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V. P. Shibaev[a]; R. V. Tal'roze[a]; I. A. Korobeinikova[a]; N. A. Plate[a]
[a] Department of Chemistry, M. V. Lomonosov Moscow State University, Moscow, USSR

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Invited Article

Cholesteric polymers in electric fields

by V. P. SHIBAEV, R. V. TAL'ROZE, I. A. KOROBEINIKOVA and N. A. PLATE

M.V. Lomonosov Moscow State University, Department of Chemistry, Moscow 119899, USSR

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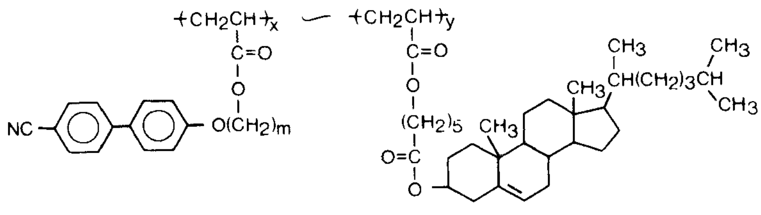
The main peculiarities of electric field-induced structural transformations in cholesterol containing comb-shaped polymers are discussed. As for low molar mass cholesterics both the changes in the texture and the untwisting of the helix can be observed. In cholesteric copolymers with a layered order of the side chains the untwisting of the helix results in the formation of a smectic-like structure. The dynamics of the helix untwisting is shown to be controlled by the mobility of the backbone.

1. Introduction

The ability of comb-shaped polymers with mesogenic side groups to change their structures in response to electric and magnetic fields prove that they are real liquid-crystalline materials. The electro-optic behaviour of nematic and smectic polymers is well studied and its main features have been reviewed [1–6]. Nematic and smectic polymers are shown to be oriented in an electric field in accord with the sign of the dielectric anisotropy ($\Delta\varepsilon$). This permits us to control their optical properties by means of external fields. However there is no information dealing with the influence of electric field on the cholesteric polymers, although the cholesteric mesophase has been shown to exist in polymeric systems [3, 6, 8]. The main reason for this is the absence of cholesteric polymers with high enough dielectric anisotropy. Such polymers have been obtained by us based on acrylic copolymers with cholesterol and cyanobiphenyl containing units [9, 10]



where $m = 4, 5$. The cyanobiphenyl groups provide the high value of the positive dielectric anisotropy and, as a result, the ability of the polymer to be aligned by an electric field.

Thus the set of polymeric materials with field controlled optic properties may be extended by the use of cholesteric polymers which selectively reflect light of different wavelengths and possesses a high sensitivity to electric fields. Some properties of the cholesteric copolymers being considered are given in table 1. The planar oriented films of copolymers I and II selectively reflect light at different wavelengths (see table 1). This serves as evidence for the formation of a cholesteric mesophase [11]. The wavelength of the selective reflection, λ_R, depends on the copolymer composition and it decreases with increasing fraction of cholesterol containing monomer units. Both λ_R and the refractive index $\bar{n}$ are enhanced, the helix pitch is increased.

Table 1. Characteristics of the cholesteric copolymers.

Copolymer	Composition, mol.% cholesterol units	η/dl g^{-1}	T_g/°C	T_c/°C	λ_R/nm (T/T_c = 0·97)	$\bar{n}$
	21	0·11	50	106	760	1·564
I	27	0·12	50	89	680	1·545
	30	0·10	55	106	600	–
	33	0·10	60	106	570	–
	16	0·10	60	108	IR	–
	19	0·16	60	107	860	1·534
II	21	0·07	60	107	810	1·529
	28	0·14	60	106	660	1·517
	36	0·10	60	104	550	–
	52	–	60	105	500	–

η, intrinsic viscosity measured in dichlorethane at 25°C.

