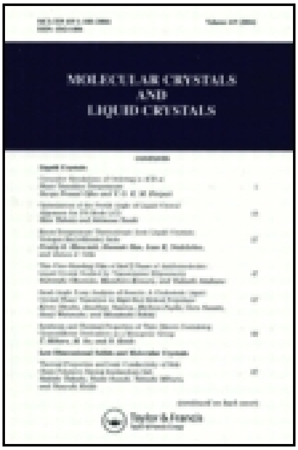

Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics

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Elastic Deformations of Liquid Crystalline Polymers and Their Monomers in Magnetic and Electric Fields

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ELASTIC DEFORMATIONS OF LIQUID CRYSTALLINE POLYMERS AND THEIR MONOMERS IN MAGNETIC AND ELECTRIC FIELDS

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Abstract A thermotropically mesogenic aromatic polyester and its low molecular weight analogue ("monomer") in the nematic phase in thin layers form homeotropic textures which can be deformed under the influence of magnetic or electric fields. The elastic orientational deformations generated here are of the threshold character (Freederiksz's transition) and are used for the determination of bend elastic constants, K_3, of the polymer and low molecular weight nematics. The optical anisotropies, $n_e - n_o$, of the samples investigated were determined from the polarized-microscopic patterns of the deformed layers. The values of $n_e - n_o$ for the polymeric and the low molecular weight nematics virtually coincide and over the investigated temperature range vary from 0.08 to 0.17. The bend constants K_3 are close in the order of magnitude for the polymer and the monomer and vary with temperature in the ranges $(5-20)\cdot 10^{-7}$ dyn and $(3-10)\cdot 10^{-7}$ dyn, respectively. The orientation of molecules of the polymer nematic in magnetic and electric fields follows the mecanism of local small-scale chain motion.

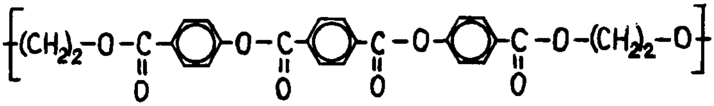
INTRODUCTION

It is known that the main property of liquid crystals distinguishing them from amorphous bodies is the presence in the liquid crystalline substance of a long-range orientational order [1] in which the axes of extended molecules are predominantly aligned parallel to the "director". The long-range order is maintained by the forces of orientational interaction of molecules counteracting elastic orientational deformations (i.e., changes in the orientation of the director) which appear in the nematic under the influence of external forces. These distortions may by described by using the three main elastic constants of the nematic, K_1, K_2 and K_3, corresponding to the splay, twist and bend deformations respectively. The elastic constants characterizing the forces of intermolecular orientational interaction in the nematic are fundamental values determining the main properties of the mesophase both in thin layers and in bulk. They affect not only the equilibrium textures observed in the microscope but also the dynamic properties of the nematic, such as mechanical [2] and thermal [3] orientational vibrations, light scattering [4], orientation in flow[5], electrodynamics [6], etc. The theories and methods of quantitative investigation of elastic deformations of low molecular weight nematics in magnetic and electric fields have been developed by the Leningrad team of physicists who have determined the values of K_1, K_2 and K_3 for p-azoxyanisol and some other mesogenes over the entire temperature range of the existence of their nematic phase [7-11]. More recently these studies have been pursued by several researchers[12-17] who have determined the values of K_1, K_2 and K_3 for some other low molecular weight nematics.

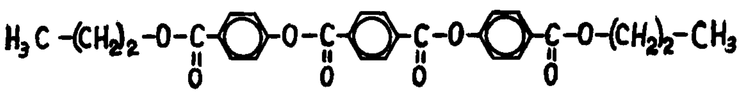
The molecules of thermotropically and lyotropically mesogenic polymers both in solution and in the nematic bulk can undergo orientation by the action of magnetic or electric fields[18-21]. However, the studies in which these effects are used for the investigation of elastic deformations in polymeric thermotropic liquid crystals are virtually non-existent. The preliminary results of first investigations in this field have been reported recently[22]. More recently these investigations have been continued, and their results are considered in the present paper.

