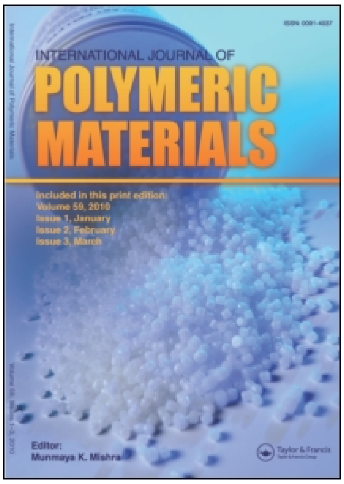

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Electrooptical and Photooptical Properties of Polymer Liquid Crystals

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Effects of electric fields on monomer liquid crystals (MLCs) and polymer liquid crystals (PLCs) are analyzed, dealing separately with nematic and cholesteric PLCs. Electrohydrodynamic instabilities affect the behavior of these systems. Thermooptical recording depends on the magnitude of the thermooptical effects. Information recording can be alternatively performed on the basis of photoorientation and the photoinduced birefringence. Capabilities and limitations of these techniques are pointed out.

Keywords: Electric fields; monomer liquid crystals; MLCs; polymer liquid crystals; PLCs; nematics; cholesterics; electrohydrodynamic instabilities; thermooptical recording; thermooptical effects; information recording; photoorientation; photoinduced birefringence

1. INTRODUCTION

During the last decade, the interest in electroactive and photoactive liquid crystalline (LC) polymer materials from both fundamental and applied points of view has been constantly growing. Indeed, possible technological uses for PLCs have been pursued with unusual vigour, obviously a consequence of the great technological impact of their counterparts of MLCs in the field of electrooptical displays [1]. Certainly, much of the research on PLCs has been intimately bound up with materials science and the quest of polymers with materials structures tailored for the best combination of physical properties deriving from

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the fluid but anisotropic behaviour of liquid crystals and the macromolecular specific properties of polymers.

The basic feature of PLC is their dual nature, enabling one to combine in a single material the properties of macromolecular compounds (with their ability to form films, glasses, fibres and coatings) and the mesomorphic properties of MLCs. It is well-known that a specific property of MLCs is the ability to undergo structural transformations under the effect of electric and magnetic fields as well as light irradiation. PLCs containing mesogenic groups also can be oriented by the action of external fields similar to MLCs, however this oriented structure can be frozen in a solid upon cooling the sample, with the anisotropy of the physical properties peculiar to the MLCs [2–9]. This feature opens up new possibilities for regulating and controlling the supramolecular structure of polymers, practically leading the creation of new types of materials performing in the LC state the necessary "commands" given, as a rule, by means of electric, magnetic or optical signals [7, 10, 11].

However, among a wide range of LC polymers synthesized a long way from each polymer may perform the functions of electro- or photosensitive material. Usually macromolecules of such polymers must contain electrosensitive or/and photoactive molecules or their fragments chemically "incorporated" in macromolecules. In other words, this pathway is an example of the creation of functionalized polymers which, in many respects, do act in accordance with the "guest-lost" principle. Therefore, depending on the concentration of the guest molecules (or their fragments), the response of the polymer matrix as a whole may be different. Nevertheless, as a result of the external field action, a certain close mutually-concerted interaction between "guest" molecules and the matrix structure is most often established which on the whole determines the behavior of the whole complex macromolecular system.

On the other hand, in studying the orientation of PLCs in external fields, the questions arise as to whether the electro- and phto-sensitive groups or their fragments are oriented independently on the polymer chains, or are the main chains of the marcomolecules also involved in the orientational process?

All of these questions are very important in connection with the possibility for creating LC materials with desirable as well as locally-regulated optical properties which could be easily and reversibly (or sometimes irreversibly) changed under an action of external electric field and light illumination [11,12].

This article predominently deals with PLCs bearing mesogenic side groups chemically linked to the backbone *via* spacers (so called comb-shaped PLCs) [2–4]. These polymers have attracted increased interest due to their possible applications as electro- and photo-optical regulated media [3, 4, 8, 11, 13–15]. The LC nature of these compounds, due to the side mesogenic groups existence forming the mesophase, permits one to use external fields for their orientation and for controlling their structure in the LC state. It opens up interesting and wide possibilities for obtaining polymer films as well as thin coatings with unusual optical properties, such as optical phase plates, polarization wedges, phasic cylindrical or spherical lenses, diffraction patterns and other no less interesting passive optical elements.

Photochromic PLCs opens up another possibility for creating photosensitive materials structure of which can be regulated by light or laser illumination. Such polymers can be considered as a new class of high-quality laser-addressed thin layer materials for reversible optical data storage and holography, for creation of optical discs and integrated optics-fields wave guides, as well as new modulators and optical switches.

This paper reviews the results of studies in the field of electrooptical and photooptical phenomena taking place in side chain PLCs.

2. ELECTRIC FIELD EFFECTS

2.1. Monomer Liquid Crystals

One the most unique and attractive properties of MLCs is their capacity to change their optical properties under the action of an external electric field of low voltage (1–5 Volts) and low power (10^{-4}–10^{-6} W/cm^2). Namely, the existence of ensembles of molecules possessing higher anisotropy of polarizability as compared with the individual molecules predetermines their higher energy of interaction with the electric field, exceeding the energy of the disorienting influence of temperature ($\sim kT$). The relatively low viscosity of MLCs and considerable high energy of their interaction with the electric field (exceeding kT) which ensures the macroscopic turning of the director sharply changing the optical properties of the anisotropic layer of the liquid crystal [1,16].

From the point of view of the electrooptical behaviour of all LC compounds (MLCs and PLCs) an existence of longitudinal or transversal dipole moment in the molecule (or in the side branching of the macromolecule), defining the anisotropy of dielectric susceptibility $\Delta\varepsilon = \varepsilon\| - \varepsilon\perp$ (where $\varepsilon\|$ and $\varepsilon\perp$ – are the dielectric constants of a liquid crystal measured along an external field and perpendicular to the field, or director **n**, respectively) is necessary.

Due to the anisotropy of the dielectric susceptibility, $\Delta\varepsilon$, the Helmholtz function of an ensemble of liquid crystal [1, 17]:

$$F = \int F_0 \cdot dV \tag{1}$$

(where F_0 is the Helmholtz function density; V – is the volume of the liquid crystal) is a minimum in the electric field at the definite director orientation in respect to the vector of the electric field $\vec{E}$. Director **n** tends to align itself along the field if $\Delta\varepsilon > 0(\mathbf{n}\|\vec{E})$ and perpendicular to it ($\mathbf{n} \perp \vec{E}$), provided that $\Delta\varepsilon < 0$.

The process of the field induced reorientation of the director **n** is usually described by the three typical geometries (Tab. I) corresponding to the three distortion types (splay, bend and torsion) and described by a certain combination of the elastic moduli K_{ii} (the so-called Frederiks transition).

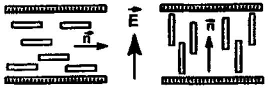
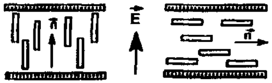
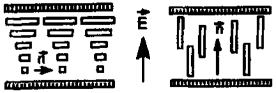
For the deformations shown in Table I the distortion-free Helmholtz function density F_0 of the nematic crystals follows from [1, 17]

$$\begin{aligned} F_0 = 1/2\,[K_{11}(\mathrm{div}\mathbf{n})^2 + K_{22}(\mathbf{n}\cdot\mathrm{rot}\mathbf{n})^2 \\ + K_{33}(\mathbf{n}\times\mathrm{rot}\mathbf{n})^2 - 1/2\,[\varepsilon_0\Delta\varepsilon(E\mathbf{n})^2] \end{aligned} \tag{2}$$

where the constants K_{ii} describe the elastic restorting forces in the three deformation pattern of Table I: splay (K_{11}), twist (K_{22}) and bend (K_{33}).

