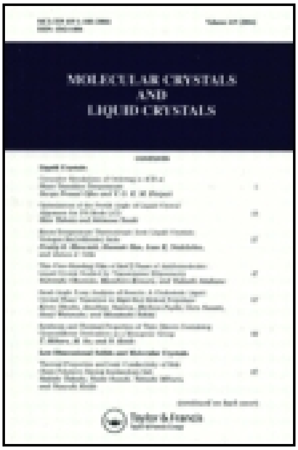

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Electrooptical Properties of Main-Chain Mesogenic Polymers in Nematic State and Dilute Solutions

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Electrooptical Properties of Main-Chain Mesogenic Polymers in Nematic State and Dilute Solutions

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Electrooptical and dielectric properties of two aromatic polyesters with hexaethyleneglycol spacers (as well as their low molecular weight structural analogues) were studied in dilute solutions and in nematic state using the methods of flow birefringence, equilibrium electric birefringence, and orientational elastic deformations in electric fields. It was shown that the macromolecules under investigation orientated in the electric field according to the small-scale mechanism, and the Kerr constant K values are in good agreement with the dipole structure of their molecules. The sign of dielectric anisotropy $\Delta\varepsilon$ for the polymer nematics under investigation coincides with the sign of K in dilute solutions. The values of $\Delta\varepsilon$ for polymer nematics are close to the same characteristics for their low molecular weight structural analogues. The comparative analysis of the data obtained for these polymers in dilute solutions and in the nematic state is carried out.

Keywords Nematics, electrooptics, dielectric properties

INTRODUCTION

It is well known that the structure and length of flexible spacers in mesogenic macromolecules can profoundly affect the type and physical properties of mesophases [1–8]. In this connection it is very important to investigate the

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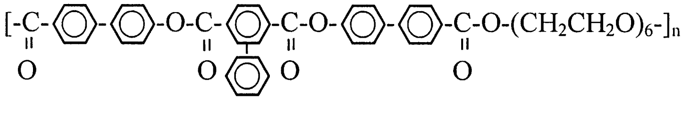
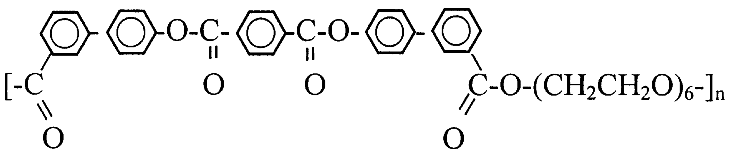
effect of the character of spacer insertion into mesogenic macromolecules on dipolar-conformational, optical, electrooptical, and dielectric characteristics of their solutions and melts.

In the present work comparative studies of two thermotropically mesogenic aromatic polyesters with hexaethyleneglycol spacers in dilute solutions and nematic melts were carried out. Their structural formulas are given below.

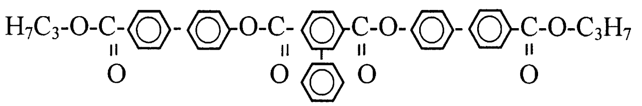


APE 1

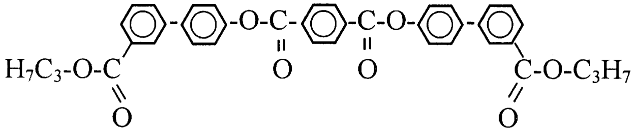


APE 2

Two low molecular weight compounds, structural analogies of APE 1 and 2, were also investigated.



AE 1



AE 2

The polymers were synthesized under the procedure described in detail in Bilibin and Stepanova [9]. Their hydrodynamic properties were studied [10, 11]. Elastic properties of their nematic melts were described in Andreeva et al. [12].

EXPERIMENTAL

Flow birefringence (FB) was studied in a titanium dynamo-optimeter with an inner rotor 3 cm in diameter and 3.21 cm high. The gap between the rotor and the stator was 0.022 cm. A photoelectric recording scheme with modulated ellipticity of light polarization was used to increase sensitivity [13]. A He-Ne laser was the light source (light wavelength was $\lambda = 6328 \times 10^{-8}$ cm). Elliptical rotating compensator had relative phase difference $\Delta\lambda/\lambda = 0.036$. FB measurements were carried out at a temperature 20°C, and for this purpose forced water thermostating of the instrument was applied.

