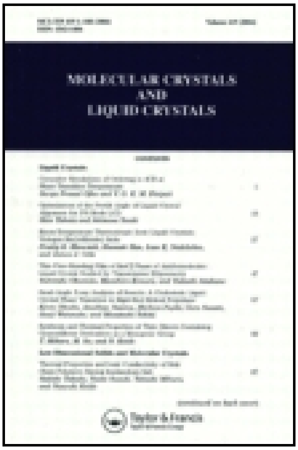

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Elastic Constants and Order Parameters of Comblike Copolymers

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Elastic Constants and Order Parameters of Comblike Copolymers

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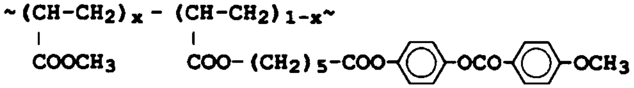
Orientational elastic deformations of nematic phase of comblike copolymers in a magnetic field were studied. The temperature dependences of birefringence Δn, order parameter S and splay elastic constant K_1 were determined. It is shown that with increasing of the molar fraction of nonmesogenic component from 0 to 0.4, the parameter S depends on copolymer composition x only near the phase transition point nematic – isotropic melt, at which S decreases with increasing x. For a copolymer with $x = 0.51$ at all temperatures, a decrease in the order parameter is detected. In the investigated temperature range the values of constant K_1 do not depend on copolymer composition. The results are compared with characteristics of thermotropic linear aromatic polyesters.

Keywords: copolymer; order parameter; orientational elastic constants

It is known that modern liquid crystals (LC) materials are mixtures, and the combination of their components and compositions leads to the needed physical chemical properties. However, phase separation often takes place because of low solubility or low compatibility of components. Besides, the compositions are sensitive to the influence of temperature, which can result in appreciable changes of properties of LC. The use of LC copolymers makes it possible to overcome successfully all these defects. In the copolymers the combination of chemically and structurally different elements is possible without phase separation. Varying the fraction of each component, it is possible to obtain materials with the necessary combination of properties.

The method of Freedericksz transitions in a magnetic field[1] was used in this work to study thermotropic mesogenic comblike copolymers (C-x) for following the influence of copolymer composition on the properties of the mesophase formed by them. The copolymer structure is as follows:



The molar portion of the nonmesogenic component x ranges from 0 (homopolymer) to 0.51. The values of molecular weight M and intrinsic viscosity [η] of the copolymers investigated are given in Table 1. The values of M lie in the Gaussian region, and therefore the molecular weight dependence of properties of investigated LC will be neglected below.

So far only homopolymers were investigated by the method of orientational elastic deformations[2-8]. The results suggested that the forces of intermolecular orientational interaction in high molecular weight nematics are related to a considerable extent to the size of the mesogenic group (or the mono-

Table 1 Characteristics of the copolymers investigated

Copolymer	x	M	[η] (dl/g)	T_g (°C)	T_{TDK} (°C)	T_{IN} (°C)
C-00	0	29000	0.095	31	54	142.0
C-08	0.08	25000	0.075	27	57	130.5
C-14	0.14		0.092	28	58	126.5
C-25	0.25	23000	0.086	29	-	112.0
C-40	0.40		0.117	30	-	94.0
C-51	0.51	21000	0.147	30	-	71.0

meric unit) and are virtually independent of chain length[3-5].

The Table 1 lists the values of phase transition temperatures. With increasing x the range of the existence of the nematic phase decreases because of the decrease in the temperature of isotropic melt – nematic transition T_{IN}. The glass transition temperature T_g is virtually independent on copolymer composition. At $x > 0.51$ the nematic phase disappears and copolymers become amorphous.

The phase behaviour of the homopolymer has already been discribed[9]. After a prolonged (several weeks) annealing of the nematic phase, C-00 at a temperature $T \sim T_g + 10°C$ forms the new highly odered Two Dimensional K (TDK) phase with the melting temperature $T_{TDK} = 54°C$. A detailed X-ray analysis of this phase is given in reference[10]. The TDK-phase was detected in C-x, but the "dilution" of the polymer chain by the amorphous component suppresses its formation in copolymers (at $x > 0.2$).