If the distortion corresponds to the "pure" splay, "pure" twist and "pure" bend deformation, such deformations are called S (when div

TABLE I Orientational effects in nematic liquid crystals

Orientation molecules in electrooptical cell Initial state Ultimate state	*Threshold voltage, E_0*	*Response times, τ_{on} and τ_{off}*
Splay effect ($\Delta\varepsilon > 0$) 	$E_0 = \pi(4\pi K_{11}/\Delta\varepsilon)^{1/2}$	$\tau_{\text{on}} = (4\pi\gamma_1 d^2/(\Delta\varepsilon E^2 - 4\pi^3 K_{11}))$ $\tau_{\text{off}} = (\gamma_1 d^2/\pi^2 K_{11})$
Bend effect ($\Delta\varepsilon < 0$) 	$E_0 = \pi(4\pi K_{33}/\Delta\varepsilon)^{1/2}$	$\tau_{\text{on}} = (4\pi\gamma_1 d^2/(\Delta\varepsilon E^2 - 4\pi^3 K_{33}))$ $\tau_{\text{off}} = (4\pi\gamma_1 d^2/\pi^2 K_{33})$
Twist effect ($\Delta\varepsilon > 0$) 	$E_0 = \pi((4\pi/\Delta\varepsilon)\ [K_{11} + (1/4)(K_{33} - 2K_{22})])^{1/2}$	$\tau_{\text{on}} = (4\pi\gamma_1 d^2/(\Delta\varepsilon E^2 - 4\pi^3 K_{11} + 1/4(K_{33} - K_{22}))$ $\tau_{\text{off}} = (\gamma_1 d^2/(\pi^2 K_{11} + 1/4(K_{33} - 2K_{22}))$

$\mathbf{n} \neq 0$), T (when $\mathbf{n}\cdot\mathrm{rot}\mathbf{n} \neq 0$) and B (when $\mathbf{n}\cdot\mathrm{rot}\mathbf{n} \neq 0$) deformations, respectively (Tab. I).

The left part of Eq. (2) in brackets corresponds to the elastic deformation of the liquid crystal without the external field, the second term in brackets corresponds to an interaction of the electric field with the dielectrically anisotropic media. Referring to Eq. (2), director **n** reorients in the electric field under the action of the dielectric torque, which is proportional to the dielectric anisotropy $\Delta\varepsilon$.

The evaluation of the minimum of the free energy from Eq. (2) at the fixed boundary conditions defined by the geometry of the experiment permits the calculation of the threshold voltage E_0. These threshold values for different types of deformations are presented in Table I, where the appropriate expressions for the kinetic parameters corresponding to the orientation time (so called rise time, t_{on}) and to the relaxation time (so called decay time, t_{off}) of the electrooptical effects are presented.

As can be seen from the formulas of Table I, the threshold voltage E_0 is connected to the above mentioned elastic constants; the kinetic constants τ_{on} and τ_{off} are defined also by the rotational viscosity coefficient γ_1 of the liquid crystal. Thus, the typical switching times of MLCs are 10^{-3} s; relaxation after switching off takes place much more slowly (decay time, $\tau_{\mathrm{off}} \sim 10^{-2} - 10^{-1}$ s).

The typical values of the elastic constants K_{ii} and the rotational viscosity coefficients, γ_1, for the usual MLC nematics are of the order of $10^{-11} - 10^{-12} N$ (1 dyne $= 10^{-5} N$) and $0.01 - 0.2\,\mathrm{Pa{\cdot}s}$ respectively. As for the ratios of the elastic moduli they are as follows [1,16]:

$$\begin{aligned} 0.5 &< K_{33}/K_{11} < 3.0 \\ 0.5 &< K_{22}/K_{11} < 0.8 \end{aligned} \tag{3}$$

The temperature dependence of the elastic moduli correlates with that of the square of the order parameter s:

$$K_{ii} \sim s^2(T); \quad i = 1,2 \,\mathrm{and}\, 3 \tag{4}$$

A knowledge of the numerical values of all these constants are very important due to the understanding of the static, as well as the dynamics performance of LC displays.

2.2. Polymer Liquid Crystals

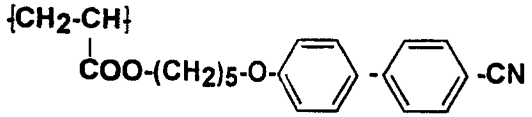
2.2.1. Nematic Polymers

As is shown in many publications, the bahavior of PLCs in an electric field is usually described in the framework of the same approach which has been considered in the preceding section [1–4, 9–11, 13–17]. In general, in analogy with MLCs, an electric field can reorient nematic PLCs according to the sign of their dielectric anisotropy $\Delta\varepsilon$ (the so called Frederiks transition). In turn, the sign of $\Delta\varepsilon$ depends on the direction of dipole moment of the electroactive mesogenic side chains. The macromolecular nature of PLCs permits the incorporation a variety of mesogenic groups in the same macromolecules differing in dipole moment direction (Fig. 1).

The study of such copolymers containing mesogenic fragments with negative and positive anisotropy of dielectric susceptibility ($\Delta\varepsilon$) is of a considerable interest for creating LC systems with controlled values and signs of $\Delta\varepsilon$ as well as and for elucidation of the regularities of their electrooptical behaviour. However, unfortunately the majority of electrooptical studies have been performed with the copolymers monomeric units of with similar sign of $\Delta\varepsilon$.

Some regularities of electrooptical behaviour of such homopolymers and copolymers are briefly considered below.

The ability of PLCs to orient in static and alternating electric fields was established for the first time in the studies [18–22]. Figure 2a shows the orientation process of the unoriented sample of an acrylic polymer containing cyanobiphenyl mesogenic groups I



(I)

under the influence of an electric field [13, 22]. The orientation process was identified by the change in the optical characteristics of the LC film (transparency, birefringence) placed between two glass plates with the electrically conducting transparent coating of SnO_2, similar to the conventional electro-optical cell. Measuring the intensity of the transmitted light as a function of time at different voltages one can observe how the initial unoriented and turbid polymer film is

