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ORIENTATIONAL ELASTIC CONSTANTS OF POLYMER COMBLIKE NEMATIC

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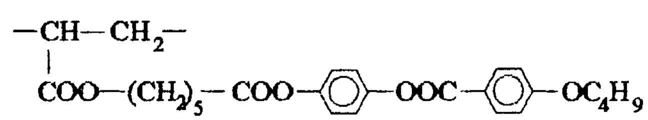
Abstract Elastic deformations of uniformly orientated layers of thermotropic polymeric comblike nematic in magnetic field were studied using the method of Freedericksz transitions. The temperature dependences of splay K_1 and bend K_3 elastic constants and optical anisotropy were determined. On changing of the relative temperature $\Delta T = T - T_c$ from -0.5 to -60°C, the optical anisotropy increases from 0.05 to 0.1. This experimental fact shows double increase of order parameter. It was found that in investigated temperature range the splay constant values are slightly more then the bend constant values ($K_1/K_3 \sim 0.8$).

Several recent papers[1-4] deal with the behavier of polymer nematics in bulk in external magnetic fields. Aromatic polyesters, both main-chain LC polymers[1,2] and combined main-chain/side-chain LC polymers[3,4] were investigated. It has been shown[1-4] that birefringence Δn and bend elastic constants K_3 of these polymer nematics do not depend on the chain length. Moreover, the values of K_3 coincide in the order of magnitude with those which are usually obtained for low molecular weight thermotropic nematics[5,6].

In this work the method of Freedericksz transition[7,8] was used to study orientational elastic deformations in the magnetic field of a polymer nematic[9]



The mesogenic groups of this nematic are located only in the side chains and are separated from the main chain by a long flexible fragment.

An unfractionated sample with intrinsic viscosity $[\eta] = 0.065$ dl/g (solvent - dioxane), molecular weight $M_w = 5.2\ 10^4$, and polydispersity parameter $M_w/M_n = 2.0$ was investigated. Phase transition temperatures were determined by using polarization microscopy and DSC. The polymer passes into the LC state at $T_g = 42°C$ and melts into isotropic phase at $T_o = 127°C$. In the range from 127 to 65°C the polymer exists in the stable nematic phase.

The procedure of investigations of plane-convex uniformly oriented layers of polymer nematics applied here has been described in detail[1]. Quartz plane glasses and plane-convex lenses with curvature radii R of 1.61 and 2.00 cm were used. Mesurements were carried out in a magnetic field with a strength of up to 25000 Oe. The temperature T of the sample placed in a special oven was controlled to within 0.5°C.

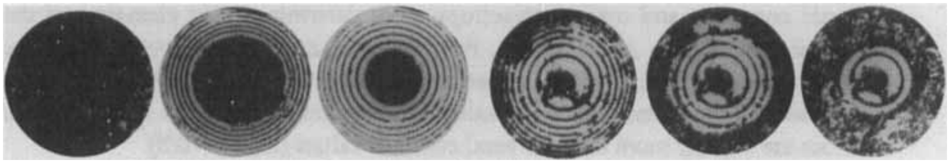


FIGURE 1 Polarizing-microscopic patterns of the polymer under investigations.

It was possible to obtain for this polymer both homeotropic and planar uniformly oriented textures. Figure 1 shows polarizing micrographs of homeotropic and planar textures in the absence and presence of a deforming field in crossed polaroids. Deformations appearing in the polymer nematic under the effect of a magnetic field applied normally to the director are of the pronounced threshold character. The critical boundary separates the deformed and non-deformed sample parts. In the case of a planar texture, interference rings are retained in the nondeformed part and disappear in the deformed part. For the homeotropic layer, these rings are observed in the deformed part. When magnetic field strength increases, the radius of the critical boundary r_c and, correspondingly, the critical thickness $z_c = r_c^2 / 2R$ decreases.

