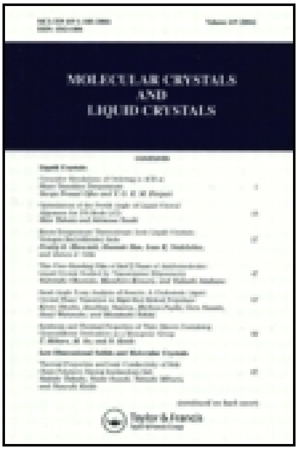

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Orientational Elastic Deformations of Main-Chain LC Aromatic Polyesters and Low Molecular Weight Nematics in a Magnetic Field

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Orientational Elastic Deformations of Main-Chain LC Aromatic Polyesters and Low Molecular Weight Nematics in a Magnetic Field

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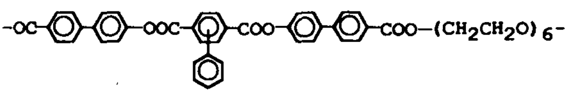
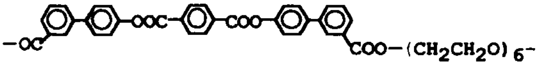
Orientational elastic deformations in a magnetic field were investigated in the nematic phase of polyphenylterephthaloyl-bis-(4-oxybiphenyl-4'-carbonyl), polylterephthaloyl-bis-(4-oxy-biphenyl-3'-carbonyl), and their low molecular weight analogues. Temperature dependences of birefringence Δn were obtained and used to evaluate the degree of orientational order S. The splay and bend elasticiy constants, $K_1$and K_3, were determined.. The elongation of the rigid mesogenic core in polymer molecules leads to an increase in the K_3/K_1 ratio, just as in the case of low molecular weight nematics. No effect of molecular weight on the values of Δn and K_i was detected.

Papers [1-4] presented the results of investigation of orientational elastic deformations in magnetic and electric fields of thermotropically mesogenic linear aromatic polyesters (APE). For these APE the structure of the rigid mesogenic core was the same: three phenyl rings separated by ester groups (so-called "triades").

This work considers elastic deformations in a magnetic field in the nematic phase of linear APE the mesogenic cores of which contain biphenylene groups



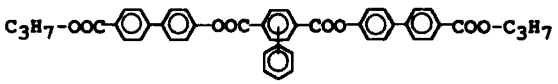
$-OC-C_6H_4-C_6H_4-OOC-C_6H_3(C_6H_5)-COO-C_6H_4-C_6H_4-COO-(CH_2CH_2O)_6-$ APE5-p



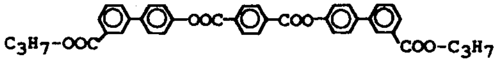
APE5-m

The structures of the two investigated APE differ in the character of insertion of biphenylene units into the chain.

The following low molecular weight nematics were also studied:



AE5-p



AE5-m

Table 1 lists the molecular weights M_{sD} of APE fractions under investigation according to data in refs[5,6]. This Table also gives the temperatures of phase transitions: isotropic melt (I) - nematic (N) T_{IN}, nematic– smectic (S) T_{NS}, and the crystallization temperature T_{cr}. These temperatures were determined by polarizing microscopy.

TABLE 1 Molecular characteristics and phase transition temperatures

Samples and their number		M_{sD}	T_{IN} °C	T_{NS} °C	T_m °C	T_{cr} °C
APE5-p	I	20200	160		85	
	II	10800	161		75	
	III	10100	154		71	
	IV	5300	151.5		65	
APE5-m	V	10400	161.5	143.5	95	
	VI	2300	148	125	92	
AE5-p	VII	642	236		76	
AE5-m	VIII	568	186			142

The procedure of investigations of orientational elastic deformations in a magnetic field has been described in detail in refs[1-3,7]. Only homeotropic textures could be obtained for polymers, only planar textures - for AE5-m , and both types of textures - for AE5-p. The sample was observed under a polarizing microscope in parallel light beams normal to the layer plane. Orientational elastic deformations appearing in the nematic under the influence of magnetic field are of the threshold character: a maximum critical thickness z_c exists for a layer in which deformation in a magnetic field of strength H_c is possible. According to Freedericksz' law [7], the product z_cH_c is constant at a given temperature and determines the ratio of elasticity constant K_i to specific diamagnetic anisotropy $\Delta\chi$

$$z_cH_c = \pi(K_i/\Delta\chi)^{1/2} \qquad (1)$$

where i = 1, 3. Splay K_1 and bend K_3 elasticity constants can be obtained by studying the deformations of planar and homeotropic layers, respectively.