Equilibrium electric birefringence (EB) was studied in rectangular-pulsed electric fields by a method described in detail in Tsvetkov and Tsvetkov [14]. Measurements were carried out in a glass Kerr cell with titanium electrodes 3 cm in length along the light beam path, with a gap of 0.03 cm between them. Just as in FB studies, a photoelectric recording scheme with modulated ellipticity of light polarization was applied using an elliptical rotational compensator $\Delta\lambda/\lambda = 0.01$ and a He-Ne laser as the light source.

Electrooptical characteristics of nematic phase were studied by the method of orientational elastic deformations in electric and crossed (i.e., magnetic and electric) fields described in detail in Tsvetkov et al. [15]. Planar-concave nematic layers with thickness up to 5×10^{-3} cm were used. To prepare homeotropically oriented nematic layers, the surfaces of glasses and transparent electrodes (tin oxide) coming in contact with the sample were treated with concentrated sulfuric acid with subsequent repeated washings in distilled water and drying.

The light source was a mercury lamp with a green filter (wave length $\lambda = 5460 \times 10^{-8}$ cm). The processes of nematic layers reorientation were carried out in electric fields using sinusoidal voltages in a frequency range from 10–500 kHz and potential difference on the electrodes up to 700 V and magnetic fields with a strength up to 6 kGs.

RESULTS AND DISCUSSION

Data obtained for APE 2 in dioxane (DO) solutions by the FB method are illustrated in Figure 1, which shows the dependence of birefringence Δn on shear stress $\Delta\tau$. Analogous dependencies were observed for APE 1.

This fact made it possible to determine the values of shear optical coefficient $\Delta n/\Delta\tau$ of the polymers being investigated (Table 1). According to these $\Delta n/\Delta\tau$ values, it is possible to calculate optical segmental anisotropy from the ratio [13]

$$\frac{\Delta n}{\Delta\tau} = \frac{4\pi}{45kT}\frac{(n^2+2)^2}{n}(\alpha_1 - \alpha_2), \tag{1}$$

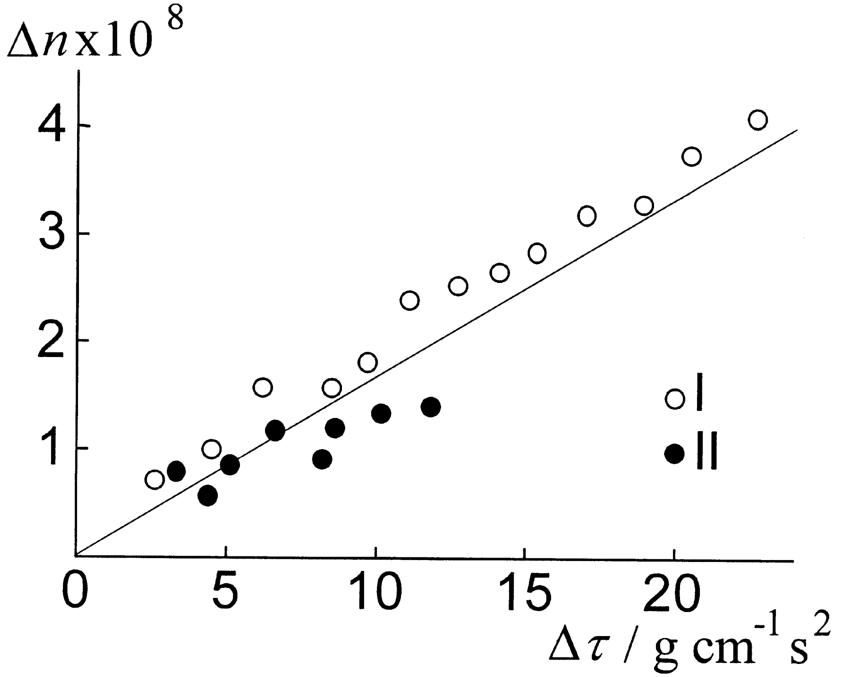


FIGURE 1 Birefringence Δn vs. shear stress $\Delta\tau$ for APE 2 in dioxane. I = fraction 2 ($c = 1.07 \times 10^{-2}$ g/cm^3), II = fraction 1 ($c = 0.77 \times 10^{-2}$ g/cm^3).

where n is the refractive index of the solvent. Table 1 also lists the molecular weights M_{SD} of APE fractions under investigation determined within 10% by using the diffusion-sedimentation analysis [10, 11].