Similar to some known cholesteric copolymers [11–15] the cholesterol containing units serve as a chiral additive and twist the optically inactive liquid crystal structure formed by the cyanobiphenyl mesogens. The helical twisting power $A = dP/dx$ (where, P is the pitch of the helix and x is the mole fraction of cholesteryl monomer units) was determined to be of about 7·5–8 μm^{-1} mol^{-1}. It is lower than that for some other cholesteric polymers ($A \approx 10\,\mu$m^{-1}mol^{-1}) [13] but it is of the same value as the twisting power of low molar mass cholesteric mixtures with nitrile containing Schiffs base [16]. Compared to systems without polar groups the specific (dipole–dipole) interaction between the mesogens with CN groups seems to hinder the helical twisting in copolymers being considered. That is why the helical twisting power is relative low.

Nevertheless, the helix pitch, P, increases with temperature (see figure 1). Such a temperature dependence of P may be explained by the model suggested in [17]. This considers the correlation between the helix pitch and the temperature, special interactions being disregarded. In this case the change of the second rank orientational order parameter, S, should result in the change of the twisting angle. From figure 2 we can see the decrease of S, which was calculated using Haller's approximation [18, 19], when the temperature is increased. The comparison of S values for copolymers and for the corresponding cyanobiphenyl containing homopolymers shows that the local order in cholesteric systems at relatively high temperatures is identical to that in nematic (m = 4) and smectic (m = 5) homopolymers. The difference resulting from the change of the spacer length vanishes with the incorporation of cholesterol monomer units in the copolymers (see figure 2).

The cholesteric mesophase of copolymers possesses a pronounced layered order. This can be seen from the small angle X-ray scattering patterns; the corresponding values of interplanar spacings, d, are given in table 2. Comparing d, with that for

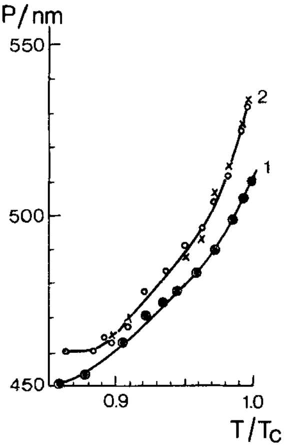


Figure 1. Temperature dependence of the pitch of the cholesteric helix for copolymers I (1) and II (2) containing, respectively 21 and 19 mol. % of cholesterol units with a degree of polymerization of 50 (○) and 160 (x).

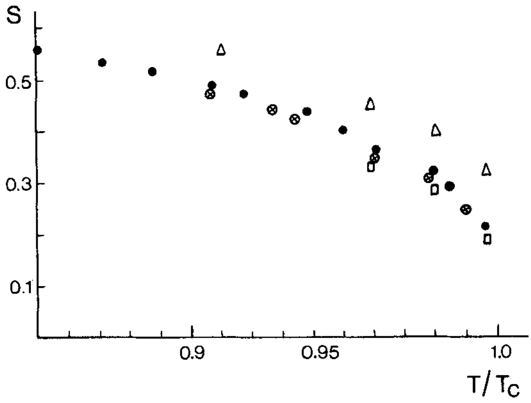


Figure 2. The order parameter, S, as a function of temperature for cyanobiphenyl containing homopolymers with $m = 4$ (△) and 5 (□) and for copolymers I (●) and II (⊗), containing 21 and 19 mol. % of cholesterol units, respectively.

Table 2. X-ray data for cholesteric copolymers I and II (23°C).

Composition of copolymer, mol.% of cholesterol units		Interplanar spacings/Å				
		$d_1 \pm 1$	$d_2 \pm 1$	$d_3 \pm 1$	$d_4 \pm 0{\cdot}5$	$d_5 \pm 0{\cdot}1$
	21	–	–	–	–	5·5
	30	42	–	–	–	5·5
I	33	42	28	22	17	5·7
	41	42	27	22	18	5·7
	19	41	–	–	–	5·3
	21	41	–	–	–	5·5
II	28	42	28	21	17	5·5
	36	42	28	22	18	5·7

cholesterol containing homopolymer we can conclude that the local smectic-like structure in cholesteric mesophase is imposed by the cholesterol units. The structure of the copolymers depends on the nature of the matrix and on the fraction of cholesterol monomer units. In copolymers with a smectic-like matrix ($m = 5$) the layered structure is preserved over a wide concentration range whereas for copolymers with a nematogenic matrix ($m = 4$) the smectic order disappears when the content of cholesterol-groups is less 20 mol %. The layer structure contradicts the general idea of the cholesteric mesophase in low molar mass liquid crystals which are usually considered to be a twisted nematic phase. A model for the structure of the comb-shaped polymers in the cholesteric state has been suggested in [13, 20, 21]. It demonstrates the possibility of the coexistence of small smectic regions having the size of about 10^2 Å with the macroscopic cholesteric order possessing the helix pitch over 300 nm.