EXPERIMENTAL

Two substances were used for the investigations: an aromatic polyester (APE)



and a low molecular weight analogue of its repeat unit (AE"monomer")



The syntesis of these compounds has already been described [23]. The low molecular weight compound, AE, is in the nematic liquid-crystalline state in the temperature range 190-215°C.

The APE under investigation is a para-aromatic polyester in which rigid mesogenic (ester-aromatic) nuclei are separated by flexible diethylene glycol chain parts. The molecular weight of the sample M (according to viscometric data and diffusion of its dilute solutions) is $4 \cdot 10^3$ and its intrinsic viscosity in dichloroacetic acid is 0.41 cm^3/g. The polarizing microscopic investigations showed that at $T = 200°C$, APE melts from the crystalline into the nematic phase which passes into the isotropic phase at $T = 320°C$.

An indispensable condition for the quantitative study of elastic orientational deformations in the nematic is the formation of a texture with a director uniformly oriented in the sample and having a definite character of orientation on the sample boundaries. For low molecular weight nematics, the methods of preparation of these textures are well known and it was possible to obtain the homeotropic texture (director is normal to the glass surface) in the nematic phase of the monomer without difficulty.

In the case of polymer APE the situation was more complex. The homeotropic structure in the layers of the polymer nematic could by obtained only by a special treatment of polished surfaces of the quartz glasses and the application of wedge-shaped polymer layers. The thickness of these layers, however did not exceed 0.1 mm (Fig.3).Nevertheless, it was found to be sufficient for the quantitative investigation of deformation of these layers in magnetic and electric fields.

In the investigations carried out in the magnetic fields, Freedericksz's and Zolina's method[7] was used, and in the investigations in the electric fields, Freedericksz's and Tsvetkov's method [9, 10] was applied. In both cases wedge-shaped, planar and spherical surfaces of the quartz glasses were employed (Fig.1). The layer thickness Z was determined from the ratio $Z = r^2/2R$ where R is the radius of the spherical glass surface and r is the distance between the investigated point of the preparation and its centrum.

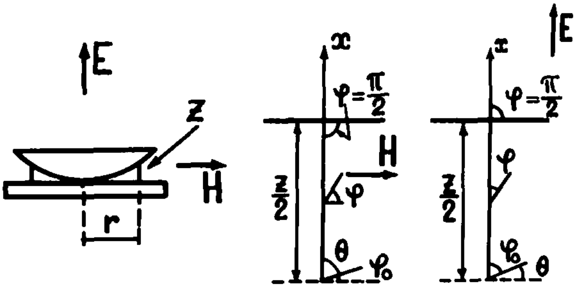


FIGURE 1. Scheme illustrating the deformation of the homeotropic layer of the nematic liquid crystal in the magnetic H and electric E fields.

The theoretical basis of the experiment is the Freedericksz - Zocher equation [8]

$$K\frac{d^2\varphi}{dx^2}=\Delta\chi H^2\sin\varphi\cos\varphi \tag{1}$$

describing the equilibrium conditions between the deforming forces of the magnetic field H and the elastic forces of the nematic.

Here x is the coordinate normal to the layer plane, φ is the angle between the field direction in which the magnetic susceptibility of the anisotropic substance is maximum. $\Delta\chi$ is the absolute value of the difference $\chi_\parallel - \chi_\perp$ between the two principal magnetic susceptibilities $\chi_\parallel$ (parallel to the director) and $\chi_\perp$ (perpendicular to the director) per unit volume.

An expression analogue to eq.(1) can also be written for the case of the electric field [9, 10] with the replacement of H by E (field strength) and that of $\Delta\chi$ by $\Delta\varepsilon/4\pi$ where $\Delta\varepsilon$ is the absolute value of the difference between principal (with respect to the director) dielectric permittivities, $\varepsilon_\parallel$ and $\varepsilon_\perp$, of the nematic. K is the elastic constant of the nematic.

