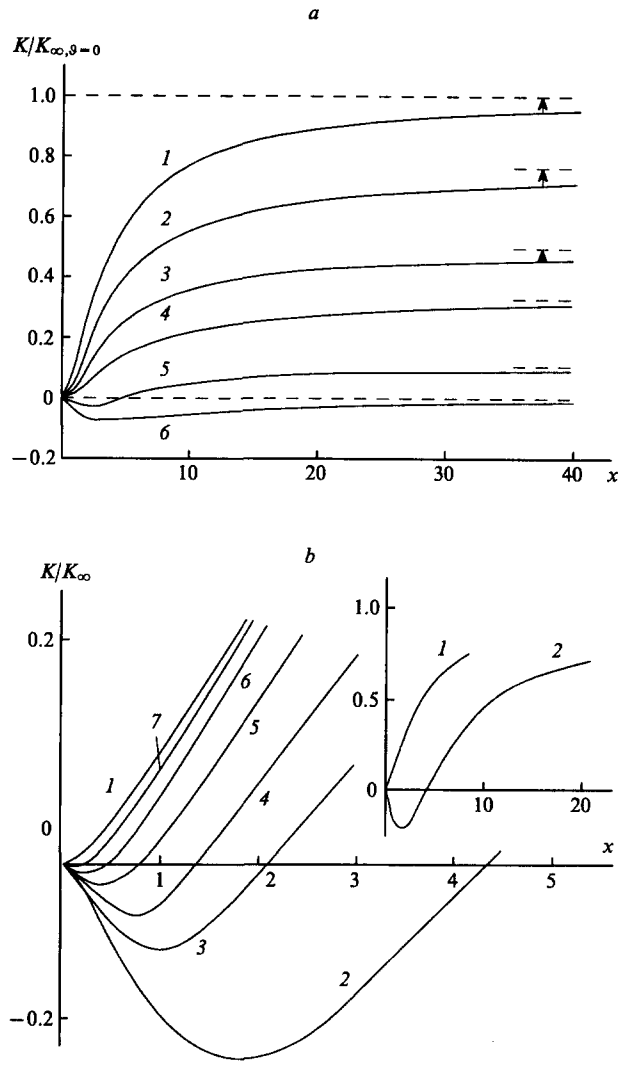


Figure 3. Plots of the relative Kerr constant against x for a kinetically rigid vermiform chain with $\alpha = 1$ (*a*) and different values of α (*b*): ϑ is the angle between the dipole of the monomer unit and the direction of the chain a: $\vartheta = 0°$ (*1*), 30° (*2*), 45° (*3*), 54.43° (*4*), 70° (*5*), 90° (*6*); *b*: $\vartheta = 0°$ (*1*), 70° (2–7); $\alpha = 0$ (*1*), 1.0 (*2*), 1.5 (*3*), 2.0 (*4*), 3.0 (*5*), 5.0 (*6*), 10.0 (*7*).

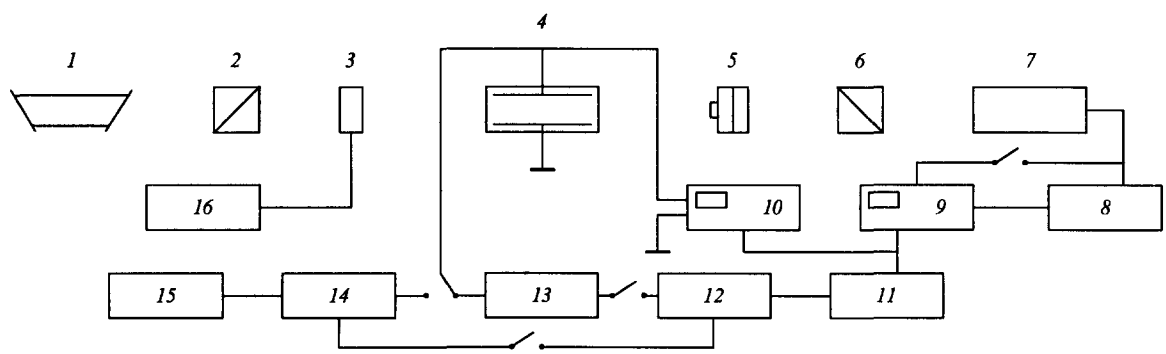


Figure 4. Apparatus for measuring the EBR by the compensation method in pulsed (sinusoidal and rectangular) electric fields: (*1*) helium–neon laser (λ = 632.8 nm); (*2*) and (*6*) polariser and analyser (Franck–Ritter prisms); (*3*) piezoceramic modulator of the ellipticity of the polarised light; (*4*) Kerr cell; (*5*) elliptical compensator with a path difference of 0.01 λ; (*7*) photodetector; (*8*) selective system; (*9*) and (*10*) oscillographs; (*11*) pulse delay generator; (*12*) rectangular pulse generator; (*13*) rectangular pulse former; (*14*) sinusoidal pulse former; (*15*) sinusoidal voltage generator; (*16*) generator for exciting the oscillations of the modulator.

already been described in detail.[31,32] The light flow Φ emerging from the analyser depends on the difference in phase between the mutually perpendicular oscillations of the two light waves created by the passage of light through the birefringent elements of the system. The azimuths of the optical axes of the birefringent layer and of the modulator form an angle of $\pi/4$ with the axis of the polariser. At low phase differences $\delta \ll 1$ we have the following expression for the light flux at the outlet to the photodetector:[31]

$$\Phi = \Phi_0 \frac{(\delta_E + \delta_m + \delta_0 \sin 2\varphi)^2}{4} . \quad (37)$$

Here Φ_0 is the amplitude of the light flux at the inlet to the system, δ_E is the phase difference generated by the solution ($\delta_E = 2\pi l \Delta n/\lambda$, where l is the optical length of the birefringent layer, and λ is the optical wave length), δ_0 and φ are the phase difference and the azimuth angle of the optical axis of the compensator, and $\delta_m = \delta_{m_0} \cos \Omega t$ is the phase difference introduced by the modulator ($\delta_{m_0} \ll 1$, $\Omega/2\pi = 5 \times 10^5$ Hz).

By using a selective system, tuned to the modulation frequency Ω, we can isolate the component of the light flux Φ',

$$\Phi' = \frac{\Phi_0}{2} (\delta_E + \delta_0 \sin 2\varphi) \delta_{m_0} \cos \Omega t , \quad (38)$$

which is linearly dependent on the azimuth angle φ of the rotation of the compensator. The compensation condition is defined by the expression

$$\delta_E = -\delta_0 \sin 2\varphi_c , \quad (39)$$

where φ_c is the azimuth angle for compensation.

In measurements of the growth and decay of the EBR the selective system is switched off, and the signal from the photodetector is taken directly to the input of the oscilloscope amplifier. However, the compensation condition (39) at the instant corresponding to the beginning of the pulse (determined by the time-delay of the master generator) stays unchanged. Under these conditions a signal at double the modulation frequency Ω is observed on the oscilloscope screen at the compensation instant.

Under the influence of an electric field of intensity $E = E_0 \cos \omega t$ the oscillations of the two light waves linearly polarised parallel and perpendicular to the voltage vector in the Kerr cell acquire a phase difference

$$\delta_E = \frac{\bar{\delta}_{E_0}}{2} + \left(\frac{\tilde{\delta}_{E_0}}{2}\right) \cos(2\omega\tau - \psi) , \quad (40)$$

where $\bar{\delta}_{E_0}$ is the phase difference characteristic of the constant component of the EBR, and $\tilde{\delta}_{E_0}$ is the amplitude of the oscillations in the EBR of frequency 2ω. These two values coincide under equilibrium conditions at low enough frequencies ω, and $\psi = 0$, but they differ in the frequency dispersion region corresponding to the Kerr effect.

The amplitude Φ of the oscillations in the flow of frequency Ω is linearly dependent on $\bar{\delta}_{E_0}$ and on $\sin 2\varphi$, and vanishes at the compensation point[31]

$$\bar{\delta}_{E_0} = -2\delta_0 \sin 2\varphi_k . \quad (41)$$

Eqn (41) is valid also when a sinusoidally pulsed field is applied.

The magnitude and the sign of the Kerr constant can be determined from Eqns (39) and (41). Various designs of the Kerr cell have been proposed.[28,29] In studies of the EBR in solutions of many rigid-chain polymers glass tubes fitted with titanium electrodes and with quartz side windows (held in position with springs or with adhesive) are most convenient. The length of the electrodes varies between 1 and 10 cm, and the interelectrode gap between 0.33 and 1.2 mm, depending on the chosen solvent.

The compensation method of measuring EBR by modulating the ellipticity of polarisation of the light gives the Kerr constants, the characteristic growth and decay times of the EBR, and also the dispersion relaxation times τ, with relative errors of 10%, 30%, and 20% respectively.

III. Transient electrical birefringence in solutions of rigid-chain polymers. Experimental data

1. Study of the dynamics of macromolecules in rectangular-pulse electric fields

Most of the recent studies of the rotational mobility of polymer molecules by the transient EBR method have used rectangular-pulse fields.[18,19,33-40] The free relaxation of the EBR following the removal of the field is usually monitored. The study of macromolecular dynamics by the free relaxation method offers information on the rotational mobility and on the conformational characteristics of polymer chains, and in this case, as was stated above, the nature of their orientation and of the observed EBR are unimportant. The combined study of the EBR growth and decay processes offers more information.

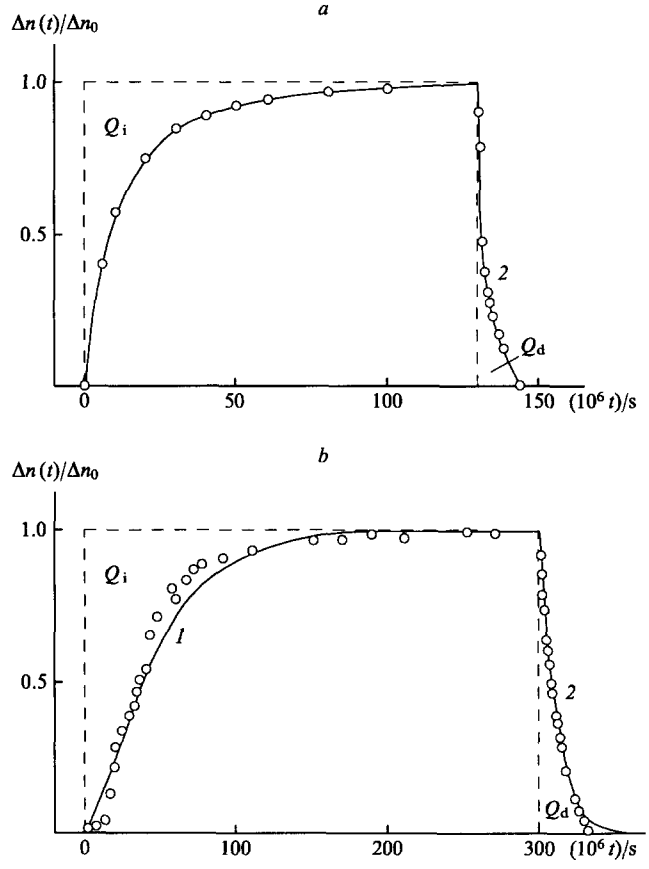


Figure 5. Time dependence of the relative EBR from the instant of switching on (*1*) and off (*2*) a rectangular electric pulse for a solution of the poly(butyl isocyanate) fraction with $M = 58 \times 10^3$ in tetrachloromethane[41] (*a*) and for a sample of polyamidohydrazide ($M = 26.6 \times 10^3$) in dimethyl sulfoxide[42] (*b*). Concentration of solution/g cm^{-3}: (*a*) 1×10^{-4}; (*b*) 0.11×10^{-2}.

Plots of the growth and decay of EBR following the instantaneous switching on and off of an electric field are shown in Fig. 5 for poly(butyl isocyanate) and poly(amido hydrazide). It can be seen that the growth of the EBR is markedly slower than its decay. This behaviour is characteristic of most of the rigid-chain polymers in which

Table 1. Dynamic characteristics of rigid-chain polymers in dilute solutions, obtained by the transient EBR method.