The data in Table 1 show that the positive value of $\Delta n/\Delta\tau$ and, correspondingly, the optical anisotropy of the Kuhn segment $(\alpha_1 - \alpha_2)$ are greater for APE 1 than for APE 2, which is due to the higher value of equilibrium rigidity of APE 1 [10, 11].

The results obtained in the investigation of EB for solutions are illustrated in Figure 2, which shows the dependencies of birefringence Δn on the square of the strength of a rectangular pulsed electric field E^2. According to these dependencies, the characteristic Kerr constants of the compounds under investigation were obtained from the equation

$$K = \lim_{E\to 0,\, c\to 0} (\Delta n / cE^2), \tag{2}$$

TABLE 1 Electrooptical characteristics of solutions of the compounds under investigation in dioxane

Polymer	*Fraction*	M_{sD} (g/mol)	$\Delta n/\Delta\tau \times 10^{10}$ $(g^{-1}s^{2}cm)$	$(\alpha_1 - \alpha_2) \times 10^{25}$ (cm^3)	$K \times 10^{10}$ $(g^{-1}cm^5(300\,V)^{-2})$	T_{NI} $(^\circ C)$	T_{NS} $(^\circ C)$	T_m $(^\circ C)$	T_{cr} $(^\circ C)$
APE 1	1	36,000				162		87	
	2*	20,200	22	350	−0.20	160		85	
	3	10,800				161		75	
	4	10,100	22	350	−0.21	154		71	
	5	5,300				152		65	
APE 2	1	14,000	15	240	0.44	162	147	95	
	2	10,400	15	240	0.48	161	144	95	
	3	2,300				148	125	92	
AE 1		638				236			
AE 2		638			0.42	186			142

*not fractionated sample.

T_{NI}, isotropization temperatures; T_{NS}, nematic-smectic transition temperatures; T_m, melting temperatures; T_{cr}, crystallization temperatures.

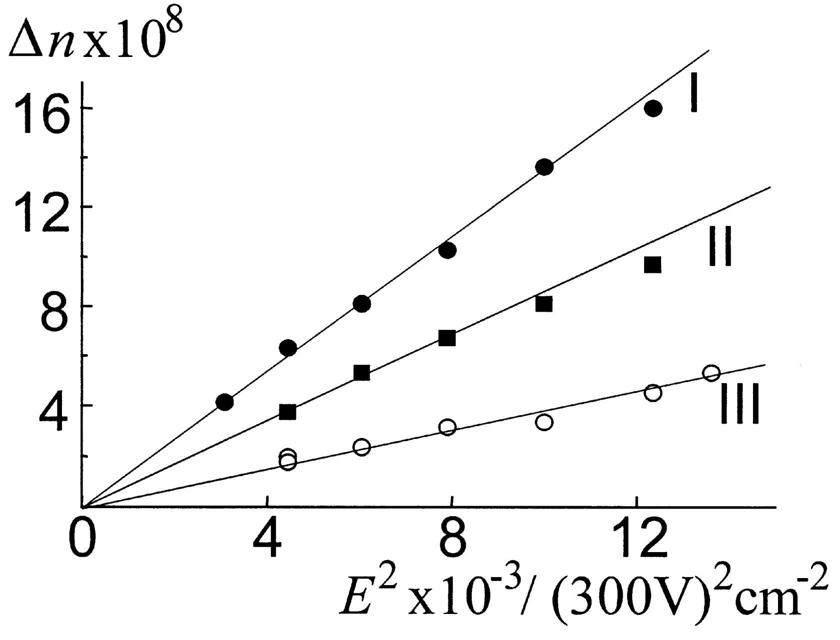


FIGURE 2 Δn vs. square of electric field strength E^2 for fraction 2 of APE 2 in dioxane. Solutions concentrations $c = 2.11 \times 10^{-2}$ g/cm^3 (I), 1.07×10^{-2} g/cm^3 (II), straight line (III)-dioxane.

where Δn is the excess difference (of the solution above solvent) between refractive indices of extraordinary and ordinary light beams and c is the solute concentration (g/cm^3).