2. Texture transformations in an electric field

The application of an AC electric field with a frequency of 1 kHz to a planar oriented polymer cholesteric parallel to the helix axis is accompanied by large changes of the optical properties. In figure 3 the transmittance spectra for copolymer I, containing 21 mol. % of cholesterol units are shown; these were measured in electric fields of different intensity. With increase in the voltage the peak corresponding to λ_R broadens and is shifted into a region of shorter wavelength. This can also be seen from the experimental dependence of λ_R on the voltage (see figure 4). Analysis of the

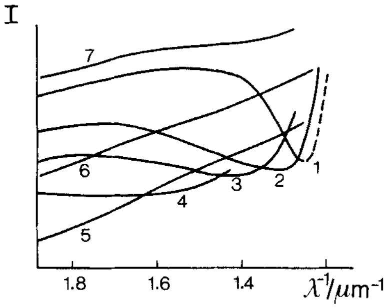


Figure 3. The transmittance spectra of copolymer I (21 mol. % of cholesterol units) at different voltages: O (1), 15 (2), 20 (3), 25 (4), 40 (5), 80 (6) and 120 V (7) (T/T_c = 0·99).

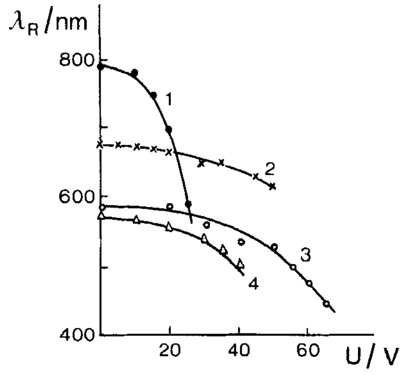


Figure 4. The wavelength of selective light reflection as a function of voltage for copolymer I, containing 1–21 (102°C), 2–27 (89°C), 3–30 (92°C) and 4–33 mol. % of cholesterol units (95°C).

transmittance in the short wavelength region beyond the selective reflection zone shows that application of the electric field results in the decrease of the transmittance. Further increase of the voltage does not change the transmittance in a certain voltage interval. But then the transmittance increases up to a value typical for the isotropic melt.

The decrease in the transmittance at the initial part of the curves in figure 5 shows the transparent planar texture to be destroyed by the electric field. This is confirmed by direct optical observations. The scattering confocal texture is stabilized in a certain voltage range. The simultaneous shift of the selective reflection maximum to the short wavelength range seems to be related with a change of the initial orientation of the cholesteric helix. The helix axis changes its parallel position relative to the field direction into one in which it is normal to the field with the simultaneous formation of the confocal texture. The main reason for these texture transformations is the influence of the cyanobiphenyl mesogens on the dielectric anisotropy of the copolymer as a whole. The calculated values of $\Delta\varepsilon$ are given in table 3. The side chains

Table 3. Dielectric anisotropy and threshold voltage for helix untwisting of cholesteric copolymers.

	Composition of copolymer, mol.% of cholesterol units	η/dl g^{-1}	P/nm (T/T_c = 0·97)	$\Delta\varepsilon$	U_0/V
	21	0·11	490	-	75
I	30	0·10	400	-	130
	33	0·10	380	-	140
	19	0·16	560	4·1	100
II	21	0·07	520	4·0	125
	28	0·14	440	3·6	140
	36	0·10	370	3·2	165