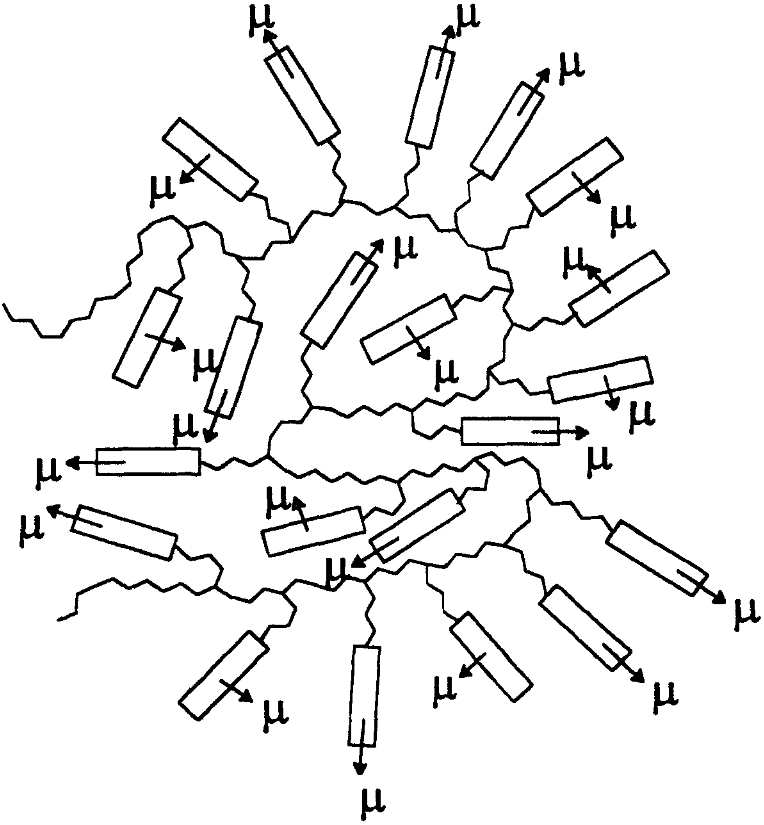


FIGURE 1 Schematic representation of comb-shaped macromolecule containing polar mesogenic groups distinguished by the dipole moment directions, μ.

transformed into the oriented and completely transparent film (Fig. 2, a, c, d). Between the crossed polarizers of an optical microscope the sample becomes completely dark and the X-ray diffraction pattern and conoiscopic picture of the film confirm the high degree of mesogenic group orientation. Such a transparent film in essence is similar to an anisotropic uniaxial monocrystal with the axis direction coinciding with the electric field direction.

The reciprocal rise time is universally proportional to the square of the voltage value (Fig. 2b), which is in a good agreement with the general Eq. (2) (see the second term in brackets). It proves that this orientational process is a result of the field effect.

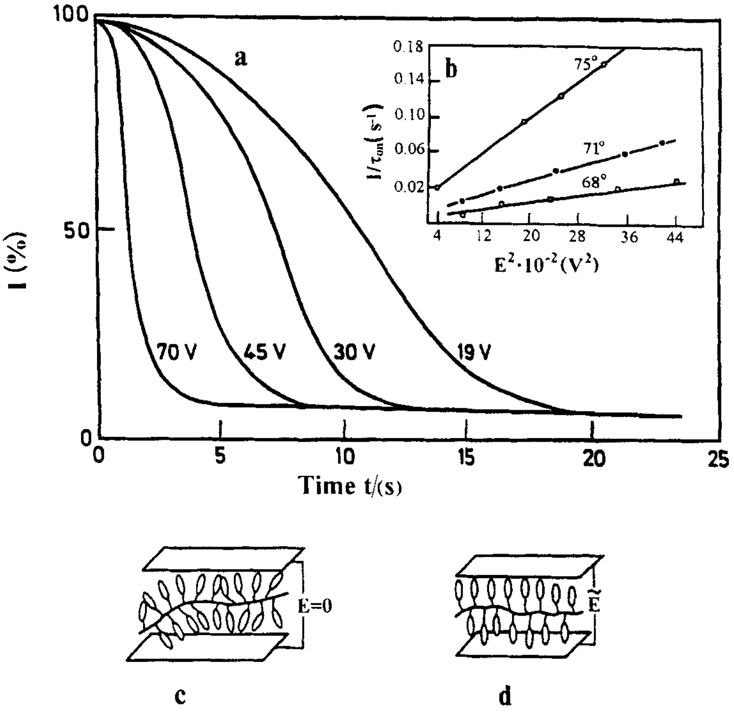
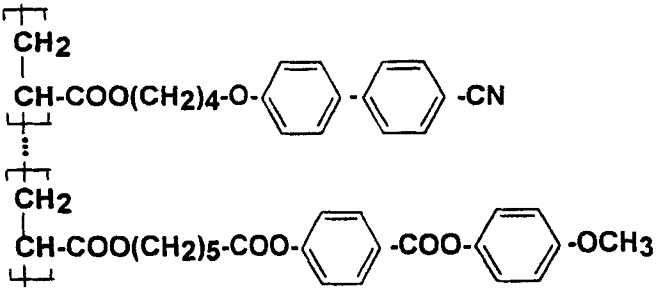


FIGURE 2 (a) Kinetics of the orientation of the unoriented polymer I upon application of an electric field at different voltage ($f = 50\,\mathrm{Hz}$; $T = 75°\mathrm{C}$) (the optical transmission in crossed polarizers is given as a function of time); (b) reciprocal rise time as a function of the voltage square at different temperatures, °C; (c, d) schemes of mesogenic groups orientation before and after the application of an electric field.

Another example showing the kinetics of the orientation of a sample of a copolymer II with a planar orientation (Fig. 3) given by special treatment of the surface of the electrooptical cell [13].

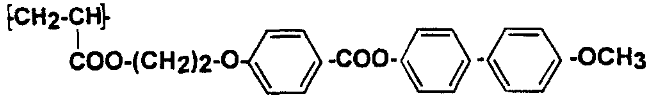


(II)

In this case, the peaks on the curves correspond to the director reorientation process from the planar texture trough disoriented texture to the homeotropic orientation (Fig. 3). After that the overall decrease of the light intensity during orientation indicates the orientation of the director along the direction of the field.

The analysis of these results gave grounds for the analogy of the observed electrooptical effects and the above mentioned *s*-effect, known for nematic MLCs with $\Delta\varepsilon < 0$.

A transition similar to the *B*-effect (see Tab. I) in an electric field was also observed in the nematic polymer III



(III)

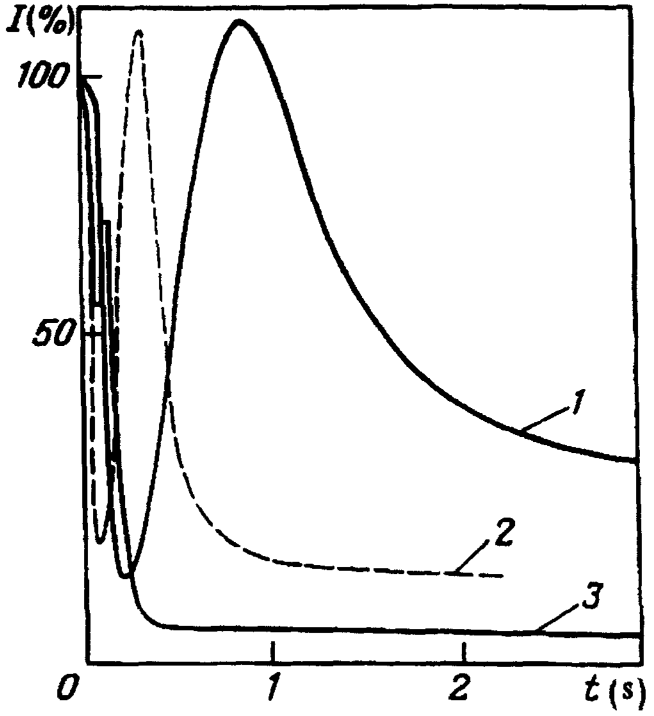
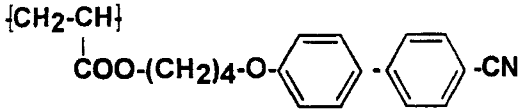


FIGURE 3 Kinetics of the orientation of the planary-oriented copolymer II at the different voltage (1) 11 V; (2) 20 V and (3) 30 V at T/T_{cl} = 0.91 (the optical transmission in crossed polarizers is given as a function of time).

characterized by low negative dielectric anisotropy ($\Delta\varepsilon \approx -0.3$), that is evidence in close favour of electrooptical behaviour MLCs and PLCs [24]. However there are at least three principal differences from the conventional nematics.