Characteristic Kerr constants for APE 1 and APE 2 are given in Table 1. It is clear that the absolute values of K for these polymers are not high, which is the result of a considerable equilibrium and kinetic flexibility (small-scale mechanism of macromolecular orientation in external fields) of their macromolecules. However, the difference in signs of the Kerr constant for APE 1 and APE 2 should be emphasized. Let us consider this difference in greater detail. It is logical to assume that electrooptical properties of these polymers in solutions are mainly determined by the dipolar anisotropic structure of their mesogenic cores. In order to test this assumption experimentally, the EB of AE 2 in DO was investigated. The K value obtained for AE 2 is given in Table 1. This K value coincides within experimental error with the corresponding value for the APE 2 polymer. This coincidence results from the small-scale reorientation of APE 2 macromolecules in the EB phenomenon, which proceeds by the mechanism of virtually independent rotation of polar and anisotropic mesogenic cores in an electric field. Unfortunately, insufficient amounts of AE 1 prevented its investigation in solutions. However, the absence of EB dispersion (in the frequency range up to 1 MHz) in solutions of both APE 2 and APE 1 shows unequivocally that reorientation of their macromolecules in an electric field is of the small-scale character.

It should be pointed out that the Kerr constant sign for APE 1 is negative. This is caused by the dipolar structure of the mesogenic core. In this structure, the four polar ester groups are inserted in pairs opposite each other. Therefore, the longitudinal component of the dipole of the mesogenic core is absent. In contrast, the normal component of this dipole is relatively great and determines the negative sign of EB.

The sign of *K* for APE 2 and its low molecular weight structural analogue AE 2 is positive. This is not typical of *para*-aromatic polyesters. In the structure of the repeat unit of APE 2 (and in that of the AE 2 molecule), two terminal ester groups forming a part of the mesogenic core are bound in the *meta*-position and not in the *para*-position. This explains the positive EB sign for these substances. It will be elucidated by a scheme (Figure 3) that takes AE 2 as an example. Two central OCO groups included in the *para*-position opposite each other cannot provide contribution to the longitudinal component of the dipole of the mesogenic fragment and will not be considered. The structure of the mesogenic core

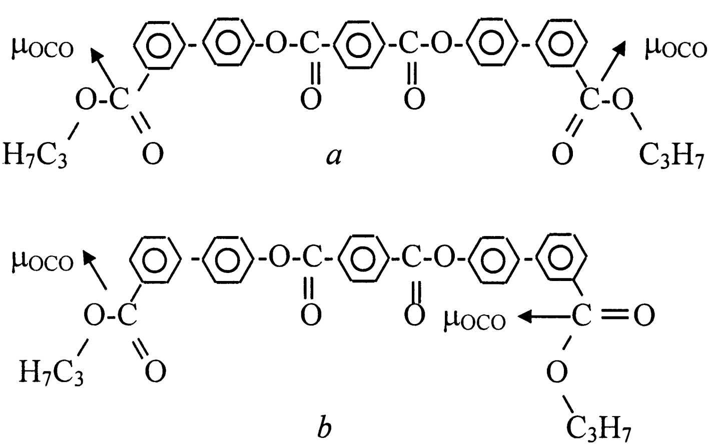


FIGURE 3 Possible conformations of AE 2. Conformation (b) can be obtained from conformation (a) by rotating one of the terminal OCO groups.

of AE 2 (Figure 3a) is of such a type that all longitudinal components of dipoles of OCO groups are mutually compensated for. Therefore, in the case of this conformation the sign of K should be negative. This contradicts experimental data. However, conformations similar to that shown in Figure 3b are also possible (this conformation can be obtained by rotating one of the OCO groups). The specific feature of mesogenic core conformation shown in Figure 3b is the considerable longitudinal component of the dipole in the OCO group along the mesogenic fragment, which causes the positive EB sign. Hence, it may be said that an important part in the conformers set of the mesogenic core of AE 2 and APE 2 consists of structures similar to that shown in Figure 3b.