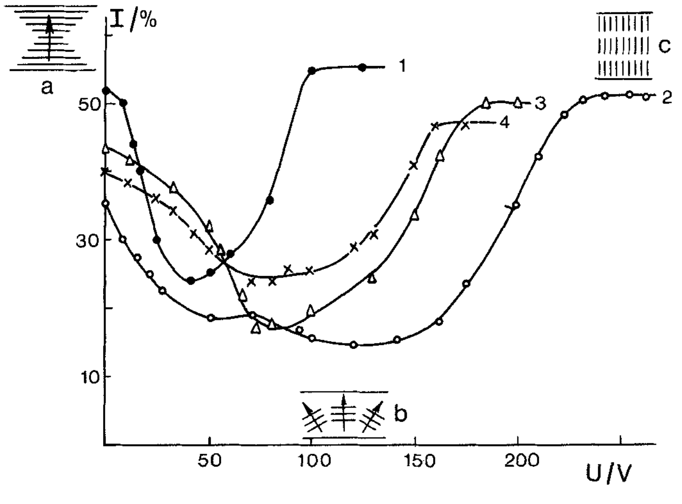


Figure 5. The transmittance as a function of voltage for copolymers I containing 21 (λ_R = 555 nm, T/T_c = 0·99) (1), 27 (λ_R = 625 nm, T/T_c = 0·98) (2), 30 (λ_R = 455 nm, T/T_c = 0·97) (3) and 33 mol.% of cholesteryl units (λ_R = 440 nm, T/T_c = 0·98) (4). a, b and c, Schemes for the arrangement of the mesogenic groups and of the helix axis (this is shown by the arrow) in the helix untwisting process: a, initial planar cholesteric texture; b, confocal cholesteric texture; c, homeotropic smectic texture.

of the macromolecules, arranged normal both to the helix axis in the planar sample and to the field direction, try to reorient the helix in accordance with the positive sign of $\Delta\varepsilon$ for the liquid crystal. An additional increase of the field voltage destroys the confocal texture and a new optically inactive transparent texture is formed. Its optical properties are identical to those of the homeotropic structure of uniaxial nematics and orthogonal smectics.

Thus in comb-shaped cholesteric copolymers with $\Delta\varepsilon > 0$ the following sequence of the texture transformations can be seen in an increasing electric field: planar cholesteric texture—confocal cholesteric texture—homeotropic texture.

2.1. *Untwisting of the cholesteric helix*

Homeotropically oriented films of cholesterol containing copolymers, at room temperature, are characterized by X-ray scattering patterns shown in figure 6. The wide angle diffuse reflection is located at the equator of the X-ray diffraction pattern. This means that the side chains of the macromolecules are oriented along the field direction and normal to the film plane. The cholesteric helix seems to be untwisted in an electric field and the resulting structure is frozen in when being cooled below the glass transition temperature, T_g. In some cases the resulting mesophase structure differs from the nematic. If the initial cholesteric possesses a local layer order (see table 2) the small angle, meridional reflections appear in the X-ray patterns of the untwisted cholesteric polymer (see figure 6(*b*)). This illustrates the formation of the smectic structure. It means that, unlike low molar mass liquid crystals, the electric field induces both the cholesteric → nematic and cholesteric → smectic phase transitions.

The dielectric interaction of the polymer cholesterics with an electric field obviously results in the untwisting of the cholesteric helix. This process is characterized by a threshold voltage for the untwisting of the whole helix. As a measure of threshold voltage, U_0, the minimum value of the voltage at which the transmittance is maximum has been taken. The decrease of U_0 with increase in the number of cyanobiphenyl units results from the increase of both the dielectric anisotropy and the helix pitch. However the frequency dependence of threshold voltage (see figure 7) may be accounted for by the change of $\Delta\varepsilon$ only. The asymptotic shape of the curve $U_0 = \varphi(f)$ indicates that in the cholesteric sample as well as nematic comb-shaped polymers [1] the change of