The values of z_c in Fig.1 are plotted vs. $1/H_c$. The slope of each curve determines the value of z_cH_c and , correspondingly, that of $K_i/\Delta\chi$ at a temperature $\Delta T = T - T_{IN}$.

Polarizing micrographs of an undeformed planar layer or those of a

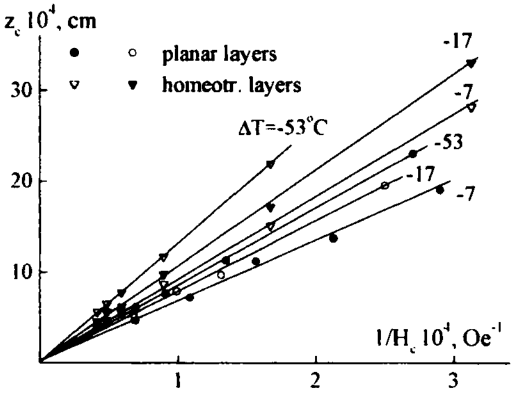


FIGURE 1 Dependence of critical layer thickness z_c on $1/H_c$.

homeotropic layer deformed by a magnetic field were used to determine the difference between two main refractive indices of the nematic $n_e - n_o = \Delta n$. The dependences $\Delta n(z)$, obtained for deformed homeotropic layers were used to determine the K_3/K_1 ratio with the application of Saupe's theory [8]. This made it possible to estimate the values of K_1 for polymer nematics for which it was not possible to obtain planar textures.

The values of optical anisotropy Δn are presented in Fig.2 as a functions of temperature ΔT. If birefringence values are not very high, these dependences can be described by the approximate equation[9]

$$\Delta n = (2\pi/3n)(n^2 + 2)N_A(\Delta\alpha/M_o)\rho S \qquad (2)$$

where S is the degree of orientational order, n is the mean refractive index, ρ is the nematic density, M_o is the molecular weight, and $\Delta\alpha$ is the polarizability anisotropy of nematic molecules. It is known that over a wide temperature range the values of n and ρ for nematic liquid crystals change only slightly (see, e.g.[9,10]). Hence, the dependence of Δn on ΔT reflects to the first approximation the temperature dependence of the degree of orientational order S of the nematic.

It has been shown[1-3] that the monomer unit is the main structural element responsible for equilibrium orientational and elastic properties of high molecular weight nematics. Consequently, the values of $\Delta\alpha/M_o$ for the polymer in Eq. (2) can be taken to be values referring to the monomer unit.

For LC investigated, the value of $\Delta\alpha$ is determined to a considerable extent by the polarizability anisotropy of para-aromatic mesogenic cores. Hence, it may be expected that the values of $\Delta\alpha/M_o$ for these LC also coincide and the differences in Δn are determined by different values of the orientational order parameter S.

For APE5-p and APE5-m, the temperature dependences of birefringence Δn coincide within experimental error (Fig. 2). For low molecular weight nematics near the phase transition point I-N the values of Δn for AE5-m are much lower than those for AE5-p. When temperature decreases, this difference becomes smaller, and at $\Delta T \sim -30^{\circ}C$ the values of Δn for AE5-m and AE5-p virtually coincide (Fig. 2).

The values of S for AE5-m can be determined using the fact that after crystallization a "planar" region with a system of interference rings was retained in the AE5-m sample under investigation. This made it possible to estimate the value of birefringence of the crystalline phase: $\Delta n_{cr} = 0.24 \pm 0.1$. Assuming that AE5-m forms a uniaxial crystal, it is possible to find $S \approx \Delta n / \Delta n_{cr}$ (Fig.2).