Fraction, polymer sample	Solvent	$10^{-2}[\eta]/cm^{-3}\,g^{-1}$	$10^{-3}M$	$10^{6}\tau_0/s$	$10^{6}Q_g/s$	$10^{6}\tau/s$	F	Ref.
Fractions								
cellulose nitrate	Cyclohexanone	2.6–16.5	130–822	13.5–270	–	–	0.38–0.76	38
cyanoethylcellulose	"	2.3–7.4	104–317	11–23	–	22–63	0.2–1.5	39
diphenyl substituted poly(phenylene terephthalate)	Dichloroacetic acid	1.7–6.45	14–86	3–68	–	–	0.3–0.4	40
poly(butyl isocyanate)	Tetrachloromethane	0.35–65	8.4–700	2–320	8–640	0.7–650	0.08–1.5	41
polyamidobenzimidazole	Dimethylacetamide	0.46–5.25	4–45	1–5	–	0.38–11	0.1–0.44	42
polyamidohydrazide	Dimethyl sulfoxide	0.85–5.7	8.6–46	0.7–7	4–20	2.4–17	0.14–0.7	42
cellulose acetobenzoate	Dioxan	0.16–1.75	13–198	–	–	1–22	0.03–0.37	43
cellulose acetocinnamate	"	0.1–6.5	7.7–878	–	–	0.63–200	0.04–0.91	44
cellulose carbanilate	"	0.09–0.78	14–107	–	–	0.3–4.5	0.18–0.43	45
cellulose carbanilate	"	0.1–2.1	10–195	–	–	0.22–19.6	0.12–0.53	[a]
Samples of cellulose carbanilate	"	1.6–11.5	340–4070	–	–	23–265	0.6–4.5	46
Samples of cellulose carbanilate	Dioxan	4.0	–	–	–	60	0.67	47
	Ethyl acetate	3.1	400	–	–	15	0.73	47
	Cyclohexanone	2.7	–	–	–	40	1.17	47
	Dimethylacetamide	2.6	–	–	–	18	1.06	47
Fractions								
cellulose nitrate	Dioxan	0.97–2.0	34–77	–	–	0.9–6.6	0.6–1.0	48
poly(chlorohexyl isocyanate)	Tetrachloromethane	0.4–3.8	8.8–159	–	–	0.8–227	0.23–0.54	49
Sample of poly(butyl isocyanate)	Tetrachloromethane – pentafluorophenol mixture (0%–10% mole fraction)	24–3.6	230	–	–	260–20	0.39–0.83	50
Samples of cellulose acetodiphenyl acetate	Dioxan	1.7–3.2	–	–	–	16–98	–	51
Sample								
ethylcellulose	"	2.5	80	–	–	14	0.29	52
benzylcelluose	"	0.6	30	–	–	1	0.38	52
cellulose diphenylphosphonocarbamate	"	4.9	1000	–	–	118	0.83	52
cellulose butyrate	"	6.5	780	–	–	236	0.43	52

[a] Data obtained in our laboratory.

the EBR is determined by the presence of a large steady dipole moment in the molecules.

The slight deviation of the experimental points in Fig. 5 from the theoretical curves for a monodispersed ensemble of rigid dipolar molecules indicates a relatively small polydisperseness of the sample in relaxation times. From the $\Delta n(t)/\Delta n_0$ curves obtained in this way we can determine the growth and decay times of the EBR whose values (extrapolated to infinite dilution) are listed in Table 1.

As can be seen from Table 1 the $\langle\tau_0\rangle$ values are strongly dependent on the molecular mass M, which is typical of rigid-chain polymers. The ratio $Q_g/\langle\tau_0\rangle$ is close to 4 for most of the fractions of poly(butyl isocyanate) and poly(amido hydrazide), as required by the theory for kinetically rigid dipolar molecules or particles. However, for the fractions of these polymers having the highest molecular mass we find $Q_g/\langle\tau_0\rangle < 4$. Two interpretations of this observation are possible. First, according to Eqns (11) and (12) the ratio $Q_g/\langle\tau_0\rangle$ should be less than 4. The development of kinetic flexibility in the macromolecules when M becomes very large can lead to the same result. An unambiguous choice between these two alternative explanations can be made by using only electric fields of variable sign, which immediately show whether or not the molecule has a substantial induced dipole. Studies based on sinusoidal-pulse electric fields[41,42] have indicated a preference for the second of these alternatives, which was shown to be responsible for a decrease in the ratio $Q_g/\langle\tau_0\rangle$.

2. Study of the dynamics of rigid-chain polymeric molecules in sinusoidal and in pulsed sinusoidal electric fields

As pointed out above, unambiguous conclusions on the nature of the EBR can be formulated by using electric fields of varying sign. Sinusoidal fields are the most convenient for this purpose. An additional advantage of a sinusoidal field as compared with a rectangular pulse field is that in studies of the dynamics of macromolecules of relatively low molecular weight in solutions the relaxation times can be so small as to be impossible to measure reliably by the free relaxation method. This shortcoming is almost totally eliminated in the method of determining τ in sinusoidal fields, which can be used at any frequency in the radio-frequency band: in other words, the sinusoidal field method can be used to determine τ over a much wider range of values.

The dynamics of macromolecules in electrically conducting polar solvents can be studied only in pulsed sinusoidal electric fields.

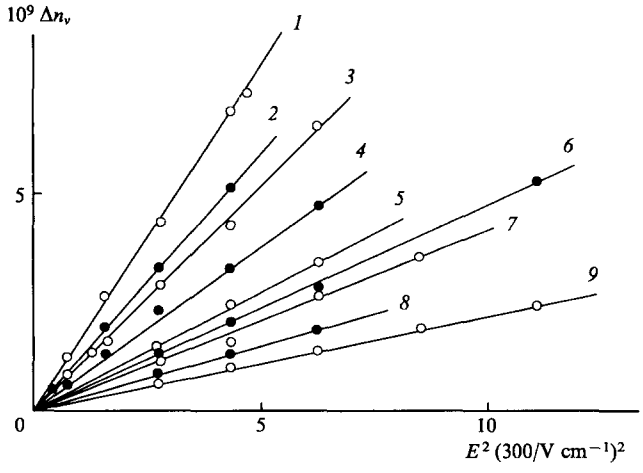


Figure 6. Dependence of the EBR on the effective intensity of a pulsed sinusoidal field for a solution of a sample of polyamidobenzimidazole ($M = 43 \times 10^3$) in dimethylacetamide ($c = 0.23 \times 10^{-2}$ g cm^{-3}) at different frequencies;[42] ν/kHz: (*1*) 0.5, 1, 3; (*2*) 7; (*3*) 10; (*4*) 20; (*5*) 50; (*6*) 70; (*7*) 100; (*8*) 200; (*9*) solvent at the same frequencies.

In Fig. 6 we show as an example the dependence of Δn on the square of the effective voltage of a pulsed sinusoidal field for a sample of polyamidobenzimidazole in dimethylacetamide. These plots can be used to determine the constant K_v of the polymer [Eqns (16) and (17)] for a fixed frequency ν of the pulsed field.

Figs 7 and 8 show dispersion plots of $\Delta n_v/\Delta n_0$ and of $K_v/K_{v\to 0}$ (where $K_{v\to 0}$ is the equilibrium value of the Kerr constant) against lg ν for several rigid-chain polymers. Similar data for other samples can be found in published reports.[13,53] It can be seen that all the plots in Figs 7 and 8 decay almost to zero as the frequency of the sinusoidal field is increased, and that they are strongly shifted towards lower frequencies by an increase in the molecular mass M of the polymers. These observations suggest that the mechanism mainly responsible for the observed EBR in solutions of rigid-chain polymers in both polar and non-polar solvents is a large-scale rotation of their dipolar molecules under the influence of the applied electric field. Furthermore, in the region of frequencies corresponding to the dispersion of the EBR dispersions of the dielectric increment $\Delta\varepsilon$ of the solutions have also been observed for cellulose poly(chlorohexyl isocyanate)[55] and carbanilate,[56] the dielectric dispersion curves almost coinciding with those of the Kerr effect. This indicates an identity of the molecular motion mechanisms and corresponds to the dispersion equation (17) for kinetically rigid molecules.

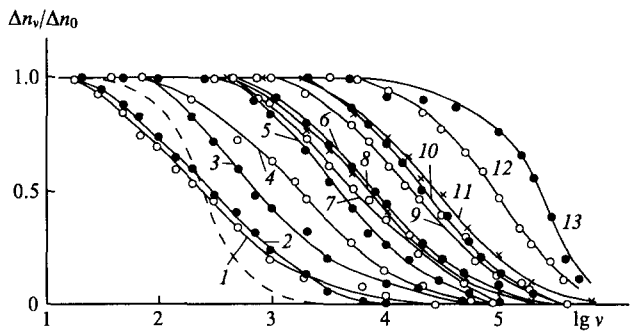


Figure 7. Dispersion plots of the EBR for the poly(butyl isocyanate) fractions in tetrachloromethane. The broken line is the Debye dispersion curve[41] with a relaxation time τ for the fraction *1*. 10^{-3} M: (*1*) 770; (*2*) 700; (*3*) 200; (*4*) 103; (*5*) 86; (*6*) 58.9; (*7*) 57.8; (*8*) 48.4; (*9*) 29.6; (*10*) 28.6; (*11*) 21.2; (*12*) 10.9; (*13*) 8.4; concentration of solutions 1×10^{-4} g cm^{-3}.

3. Kinetic and equilibrium rigidity of polymeric molecules

By using dispersion curves the 'mean' dispersion relaxation time τ can be calculated by Eqn (18). Typical concentration dependences of τ are shown in Fig. 9. Analogous data for several rigid-chain polymers have been published recently.[37] Values of τ for several rigid-chain polymers extrapolated to infinite dilution are shown in Table 1.

As can be seen from Table 1, the relaxation times τ increase rapidly as the molecular mass M of the polymers is increased. The model coefficient F can be calculated by using Eqn (23) in conjunction with the characteristic viscosities $[\eta]$.

An analysis of the dependence of F on the molecular mass for different classes of polymer is of interest. In a homologous series of fractions of a given polymer we note a tendency for F to increase with M in keeping with the accompanying change in the shape of the molecule from rod-shaped to tangle-shaped. Furthermore, it has been shown that in the fractions of these polymers having the highest molecular mass the F values exceed the maximum theoretical value for rigid particles. This is evidence of a weakening of the dependence of τ on M at high values of M. The weakening can be attributed to the general conditions of orientation and deformation of the chain molecule moving in an electric field.[57] Since τ_{or} increases with M in proportion to $M[\eta]$,