1. All PLCs have elevated viscosity, which depends on the degree of polymerization (DP). Namely this "polymeric nature" of the LC phase is responsible for the slowing down of all dynamic and relaxation processes carried out in PLCs under the influence of the external fields, including electric fields. For example, a 100 fold increase in the DP is accompanied by almost a 200 fold increase of the rise time (τ_{on}) [25]. This indicates that kinetics parameters of orientational process are defined mostly by macroscopic viscosity of a polymer. The calculation of γ_1 for the acrylic polymer IV of the same chemical nature that polymer I



(IV)

   from NMR data [26, 27] has shown that the values of γ_1 varied from 10^2 Pa·s to 10^4 Pa·s under changes of DP from 200 to 2500. These γ_1 values exceed the appropriate values of γ_1 of LMM liquid crystals by 2–4 orders of magnitude.
2. A majority of studies on orientational phenomena of PLCs in electric fields were carried out on unoriented (polycrystalline) samples. The elevated viscosity of PLCs and the existence of a polymer backbone are factors responsible for certain difficulties in the preparation of the perfect and the homogeneous initial texture of PLCs. At the same time, a strict quantitative estimation of such significant parameters as the threshold voltage E_0, τ_{on}, and τ_{off} times of the Frederiks effect are feasible only for polymer samples with homogeneous oriented initial texture (planary, homeotropic or twist). The textures of this sort can be obtained with the use of the same methods of treatment for the cell surface as in the case of MLCs. However, in the case of PLCs thee types of treatment of the glass plates of electrooptical cell should be supplemented with the prolonged annealing of the samples – sometimes it takes tens of hours or several days; the annealing time is defined by the DP.

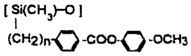
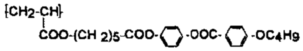
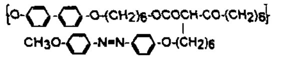
3. Contrary to the conventional MLCs, which are reoriented relatively rapidly after applying the electric field, the PLCs relax very slowly and their oriented structure can be easily "frozen" (fixed) in the solid after cooling.

In spite of the above-mentioned features of PLCs, exhibited at their electrooptical behaviour, analysis of our own and the literature data showed a series of analogies between MLCs and PLCs. First of all this is particularly true in regard to the elastic properties. Strange as it may seem, for both the main chain and side chain thermotropic PLCs, the values of the elastic moduli seem to be of the same order of magnitude as for their MLC counterparts [28 – 34].

Unfortunately in the light of the above mentioned difficulties of homogenous texture preparation, there is little few data concerning the determination of elastic moduli for the thermotorpic PLCs; some of them are shown in Table II.

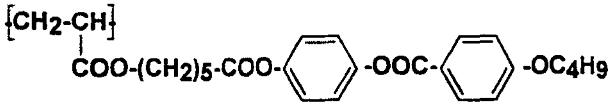
As can be seen from Table II, the values of the elastic moduli for different distortion types of PLCs (K_{11}, K_{22} and K_{33}) are very close to the appropriate elastic moduli of [1,16] . (1 dyne = $10^{-5}\,N$). As for the typical ratios of the elastic moduli, it is now difficult to make an

TABLE II Elasticity constants of some PLCs

N	*PLCs*	$K_{11}\cdot 10^7$, *dyne*	$K_{22}\cdot 10^7$, *dyne*	$K_{33}\cdot 10^7$, *dyne*	K_{33}/K_{11}	*Ref.*
						
1.	*n* = 4	7	–	13	1.8	
	(DP = 95)					[29]
2.	*n* = 6	8	–	7	0.9	
3.	 (DP = 115; T = 0.97T_{Cl})	7	–	6	0.86	[30]
4.	 (DP = 2-15; T = 0.97T_{Cl})	–	–	5	–	[31]
5.	Cholesteric Copolymers VII (DP = 50, 80, 160)	–	4÷7	–	–	[32, 33]

unambiguous conclusion showing the relation between molecular structure of PLCs and the numerical values of these quantities. Only some data in this direction have been recently obtained [30, 31, 34].

Next, Figure 4 shows the temperature dependence of the splay elastic constants K_{11} (curve 1) and bend elastic K_{33} constants (curve 2) for polymer nematic V obtained by orientation in magnetic field [30].



(V)

T_g=40°C $T_{N\rightarrow I}$=127°C (DP=114)

As can be seen from Figure 4 the values of K_{11} and K_{33} are really very close to the same values of elastic moduli of MLCs; however the K_{11} values exceed the K_{33} values the temperature range. At the same time, it is necessary to remind the order that the bend moduli K_{33} of

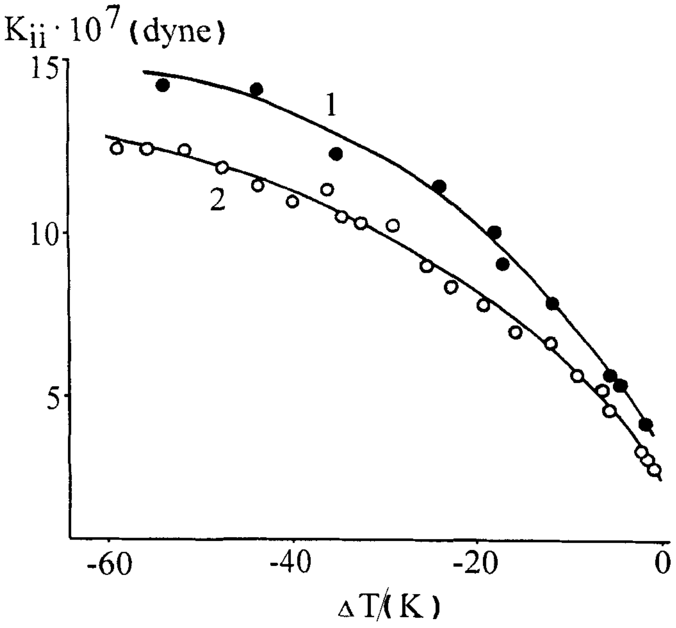


FIGURE 4 Temperature dependences of splay K_{11} and bend K_{33} elastic moduli for polymer V; (1) – K_{11} and (2) – K_{33}.

conventional nematics are usually slightly higher than their splay moduli K_{11} [1, 16].

Unfortunately, the absence of the quantitative data relating to the elastic moduli for a series of PLCs already studied, hampers even the phenomenological description of the regularities obtained. The study of the influence of the DP on the elastic moduli is also worthy of significant attention.

The electrooptical investigations of the cholesteric copolymers with different molar masses performed in [32, 33] have shown, that the change of the $\overline{\mathrm{DP}}$ with the limits of 50 to 160 has almost no effect on the value of $K_{22} \cong (4 \div 7)10^7$ dyne, which coincides (in order of magnitude) with the twist elasticity constants of low-molar-mass nematic-cholesteric mixtures.

The recent papers dedicated to the electrooptical behaviour of the PLCs and their mixtures with MLCs [35 – 37] [1] are worthy of the serious attention as far as they provide a possibility of estimating the elastic moduli everywhere over the composition region. Such an approach permits one to understand and evaluate the contribution of each structural unit of comb-shaped macromolecule (main chain, spacer and mesogenic group) to the visco-elastic properties of PLCs.