By using the Figure 1 it is possible to determine (i) the values of splay constants K_1 (from planar layers deformation) and bend constants K_3 (from homeotropic layers deformation) and (ii) the value of nematic birefringence $\Delta n = n_e - n_o$. All quantitative results discussed below refer to the equilibrium state of the system.

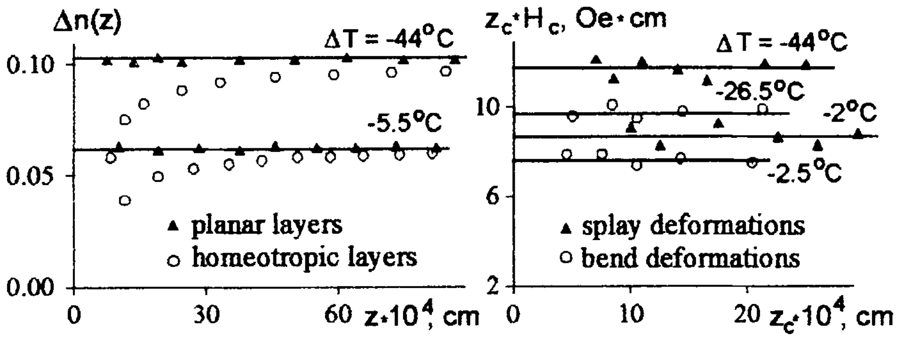


FIGURE 2 The experimental dependences of $\Delta n(z)$ on z and of $z_c H_c$ on z_c

Figure 2 shows the dependences of effective birefringence $\Delta n(z) = m\lambda/z$ (m is the number of the interference ring counted from the sample center and $\lambda = 546$ nm) on the layer thickness z. In the case of a spontaneous planar orientation, the value of $\Delta n(z)$ does not depend on z, and the mean value of $\Delta n(z)$ determines the birefringence of the nematic Δn at a given relative temperatures $\Delta T = T - T_o$. For deformed homeotropic layers, effective birefringence of $\Delta n(z)$ decreases with decreasing z from thick layers to z_c. This is due to incomplete reorientation of the director in thin layers. The limiting value of $\Delta n(z)$ in the range of large layers thickness ($z >> z_c$) gives the value of birefringence Δn for a completely oriented nematic at a given temperature.

The values of Δn are shown in Figure 3 vs ΔT. These values are in good agreement with data for low molecular weight nematics with the molecular structure similar to that of the mesogenic groups of the polymer nematic investigated here.

Birefringence of the nematic Δn is virtually a unique function of the degree of its orientational order S^{10}. In other words, the dependence of Δn on ΔT reflects the temperature dependence of the order parameter S of the polymer nematic investigated. It may be concluded from the experimental dependence shown in Figure 3 that the order parameter of this polymer nematic increases more than twice when the relative temperature ΔT decreases from -1° to -60°C.

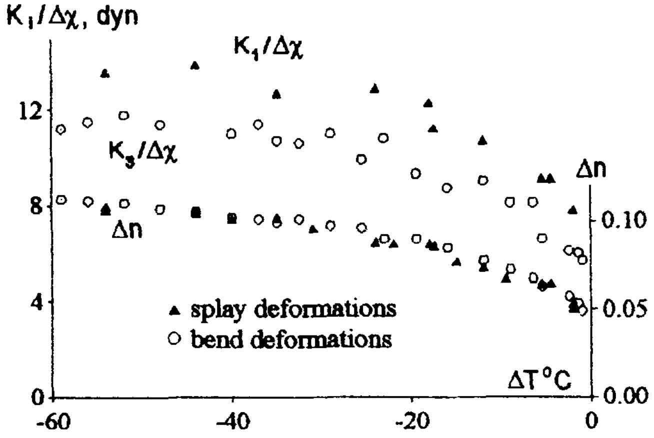


FIGURE 3 The experimental dependences of K_i / $\Delta\chi$ and Δn on the temperature ΔT

The main law determining Freedericksz transitions for splay and bend deformations is given by

$$z_c H_c = \pi (K_i / \Delta\chi)^{0.5} \qquad \text{and} \qquad i = 1, 3$$

where H_c is the magnetic field strength corresponding to critical layer thickness z_c and $\Delta\chi$ is the diamagnetic anisotropy of the volume unit of the nematic. Experimental data in FIGURE 2 indicate that the Freedericksz law is obeyed for this polymer nematic. The values of z_cH_c averaged over all thicknesses determine the $K_i / \Delta\chi$ ratio at a given relative temperature ΔT.