Under experimental conditions (Fig.1), the field H should be normal to the director of the undistorted nematic (parallel to the nematic layer) and the field E should be normal to the director of the nematic with positive dielectric anisotropy ($\varepsilon_\parallel > \varepsilon_\perp$) and parallel to the director in the case of the negatively anisotropic nematic ($\varepsilon_\parallel < \varepsilon_\perp$). Under these conditions, the integral of eq.(1) is [7,8]

$$zH\sqrt{\Delta\chi/K} = 2\int_0^{\pi/2}(1-\sin^2\theta\,\sin^2\psi)^{-1/2}d\psi \equiv 2J_1(\theta) \qquad (2)$$

Here $\theta=\pi/2-\varphi_0$ where φ_0 is the φ value at $x = 0$, i.e. in the middle of the layer (at a distance $Z/2$ from the orienting glass surfaces). In other words, θ is the deformation angle in the middle of the layer (where deformation is a maximum).

In the absence of deformation $\theta = 0$, the first elliptical integral $J_1(\theta)=\pi/2$, whereas when deformation exists, $\theta > 0$ and $J_1(\theta) > \pi/2$. Hence, eq.(2) determines the threshold type of deformation in the magnetic field experimentally found in refs[7,8]: the minimum (critical) layer thickness Z_k in which deformation in the field H is possible, is determined by eq.(3)

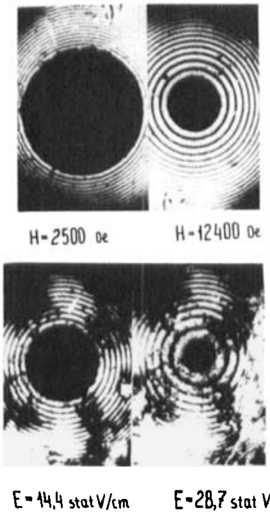
$$z_k H = \pi\sqrt{K/\Delta\chi} \qquad (3)$$

An analogous eq.(4) determines the critical thickness Z_k and the threshold character of deformation in an electric field E experimentally detected in refs [9, 10]

$$z_k E = 2\pi\sqrt{\pi K/\Delta\varepsilon} \qquad (4)$$

In this case under the experimental conditions shown in Fig.1 the value of K in eqs. (3) and (4) implies the bend elastic constant K_3.

RESULTS AND DISCUSSION



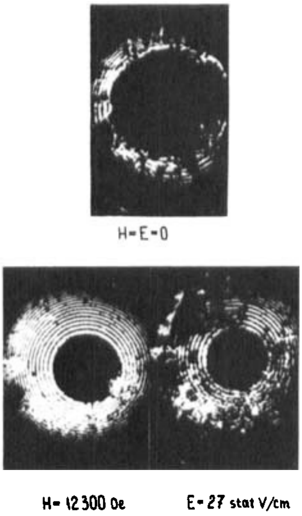


FIGURE 2. Polarizing-microscopic patterns of a low molecular weight nematic deformed by magnetic (H = 2500 Oe and H = 12400 Oe) and electric (E = 14.4 stV/cm and E = 28.7 stV/cm) fields.

FIGURE 3. Polarizing-microscopic patterns of the homeotropic layer of the polymer nematic in the absence of the field (H, E = 0) and that deformed by magnetic (H = 12300 Oe) and electric (E = 27 stV/cm) fields.

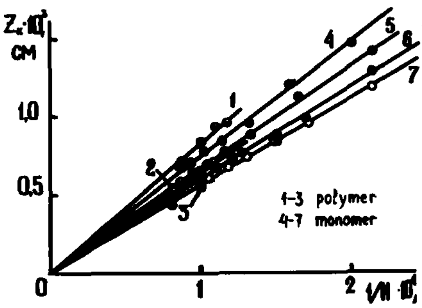
Fig.2 (top) shows the photographs of deformation pattern in the magnetic field H when the homeotropic layer of the low molecular weight nematic is observed in parallel beams of the polarized light (wavelength $5.46\cdot10^{-5}$ cm) normal to the layer plane. This pattern is fixed in the photographic camera of the polarizing microscope with crossed polarizers under the conditions when the magnetic field parallel to the layer plane is diagonal to the axes of the polaroids. The photographs show distinctly the critical boundary separating the undistorted part of the preparation (dark homeotropic part) from the distorted part in which as a result of deformation the pattern of concentric interference rings (curves of equal thickness) appeared. With increasing field strength H the critical boundary is displaced towards thinner layers.