2.2.2. Cholesteric Polymers

An electric field is a powerful method, allowing us to change not only the nematic and smectic polymers but also to strongly change the supramolecular structure of cholesteric and ferroelectric PLCs.

The electrooptical behaviour of ferroelectric chiral compounds is the subject of widespread interest in current investigations of MLCs and PLCs and are considered in other chapter of this book. We consider here the structural transformations taking place in thermotropic comb-shaped cholesteric polymers.

Using cholesteric copolymers VI and VII containing the polar cyanobiphenyl mesogenic groups responsible for the positive $\Delta\varepsilon$ sign, the authors [32, 33] describe in detail the process of the helix untwisting under an action of the electric field.

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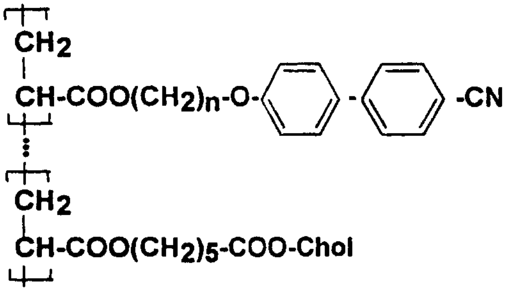
[1] These problems are considered by Simoni and Francescangeli in the same volume in detail.



n=4 (VI)
n=5 (VII)

where Chol - cholesteryl.

Figure 5 shows how the optically active planar-oriented cholesteric structure is transformed into the optically inactive homeotropically oriented texture after an applying the electric field. This process takes place in two stages.

In the first stage, the axis of the cholesteric helix changes its direction; these structural rearrangements are accompanied by a shift in the wavelength of the selective light reflection maximum (λ_{max}) to the region of shorter wavelengths. Simultaneously, the initial planar texture is transformed into a confocal texture and the overall transparency of the sample decreases (Fig. 5).

The second stage corresponds to untwisting of the helix, and the mesogenic groups are arranged along the electric field direction in accordance with the positive sign of $\Delta\varepsilon$ stipulated by CN-groups existence in the polymer. An additional increase in the field voltage destroys the confocal texture and a new optically inactive transparent texture is formed (Fig. 5). In dependence on the spacer length of the cholesteryl-containing copolymers VI and VII ($n = 4$ or $n = 5$), the structural transition induced by the electric field may be described in the framework of a cholesteric → nematic ($n = 4$) or cholesteric → smectic ($n = 5$) phase transition. Taking into account the critical electric field, *i.e.*, a threshold voltage E_0 corresponding to the untwisting of the helix, the twist elastic constants K_{22} of cholesteric copolymers have been determined [32]. These values of $K_{22} = (4 \div 7) \cdot 10^{-7}$ dyne practically do not depend on DP, similar to the polymer nematics (see Tab. II; copolymers 5) [32].

Thus, under the influence of an electric field, the supramolecular structure of polymer cholesterics may be essentially changed independent

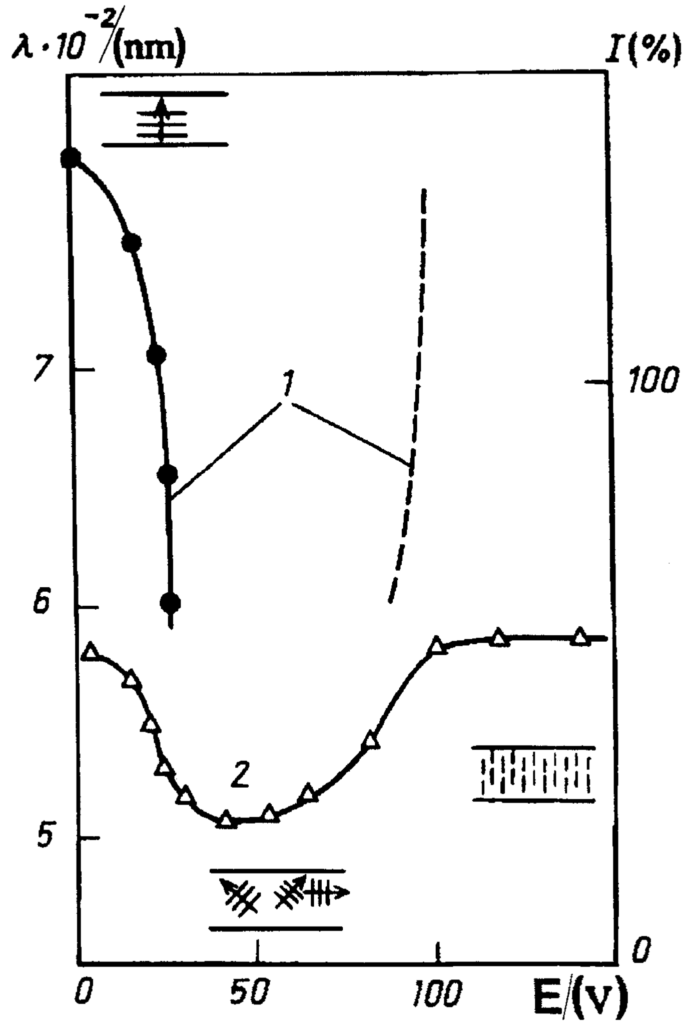


FIGURE 5 Untwisting of the cholesteric helix and schemes of the arrangement of the mesogenic groups and the helix axis. (1) Change in the selective reflection wavelength, λ, and (2) optical transparency, I, of cholesteric copolymer VI, containing 36 mol% of cholesteryl units, as a function of voltage. Initial planar texture, confocal cholesteric texture and final homeotropic orientation of mesogenic groups are shown in the figure (the arrows indicate the direction of the axis of the cholesteric helix).

of the chemical binding of the mesogenic groups to the polymer backbone; after cooling below T_g this modified texture is fixed in a solid polymer film retaining all the optical properties inherent to the cholesteric LC phase.

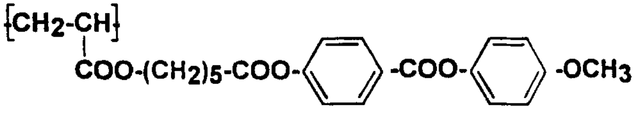
3. ELECTROHYDRODYNAMIC INSTABILITIES

The above mentioned field effects are phenomena based on the interaction of the electric field with the dielectrically-anisotropic medium and they are not associated with the electrical conductivity of the liquid crystals.

The other group of effects, known as the electrohydrodynamic instabilities (EHDI) arise due to the anisotropy of the conductivity, and correspond to a periodic deformation of the alignment of a nematic liquid crystal under the action of a direct current of low-frequency alternating current. An EHDI may be divided into two groups; those typical of isotropic fluids but observed in anisotropic phases as well as those which are specific for liquid crystals, and never observed in isotropic fluids. Only the second type of EHDI will be considered below (the so called the Carr-Helfrich instabilities) [1].

This type of EHDI can be visualized optically in the form of a very regular vortex motion which is accompanied by a strip domain optical pattern (the Kapustin-Williams domains). The scheme of EHDI appearance is shown in Figure 6. They appear in thin electrooptical cell ($d = 10 - 100\,\mu m$) and have a well defined voltage threshold independent of thickness. At voltages higher than the threshold of the EHDI, the turbulent motion of a liquid crystal acompained by a strong dynamic light scattering is usually observed.

The first observation of the Kapustin-Williams domains in PLCs was described in [38] for main chain LC polymers and later a detailed study of EHDI was conducted in [39] on the example of polyacrylate with methoxyphenylbenzoate side groups VIII



(VIII)

As can be seen from Figure 7, the threshold voltage for domain instability appearance (the conduction regime) deopends strongly on molecular mass (MM) (due to conductivity dependence on MM), which is expressed here as the intrinsic viscosity.