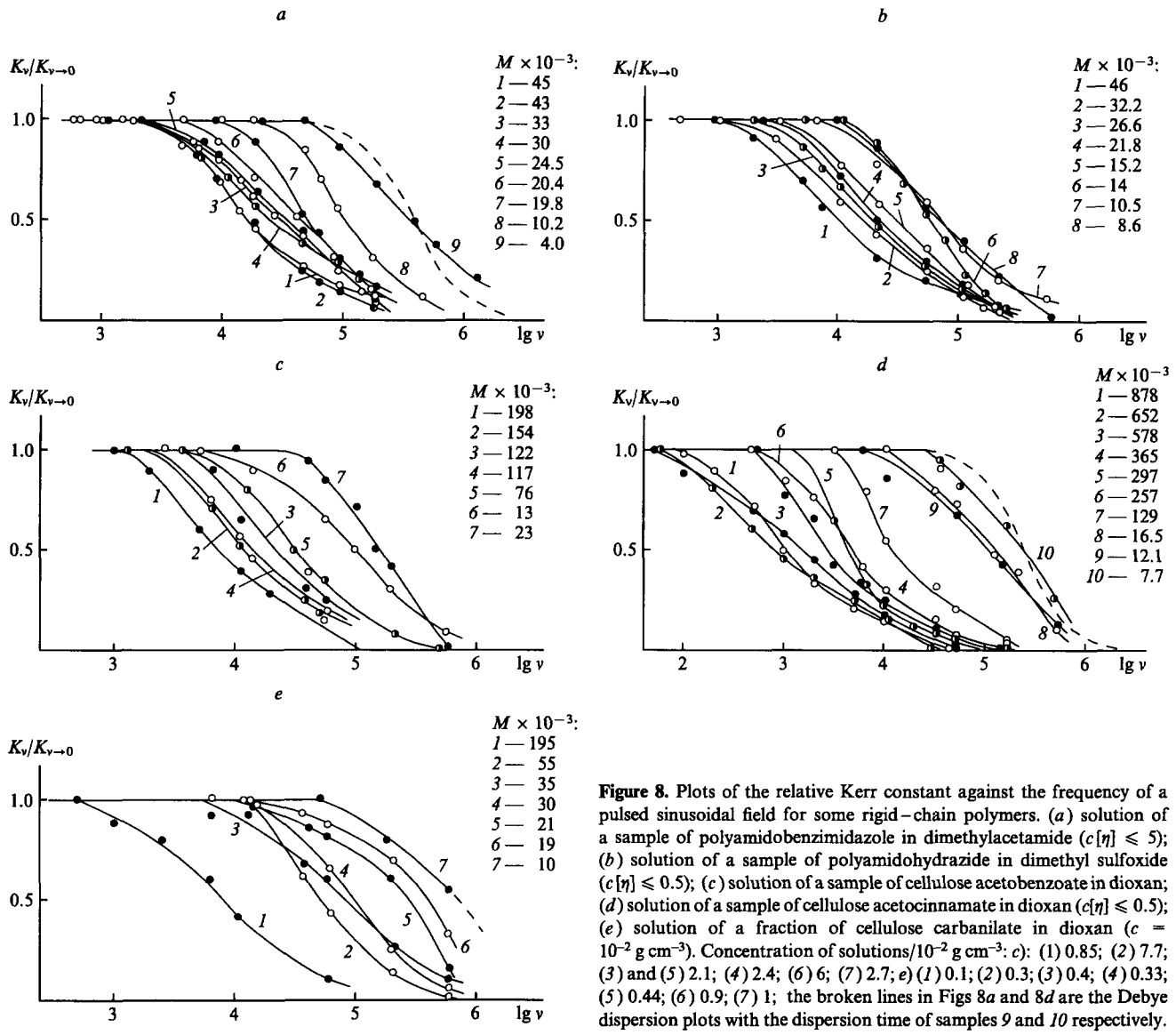


Figure 8. Plots of the relative Kerr constant against the frequency of a pulsed sinusoidal field for some rigid-chain polymers. (*a*) solution of a sample of polyamidobenzimidazole in dimethylacetamide ($c[\eta] \leqslant 5$); (*b*) solution of a sample of polyamidohydrazide in dimethyl sulfoxide ($c[\eta] \leqslant 0.5$); (*c*) solution of a sample of cellulose acetobenzoate in dioxan; (*d*) solution of a sample of cellulose acetocinnamate in dioxan ($c[\eta] \leqslant 0.5$); (*e*) solution of a fraction of cellulose carbanilate in dioxan ($c = 10^{-2}$ g cm^{-3}). Concentration of solutions/10^{-2} g cm^{-3}: *c*): (1) 0.85; (*2*) 7.7; (*3*) and (*5*) 2.1; (*4*) 2.4; (*6*) 6; (*7*) 2.7; *e*) (*1*) 0.1; (*2*) 0.3; (*3*) 0.4; (*4*) 0.33; (*5*) 0.44; (*6*) 0.9; (*7*) 1; the broken lines in Figs 8*a* and 8*d* are the Debye dispersion plots with the dispersion time of samples *9* and *10* respectively.

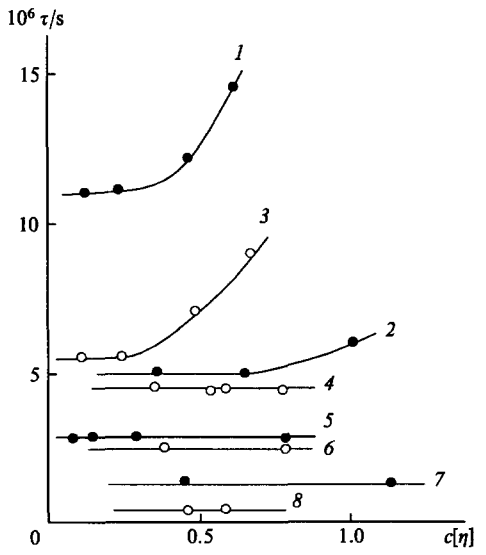


Figure 9. Plots of relaxation time against the volume fraction of the polymer in solutions of polyamidobenzimidazole in dimethylacetamide.[54] 10^{-3} *M*: (*1*) 45; (*2*) 33; (*3*) 30; (*4*) 24.5; (*5*) 20.4; (*6*) 19.8; (*7*) 10.2; (*8*) 4.

and τ_{def} is almost independent of *M*, we can expect to find $\tau_{or} > \tau_{def}$ for high enough values of *M*, and therefore the anisotropy of the solution in an electric field is produced by the deformation mechanism. The transition from an orientation to a deformation process as *M* is increased should result in an increase in *F*.

The results of Lewis, et al.[19] are of interest in this context. Starting from data on the free relaxation of the EBR in monodispersed samples of DNA of relatively high molecular mass these workers obtained the spectra of the times τ_0. The longest relaxation time in the spectrum corresponded to the large-scale motion of the DNA molecules, whereas the shortest times were determined by the small-scale motion and the corresponding deformation of the macromolecules. The largest relaxation time increased rapidly with the degree of polymerisation of the molecules, whereas the smallest was almost independent of *M*, though its contribution increased with *M*. These results are a clear illustration of the increased role of the deformation factor in the EBR of a polymer solution when *M* is increased.

A large increase in the *F* coefficient with *M* has been observed[46] in samples of cellulose carbanilate of high molecular mass ($M > 350 \times 10^3$). This effect was also treated as a manifestation of the intramolecular motion of the cellulose carbanilate molecules at large *M*, and it was described in terms of Zimm modes.[58, 59]

An increase in the *F* coefficient upon changing the nature of the solvent has been reported[47, 50] for cellulose carbanilate

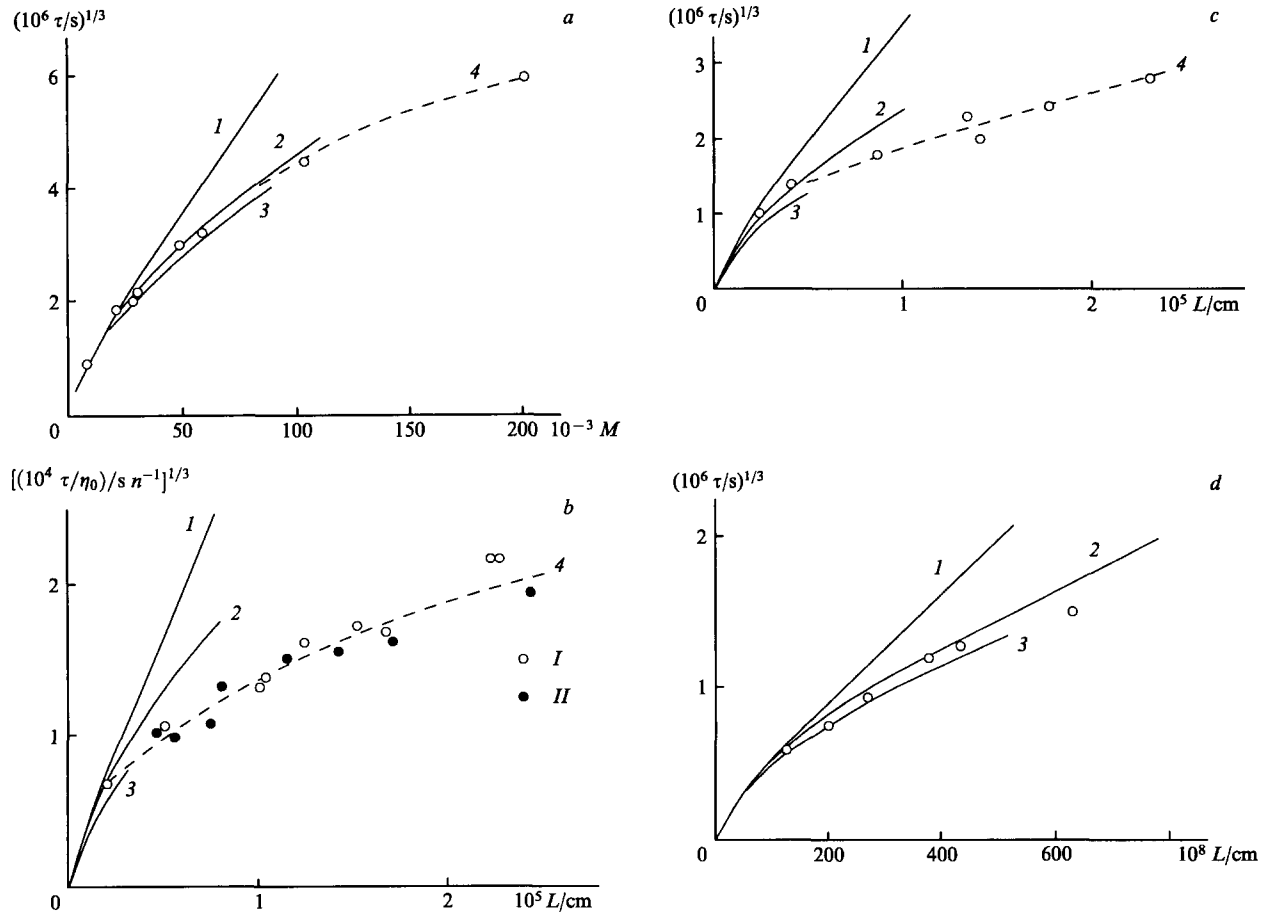


Figure 10. Dependence of the relaxation time for some rigid-chain polymers on the molecular mass (*a*) or on the chain length of the polymer (*b*–*d*). Polymers: poly(butyl isocyanate) (*a*); polyamidobenzimidazole (*b*, *I*); polyamidohydrazide (*b*, *II*); cellulose acetobenzoate (*c*) and carbanilate (*d*). Curves calculated: (*1*) for a cylindrical chain by Eqn (24), 10^8 *d*/cm: (*a*) 30; (*b*) 10; (*c*) 17; (*d*) 15; (*2*) and (*3*) for a vermiform chain in the region of $x \leqslant 5$ by Eqns (24) and (25) with 10^8 A/cm: (*a*) 900 (*2*), 700 (*3*); (*b*) 350 (*2*), 150 (*3*); (*c*) 400 (*2*), 200 (*3*); (*d*) 300 (*2*), 200 (*3*); (*4*) experimental data.

and poly(butyl isocyanate). This was treated as an increase in the kinetic flexibility of these polymers in a polar medium, resulting from the specific interactions of the macromolecules with the dipolar[47] or the aromatic[50] solvent molecules.

However, for the majority of rigid-chain polymers of not too high molecular mass the F coefficient lies between the limits predicted by the theory in the case of kinetically rigid molecules. This shows that the EBR in these solutions is due mainly to the large-scale motion of the macromolecules in an electric field.

This phenomenon allows us to use data on the transient EBR to determine the conformational characteristics (length A of the Kuhn segment) of polymers by using the theory of rotational friction in kinetically rigid vermiform chains.[17]

In Fig. 10 we show plots of the cube root of the dispersion relaxation time against the molecular mass M (or the chain length L) for several rigid-chain polymers. In addition to the experimental data we show theoretical dependences for a straight cylinder and for vermiform chains of the same diameter. The presence of experimental points in the region of $x < 1$ allows us to determine the hydrodynamic diameter of these macromolecules. These results can be obtained from measurements by molecular hydrodynamics methods (translational diffusion, viscometry).

Table 2. Conformational characteristics of some rigid-chain polymers in dilute solutions.

Polymer	Solvent	From transient EBR data			From hydrodynamic and diffraction data		
		10^8 *d*/cm	10^8 A/cm	Ref.	10^8 *d*/cm	10^8 A/cm	Ref.
Poly(butyl isocyanate)	Tetrachloromethane	30	800±100	41	28	840	60
Polyamidobenzimidazole	Dimethyl acetamide	–	250±100	42	5	130–260	61
Polyamidohydrazide	Dimethyl sulfoxide	–	250±100	42	9	160–190	62, 63
Cellulose acetobenzoate	Dioxan	–	300±100	43	17	210	64
Cellulose carbamate	"	15	250±50	[a]	11–16	240	65, 13

[a] Data obtained in the writers' laboratory.

These constructions can be used to determine the equilibrium rigidity (the length A of the Kuhn segment) in the polymers. The results are shown in Table 2, together with data obtained by molecular hydrodynamics and light scattering methods, included for comparison.

It is evident from Table 2 that the data obtained by the transient EBR method for rigid-chain polymers (in both polar and nonpolar solvents) agree reasonably well with the results of other methods, and can be used for a quantitative characterisation of the conformation properties of macromolecules.

IV. Steady electrical birefringence in solutions of rigid-chain polymers. Experimental data

1. The problem of choosing the internal field multiplier

As we know, many rigid-chain polymers are soluble only in strongly polar solvents, and therefore when discussing the electro-optical properties of macromolecules in these solvents we must allow for the difference between the electric field externally applied to the solution and the electric field experienced by the solvent molecules and by the macromolecules of the polymer dissolved in it. Formally this difference can lead to a definition of a suitable 'internal field' multiplier, which can be reasonably assumed to be the same for studies of dilute solutions of rigid-chain polymers in low-molecular polar solvents and for studies of the electro-optical properties of the solvents themselves.