Fig.2 (bottom) shows the interference patterns of the same sample in the sinwave (frequency 8.10^{4} Hz) electric field E. The sinwave fields were applied in order to avoid hydrodynamic instabilities appearing in the nematic in constant electric fields as a result of electric conductivity of the substance [24]. The field is normal to the layer plane (parallel to the director in the undistorted homeotropic part of the preparation). The critical boundary of deformation is as distinct as in the magnetic field, and the interference pattern indicates that the dielectric anisotropy of the investigated nematic is negative in sign. In this case, apart from interference rings (similar to those in the magnetic field), a dark cross is visible. Its branches are parallel to the axes of crossed polaroids. This pattern indicates that the orientation of molecular axes in the deformed layer of the nematic is conoscopic [10].

Photographs in Fig.3 illustrate the results obtained in the investigation of the polymer nematic, APE. Fig.3 top shows the pattern of the planar-concave layer in crossed polaroids in the absence of the field. Although the normal homeotropic orientation of the director is not extended to the entire visible preparation, it is sufficiently well expressed in its considerable central part. This fact makes it possible to study the deformation of liquid-crystalline layers in magnetic and electric fields with the same geometry of experiments as in the case of the low molecular weight monomer. Fig.3 bottom, left-hand shows a preparation of the nematic APE in the magnetic field $H = 12.3 \cdot 10^3$ Oe. The observed interference pattern corresponds to those obtained for the low molecular weight AE under similar conditions although differs from them in a slightly lower homogeneity of the field of vision. Fig.3 bottom, right-hand shows the deformation pattern of the same preparation of the polymer nematic in the electric field $E = 27$ stV/cm. The interference rings appearing in the distorted part of the preparation indicate that the dielectric anisotropy of the liquid-crystalline polymer is also negative just as in the case of the monomer. However, the structure of the deformed polymer nematic is less homogeneous than that of its monomer, and in this case the conoscopic orientation of molecular axes (dark cross) is olmost negligible.

The macroscopic inhomogeneities in the polymer nematic manifested upon its deformation can by partly due to the presence of impurities in the polymer substance, However, it is not less probable that the specific structure of the polymer may play a certain role in their formation. In this structure, the mesogenic nuclei of the polymer form a part of long polymer chains. The reorientation of these nuclei in the magnetic or electric fields inevitably leads to the conformational rearrangement considerable parts of the polymer chain. As a result, the reorientation time becomes much longer, and macroscopic inhomogeneities in the texture of the polymer nematic can appear.

The reorientation time of the polymer nematic (after the field is switched on) exceeds many times that of the monomer liquid crystal. It increases drastically with increasing molecular weight and decreasing temperature of the sample. In the case of the APE investigated, the equilibrium (stable in time) patterns of the critical boundary were obtained by maintaining the preparation in a constant field for the period ranging from a few minutes to several tens of minutes. Only the equilibrium values of critical thicknesses, Z_k, were used as quantitative data.



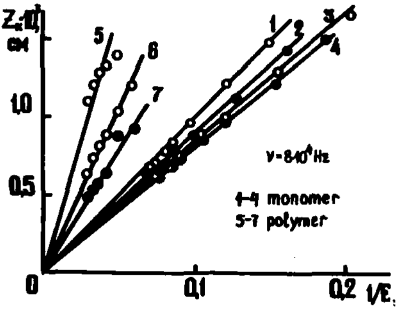


FIGURE 4. Critical thickness Z_k VS inverse magnetic field strength, 1/H, for a polymer nematic (1, 2, 3) and a low molecular weight nematic (4, 5, 6, 7) at different temperatures T°C.