With the increase of the electric field frequency the threshold voltage required for the domain appearance sharply increases. (Fig. 8). On the other hand, at higher voltages the domain become unstable and the polymer films passes into the dynamic light scattering mode

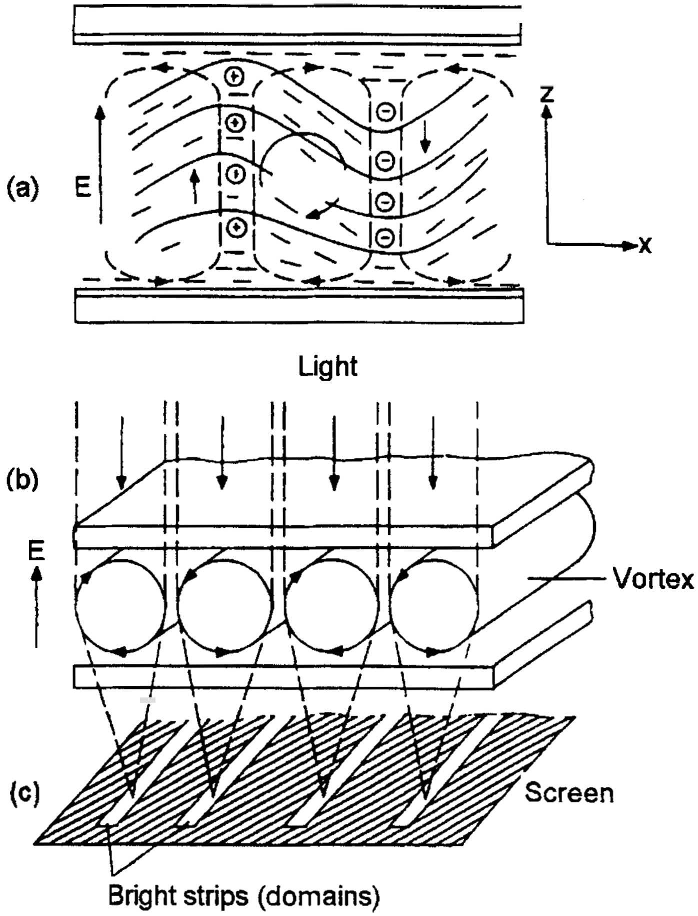


FIGURE 6 Schematic representation of electrohydrodynamic instabilities in nematic liquid crystal. (a) Onset of the instability; (b) the vortex motion of a liquid crystal and (c) the black and white stripes in the screen plane (domain structure).

characterized by the turbulent motion of a LC melt. This type of frequency of threshold voltage enables one to perform the switching operations with optical characteristics of polymeric films.

The use of the electric field for orientation of PLCs suggests the new and wide range of possibilities for the creation of new types of polymeric films with interesting and desirable optical properties. Such highly-oriented films may be obtained by the action of an electric field

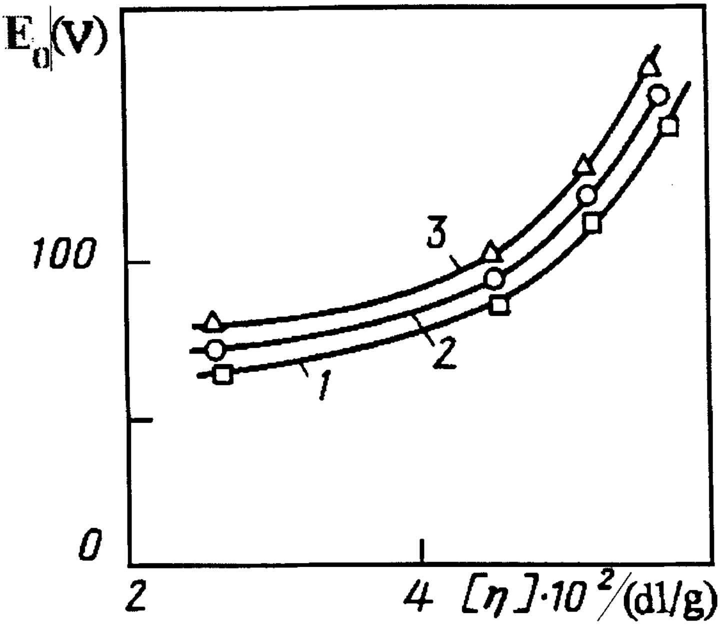


FIGURE 7 Influence of the intrinsic viscosity of LC polymers VIII (measured in dichlorethane at 25°C) on the threshold voltage, E_0, of domain formation at different frequencies of electric field: (1) 0.5 kHz; (2) 1 kHz and (3) 3 kHz.

in the LC state in an appropriate temperature range with the successive fixation of such structures in the solid by cooling the sample below the glass transition temperature.

In Table I there were presented the main types of nematic structures, well-known for MLCs: homeotropic, planar and twist textures. Such structures may also be obtained in PLCs by the certain specific methods. For example, polymeric films with planar texture constitute the phase plates; their optical properties are characterized by the difference in the course $\Delta\Phi = \Delta nd$, where $\Delta n = n_{\|} - n_{\perp}$ is the optical anisotropy; *i.e.*, the difference in the refractive indices of light for polarization parallel ($n_{\|}$) and the perpendicular ($n_{\perp}$) to the optical axis, where d is the thickness of the plate.

In such polymeric films, the values of $\Delta\Phi$ may be modulated on the coordinate both in the thickness of the sample and along the plane of the film. This gives us the possibility of obtaining polarization wedges and phase cylindrical or spherical lens. Some examples of different

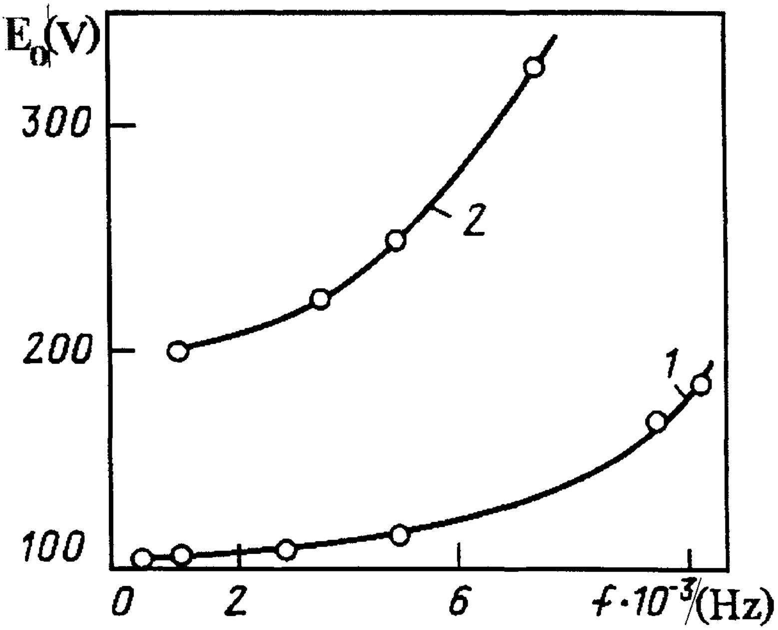


FIGURE 8 Influence of the electric field frequency on the threshold voltage of (1) EHDI domain appearance and (2) dynamic light scattering measured at 115°C for polymer VIII.

mesogenic group arrangements in such films, corresponding essentially to the supramolecular structure of the "frozen mesophase" are presented in Figure 9. All these structures shown in this Figure may be created by applying to the layer of the PLC an electric field the voltage of which changes along the plant of the layer. This can be accomplished, for example, by the use of electrodes with distributed resistance, and subsequent cooling of the film below the glass transition point.