In the expression for the molar Kerr constant ${}_mK$ defined by Eqn (4) allowance for this difference is made by introducing an internal field multiplier of the Lorenz type, $[(\varepsilon + 2)/3]^2$.[66] As was stated above, the results obtained from the expressions (4) and (7) agree well with the experimental data for substances studied in the gas phase,[3] and the agreement is reasonable for substances (both polar and nonpolar) dissolved in a nonpolar solvent.[67,68] However, attempts to apply these equations to concentrated polar liquids (while retaining the Lorenz multiplier) led to unacceptable results.[69,70,71]

An analogous situation was observed in studies of the dielectric properties of polar liquids. The widely used Debye theory,[72] which relates the dielectric permittivity ε of a liquid to the polarisability δ and dipole moment μ of its molecules, and which uses a Lorenz internal field multiplier, was found not to be applicable to undiluted polar liquids because it leads to physically unacceptable values of μ calculated from experimental values of ε. Much better results were obtained by using Onsager's theory,[73] which offers a more successful macroscopic model of the dielectric properties of a polar liquid by allowing for the long-range electrostatic interactions of the polar molecules, averaged over the volume of the liquid. The difference between the electric field applied to the sample and the electric field acting on an individual molecule was allowed for by using two multipliers: for the internal field P (the cavity field) and for the reactive field Q:

$$P = \frac{3\varepsilon}{2\varepsilon + 1}\ ; \qquad Q = \frac{(n^2 + 2)(2\varepsilon + 1)}{3(2\varepsilon + \varepsilon^2)}\ . \tag{42}$$

Onsager's theory can be used to calculate with acceptable precision the dipole moments of the molecules of polar liquids from the dielectric permittivity of the liquid.[74]

Further attempts to improve Onsager's model theory by introducing corrections for the non-sphericity of the molecules[75] or by allowing for the orientational correlations between nearest neighbours[76,77] proved to be ineffective because the final equations included unknown structural parameters of the liquid.

The successful application of the Onsager theory to describe the dielectric polarisation of polar liquids stimulated attempts to apply it also to the Kerr effect in the same systems. In some special cases these attempts were successful.[78]

According to currently held views[79-82] the EBR in polar liquids can be influenced by molecular 'hyperpolarisability'. It is assumed that in a polar liquid the field acting on a molecule from long-range and short-range neighbours is many orders of magnitude greater than the external field E (both electrical and optical) used in studies of the Kerr effect. Therefore the effective polarisability of the molecules γ_e in the electric field should be treated as a series in powers of E.

A two term expression for the specific Kerr constant has been obtained[80,81] by using this approach and allowing for the internal field by Onsager's theory in the special case of a molecule having a dipole moment μ parallel to its optical symmetry axis. The first (quadratic) term depends on μ and is proportional to the optical anisotropy of the molecule, whereas the second term is proportional to the first power of μ and provides a contribution for the hyperpolarisability in the Kerr effect. According to Buckingham[82] the first term plays a dominant role in the equation for K_ρ in the case of molecules in which $\mu \approx 1$ D, and the contribution from the second term is only $\sim 15\%$.

This allows us to ignore hyperpolarisability effects and to base the discussion of the EBR on the more general and more firmly established expressions (2), (4), and (7), replacing the Lorenz multiplier $(\varepsilon + 2)/3$ by the Onsager multiplier PQ:

$$K_\rho = \frac{\pi N_A}{135kTM}(PQ)^2\frac{(n^2+2)^2}{n} \times \left[\sum_{i,j=1}^{3}(\gamma_i - \gamma_j)(\delta_i - \delta_j) + \frac{1}{kT}\sum_{i,j=1}^{3}(\gamma_i - \gamma_j)(\mu_i^2 - \mu_j^2)\right]. \tag{43}$$

Eqn (43) is formally applicable to both polar and nonpolar liquids, since for the latter $\varepsilon = n^2$ and the multiplier PQ reduces to the Lorenz multiplier.

We have recently tested[83] Eqn (43) with a wide range of substances. Experimental values of K_ρ for polar and for nonpolar liquids were used in conjunction with (43) to calculate the optical anisotropies of the molecules. The results were compared with published data[3,68,84] or with data calculated by the valence-optical approach. This analysis led to the conclusion that the Onsager internal field multiplier can be used to describe the electro-optical properties of low-molecular liquids.

On the basis of these results[83] we obtained[85] an expression for the molar Kerr constant of polar liquids by using the Onsager internal field multiplier.

$${}_mK = K_\rho M\frac{2n}{3(n^2+2)^2(PQ)^2} \equiv \frac{2}{3}K_\rho Mn\left[\frac{2\varepsilon + n^2}{\varepsilon(n^2+2)^2}\right]^2. \tag{44}$$

Obviously, Eqn (44) is applicable also to non-polar liquids ($\varepsilon = n^2$), since under these conditions it reduces to Eqn (4). For an experimental demonstration of the validity of Eqn (44) we can examine the data in Table 3, which lists the ${}_mK$ values for several liquids calculated[85] from the K_ρ, ε, and n values by using the expressions (4) and (44). For comparison the table also gives the ${}_mK$ values obtained in dilute solutions in nonpolar tetrachloromethane or in the gas phase. It can be seen that the ${}_mK$ values calculated by using the Onsager internal field multiplier are reasonably well correlated with the values obtained in a dilute solution or in the gas phase, whereas the ${}_mK$ values calculated by Eqn (4) for polar substances are smaller (by a large factor) than the values for a solution or a gas.

We may therefore conclude that the Onsager internal field multiplier can justifiably be used to describe the electro-optical properties of low-molecular-mass polar or nonpolar liquids as well as those of rigid-chain polymers dissolved in these media.

2. Dependence of the Kerr constant on the molecular mass

According to the theory of the Kerr effect in solutions of vermiform chains the characteristic Kerr constant of rigid-chain polymers should be sensitively dependent on the molecular mass [Eqns (33), (34), and (36)]. The expected dependences have been observed in cellulose poly-γ-benzyl-L-glutamate,[87] poly-

Table 3. Calculated (I, II) and experimental values (III, IV) of ${}_mK$ for various substances.

Substance	ε	n	$10^{12}\,K_\rho/g^{-1}\,cm^5\,(300\,V)^{-2}$ (Ref.[85])	$10^{12}\,{}_mK/g^{-1}\,cm^5\,(300\,V)^{-2}$			
				in liquid [a]		in solution [68, 86]	in gas [3, 86]
				I	II	III	IV
Benzene	2.2	1.50	2.4	5.2	5.2	7	17
Chlorobenzene	5.6	1.53	66	64	125	137	190
o-Dichlorobenzene	11	1.55	170	70	334	362	–
m-Dichlorobenzene	5	1.55	37	53	89	74.7	–
p-Dichlorobenzene	2.4	1.53	10	36	36	38.9	–
o-Dibromobenzene	7.5	1.61	75	90	235	288	–
Nitrobenzene	35	1.56	1960	84	2780	1070	1330
Phenyl isothiocyanate	20	1.64	452	56	616	1230	–
1-Bromonaphthalene	4.8	1.66	33.6	66	100	213	–
Pyridine	12.3	1.51	123	24	139	150	–
Cyclohexanone	15.7	1.45	84	14	128	184	–
1,4-Dioxan	2.3	1.42	0.39	10	1.0	1.0	–
Nitromethane	36	1.38	55	1.3	56	89	55
Acetonitrile	37	1.35	353	5.3	256	239	–
Dimethyl sulfoxide	45	1.48	202	3.6	212	144	–
Dimethylacetamide	40	1.44	300	7.7	383	355	–
Acetone	21.5	1.36	90	5.2	94	107	99
Ethyl methyl ketone	18	1.38	85	8.3	107	88.2	–
Ethyl acetate	6.4	1.37	10.9	7.4	20.4	20.1	–
Chloroform	4.8	1.45	−12.7	−17	−30.8	−28.5	−26
Tetrachloroethane	8.2	1.45	−11.9	−9.8	−34.3	−15.2	–

[a] I, calculated by formula (4); II, calculated by formula (44).

(chlorohexyl isocyanate),[49] and nitrate,[38, 48, 88, 89] and in cyanoethylcellulose,[39] and cellulose carbanilate.[90]

Some interesting results were reported by Kolomiets, et al.[91] For the nitrates of flax cellulose in ethyl acetate and in cyclohexanone a change in sign of the Kerr constant with increasing molecular mass of the polymer was observed, as predicted by Eqn (33). This observation demonstrates the difference between the contributions to the EBR from the longitudinal and the transverse components of the dipole moments of the monomer units, and also reflects the accumulation of the longitudinal components of the molecular dipole $\mu_{0\parallel}$ when the chain length is increased.

In all the work discussed above the experimental points describing the homologous dependence of the Kerr constant for the polymer can be reconciled with the theoretical curve (33), which allows the A parameters of the equilibrium rigidity of the molecular chains to be determined. The values of A are shown in Table 4: they are reasonably well correlated with the lengths of the Kuhn segment, determined by hydrodynamic methods.

In Fig. 11 we show as an example plots of K against M for cellulose poly(butyl isocyanate) in tetrachloromethane,[92] for cellulose acetobenzoate,[43, 94] acetocinnamate,[44] and carbanilate in dioxan, and also the theoretical dependences (33) for the corresponding values of A and K_∞. The values of A for these polymers are given in Table 4.

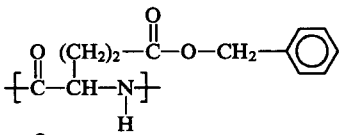
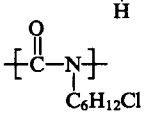
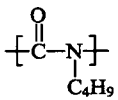
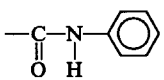
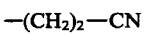
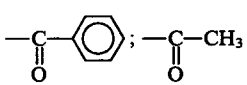
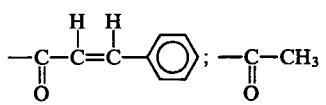
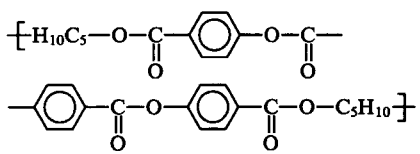
Interesting results have been reported[99, 101, 103, 105, 106] for various aromatic polyesters, mesogenic in the main chain. The mesogenic nuclei in these macromolecules are a sequence of ester groups separated by benzene rings introduced into the chain in the *para* position. Introducing into the same chain (as 'spacers') methylene groups which make the chain more flexible, as well as benzene rings in *meta* and *ortho* positions, markedly lowers the equilibrium rigidity of the chain. Furthermore an aromatic polyester containing an *ortho* benzene ring as a spacer[105] is known to orient itself in an electric field by the small-scale motion mechanism. At the same time an aromatic polyester with a decamethylene spacer,[99] in spite of its relatively low equilibrium rigidity, orients itself in an electric field by the large-scale motion mechanism (as a result of the accumulation of the longitudinal components of the dipoles of the monomer units as the chain length is increased).

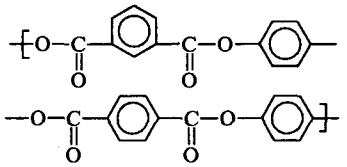
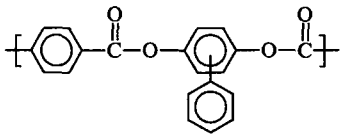
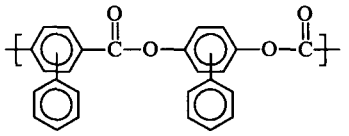
A large difference between the longitudinal-dipolar and the transverse-dipolar rigidity has been observed in mesogenic aromatic polyesters. This effect is illustrated by Eqn (33), which takes account of this difference by using the factor α. The difference is specially notable in the polyester 13 (Table 4), for which $\alpha \approx 3$. This finding is not unexpected, since the molecule of the polymer 13 is a good representation of the ideal *para*-aromatic polyester, i.e. it is structurally close to the ideal 'crankshaft' model. In Fig. 12 we show the molecular mass dependences of K for mesogenic polyesters.

We have studied[107] the equilibrium electro-optical properties of two aromatic polyamides: polyamidobenzimidazole and polyamidohydrazide, which are soluble only in strongly polar (conducting) solvents such as dimethylacetamide and dimethyl sulfoxide. A study of the kinetics of the orientation of these polymers by the transient EBR method showed that their molecules become oriented in an electric field by a large-scale mechanism. The Kerr constant for these substances shows a marked dependence on the molecular mass, characteristic of rigid-chain polymers. However, the experimental points cannot be fitted to the theoretical dependence (33) for any set of adjustable parameters. This is interpreted as a manifestation of an orientational correlation between the polar molecules and the dipolar bonds of the polymer chain.

We have calculated[107] the longitudinal component of the macromolecular dipole $\langle\mu_\parallel^2\rangle^{1/2}$ in these polymers. It was found to increase steeply as the chain length is increased (curve *1* of Fig. 13). Curve *2* of the same figure is the theoretical dependence for $\langle\mu_\parallel^2\rangle^{1/2}$, which can be calculated from the geometrical parameters of the macromolecules. It can be seen that curves *1* and *2* approach each other only in the region of small M, and that they are strongly divergent for large M. The large values of $\mu_\parallel^2$, for polyamidobenzimidazole and polyamidohydrazide cannot be attributed wholly to their dipole structure, and must be explained at least

Table 4. Length of the Kuhn segments of some rigid-chain polymers, determined by the equilibrium EBR method (A_1) and by hydrodynamic methods (A_2).