T = 1) 189°C, 2) 267°C, 3) 287°C, 4) 212.5°C, 5) 209°C, 6) 200°C, 7) 194°C.

FIGURE 5. Critical thickness Z_k VS inverse electric field strength, I/E, for the low molecular weight nematic (1-4) and the polymer nematic (5-7) at different temperatures T = 1) 194°C, 2) 200°C, 3) 209°C, 4) 212°C, 5) 267°C, 6) 217°C, 7) 189°C.

Fig.4 shows the values of the critical thicknesses Z_k versus inverse values, I/H, of the applied magnetic field H for liquid crystals AE and APE. Fig.5 shows similar dependences for deformations in electric fields (Z_k as a function of I/E). The experimental points corresponding to a certain temperature closely fit one straight line passing through the origin in accordance with the threshold character of deformations pre-

TABLE 1 Diamagnetic $\Delta\chi$ and dielectric $\Delta\varepsilon$ anisotropies and elastic bend constants K_3 of the low molecular weight and the polymer nematics at different temperatures.

T^oC	T_0-T	$\frac{K_3}{\Delta\chi}$	$-(K_3/\Delta\sigma)\cdot 10^5$		$\Delta\chi\cdot 10^7$	$K_3\cdot 10^6$	$-\Delta\varepsilon$	
			80kHz	700kHz	AAB	dyn	80kHz	700kHz
				Monomer AE				
194.5	20.5	5.4	0.97		1.8	1.0	1.3	
200	15	4.3	0.80		1.7	0.7	1.2	
205.5	9.5	3.9	0.77		1.5	0.6	1.0	
209	6	3.6	0.73		1.3	0.5	0.8	
212.5	2.5	3.1	0.65		1.0	0.3	0.6	
				Polymer APE				
189	131	7.5	2.6	-	(2.9)	(2.2)	(1.1)	
215	105	-	3.1	2.0	(2.8)	-	(0.81)	(1.3)
217	103	7.2	4.7	-	(2.8)	(2.0)	(0.53)	
243	77	7.0	12	-	(2.5)	(1.8)	(0.18)	
247	73	6.2	-	-	(2.5)	(1.6)	-	
267	53	4.4	12	2.8	2.25	1.0	0.10	0.45
270.5	49.5	-	16	3.3	-	0.9	0.07	0.35
274	46	4.0	-	5.0	2.1	0.8	-	0,21
287	32.5	3.3	-	5.0	2.0	0.66	-	0.17

dicted by eqs.(3) and (4). According to eq.(3) or (4), the slope of each straight line determines the ratios $K_3/\Delta\chi$ or $K_3/\Delta\varepsilon$ at a fixed temperature. The values of $K_3/\Delta\chi$ and $K_3/\Delta\sigma$ (where $\Delta\sigma = \Delta\varepsilon/4\pi$) obtained in this manner are given in Table 1.

For further discussion of the properties of the liquid-crystal-line monomer and polymer, it is essential to compare the parameters of orientational order S in their mesophases. It is known that diamagnetic $\Delta\chi$ or optical $\Delta n_0 = n_e - n_0$ anisotropies of the mesophase may serve as the most direct characteristics of the value of S^1.

The average value of birefringence of a layer with a thickness Z of a preparation deformed by the field can be determined from the simple equation

$$n_e' - n_o \equiv \Delta n = m\lambda/Z \tag{5}$$

where m is the number of the dark interference ring (reckoned from the critical boundary) corresponding to the thickness Z and λ is the wavelength of the applied light. In Fig.6 the values of Δn measured in a strong magnetic field ($H = 12.3\cdot10^3$ Oe) are shown as functions of the relative layer thickness Z/Z_k for the monomer and polymer nematics at various temperatures. A decrease in Δn with decreasing layer thickness reflects the incomplete reorientation of the director in thin layers in the field H. The limi-