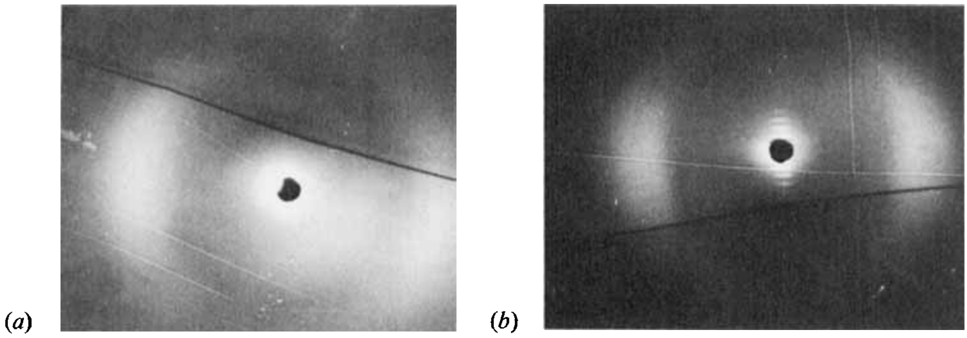


Figure 6. X-ray scattering patterns of copolymers I, containing 21 (*a*) and 41 (*b*) mol. % of cholesterol-units after application of an electric field and freezing below T_g.

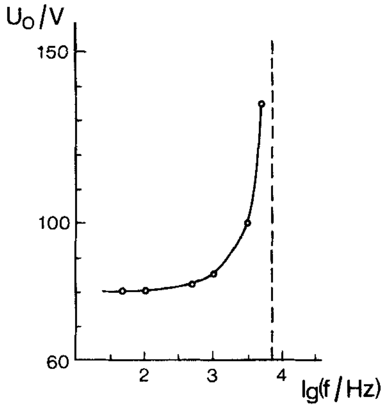


Figure 7. The threshold voltage as a function of frequency for the copolymer II (19 mol. % of cholesterol units) at T/T_c of 0·95.

the sign of the dielectric anisotropy takes place in the comparatively low frequency range. For example, in copolymer II (21 mol.% of cholester-units) at 82°C the untwisting of the helix cannot be observed at frequencies above 7 kHz.

According to the similarity of the field behaviour of comb-shaped polymers and low molar mass cholesterics the elastic constant K_{22} for copolymers has been evaluated. The well-known relation between U_0 and the general characteristics of cholesterics ($\Delta\varepsilon$, P, K_{22})

$$U_0 = \frac{\pi^2 d}{2P}\sqrt{\left(\frac{4\pi K_{22}}{\Delta\varepsilon}\right)},$$

has been used. The values of K_{22} for copolymers II depend weakly on the copolymer composition and are of about (5–7) × 10^{-12} N at T/T_c of 0·97. They are of the same order of magnitude as the corresponding elastic constants of low molar mass cholesteric–nematic mixtures.

3. Kinetic characteristics of the helix untwisting process

In figure 8 the kinetic curves of the transmittance change for cholesteric copolymers in an electric field are given. At comparatively low voltages this process may be described by only one characteristic time (see curve 1). At higher voltages the kinetic curves are more complicated. When comparing these curves with those given in figure 5 as a function of the voltage we can conclude that the initial part of the

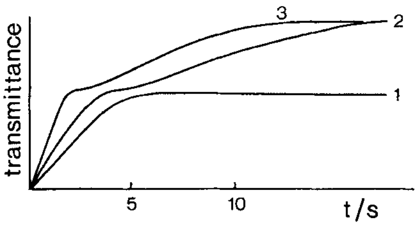


Figure 8. The time dependence of the transmittance for the copolymer II (28 mol. % of cholesterol units) at 90 (1), 120 (2) and 140 V (3) (T = 89°C).

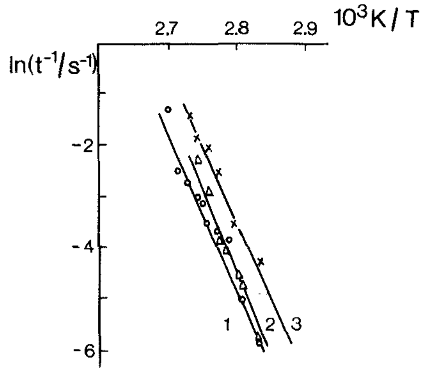


Figure 9. The reciprocal of the time for helix untwisting as a function of the reciprocal temperature for copolymers II containing 21 (1), 30 (2) and 33 (3) mol. % of cholesterol units.