The study of orientational elastic deformations carried out by a procedure described in detail previously[1-3]. Plane-convex LC layers formed by a planar and spherical surfaces of quartz glasses were used. The homogeneous planar textures were obtained by rubbing the surfaces of glasses and lenses. Mesurements were performed in a magnetic field with a strength H of up to 16000 Oe. Sample temperature T was controlled to within 0.5°C.

The using experimental method makes it possible to determine the values of the splay elastic constant K_1 and the birefringence Δn of nematics.

Fig. 3 shows the dependences of Δn on the relative temperature $\tau = T/T_{IN}$. The values of Δn obtained for copolymers are in a good agreement with those for high[5] and low[11-12] molecular weight nematics with similar structure of mesogenic groups.

Birefringence Δn of copolymers decreases with increasing molar fraction

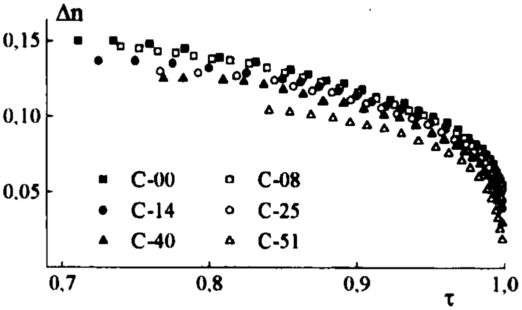


FIGURE 1 The temperature dependences of birefringence Δn.

x of the nonmesogenic component (Fig. 1). This change in Δn may be caused as by a decrease in the degree of intermolecular orientational order S of the nematics so by a decrease in the polarizability anisotropy Δα of their molecules. In fact, the dependences Δn(τ) may be discribed by the approximate equation[11]

$$\Delta n = (2\pi/3n)(n^2 + 2)N_A(\Delta\alpha/M)\rho S \qquad (1)$$

The density ρ and optical factor $(n^2 + 2)/3n$ weakly depend on temperature and composition of copolymer.

The value of Δα for LC investigated are determined to a considerable extent by the polarizability anisotropy of phenylene rings of mesogenic groups of the molecules. The contribution of the polarizability anisotropy of the non-mesogenic component to the values of Δα is smaller by almost two orders of magnitude. Therefore, the Δα/M ratio for copolymers decreases with decreasing fraction of mesogenic groups, which leads to the corresponding decrease in birefringence Δn of LC.

With increasing the molar fraction of nonmesogenic component from 0 to 0.40, the value of Δn decreases linearly. In this case in the temperature range $\tau \leq 0.96$ this value decreases as many times as the mass fraction of optically anisotropic phenylene rings decreases. This fact suggests that in the temperature range considered the order parameter S is virtually independent of copolymer composition. At $\tau > 0.96$ the value of Δn decreases much more than the mass fraction of phenylene rings. Hence, in the temperature range $\tau > 0.96$, the value of S depends on copolymer composition decreasing with increasing x.

The values of order parameters S for a homopolymer have previously been determined by wide-line 1 NMR spectroscopy[9]. The temperature dependence of S for C-00 is shown in Fig. 2 according to data in ref.[9]. It can be compared to the results obtained in the present work in the study of birefringence. For this purpose the scale of Δn (Fig. 1) must be transformed into the scale of S. The best agreement of the results obtained by the two methods is attained if S is taken to be equal to 0.5 at $\Delta n = 0.096$ (Fig. 2a).

It follows from the above that in the range of $\tau < 0.96$ the dependence of S on τ shown in Fig. 2a reflects the change in parameter S with temperature

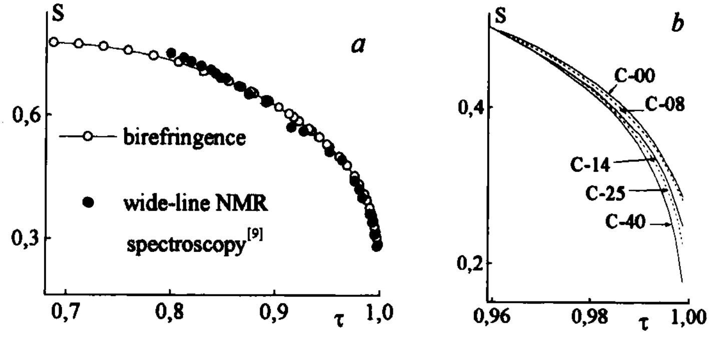


FIGURE 2 The dependences of S on relative temperature τ.

for C-08, C-14, C-25, and C-40. At higher temperatures the values of S for copolymers can be determined by transforming the dependences $\Delta n(\tau)$ into the dependences $S(\tau)$ taking into account the value of Δn and S in the range $\tau < 0.96$. The result of this transformation is shown in Fig. 2b.