	Polymer	Structural formula	Solvent	$10^8 A_1$/cm	Ref.	$10^8 A_2$/cm	Ref.
1	Poly-γ-benzyl-L-glutamate		Dichloroethane	1600	87	2200	94
2	Poly(chlorohexyl isocyanate)		Tetrachloromethane	540	49	500	95
3	Poly(butyl isocyanate)		"	720	92	840	60
4	Cellulose carbanilate		Dioxan	210	90	240	13, 65
5	Cyanoethylcellulose		Cyclohexanone	260	39	290	96
6	Cellulose nitrate (10.7% N)		Dioxan Ethyl methyl ketone	155 –	48, 90 –	– 130	– 48
7	Cellulose nitrate (13.4% N)		Cyclohexanone Acetone Ethyl acetate	310 310 360	88 88 91	– – 300	– – 97
8	Cellulose nitrate (12.1% N)		Cyclohexanone	180	38	180	98
9	Cellulose acetobenzoate		Dioxan	210	93	210	64
10	Cellulose acetocinnamate		"	300	44	230	
11	Polydecamethylene terephthaloyl-dip-*p*-hydroxybenzoate		Trifluoroacetic acid	50	99	50	100

12	Aromatic polyester with *p*- and *m*-phenylene rings in the chain		Dichloroacetic acid	120	101	120	102
13	Monophenyl substituted poly-*p*-phenylene terephthalate		"	380	103	380	104
14	Diphenyl substituted poly-*p*-phenylene terephthalate		"	260	40	260	40
			Dioxan	–	–	260	40

[a]Data obtained in our laboratory

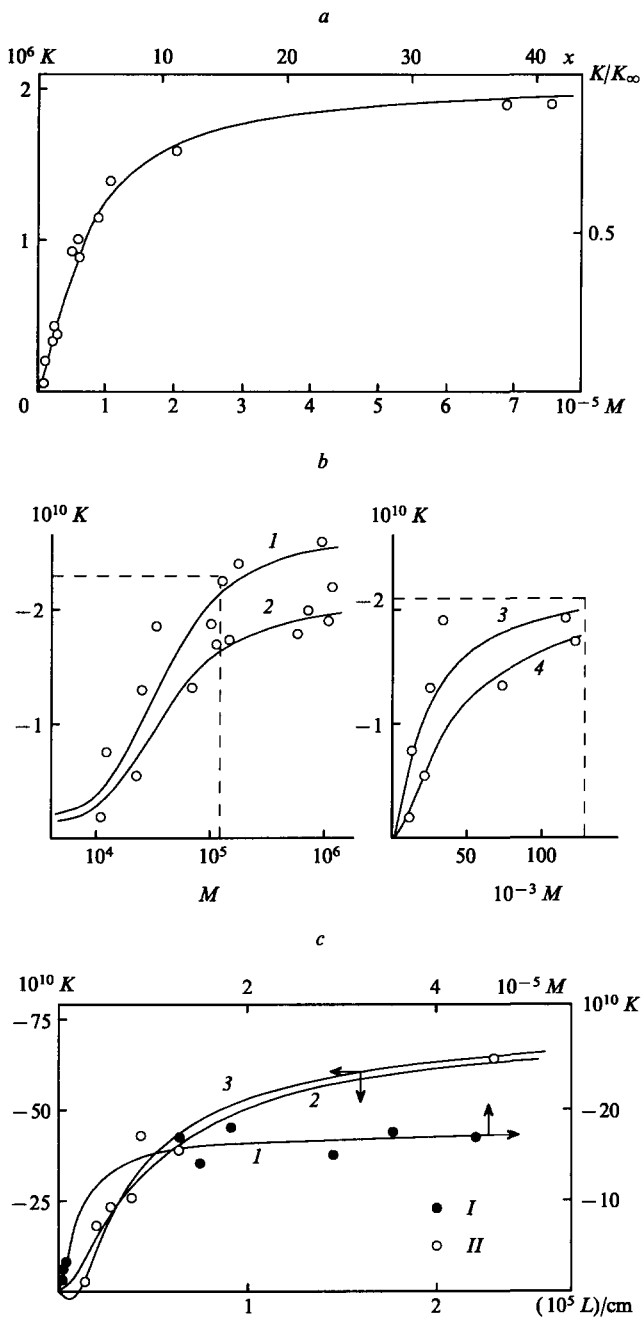


Figure 11. Plots of the Kerr constant for cellulose polybutylisocyanate in tetrachloromethane (*a*) and cellulose acetobenzoate (*b*) against the molecular mass, and also for cellulose acetocinnamate (*c*, *I*) and carbamate (*c*, *II*) in dioxan against the chain length. The points are experimental, the curves are calculated by formula (33). $10^{10} K/g^{-1}$ cm^5 (300 V)$^{-2}$: (*a*) 2.1 × 10^4; (*b*) −2.6 (*1*), −2.0 (*2*), −2.3 (*3*, *4*); (*c*) −18 (*1*); −7.5 (*2*, *3*); ϑ/deg: (*a*) 0; (*b*) 0 (*1*–*4*); (*c*) 0 (*1*–*2*), 70; α = 3 (*3*); $10^8 A$/cm: (*a*) 720; (*b*) 210 (*1*, *2*); 150 (*3*); 270 (*4*); (*c*) 300 (*1*); 250 (*2*); 200 (*3*).

partially by the influence of the strongly polar solvent on the electro-optical properties of the polymer chains.

Even more unexpected and instructive results have been obtained[40] for the diphenyl-substituted poly(*p*-phenylene terephthalate) (compound 14 in Table 4). This polymer differs from compound 13 by the presence of an additional benzene substituent in the self-repeating unit of the main chain. This additional benzene ring greatly improves the solubility of the polyester, which becomes soluble even in the nonpolar dioxan. Its

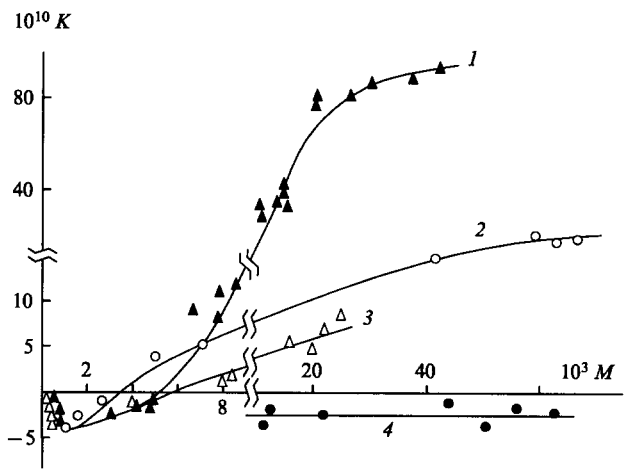


Figure 12. Dependence of the Kerr constant on the molecular mass for aromatic polyesters.[106] Polymer number (see Table 4); (*1*) 13; (*2*) 11; (*3*) 12; (*4*) analogue of 13, containing a benzene ring in the *ortho* position as a spacer; the points are experimental, the curves are calculated by Eqn (33) for α = 3 (*1*), 1 (*2*), 1.3 (*3*).

solubility is even higher in various polar solvents: for example, in dichloroacetic acid. In Fig. 14 we show the molecular-mass dependence of the Kerr constant for this polyester in dichloroacetic acid. It can be seen that K increases steeply with M, as expected for rigid-chain polymers oriented by a large-scale mechanism in an electric field. Furthermore K changes sign during the growth, suggesting an accumulation of the longitudinal components of the dipoles of the monomer units and a weakening of the correlation of the dipole formed by the normal components $\mu_{0\perp}$ with the direction of the vector $\boldsymbol{h}$ when M is increased. Lastly, the experimental points can be fitted to the theoretical curve with a reasonable choice of the parameters ϑ, A, and α.

However, in the nonpolar dioxan the Kerr constant of this polyester is almost unaffected by an increase in M, and remains close to the K value of the corresponding monomer. Furthermore

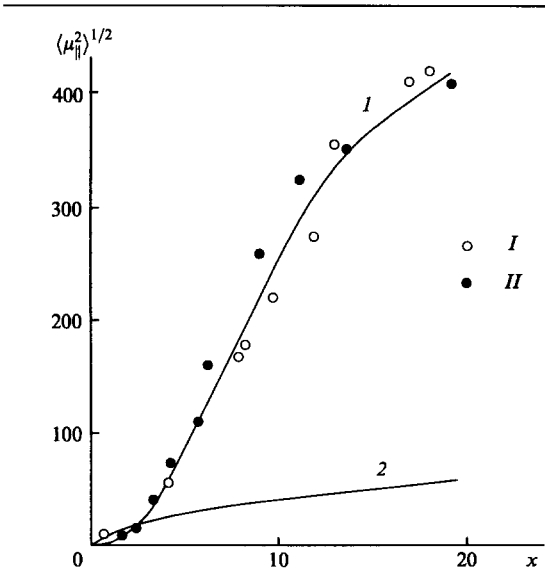


Figure 13. Dependence of the longitudinal component of the dipole moment of macromolecules $\langle\mu_\parallel^2\rangle^{0.5}$ in the direction of the vector $\boldsymbol{h}$ connecting the ends of the molecule upon the reduced chain length $x = 2L/A$: (*1*) experimental dependence for polyamidobenzimidazole (*I*) and poly-amidohydrazide (*II*); (*2*) theoretical dependence for a vermiform chain with $\mu_{0\parallel} = 1.5$ D.

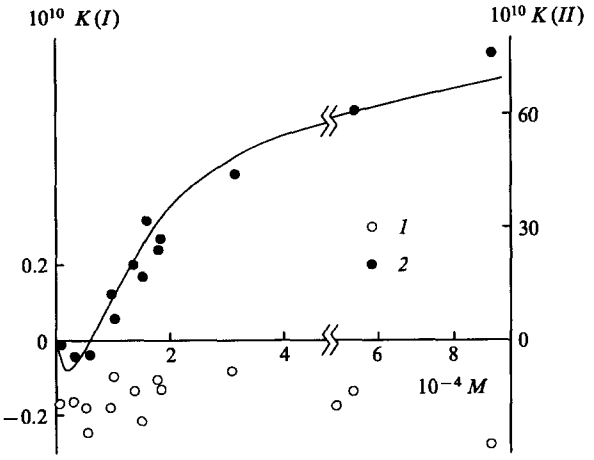


Figure 14. Dependence of the Kerr constant on the molecular mass for diphenyl-substituted poly(*p*-phenylene terephthalate) in dioxan (*1*) and in dichloroacetic acid (*2*). The points are experimental; the curve is the theoretical dependence according to Eqn (33) for $\alpha = 3$ and $K_\infty = 80 \times 10^{-10}$ g^{-1} cm^5 (300 V)$^{-2}$.

it is negative, i.e. its sign is the opposite of the sign of the flow birefringence of the same solution, and its magnitude is very small (see Fig. 14). All this suggests a small-scale orientation of the polyester (in its equilibrium state of rigidity) when exposed to an electric field in a nonpolar solvent. Noting the dipolar structure of the macromolecules of this polymer we can expect to find a substantial perpendicular component of the dipole of the monomer unit $\mu_{0\perp}$, with a negligibly small longitudinal component $\mu_{0\parallel}$. Data obtained by the steady EBR method for solutions of the *para-aromatic* polyester in dioxan point to the same conclusion, suggesting that in a solution of this polymer the EBR is due to the local reorientations of $\mu_{0\perp}$ accompanying the rotations round the *para*-aromatic axes.

The electrical birefringence in solutions of the same polymer in dichloroacetic acid is produced by the large-scale motion mechanism. This shows that a strongly polar solvent not only alters the dipole structure of the macromolecule, inducing the appearance of a substantial $\mu_{0\parallel}$ component, but also affects the process by which the EBR is created, replacing the small-scale by a large-scale mechanism. The latter effect may be due to an orientational correlation between the dipolar molecules of the solvent and the polar units of the polymer chain, leading to the formation in the polymer chain of an 'effective' electro-optical dipole which determines the mechanism, magnitude, and sign of the EBR in solutions of the polyester in a polar solvent.

3. Effect of polar solvents on the electro-optical properties of polymer chains

The results discussed in the previous section show that a polar solvent can strongly affect the electro-optical properties of rigid-chain polymers. This phenomenon has been examined in our laboratory[108] by studying the viscometric, dynamo-optical, and electro-optical characteristics of a cellulose carbanilate sample ($M = 4 \times 10^5$, degree of substitution 2.7), which is readily soluble in both the nonpolar dioxan and in various polar solvents such as ethyl acetate, cyclohexanone, and dimethylacetamide.