An important advantage of PLCs as compared with MLCs is the possibility of superimposing one formed layer of the PLCs with certain optical properties to the surface of another which allows one to construct complex optical systems of low thickness. The possibility of obtaining thin polymeric films with exotic and various variants of the mesogenic groups arrangements allow us to consider the PLCs as prospective materials for the creation of new passive optical elements.

However, in addition to the possible use of PLCs as materials of passive optical elements (when the optical properties of these materials

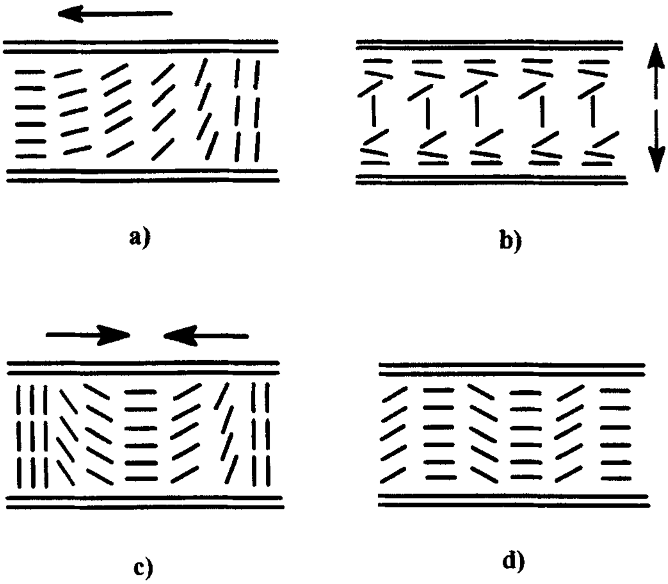


FIGURE 9 Various types of mesogenic groups arrangements in electrooptical cell which may be used to create passive optical elements. Arrows indicate direction of the Δn gradient. (The main chains of macromolecules are omitted for simplicity).

set once by the external fields in the preparative stage are in the main "exploited"), PLCs may be used in active controlled elements. In this case external factors such as temperature, electric field and light, act as controlling signals. In this way such LC films may be used, for example as materials for recording of information.

4. THERMOOPTICAL EFFECTS (THERMOOPTICAL RECORDING)

The capacity of PLCs for orientation in an electric field with subsequent fixing of a frozen homeotropic or planar texture in the glassy matrix make it possible to use such polymers as materials for recording and displaying information.[2]

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[2] These problems are also considered in the Chapter 13 "Optical Storage" by Th. Fuhrmann and J. Wendorff.

The use of PLCs for thermooptical recording of information was demonstrated for the first time by Russian scientists at the Moscow State University as illustrated by polyacrylic polymer I readily orienting in an electric field (see Fig. 2) [40–43].

The principle scheme for information recording is shown in Figure 10. On a transparent film of a homeotropically oriented polymer (20–40 μm thick), using a focused laser beam, spots of local overheating of the polymer above its clearing temperature (T_{cl}) are created. At these spots, the LC polymer melts passing into an isotropic melt, disturbing the monodomain orientation of the mesogenic groups. Cooling the sample, for example, through simple removing of the laser beam leads to the formation on the transparent film of a strongly light-scattering polydomain texture which corresponds to the recording of certain bits of information. Illumination of the polymeric film with a defocused laser beam allows the recorded image to be projected onto a screen.

Figure 11 gives examples of recording different geometrical figures on polymeric film. The introduction of a dye of the anthraquinone series into polymer I and the use of a laser beam with $\lambda = 1.06\,\mu m$ allows information to be recorded with high contrast (1:120) and quite good resolution of the order 100 and more elements per line at the scanning rate of the laser beam ~0.45 cm/s [4].[3]

The information (or image) thus recorded may be kept for a long time if the sample of the LC polymer is preserved below the glass transition temperature where the relaxation rate is negligibly small.

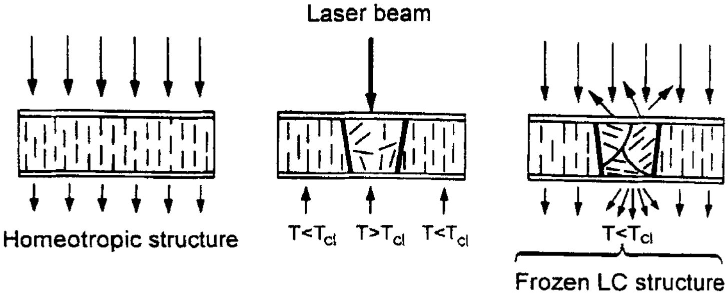

FIGURE 10 Scheme of thermooptical recording (thermoadressing) on the homeotropically oriented LC polymer.

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[3] This work was undertaken by Mr. A. N. Drozhzhin and Dr. S. G. Kostromin.

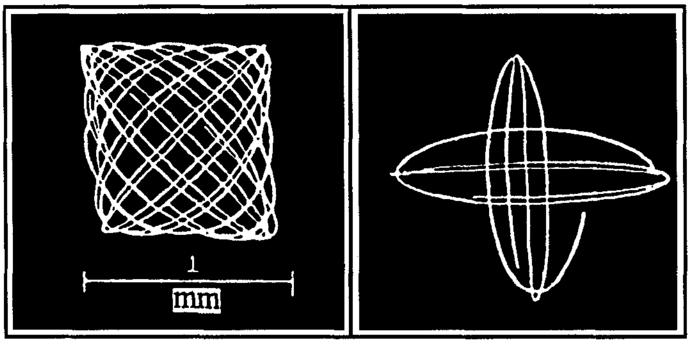


FIGURE 11 Photomicrographs showing the typical examples of thermooptical recording on a homeotropically oriented film of polymer I. (Film thickness 30 μm, laser power 2.6 mW, scanning speed 10 mm/s).

The symbols obtained in the above mentioned way could be erased by switching on an alternating electric field applied to the electro-optical cell ($U = 100\,\mathrm{V}; f = 50\,\mathrm{Hz}$) or by heating the sample above the clearing point.

Taking into account also the publications by Coles [44] and Mc Ardle [45], concerning the thermorecording on the oriented films of the side chain polysiloxanes one can consider nematic and smectic comb-shaped polymers as the perspective materials for archival memory (microfiches, carthography *etc.*).

The interesting possibilities of the use of thin layers of cholesteric LC polymers deposited on carbon dispersed black polyethylene terephtalate film for thermooptical recording were demonstrated in the studies carried out by Japanese scientists [46].

In this case, the authors of [46] instead of a laser beam, used a thermal head, which locally heated the cholesteric layer. The written state is induced by rapid heating and cooling cycle due to heat pulse application and rapid thermal head scanning. In the activated, heated region, the initial planar alignment becomes random and polydomain, so that light scattering occurred, *i.e.*, the written spot is in a light scattering area. As a result, a white image appears on the uniformly colored (green or red) background. The sensitivity of such a cholesteric film is around 0.15 mJ/dot input energy density. The resolution is more than 8 dots/mm. The constant ratio gradually increased with increasing input energy density and saturated at about 0.3 mJ/dot.