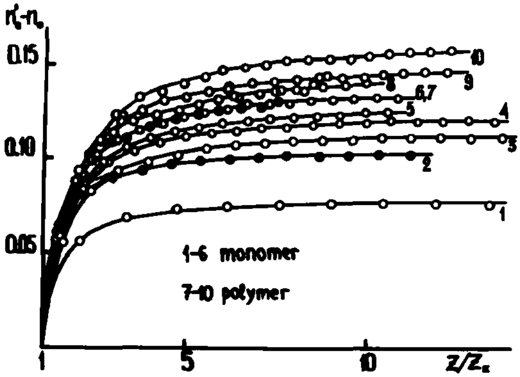


FIGURE 6. Effective optical anisotropy of low molecular weight (1-6) and polymer (7-10) nematics deformed by the field H = 12500 Oe is relative layer thickness Z/Z_k at different temperatures T°C.

T = 1) 213°C, 2) 208°C, 3) 205.5°C, 4) 201.5°C, 5) 197.5°C, 6) 191°C, 7) 287°C, 8) 280°C, 9) 266°C, 10) 248°C

ting value of Δn attained at large Z/Z_k gives the value of $\Delta n_o = n_e - n_o$ for the completely oriented nematic at a corresponding temperature. In order to determine reliably the limit of curves in Fig.6 at high Z/Z_k ratios, the extrapolation equation is used [7]

$$\Delta n/\Delta n_o = 1 - (2Z_k/\pi Z) J_2(\theta) \qquad (6)$$

Here $J_2(\theta)$ is the elliptical integral of the second kind and θ is the angle of orientational deformation in the middle of the layer. The value of θ is determined from the equation $J_1(\theta) =$

$=\pi Z/2Z_k$ where $J_1(\theta)$ is the elliptical integral of the first kind contained in eq.(2). The following expression may serve as a good approximation for eq.(6):

$$\Delta n/\Delta n_0 = 1 - 2Z_K/\pi Z \qquad (7)$$

The values of $n_e - n_o$ for the nematic phase of the monomer and the polymer obtained by this procedure are given in Table 2 and shown as fun-

TABLE 2. Difference between two principal refractive indices $n_e - n_o$ of low molecular weight and polymer nematics at different temperatures.

T^oC	$(T_o - T)^oC$	$n_e - n_o$
	Monomer AE	
213	2.0	0.084
208	7.0	0.111
205.5	9.5	0.122
201.5	13.5	0.130
197.5	17.5	0.136
191	24.0	0.145
	Polymer APE	
287	33	0.145
280	40	0.152
266	54	0.158
248	72	0.172

ctions of temperature (reckoned from the temperature T_0 of the transition into the isotropic phase) in Fig.7 (curve 1). It is noteworthy that the experimental points for the polymer and the monomer fall along the same curve. This fact implies that the degrees of orientational order for the polymer and monomer nematics in the corresponding temperature range virtually coincide.

The absolute values of the optical anisotropy, $n_e - n_o$, of the ester-aromatic nematics are twice lower than that for azoxyanisole [8] and other nitrogen-containing compounds [7].

The coincidence of the values of Δn_0 (and, correspondingly, of S) for liquid-crystalline AE and APE implies that the values of their diamagnetic anisotropies $\Delta\chi$ also coincide in the corresponding temperature ranges.

The absolute values of $\Delta\chi$ for AE (and correspondingly for APE) can be determined by using the data published in ref.[25] in which it has been shown that the molar magnetic anisotropies of various nematics are determined by the number of benzene rings in their molecules, whereas the values of $\Delta\chi$ calculated per unit volume virtually coincide in the corresponding temperature ranges. In particular, the values of $\Delta\chi$ for anisalaminoazobenzene (the mesogenic nucleus of its molecule contains three benzene rings just as in the case of AE and APE) are given in Table 1 according to the data of ref.[25], and the temperature dependence of $\Delta\chi$ for this nematic is shown by curve 2 in Fig.7. According to the above considerations, the same curve also describes the dependence of $\Delta\chi$ on $T_0 - T$ for AE and APE.