curves corresponds to a textural transformation and the second is related with the untwisting process. As for the orientation field effects in nematic and smectic polymers the time taken to untwist the helix increases with increase of the polymer chain length. At the same time the strong temperature dependence of the untwisting time permits us to calculate an apparent activation energy for the process (see figure 9). This is equal to 200–250 kJ/mol and does not depend on the polymer chain length for samples with a degree of polymerization of between 50 to 160. This combination of experimental data leads us to conclude that the untwisting of the helix formed by the packing of the mesogenic side groups must be regarded as the process which is kinetically controlled by the change of the untwisting time with the lengthening of the polymer backbones and so the macromolecule as a whole to be involved in the rearrangement movement [22].

When the electric field is switched off the structure relaxes to the initial state. The change of the transmittance shown in figure 10 demonstrates the course of the relaxation process. Curve 1 indicates the reverse process to be the stage of defect accumulation (induction period). During the induction period (τ) in the homeotropically oriented sample some defects appear and helix twisting starts at these. The

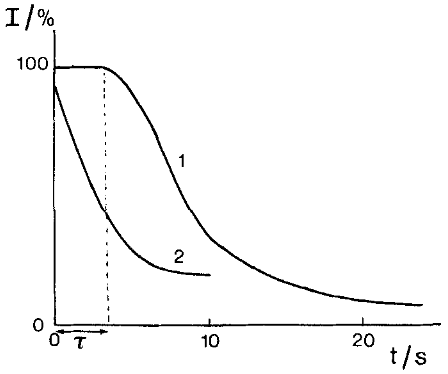


Figure 10. The change of transmittance during the relaxation of the cholesteric structure of copolymer II (28 mol. % of cholesterol units) initially oriented in an electric field at 130 (1) and 100 V (2) ($T_c - T_{exp} = 6°C$).

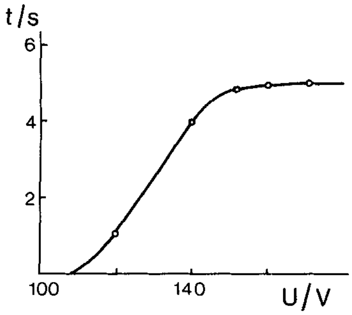


Figure 11. The induction period as a function of the voltage of the helix untwisting in copolymer II (28 mol. % of cholesterol units) at 95°C.

induction period depends essentially on the untwisting voltage (see figure 11). At relatively low voltages some small helical regions are preserved in the macroscopically oriented homeotropic films. In this case the relaxation process proceeds without an induction period (see figure 10, curve 2). The greater the voltage the less is the number of defects and the greater is τ. At a certain voltage τ reaches an upper value which is not changed with additional increase of the voltage. This is similar to the absence of defects in the macroscopically oriented sample. Relaxation back to the initial, planar texture is difficult. That is why the confocal texture is formed initially and this is transformed into the planar texture by means of long annealing.

It should be pointed out, that the induction period depends strongly on the temperature. This permits us to increase the memory time by cooling the sample. The polymer structure created by the electric field may be frozen in the sample below T_g.

Analysis of the cholesteric polymer behaviour under the influence of an electric field permits us to describe the electro-optic phenomena in polymer cholesterics. With the aid of an AC electric field the texture rearrangement and the untwisting of the helix may be realized independently of the chemical binding of the mesogenic groups to the polymer backbone. The ambivalent character of such polymers must be stressed: in the static state and at thresholds the similarity with low molar mass liquid crystals is manifested. From the dynamic viewpoint they behave as real polymers. The textural and structural transformations are realized only because of the liquid crystallinity in the side chains of the macromolecules; this is kinetically controlled by the chemical structure and mobility of the backbone. The low elastic constant of the cholesteric phase similar to that in low molar mass liquid crystals combined with large positive dielectric anisotropy permit us to control the structure and optic properties of polymeric systems in spite of the chemical bonds between the mesogenes and polymer chains which yield a high viscosity to the liquid crystal polymer as a whole.

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