The dependence of the value of $K_1/\Delta\chi$ and $K_3/\Delta\chi$ on ΔT are shown on Figure 3. Over the entire temperature range investigated the experimental points corresponding to splay elastic constants lie slightly above the points for bend elastic constants, i.e. $K_3/K_1 < 1$. A similar ratio of these constants has been obtained by C.Casagrande[11] and W.Rupp[12] for the polymer nematics with a comblike structure.

It is not always possible to obtain both planar and homeotropic orientations for the same nematic. In these cases Saupe's theory[13] is used to determine the K_3/K_1 ratio. This theory makes it possible to estimate this ratio from experimental investigations of only one deformation type (for either planar or homeotropic layers). The validity of this theory, at least for low molecular weight nematic LC has been confirmed in several papers[13,14]. Saupe's theory has been used in the investigation a polymer nematic by

W.Rupp[12]. For the polymer nematic investigated in the present work, the K_3/K_1 ratio was obtained from ***independent*** investigations. Over the entire temperature range investigated, this ratio is aproximately 0.8.

This experimental fact requires additional checking. First, it should be born in mind that the K_3/K_1 ratio can be determined not only by the properties of this LC as such but also by its bonding to the support[5,6]. Weak bonding is known to lead to too low experimental values of elastic constants[5]. Moreover, a considerable error in the determination of the $K_1/\Delta\chi$ ratio should not be overlooked either. This error is due to the relatively low value of Δn for this nematic.

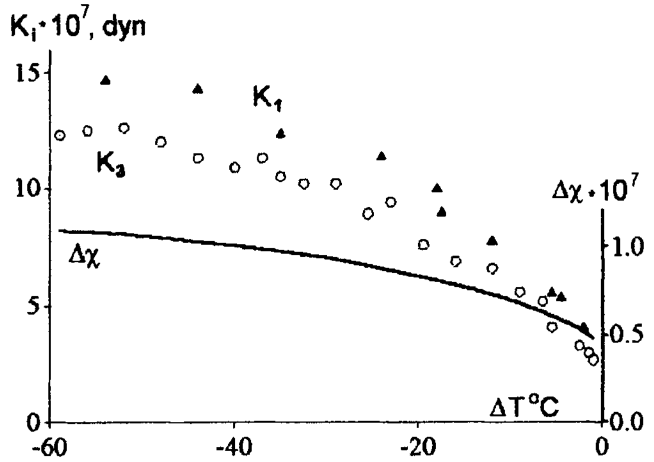


FIGURE 4 The dependences of $\Delta\chi$ and the constants K_i on the temperature ΔT

In order to determine the absolute values of K_1 and K_3 from the experimental values of $K_1/\Delta\chi$ and $K_3/\Delta\chi$, specific diamagnetic anisotropy $\Delta\chi$ should be known. It can be estimated by the method proposed in papers[2,15] using the experimental values of molar diamagnetic anisotropy $\Delta\chi_\mu$ for several nematics[15] and taking into account the fact that the mass fraction of aromatic rings in this polymer is 33.5% and its density ρ isabout 1.4 g/cm^3. The values of $\Delta\chi$ calculated in this way are shown in Figure 4.

The temperature dependence of the values of K_i determined from the experimental values of $K_i/\Delta\chi$ and $\Delta\chi$ are shown in Figure 4. The values of K_1 and K_3 are close in the order of magnitude to those for low molecular weight nematics (however, for the latter K_3 is usually greater than K_1)[5,6]. The bend elastic constants for this comblike polymer are close to those for high molecular weight nematics investigated previously[1-4].

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