Taking into account the above considerations about the value of $\Delta\alpha/M_o$, one may expect that to the first approximation for APE5-p, APE5-m and AE5-p the value of birefringence Δn_o of a completely ordered structure (S=1)

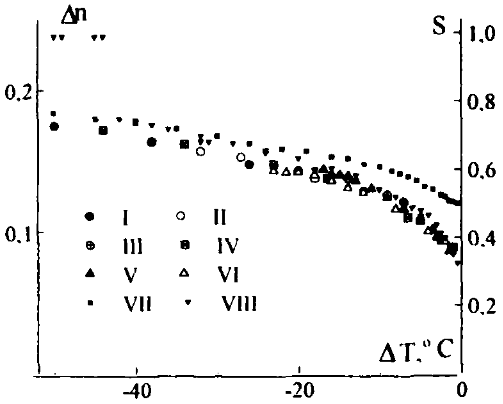


FIGURE 2 Temperature dependences of optical anisotropy APE5-p (I - IV), APE5-m (V-VI), AE5-p (VII) and AE5-m (VIII).

is close to Δn_{cr} for AE5-m. Hence, it is possible to estimate the values of $S \approx \Delta n/\Delta n_0$ for these nematics (Fig.2).

To determine the absolute values of the elasticity constant K_i from experimentally found values of $K_i/\Delta\chi$, it is necessary to know the specific diamagnetic anisotropy $\Delta\chi$ of the nematic being investigated. The character of the dependence of $\Delta\chi$ on ΔT almost completely corresponds to curve $S(\Delta T)$ (i.e. $\Delta n(\Delta T)$) in Fig. 3 because the value of $\Delta\chi$ is a

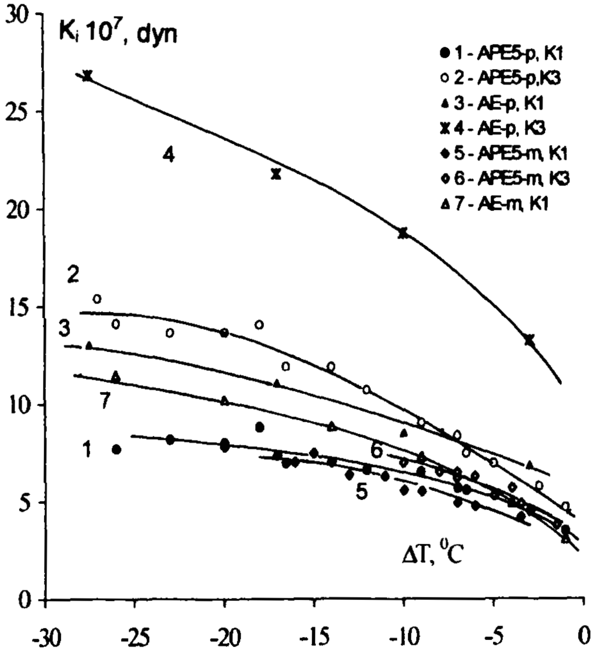


FIGURE 3 Temperature dependences of elasticity constants K_i.

unique function of ΔS [12]. The absolute values of $\Delta\chi$ were determined by the method applied in [13,1-3]. Using calculated values of diamagnetic anisotropy $\Delta\chi$ and experimental values of $K_1/\Delta\chi$ and $K_3/\Delta\chi$, we obtain the values of splay and bend constants (K_1 and K_3). The temperature dependences of K_i are shown in Fig. 3. It can be seen that for both polymers the values of K_1 (curves 1 and 5) and K_3 (curves 2 and 6) are much lower than the corresponding values of K_i (curves 3, 4, 7) for their low molecular weight models.

For polymer LC investigated the values of bend constants depend on the type of attachment of flexible groups to mesogenic cores. The values of K_3 for APE5-m (curve 6) are 20 – 30% lower than those for APE5-p (curve 2). The points corresponding to splay constants K_1 (curves 1 and 5) for both polymers fall on the same curve within experimental error.

In the case of low molecular weight nematics, at all temperatures the values of K_1 are slightly higher for a compound with end groups in the para-position (curves 3 and 7).