An analysis of these results suggests that the equilibrium rigidity of the polymer chain is decreased when a nonpolar solvent is replaced by a polar solvent. This is because the mechanism of formation of the equilibrium rigidity of the macromolecules of cellulose esters is strongly influenced by the interaction between side groups (substituents in neighbouring glucoside rings of the chain), which powerfully suppresses the intramolecular rotations. The bonds produced by the interaction of the side groups are weakened (and become easily broken) under the influence of the polar solvent molecules, capable of forming intermolecular bonds. A decrease in the optical anisotropy of the monomer unit of cellulose carbanilate in ethyl acetate has been noted and ascribed to microform effects.

The most interesting results were obtained in a study of the equilibrium electro-optical properties of cellulose carbanilate in various solvents. It was found that the Kerr constant of this polymer increases steeply with the polarity of the solvent (Table 5). The transient EBR data unambiguously show that the Kerr effect in solutions of this polymer is determined, in all the solvents examined, by the large-scale motion of its macromolecules under the influence of the electric field produced by the presence of a steady dipole moment in its chain.

In the calculation of the longitudinal component of the dipole moment of the monomer unit $\mu_{0\parallel}$ of cellulose carbanilate in various solvents allowance was made for two effects in addition to those mentioned above. Firstly, the molecular mass of the experimental sample is relatively high, and therefore its molecules are in a Gaussian tangle conformation and the EBR of its solutions is determined only by the longitudinal component of the dipole in the monomer unit $\mu_{0\parallel}$ [see Eqn (34)]. Secondly, we must note that in the description of the electro-optical properties of rigid-chain polymers in polar solvents it is reasonable to use the Onsager internal field multiplier. In these circumstances Eqn (34) can be re-written

$$K_\infty = (PQ)^2 2\pi N_A (n^2+2)^2 S^2 \Delta a \frac{\mu_{0\parallel}^2}{135 n (kT)^2 M_0} . \qquad (45)$$

Starting from (45) we calculated the $\mu_{0\parallel}$ values shown in Table 5. It can be seen that these values increase rapidly with the dipole moment of the solvent molecules. At the same time the $\mu_{0\parallel}$ value obtained for cellulose carbanilate in dioxan is reasonably well correlated with the dipole structure of the polymer chain. The large values of $\mu_{0\parallel}$ for cellulose carbanilate in polar solvents cannot be explained in terms of a single dipole structure of the macromolecule, and must be treated as effective quantities, denoting the presence of orientational correlations between the polar molecules of the solvent and the dipolar bonds in the polymer chain.

Table 5. Electro-optical characteristics of the solvents (ε, μ, K_ρ) and of the solutions (K,$\mu_{0\parallel}$) of cellulose carbanilate.

Solvent	ε	μ/D	$10^{12} K_\rho$/ g^{-1} cm^5 (300 V)$^{-2}$	$10^9 K$/ g^{-1} cm^5 (300 V)$^{-2}$	$\mu_{0\parallel}$/D
Dioxan	2.3	0	0.39	−7	0.95
Ethyl acetate	6.4	1.8	11.1	−10	1.4
Cyclo-hexanone	16	2.8	86.2	−45	2.8
Dimethyl-acetamide	40	3.8	351	−200	5.6

The present writers have recently carried out additional studies, aimed at explaining the effect of polar solvent molecules on the electro-optical properties of rigid-chain polymer molecules. The cellulose carbanilate sample ($M = 195 \times 10^3$, degree of substitution 2.3) was studied by viscometric, dynamo-optical, and electro-optical methods in mixed solvents (dioxan–ethyl acetate). The relative mole fraction of the components f was varied from 0 to 1. A dispersion of the EBR in the radio-frequency range was observed in all the solutions, the dispersion curves falling almost to zero whereas the relaxation times were reasonably well correlated with the size of the macromolecules. These observations suggested a large-scale motion in the orientation of the cellulose carbanilate macromolecules in an electric field for all the mixed solvents examined.

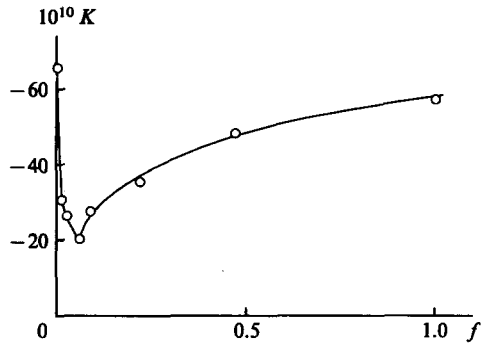


Figure 15. Plot of the Kerr constant of cellulose carbanilate (M = 195 × 10^3) against the mole fraction of ethyl acetate in the ethyl acetate–dioxan mixed solvent.

The dependence of the Kerr constant of the ester on the mole fraction f of ethyl acetate is shown in Fig. 15. The changes in K with f are strongly non-monotonic. In principle this behaviour could be due to changes in the dipole moment of the molecule, in its equilibrium rigidity, and in its optical anisotropy with changes in composition of the solvent. An analysis of these results led to the conclusion that all three parameters listed above are operating in the system. Noting that the molecular mass of the sample is relatively high, i.e. that the macromolecule is in the conformation of a Gaussian tangle, we can calculate $\mu_{0\parallel}$ from Eqn (45), allowing for changes in both S and Δa.

The dependence of $\mu_{0\parallel}$ for cellulose carbanilate on the mole fraction f of ethyl actate is shown in Fig. 16. The non-monotonicity of the changes in $\mu_{0\parallel}$ is evident. We specially note that for $f \geqslant 0.1$ $\mu_{0\parallel}$ value increases (within experimental error) almost linearly with f. This observation evidently suggests that the effective electro-optical dipole formed by the polar polymer chain with the dipole moments of the ethyl acetate molecules increases in direct proportion to the number of molecules of the polar component in the mixed solvent. The slight decrease in $\mu_{0\parallel}$ with increase of f at $f < 0.1$ can be ascribed to the partial screening of the dipole moment of the macromolecule by the polar solvent molecules.

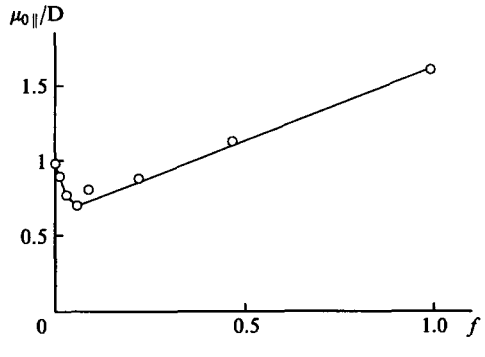


Figure 16. Plot of the longitudinal component of the dipole moment of the monomer unit of cellulose carbanilate against the mole fraction of ethyl acetate in a mixed ethyl acetate–dioxan solvent.

From the whole of this discussion we may conclude that the EBR in solutions of rigid-chain polymers is determined not only by the polar structure of their macromolecules but also (and to a large extent) by the dipole structure of the chosen solvents, the latter factor playing a dominant role in the case of strongly polar liquids. This can lead to a change in the dipole moment of the polymer chain, and also (as was pointed out above) to a change in the very nature of the observed EBR, depending on the choice of solvents. Therefore we can obtain quantitative information on the magnitude and direction of the dipole in the monomer unit of the macromolecules of rigid-chain polymers using only nonpolar solvents.

V. Effect of the structure of side groups and of the degree of substitution on the electro-optical properties of cellulose esters

Cellulose esters are an important class of polymers of the rigid-chain type. One property of these materials is particularly attractive to research workers: the possibility of changing the electro-optical characteristics of their molecules over a reasonably wide range by varying the chemical structure of the substituents and the extent of the esterification reaction (i.e. the average degree of substitution γ).

It has been firmly established [38, 49, 52, 88, 97, 98, 109] that both the optical shear coefficients $\Delta n/\Delta\tau$ in FBR effects and the Kerr constants for cellulose nitrates are sensitively dependent on the degree of substitution. Thus, for cellulose nitrate containing 10.7% of nitrogen the optical shear coefficients $(\Delta n/\Delta\tau)_\infty$ and the Kerr constant K_∞ in the Gaussian region are small and positive.[48, 109] At the same time in nitrates containing a larger percentage of nitrogen $(\Delta n/\Delta\tau)_\infty$ and K_∞ are negative, and K_∞ is greater by two orders of magnitude (in absolute value) than K_∞ for the less highly substituted nitrate.[38, 52, 88, 97, 98] The same papers point out a steep increase in the dipole moment of the monomer unit μ_0 of the cellulose nitrates with the nitrogen content of the side groups, but these results should be viewed with caution because they were obtained in a strongly polar, electrically conducting solvent, cyclohexanone, and this could introduce significant errors in the dipolar characteristics of the polymer chains.

We have reported [51] a study of the optical and the electrical properties of two substituted cellulose esters (the acetodiphenylacetate and the acetocinnamate) as a function of their degree of substitution. The measurements of EBR, FBR, and viscosity were carried out in a nonpolar, poorly conducting solvent (dioxan), and the molecular masses of the polymers corresponded to the Gaussian region. In both these cellulose esters we observed a steep increase in the optical shear coefficients $(\Delta n/\Delta\tau)_\infty$ and in the Kerr constant K_∞ upon increasing the degree of substitution γ (with respect to the benzene-containing radical). The results are shown in Fig. 17. The nonlinearity of the plot of $(\Delta n/\Delta\tau)_\infty$ against γ for cellulose acetodiphenylacetate may be related to a change in the rigidity of the polymer chain with changes in γ or to an incomplete equivalence of the contributions to the optical anisotropy from the large diphenylacetate radicals, attached to the second and to the third or sixth carbon atom in the glucoside ring.

A study of the transient Kerr effect of these two cellulose esters showed that the mechanism mainly responsible for the EBR observed in solutions of cellulose acetocinnamate and acetodiphenylacetate at all degrees of substitution is the large-scale rotation of their macromolecules under the influence of the electric field, due to the presence of a steady dipole moment. However, as was stated above, the absolute value of K_∞ for these esters increases rapidly with γ. This dependence of the Kerr constant on the degree of substitution may be due to an increase in the optical anisotropy of the macromolecules (positive for the diphenylacetate and negative for the cinnamate) with increasing γ, as was also inferred from the dependence of $\Delta n/\Delta\tau$ on γ, or alternatively it may be due to changes in the dipole moment of the molecular chain.

By using Eqn (45) we have calculated [51] the $\mu_{0\|}$ values of the esters for different degrees of substitution γ. It can be seen from the results (Fig. 18) that in these esters $\mu_{0\|}$ increases with γ, especially in the acetocinnamate. This suggests that the dipole moment

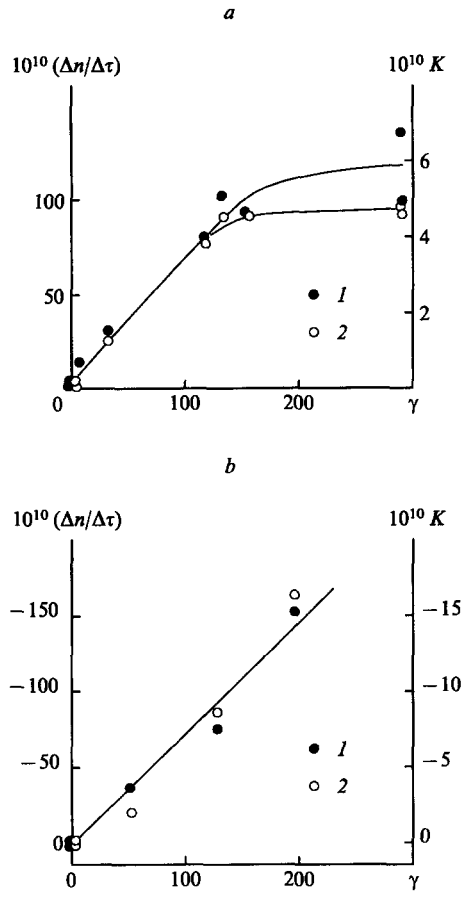


Figure 17. Plots of the optical shear coefficient (*1*) and of the Kerr constant (*2*) for cellulose acetodiphenylacetate (*a*) and acetocinnamate (*b*) against the degree of substitution.

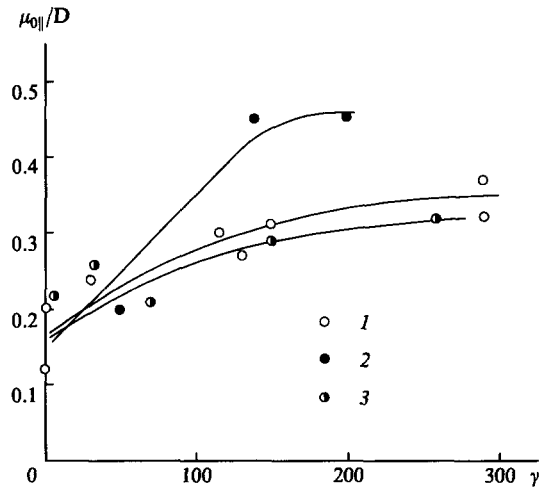


Figure 18. Dependence of the longitudinal component of the dipole moment of the monomer unit in cellulose acetodiphenylacetate (*1*), aceto-cinnamate (*2*), and acetophenylacetate (*3*) upon the degree of substitution.