The investigated APE 1 and 2, as well as AE 1 and 2, exhibit thermotropic nematic mesomorphism. Their phase behavior is determined by the polarizing-optical method described in Table 1. Dielectric properties of their nematics were investigated by the method of orientational elastic deformations in planar-concave layers [15].

The initial orientation of the APE 2 nematic was homeotropic, and its dielectric anisotropy $\Delta\varepsilon$ was positive. Therefore, its dielectric investigations were carried out in crossed magnetic H and electric E fields by the procedure used previously [8], using the equation

$$\Delta\chi H^2 + (\Delta\varepsilon/4\pi)E^2 = \pi^2 K_{33}/{z_c}^2, \tag{3}$$

where $\Delta\chi$ is the diamagnetic permittivity of the nematic, K_{33} is the bend elastic constant, and z_c, is the thickness of the layer corresponding to the critical boundary.

In the first experimental stage, the sample texture was deformed by the magnetic field in the absence of the electric field ($E = 0$ in Equation (3)), and the K_{33} value of the APE 2 nematic was determined from the experimental values of H and z_c.

In the second stage, when electric and magnetic fields are combined the critical boundary is displaced, which makes it possible to determine the threshold electric potential V_o and the $\Delta\varepsilon$ value of the nematic from the known values of E, H, and $\Delta\chi$.

For APE 1, AE 1, and AE 2 only electric fields were used in reorientation, and $\Delta\varepsilon$ was determined from Equation (3), assuming that $H = 0$ (for AE 2, K_{33} should be replaced by K_{11}, the splay elastic constant, because the sample forms the initial planar orientation).

The values of dielectric anisotropy of these nematics determined in this way are shown in Figure 4 as temperature dependencies of $\Delta\varepsilon$.

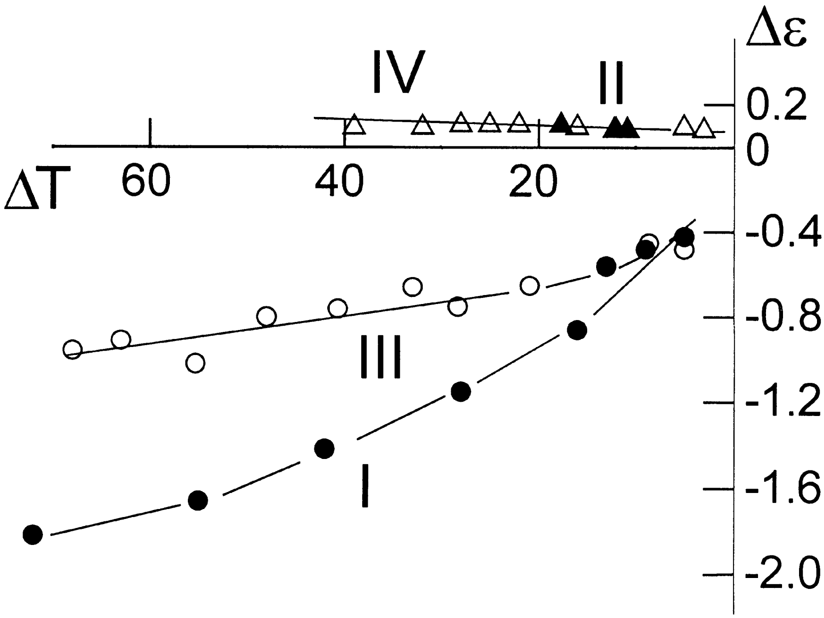


FIGURE 4 Dielectric anisotropy Δε vs. temperature ΔT for the nematics: I, APE 1 fraction 4; II, APE 2 fraction 2; III, AE 1; IV, AE 2.