For the LC investigated the ratio of bend to splay constants $K_3/K_1>1$. The temperature dependences of this ratio for AE5-p, APE5-p and APE5-m

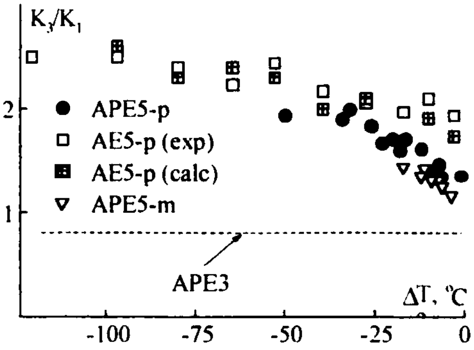


FIGURE 4 Temperature dependences of the ratio of bend to splay constants.

are shown in Fig. 4. For low molecular weight LC the points of this dependence were obtained by two procedures. In the first procedure the $K_1/\Delta\chi$ and $K_3/\Delta\chi$ ratio were determined from independent experiments by investigations of deformations of planar and homeotropic layers, and then the K_3/K_1 ratios were estimated. In the second case the K_3/K_1 ratios were determined from the results of investigations of deformations of only homeotropic layers with the application of Saupe's theory. Fig. 4 shows clearly that the values of K_3/K_1 obtained by different methods coincide within experimental error.

Relatively high K_3/K_1 values were obtained: for AE5-p with increasing distance from the phase transition point I → N, the K_3/K_1 ratio increases from 1.9 to 2.4. These values exceed more than 1.5 times those of K_3/K_1 which were obtained for a low molecular weight ester with a mesogenic "triad" [3]. The increase in the K_3/K_1 ratio with increasing length of rigid anisotropic groups of nematic molecules was repeatedly observed experimentally and is in qualitative agreement with the predictions of the theory [14].

For APE5-p and APE5-m the K_3/K_1 values are also considerably greater than unity, whereas those for APE3 investigated previously K_3/K_1 is ~0,8[3]. Hence, the increase in the length of rigid mesogenic group in APE molecules is accompanied by an increase in the K_3/K_1 ratio, just as for low molecular weight nematics.

Acknowledgments

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References

[1] V.N. Tsvetkov and I.P. Kolomiets, *Mol. Cryst. Liq. Cryst.*, **157**, 467 (1989).

[2] V.N. Tsvetkov, L.N. Andreeva, A.P. Filippov, G.S. Smirnova, S.S. Skorokhodov, and A.Yu. Bilibin, *Polymer Science*, **34**, 615 (1992).

[3] L.N. Andreeva, A.P. Filippov, V.N. Tsvetkov, and A.Yu. Bilibin, *Polymer Science*, **40**, 124 (1998).

[4] V.N. Tsvetkov, N.V. Tsvetkov, L.N. Andreeva, A.Yu. Bilibin and S.S. Skorokhodov, *Vysokomolek. Soed.*, **35 A**, 292 (1993).

[5] S.V. Bushin, E.P. Astapenko, E.V. Beliaeva, V.N. Tsvetkov, J.V. Solov'eva, and A.Yu. Bilibin, *Vysokomolek. Soed.*, **40 A,** (1998). *(in press).*

[6] S.V. Bushin, V.N. Tsvetkov, E.P Astapenko, E.V. Beliaeva, M.A. Bezrukova, and N.V. Girbasova, *Polymer Science,* **40,** (1992) *(in press).*

[7] V.K. Freedericksz and V.V. Zolina, *Z. fur Kristallogr.,* **79,** 255 (1931).

[8] A. Saupe, *Z. Naturforsh.*, **15a,** 815.(1960).

[9] Kelker H., Hatz R. *Handbook of Liquid Crystals* (Verlag Chemie, Weinheim, Deerfield, 1980).

[10] M.F. Grebenkin, A.V. Ivaschenko *Liquid Crystal Materials,*(Chemistry, Moscow, 1989).

[11] V.N. Tsvetkov *Rigid-Chain Polymers* (Plenum, New York, 1989).

[12] V.N. Tsvetkov, *Acta physicochimica URSS,* **16,** 132 (1942).

[13] V.N. Tsvetkov, and A.N. Sosnovsky, *Zh. Eksp. Teor. Fiz.,* **13,** 353 (1943).

[14] Vertogen G., de Jeu W.H. *Thermotropic liquid crystals. Fundamentals.* (Springer-Verlag, Berlin: 1988).