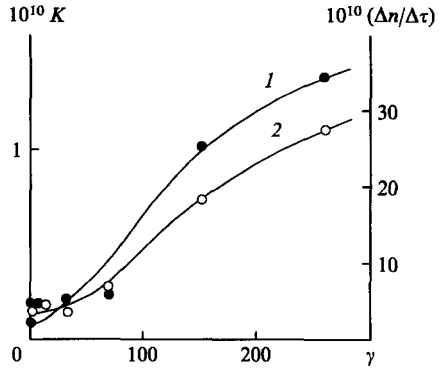


Figure 19. Plots of the Kerr constant (*1*) and of the optical shear coefficient (*2*) of cellulose acetophenylacetate against the degree of substituion.

contributed by the ester group in a side group of the glucose ring to the longitudinal component of the dipole moment of the monomer unit of the cellulose chain is strongly dependent on the structure of the side substituent. In fact, it follows from these results[51] that the presence of benzene groups in the substituent leads to an increase in the longitudinal component of the dipole of the monomer unit $\mu_{0\|}$ in the polymer chain as a result of the change in the contribution from the OCO group, whereas the presence of alkyl radicals lowers the $\mu_{0\|}$ value.

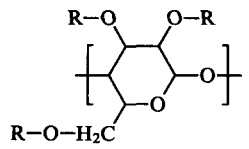
We have recently studied the effect of the degree of substitution on the electro-optical properties of cellulose acetophenylacetate in dioxan (Figs. 18, 19). The results were similar to those obtained previously.[51] The optical shear coefficients and the Kerr constants of these high-molecular samples were found to be strongly dependent on the degree of substitution γ with respect to the phenylacetate group. This dependence of $\Delta n/\Delta\tau$ upon γ is not unexpected, since the introduction of strongly anisotropic groups containing benzene rings should markedly increase the optical anisotropy of the whole molecule in comparison with that of cellulose acetate, which is not large. By using Eqn (45) we calculated the longitudinal component of the dipole moment of the monomer unit $\mu_{0\|}$ for the cellulose acetophenylacetates at different degrees of substitution (see Fig. 18). It can be seen from this figure that $\mu_{0\|}$ increases with γ. This effect should be interpreted in the same way as for the cellulose acetodiphenylacetate.

Thus we may conclude that the presence of conjugated bonds in the side chains increases the contribution from the ester group of the side chain to the overall $\mu_{0\|}$ value of the cellulose ester macromolecules.

Meaningful results were obtained for acetotritylcellulose (compound 29 in Table 6). It was found that changing the degree of substitution γ with respect to the trityl radical from 0 to 145 increases $(\Delta n/\Delta\tau)_\infty$ by an order of magnitude, whereas the Kerr constant increases by more than two orders of magnitude, corresponding to an increase in $\mu_{0\|}$ from 0.2 to 1.5 D. This large increase in $\mu_{0\|}$ suggests that the contribution to $\mu_{0\|}$ from the ether group is more substantial than the contribution from the ester group.

The other results in Table 6 also show that $\mu_{0\|}$ for compounds containing a simple ether group in a side group is usually higher than for compounds having an ester group in the side chains (exceptions to this rule are provided by the polymers 3 and 4, whose side substituents contain the strongly polar amide group). In a similar way, replacing the ester groups by hydroxyl groups increases $\mu_{0\|}$, as can be seen by comparing the data for cellulose acetobenzoate and cellulose benzoate (compounds 9 and 10). The strong effect of the structure of the side chain on the longitudinal component of monomeric dipole can be illustrated by comparing data for cellulose carbanilate and cellulose acetobenzhydroxamate (compounds 4 and 33). Passing from the structure of polymer 4 to that of polymer 33 decreases the negative value of $(\Delta n/\Delta\tau)_\infty$ and therefore also of the anisotropy Δa by a factor of two, whereas the modulus of K_∞ decreases 200-fold and $\mu_{0\|}$ decreases 10-fold.

Table 6. Electro-optical properties of some cellulose esters



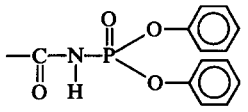
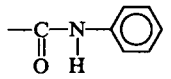
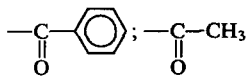
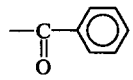
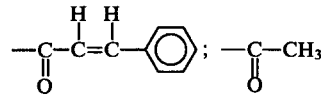
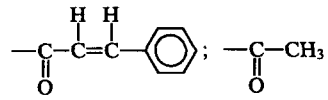
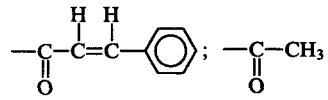
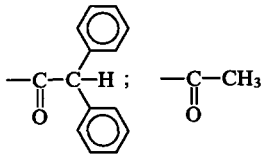
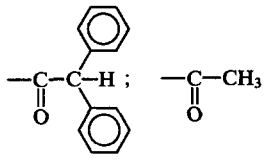
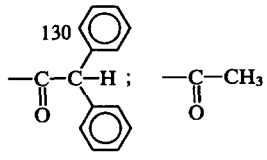
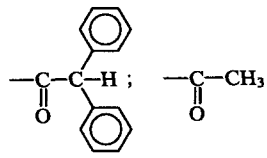
	Polymer	Structural formula of substituent radical	Degree of substitution [a]	$10^{25}\Delta a$/ cm^3	$10^{10}K_\infty$/ g^{-1} cm^5 (300 V)$^{-2}$	$\mu_{0\parallel}$/D	Ref.
1	Ethylcellulose	$-C_2H_5$	260	8	25	1	52
2	Benzylcellulose	$-CH_2-C_6H_5$	220	6	6	0.7	52
3	Cellulose diphenyl-phosphonocarbamate		200	12.5	25	1.4	52
4	Cellulose carbanilate		270	−40	−70	0.95	47
5	Cellulose nitrate	$-NO_2$	190	4.2	6	1	48, 90
6	Cellulose nitrate	$-NO_2$	230 [b]	−8.4	−550	–	38, 98
7	Cellulose nitrate	$-NO_2$	270 [b]	−9	−900	–	88, 97
8	Cyanoethylcellulose	$-(CH_2)_2-CN$	260 [b]	17.8	250	–	39, 96
9	Cellulose acetobenzoate		245 55	−26.6	−2.3	0.21	93, 110
10	Cellulose benzoate		216	−27	−7.7	0.38	[d]
11	Cellulose acetocinnamate		200 60	−38	−18	0.44	44
12	Cellulose acetocinnamate		140 160	−26	−9.4	0.44	51
13	Cellulose acetocinnamate		50 250	−9	−1.1	0.2	51
14	Cellulose acetodiphenylacetate		290 10	25.6	4.6	0.37	51
15	Cellulose acetodiphenylacetate		150 40	24	4.6	0.31	51
16	Cellulose acetodiphenylacetate		130 26.9 20	4.5	0.27	51	
17	Cellulose acetodiphenylacetate		115 130	20.4	3.9	0.3	51

Table 6 (continued).

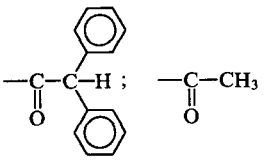
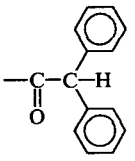
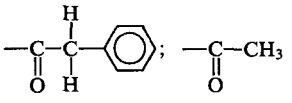
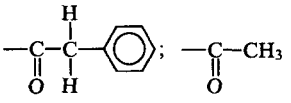
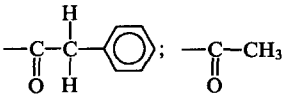
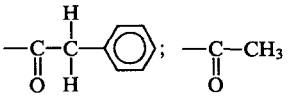
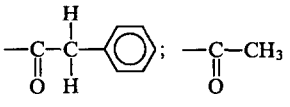
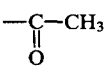
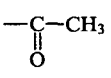
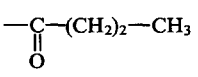
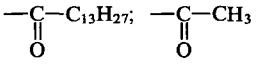
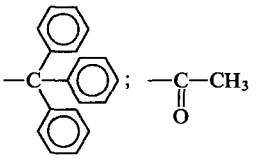
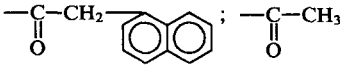
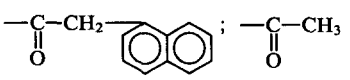
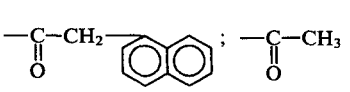
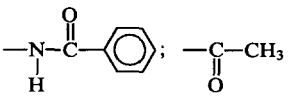
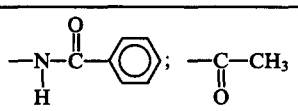
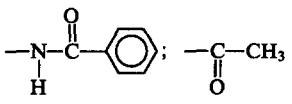
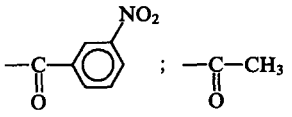
	Polymer	Structural formula of substituent radical	Degree of substitution[a]	$10^{25}\,\Delta a/cm^3$	$10^{10}\,K_\infty/g^{-1}\,cm^5\,(300\,V)^{-2}$	$\mu_{0\parallel}/D$	Ref.
18	Cellulose acetodiphenylacetate		30 270	8.1	1.3	0.24	51
19	Cellulose diphenylacetate		290	35.2	4.8	0.32	51
20	Cellulose acetophenylacetate		260 40	7.3	1.4	0.32	d
21	Cellulose acetophenylacetate		150 100	5	1.02	0.29	d
22	Cellulose acetophenylacetate		70 200	1.8	0.24	0.21	d
23	Cellulose acetophenylacetate		32 246	1.0	0.21	0.26	d
24	Cellulose acetophenylacetate		5 285	1.3	0.2	0.22	d
25	Cellulose diacetate		240	1	0.15	0.2	51
26	Cellulose triacetate		300	0.78	0.04	0.12	51
27	Cellulose butyrate		300	1.2	0.4	0.4	52
28	Cellulose acetomyristate		290[c] 10[c]	−2.2	−0.7	0.5	d
29	Cellulose acetotriphenylmethylate		145 110	22	87	1.53	d
30	Cellulose aceto-α-naphthylacetate		50 250	1.4	0.87	0.47	d
31	Cellulose aceto-α-naphthylacetate		25 275	1.4	0.18	0.2	d
32	Cellulose aceto-α-naphthylacetate		10 290	1.1	0.08	0.15	d
33	Cellulose acetobenzhydroxamate		285 15	−17.4	−0.3	0.1	d

Table 6 (continued).

Polymer	Structural formula of substituent radical	Degree of substitution[a]	$10^{25}\Delta a$/ cm^3	$10^{10}K_\infty$/ g^{-1} cm^5 (300 V)$^{-2}$	$\mu_{0\|\|}$/D	Ref.
34 Cellulose acetobenzhydroxamate		240 60	−11.5	−0.4	0.13	d
35 Cellulose acetobenzhydroxamate		170 90	−7	−0.15	0.1	d
36 Cellulose acetonitrobenzoate		25 275	−2.3	0.3	–	d

[a] If the degree of substitution is quoted in two lines the values in the second line refer to substitution by acetic acid.
[b] Solvent: cyclohexanone.
[c] Solvent: benzene.
[d] Data obtained in the writers' laboratory.

In various studies of the EBR of cellulose esters it has been assumed that the parameter $\mu_{0||}$ is determined by the dipoles of the polar O–C bonds of the glucopyranose ring in the main chain and is practically independent of the dipole structure of its side substituents.[52] The experimental information accumulated in more recent work (and discussed above) is not inconsistent with this assumption. As can be seen from the previous discussion the characteristics mainly responsible for the electro-optical properties of cellulose esters include not only the optical anisotropy but also the dipole structure of the side substituents in these molecules.

The parameter $\mu_{0||}$, which can be varied ten-fold by changes in the structure of the substituent groups and in the degree of substitution (see above), is determined by the sum of the dipole moments of all the polar bonds included in the monomer unit of the polyglucoside chain. Often the main part of this sum of moments is the contribution from the polar groups of the side substituents. Thus, in spite of the presence of some degree of rotational mobility of the polar groups in the side substituents, the dipolar contribution from these groups to the longitudinal component $\mu_{0||}$ of the dipole of the monomer unit is effectively 'fastened' in this unit and gives rise to the large-scale orientation of the polymer chain in an electric field.