Figure 4 shows that Δε of APE 1 and AE 1 nematics is negative and that of APE 2 and AE 2 is positive. The sign of EB in solutions of these compounds coincides with that of dielectric anisotropy of their nematic melts in accordance with theory of Maier and Meier [16]. The absolute Δε value of these nematics decreases with increasing temperature, which is also typical of nematic liquid crystals.

Figure 4 also shows that Δε values of APE 2 and AE 2 nematics coincide within experimental error. This fact makes it possible to draw a very important conclusion, that dielectric properties of mesogenic polymers are determined by the dipolar structure of their mesogenic cores not only in solutions but also in nematic melts. The fact that mesogenic cores in the polymer are *bound* into macromolecular chains exerts no effect on static electrooptical characteristics of polymer nematics.

For APE 1 and AE 1 nematics the values of Δε are similar in the high temperature range. However, with decreasing temperature the negative Δε of the polymer increases to an extent greater than that of its low molecular weight analogue. The reason for differences in temperature dependencies of Δε for APE 1 and AE 1 may be due to the fact that the polymer (in contrast to AE 1) exhibits not only nematic but also smectic mesomorphism. In this case it is reasonable to associate the more abrupt increase in the negative value of $\Delta\varepsilon$ for the polymer with the appearance of fluctuation cores of the smectic phase in the nematic [17].

REFERENCES

1. V. Vorländer, *Z. Phys. Chem.*, 126, 449–472 (1927).
2. A. Blumstein and O. Thomas, *Macromolecules*, 15, 1264–1267 (1982).
3. C. T. Imrie, F. E. Karasz, and G. S. Attard, *Macromolecules*, 26, 3803–3810 (1993).
4. S. Marcelja, *J. Chem. Phys.*, 60, 3599–3604 (1974).
5. J. W. Emsley, G. R. Luckhurst, G. N. Shilstone, and I. Sage, *Mol. Cryst. Liq. Cryst. (Letters)*, 102, 223–233 (1984).
6. J. W. Emsley, G. R. Luckhurst, and G. N. Shilstone, *Mol. Phys.* 53, 1023–1028 (1984).
7. N. V. Tsvetkov, V. N. Tsvetkov, V. V. Zuev, and S. A. Didenko, *Mol. Cryst. Liq. Cryst.*, 265, 487–499 (1995).
8. V. N. Tsvetkov, N. V. Tsvetkov, S. A. Didenko, and V. V. Zuev, *Mol. Cryst. Liq. Cryst.*, 265, 341–357 (1995).
9. A. Yu. Bilibin and A. R. Stepanova, *Vysokomol. Soedin., Ser. A* 40, 2218–2223 (1989).
10. S. V. Bushin, E. P. Astapenko, V. N. Tsvetkov, J. V. Soloviova, and A. Yu. Bilibin, *Vysokomol. Soedin., Ser. B* 40, 1891–1894 (1998).
11. S. V. Bushin, V. N. Tsvetkov, E. P. Astapenko, E. V. Beliaeva, M. A. Bezrukova, and N. V. Girbasova, *Vysokomol. Soedin., Ser. B* 41, 379–383 (1999).
12. L. N. Andreeva, A. P. Filippov, V. N. Tsvetkov, and A.Yu. Bilibin, *Mol. Cryst. Liq. Cryst.*, 330, 191–199 (1999).
13. V. N. Tsvetkov, *Rigid Chain Polymers* (Plenum, New York, 1989).
14. V. N. Tsvetkov and N. V. Tsvetkov, *Russian Chemical Reviews*, 62, 851–876 (1994).
15. V. N. Tsvetkov, N. V. Tsvetkov, and L. N. Andreeva, *Vysokomol. Soedin., Ser. A*. 35, 227–232 (1993).
16. V. W. Maier and G. Meier, *Z. für Naturforschung*., 16a, 262–267 (1961).
17. W. H. De Jeu, *Physical Properties of Liquid Crystalline Materials* (Gordon and Breach, New York, 1980) p. 152.