Using these values of $\Delta\chi$ and the values of $K_3/\Delta\chi$ for AE and APE one obtains for these nematics the values of elastic constants K_3 given in Table 1 and shown by curve 3 in Fig.7. The temperature ranges in which the properties of the mesophase of AE and APE could be investigated,

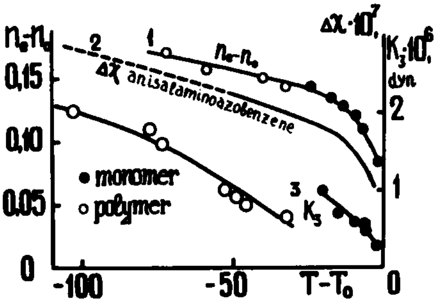


FIGURE 7. Temperature dependence of optical, diamagnetic and elastic characteristics of low molecular weight and polymer liquid crystals.
1. Optical anisotropy $n_e - n_o$ of monomer (AE) and polymer (APE) nematics.
2. Diamagnetic anisotropy $\Delta\chi$ of anisalaminoazobenzene.
3. Bend elastic constants K_3 of monomer (AE) and polymer (APE).

do not coincide. Hence, it is difficult to carry out an exact quantitative comparison of the corresponding constants K_3 under equivalent temperature conditions. However, the data show that K_3 values for the monomer and the polymer are of the same order of magnitude and close to those for other low molecular weight nematics[10,13,15].

Just as for low molecular weight nematics, for nematic APE K_3 increases with decreasing temperature, i.e., varies according to the parameter of order S. Moreover, the very wide temperature range of the existence of the nematic mesophase of APE makes it possible to carry out measurements of its elastic deformations at a temperature 130°C below T_0 and, correspondingly, to obtain under these conditions $K_3=22 \cdot 10^{-7}$dyn. This value is higher than those obtained up to the present for low molecular weight nematics.

Both the possibility of obtaining high K_3 values and the agreement with Freedericksz's law (3) over a wide range of values of the magnetic field for this polymer nematic indicate the existence of the conditions of "strong anchoring" of normal orientation of the APE director on the surface of solid glass. This result cannot be considered trivial, if it is taken into account that the size of molecules of the polymer under investigation and hence the orienting forces to which they are subjected in the magnetic field exceed by more than one order of magnitude the size of molecules of the low molecular weight nematic, AE, and correspondingly the forces exerted upon them. These facts probably agree best with the concept that the molecules of the polymer nematic are oriented in the magnetic field by small-scale local motion of its chains. In this motion the kinetic units oriented in the magnetic field are mesogenic ester-aromatic nuclei of the polymer chain. Therefore the equilibrium deformational elastic properties of polymeric and low molecular weight liquid crystals resemble each other.

By using the experimental values of $K_3/\Delta\sigma$ and K_3 given in Table 1, it is possible to determine the value of dielectric anisotropy $\Delta\varepsilon$ for both polymer and monomer liquid crystals. The values of of both samples are nemative, close to each other in the order of magnitude and decrease (in absolute value) with increasing temperature. This effect is often observed for low molecular weight nematics and can be mainly related to the corresponding decrease in the degree of order. A very drastic decrease in $\Delta\varepsilon$ with increasing temperature observed for the polymer nematic at a frequency of 80 kHz is probably due to the effect of electric conductivity of the sample complicating the interpretation of experimental data.

Both the geometry of experiments in the electric field (Fig.1) and the negative sign of $\Delta\varepsilon$ show that the longitudinal (optical) axes of molecules of both samples are oriented normally to the E field. For the low molecular weight AE, this result corresponds to the negative sign of the Kerr effect in its solutions [26]. In contrast, in the solution of APE of the corresponding molecular weight, the Kerr effect is positive [26]. This fact indicates that the orientation of APE molecules in solution due to the action of the electric field is of the large-scale type. Hence, the orientation of macromolecules in the bulk of the polymer nematic normal to the E field implies that this orientation follows the mechanism of local small-scale motion, just as in the magnetic field and in accordance with the suggestion made in another paper [27].

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