Nevertheless the appearance of a freer 'small-scale' motion of the anisotropic polar groups in the side chains cannot be excluded in the EBR of solutions of cellulose esters. An obvious example is provided by the results (unexpected for rigid-chain polymers) obtained in solutions of celluiose acetonitrobenzoate (compound 36 in Table 6). The dynamic birefringence of this polymer is negative, whereas the EBR of its solutions is positive. Further-more in the radio-frequency band its EBR does not show dispersion, and K_∞ (allowing for the degree of substitution) is close to the value of the Kerr constant for a solution of nitrobenzene in dioxan at a corresponding concentration. All these observations suggest that the EBR in solutions of this polymer is produced by a large-scale orientation mechanism involving the polar nitrobenzene groups in the side substituents.

VI. Electro-optics of solutions of branched polymers with mesogenic groups in the side chains

Specific electro-optic properties are found in solutions of polymers of the branched type, whose molecular basis is a flexible polyacrylate or polymethacrylate chain with side groups also having a chain structure and containing mesogenic fragments of aromatic esters (Table 7).

Because of their dipole structure the monomer units of polyalkylacrylates and polyalkylmethacrylates (like those of other carbon-chain polymers) do not have a component of the dipole moment parallel to the polymer chain. Accordingly, the orientation of their chains in an electric field takes place by a mechanism involving local small-scale motions of the polar groups. The electrical birefringence observed in solutions of these polymers is quite small, and its sign is not correlated with that of the FBR.[13] The equilibrium rigidity of the molecules in these polymers also corresponds to the rigidity of ordinary polymers with flexible chains.

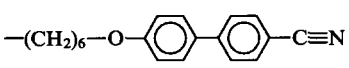
However, the physical properties of the polymethacrylate or polyacrylate chain are markedly affected if the alkyl part (R) of its side groups is replacd by the mesogenic chain of an aromatic ester (see Table 7). This leads to an increase in the equilibrium rigidity of the main chain of the resulting branched polymer to $A \simeq 50 \times 10^{-8}$ cm,[13] exceeding 2–4-fold the rigidity of typical flexible-chain polymers. This effect is related to the steric interactions of the large side groups (a phenomenon well known in other flexible-chain polymers[12]).

However, the strongest effect of mesogenic side radicals is observed in the electro-optical characteristics of branched molecules, many of which are soluble in nonpolar solvents. Thus, the study of the transient EBR in solutions of the polymers 1 and 2 (see Table 7) in a nonpolar solvent, using sinusoidal fields, showed a dispersion of the Kerr effect in the radio-frequency region ($\nu = 10^2 - 10^6$ Hz). As the frequency is increased in this band the Kerr constant falls almost to zero.[111,112] This result shows that the dominant contribution to the observed Kerr effect comes from the large-scale rotation of the dipolar macromolecules of these polymers in an electric field.

At the same time, though they show a tendency to increase with M, the F coefficients for polymer 2 exceed the theoretically maximum values for kinetically rigid molecules by a substantial factor.[112] Furthermore, for the high-molecular mass fractions of polymer 1 the relaxation time τ is independent of the molecular mass.[111] These observations show that (in addition to the rotation of the molecule as a whole) a deformation mechanism of molecular motion contributes to the development of the EBR in these polymers. Its role increases with the molecular mass of the fraction. The lack of dependence of τ on M for the polymer 1 is evidence that the condition $\tau_{or} > \tau_{def}$ applies to this polymer and that the motion of the molecular chain takes place by a

deformation mechanism, in which only part of the molecule acts as the 'kinetic unit', oriented in the electric field. However, under these conditions the rotational mobility of the kinetic unit is lower by 5 or 6 orders of magnitude than in ordinary flexible-chain polymers. Therefore this motion (though intramolecular) is similar in nature to a large-scale motion, since it is correlated through the chain.

A study of the equilibrium EBR in solutions of the polymers 1–3 (see Table 7) showed that the Kerr constant is strongly dependent on M: this behaviour is typical of monomers whose molecular chain



can accommodate an 'accumulation' of the longitudinal component μ of the monomeric dipoles. Further-more in these samples (as in compounds 4 and 5) the signs of K and of $\Delta n/\Delta\tau$ coincide in the region of high molecular masses (Table 7, see over), suggesting identical orientation mechanisms of their macromolecules in electrical and in hydrodynamic shear fields.

Thus both the transient and the steady-state electro-optical properties of branched polymers unambiguously show that the insertion of mesogenic side groups in the main methacrylate chain of polymers 1–5 (see Table 7) produces longitudinal components of the monomeric dipoles $\mu_{0||}$, uniformly oriented along the chain. The $\mu_{0||}$ values calculated by formula (45) from the Δa and K_∞ values in nonpolar solvents are shown in Table 7. They can account for only a small part of the total dipole moment μ_0 of the monomer unit of the branched macromolecule. However, these $\mu_{0||}$ components contributed by mesogenic side groups in the polymeric molecule can accumulate along its main chain and induce the orientational–polar ordering responsible for the Kerr effect in the polymer solution. The formation mechanism of the $\mu_{0||}$ dipoles uniformly oriented along the main chain of the branched polymer can be understood if one allows for the orientational interaction between the side chains, whose mesogenic nuclei contain dipolar components $\mu_\perp$ normal to these chains. In the presence of orientational order of the nematic type between the mesogenic side chains the $\mu_\perp$ components can contribute to the $\mu_{0||}$ component parallel to the main chain of the polymer.

The important role of the mesogenic structure of the side groups in the formation of the longitudinal components ($\mu_{0||}$) of the dipoles is clearly illustrated by the electro-optical properties of polymer 6 (Table 7), whose side chains are long, polar, and anisotropic, but not mesogenic. The equilibrium K values for this polymer are small and similar in order of magnitude to the K value for its monomer in tetrachloroethane, and also for low-molecular substances with a structure similar to that of its side groups. For sinusoidal fields at radio-frequencies no dispersion of the EBR has been detected [114] in solutions of the polymer. These results show that the branched molecules of polymer 6, whose side chains are not mesogenic in an electric field, behave as kinetically flexible and orient themselves by a deformation mechanism of the chain (relying on the local motion of the polar groups).

As the mesogenic nucleus of the side group in a branched polymer is moved further away from the main chain [by introducing a flexible segment (the spacer) between them] the correlation between the orientations of the main chain and of the side chains becomes less close. Therefore the large-scale motion of the macromolecule is replaced by a small-scale (local) motion, in which the orientation of the side chains in an electric field takes place as in a solution of the corresponding monomer: by the more or less independent rotation of the polar side groups. This conclusion is well illustrated by data [112] obtained for the polymer 7, whose solutions do not show radio-frequency dispersion of K: the equilibrium value of this constant is close to the K value for sample 6.

The weakening of the orientational correlation between the main chain and mesogenic side groups is of fundamental importance in demonstrating the mesomorphism of the branched polymer in a pure sample. As we know, branched polymers form a thermotropic nematic phase only if the orientation of the mesogenic side nucleus relative to the main chain is reasonably free, i.e. in the presence of a spacer. Thus, we have studied [115] the equilibrium and the transient EBR in the isotropic phase of a branched polymer containing mesogenic cyanobiphenyl groups in the side chains.

The relaxation time corresponding to a more or less independent (local) orientation of the mesogenic side groups has been obtained. Data on the equilibrium EBR confirmed these results: its magnitude and its positive sign corresponded to the magnitude and sign of the EBR in the isotropic phase (or in solution) of the mesogenic low-molecular analogue.

VII. Conclusions

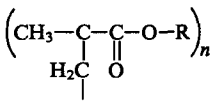
We have discussed the electro-optical properties of polymers whose macromolecules differ strongly in their equilibrium rigidity. The terms 'semirigid' and 'rigid-chain' polymers have been proposed for these materials. As we have pointed out, [116, 117] semirigid molecules cannot be treated as a class of polymers having a well defined structure. It is better to characterise them as a group of structures displaying a recognisable group of physicochemical properties. One of the most important of these properties is the large-scale orientation of the molecular chain in an electric field. The necessary condition for the appearance of this mechanism is the presence of a longitudinal component of the dipole moment of the monomer unit $\mu_{0||}$, correlated over the contour of the molecular chain.

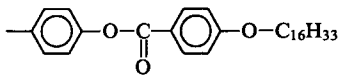
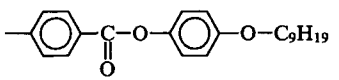
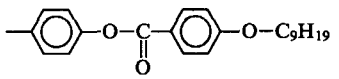
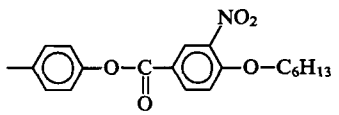
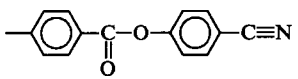
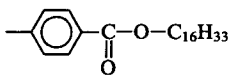
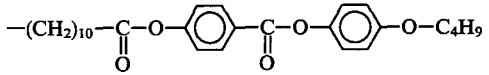
The maximum value of the Kerr effect for polymers (in the Gaussian region) is determined by the parameters $\Delta a_,$, $\mu_{0||}^2$, and S^2. Depending on the possible values of these quantities the Kerr constant can vary over several orders of magnitude in absolute value, but the signs of K_∞ and $\Delta n/\Delta\tau$ are the same whenever $\mu_{0||}$ is orientationally correlated over the chain. For many flexible-chain polymers the fundamental condition for the formation of large-scale EBR is not fulfilled, and therefore in these cases K is small and is determined by the local orientation of the monomer units, and the signs of K and $\Delta n/\Delta\tau$ are not correlated. However, even in the presence of monomeric dipoles $\mu_{0||}$ uniformly oriented over the chain the Kerr effect can be difficult to observe because S^2 (and therefore also K) is small. In addition, the presence of anisotropic and of polar side groups interacting specifically in a flexible polymer chain can produce both a slight increase in S and Δa as well as some increase in the $\mu_{0||}$ parameters, and therefore it can lead to the development in these solutions of an EBR effect by the large-scale motion mechanism. A clear example of this behaviour is seen in the branched polymers with anisotropically interacting mesogenic side groups.

The nature of the development of a longitudinal component of the dipole of the monomer unit in a polymer can differ in different systems, but in nonpolar solvents $\mu_{0||}$ for the polymer is always determined by the dipolar structure of the macromolecules. Under these conditions $\mu_{0||}$ can be strongly dependent on the polar structure of the main chain [for example, in poly(alkyl isocyanates)] as well as on the dipolar properties of the side substituents, as is clearly seen in the cellulose esters.

When polar solvents are used the origin of the $\mu_{0||}$ component is not so well understood. Under these conditions $\mu_{0||}$ can be formed by the specific interactions between the polymer and the solvent, leading to the orientational correlation of the dipolar solvent molecules and of the polar bonds in the polymer chain, and resulting in the formation of an effective 'electro-optical' dipole in the macromolecule.

In studies of the transient EBR in dilute solutions of polymers the nature of the formation of $\mu_{0||}$ is unimportant in principle. Studies of the dependence of the relaxation times on the molecular

Table 7. Electro-optical properties of some branched polymers  mesogenic groups in the side chains.

	R	Solvent	$10^{10}\,K$/ $g^{-1}\ cm^5\ (300\,V)^{-2}$	$10^{10}\,(\Delta n/\Delta\tau)$/ $cm\ s^2\ g^{-1}$	$10^{25}\,\Delta a/cm^3$	$\mu_{0\parallel}/D$	Ref.
1		Tetrachloromethane	−4 to −20	−220	−110	0.7	111
2		"	−3.4 to −8.0	−220	−110	0.43	112
3		"	−3 to −7	−50	−40	0.8	111
4		Dioxan	−7	−95	−80	0.67	113
5		Dichloroacetic acid	−4.9	−22	−20	–	113
6		Tetrachloromethane	−0.5	−35	−18	–	114
7		Dioxan	−0.9	−8.5	−7	–	112

mass for rigid-chain polymers have yielded some quantitative conclusions on the equilibrium rigidity of macromolecules without introducing data obtained by other methods, and it also allowed their kinetic rigidity to be characterised qualitatively.

An analysis of the dependence of the Kerr constant on the molecular mass in rigid-chain polymers allows us to determine the equilibrium rigidity of the chain. Under these conditions the result is relatively unaffected by the choice of solvent. The problem is simplified when the contribution to the electro-optical effect from the normal component of the dipole of the monomer unit $\mu_{0\perp}$ is small, which corresponds either to a small value of ϑ or to a large value of α. Equilibrium EBR data can be used in studies of the dipole structure of a polymer chain (the magnitude of the dipole of the monomer unit μ_0 and its slope ϑ with respect to the contour of the macromolecule) only when nonpolar solvents are chosen. To determine the angle ϑ reliably it is important to include a change in sign of the dependence of K on M, which should be observed for $\vartheta > 54°$, since unless this is done the dependence of the Kerr constant on the molecular mass is an insensitive function of the angle ϑ and cannot be used to calculate it. Unfortunately, experimental data indicating a change in sign of K upon increasing M have not so far been obtained in nonpolar solvents.

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