On passing from C-40 to C-51 the value of Δn decreases much greater than the mass fraction of aromatic rings in their molecules over the entire temperature range. Consequently, taking into account the possible change in the value of $\Delta\alpha/M$, it may be suggested that the parameter S of the nematic phase of C-51 decreases as compared to that for other copolymers over the entire temperature range investigated (in the range of $\tau < 0.96$ the decrease in S can amount to 10 – 15 %).

The value determined experimentally in the study of elastic orientational deformations of planar layers is the ratio of splay elastic constant to diamagnetic anisotropy $K_1/\Delta\chi$. In order to determine the values of K_1, it is necessary to know the value of diamagnetic anisotropy $\Delta\chi$ for LC investigated. The values of $\Delta\chi$ were estimated by the method applied previously in investigation of polymer nematic[3-6]. Taking into account that molar magnetic anisotropy of nematic is proportional to the number of benzene rings in its molecules[13], it can be easily shown[3-5] that for polymer LC $\Delta\chi \approx (x_B \times \rho \times \Delta\chi_{\mu B}/M_B) \times S$ (x_B is the mass fraction of phenylene rings in polymer molecules, and M_B is the molecular mass of benzene rings). In these calculations the average experimental values of molar magnetic anisotropy $\Delta\chi_{\mu B} = 27 \times 10^{-6}$ cm^3/mole[11,13] per benzene ring of the nematic molecules was used and it was assumed that copolymer density is the same $\rho = 1.3$ g/cm^3. Accuracy of determination of the $\Delta\chi$ value using this method is about 15%[3].

Fig. 3 shows the temperature dependences of the constant K_1 which were obtained for copolymers. Their form is typical of that for nematic LC. In

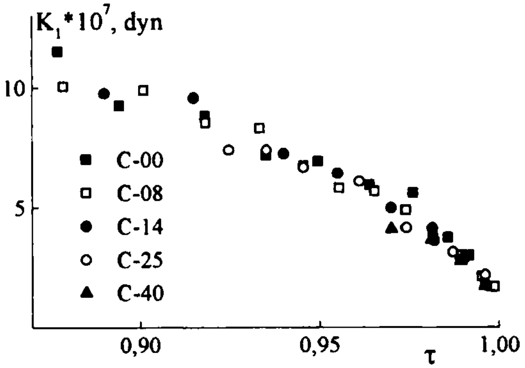


FIGURE 3 The temperature dependences of splay constant K_1.

the order of magnitude they are close to the corresponding values for low molecular weight[11,12] and polymer[5-8] nematics.

The points corresponding to different copolymers fall close to the overall curve of temperature dependence. Hence, in the temperature range investigated the splay elastic constant K_1 does not depend on copolymer composition when x increases from 0 to 0.40. This fact implies that the forces of intermolecular interaction in the nematic phase of the copolymers investigated virtually do not change when the molar fraction of the mesogenic component decreases from 1 to 0.6, i.e. when the distance between the points of attachment of mesogenic side groups to the main chain increase almost twice.

For aromatic polyesters (APE) with ethylene glycol spacers investigated previously[6], a decrease in the values of splay constant K_1 was observed when the length of the flexible fragment in the main chain increased, i.e. when the mass fraction of mesogenic groups decreased. This difference in the behaviour of high molecular weight LC is probably due to the fact that in APE molecules the distance along the chain between the mesogenic groups increases much greater than in the case of C-x copolymers. Moreover, the way insertion of mesogenic groups in the polymer molecular should also be taken into account. In APE molecules they are inserted into the main chain, whereas in copolymers investigated they are located in the side chains and linked to the main chain via a relatively long and flexible methylene chain.

Acknowledgements

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