TABLE III Comparison of some characteristics of MLCs of cholesteric (Ch) and smectic types [47] as well as a PLC used for thermooptical recording [45]

Parameters	*Ch*	*Smectic*	*PLC*
Working temperature of information recording, °C	48	38	40–100
Temperature interval of optical data storage, °C	5–48	5–38	from low temperature till T_{cl}
Diameter of bit recording, μm	20	15–20	10–20
Power of laser ($\lambda = 633$ nm), mW	3	6–10	5–10
Electric voltage at local erasure, V	–	17–25	–
Electric voltage at total erasure, V	60	60	60
Contrast	10:1	(35 ÷ 50):1	120:1
Resolution in line, number of dots	1000	1000	1000
Speed recording, $\mathrm{cm \cdot s^{-1}}$	10	5	0.5–1.0
Bit stability, months	1–2	4	years
Fatique, write/erase cycles	–	$1 \cdot 10^4$	$5 \cdot 10^3$

Table III summarizes some average technical characteristics of cholesteric and smectic MLCs in comparison with a hypothetical PLC used for thermooptical recording. As can be seen from Table III PLC is characterized by good optical fatique, long term stability, high image contrast and resolution, as well as high sensitivity ($\sim 10^{-2}\ \mathrm{J/cm^2}$).

One can suppose that an application of PLCs as thermooptical media has considerable advantages over MLCs in respect to the control of their phase state and transition temperatures as well as physico-mechanical properties.

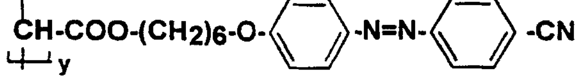
5. PHOTOOPTICAL PHENOMENA

5.1. General Remarks

The majority of the works concerning photooptical phenomena in PLCs were carried out on the copolymers containing the different photochromic groups as photosensitive fragments. Incorporation of such photochromic fragments as azobenzene, anthraquinone and spiropyran dyes "tuned" to a certain wavelength ensures their photooptical sensitivity and opens up prospects for obtaining photochromic LC polymer systems [11]. Under the action of light or laser beam the dye molecules undergo configurational (and conformational) changes independently on the phase state of photochromic copolymers.

For example, azobenzene dye molecules display a *trans-cis* isomerization under light illumination, the spiropyran groups are transformed into the merocyanine form [11, 12]. These photochemical transformation leads to changes of shape of the photosensitive units, which in their turn disturb the structural organization of the whole polymeric matrix. This results in the components of refractive index of the medium being changed, leading to the appearance of photoinduced birefringence and to the changes of optical properties of the polymeric film. In other words, using light illumination some bit of information may be recorded. In this case the phase image of the object is a consequence of spatial modulation of the refractive indices. The values of the photoinduced birefringence stored in the polymer matrix can be easily changed in respect to the electric vector of the incident light. Sometimes this method is called polarization information recording [4, 11, 12].

The first experiments concerning the applications of comb-shaped PLCs to phase and holographic recording were described by Wendorff and Eich [48, 49]. Using the films of nematic and smectic PLCs with azobenzene mesogenic groups (for example see copolymer IX), the authors observed the induced birefringence Δn of the order of $7 \cdot 10^{-3} - 1 \cdot 10^{-2}$ caused by polarized laser beam irradiation and briefly described the registered diffraction and holographic patterns.



(IX)

x=0.7, y=0.3, Tg=30°C, $T_{N \rightarrow I}$=103°C

This work probably stimulated further experimental investigations dedicated to a study of photooptical phenomena on a series of comb-shaped azobenzene [42, 50–56] and spiropyran-containing-copolymers on the basis of polyacrylates and polysiloxanes.

A majority of these and other publications have been reviewed in the books [11, 12]; that is why in this article we will concentrate our attention only on some aspects of their photooptical behaviour relating to the photoorientation of these polymers and the possibility of using these materials as optical information recording media. Let us consider photooptical behaviour of amorphous and LC photochromic copolymers containing azobenzene mesogenic fragments in the side chains.

5.2. Photoorientation of Photochromic Polymers

The reversible photochromism of aromatic azobenzene compounds is a well-known phenomenon which is explained by the *trans-cis* isomerization of molecules with respect to the $N=N$ double bond. (Fig. 12) [60]. As can be seen from Figure 12 the *trans* → *cis* isomerization (under the action of light with wave length λ_1) is accompanied by strong geometric changes; the azobenzene rod-shaped molecules are transformed into bent-shaped molecules, which can undergo a reverse transition accelerated by light with wave length λ_2.

In addition, the polar dye molecules tend to order themselves in such a way that the direction of their optical transition would be perpendicular to the electric vector of incident light. If azobenzene dichroic dyes are not chemically-linked with the polymer matrix but only

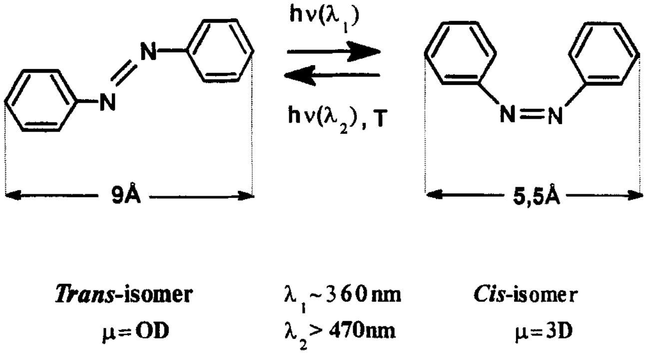


FIGURE 12 Photochemical isomerization of azobenzene (μ – dipole moment).

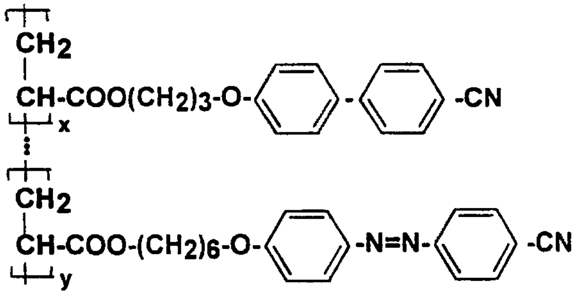
dissolved in amorphous polymer, this leads to the appearance of dichroism and photoinduced birefringence. However for the short time after switching the light illumination off the dichroism practically completely vanishes [61].

Another situation is observed for photochromic copolymers containing dye-fragments chemically (covalently) incorporated in the side chains of macromolecules. The illumination of azobenzene-containing copolymers also induces the photoisomerization of azobenzene side fragments according to the scheme presented in Figure 12. An increase in the irradiation time leads to the establishment of the photostationary equilibrium between *trans*- and *cis*-isomers [63, 64].

The establishment of a photostationary equilibrium initiates a slower process of the rotational diffusion of side dye fragments. Simultaneously, the neighboring side nonphotochromic rigid mesogenic groups are also involved in this process of reorientation, which leads to the appearance of dichroism and photoinduced birefringence Δn_{ind} in the sample.

Analysis of UV/VIS and IR-dichroitic measurements was widely used to characterize the alignment of side groups of amorphous and LC comb-shaped polymers both with respect to the electric vector of actinic light and with respect to the degree of orientational order, S [63–66].

Figure 13 shows the polarized UV/VIS spectra and angular dependence of the absorbance at 380 nm corresponding to $\pi \rightarrow \pi^*$ transition of the *trans*-azobenzene groups before and after irradiation of LC copolymer X being in amorphousable state.



(X)

y=0.2; x=0.8

As can be seen from Figure 13, the isotropic distribution of the UV-absorbance in the initial state demonstrates that there is no preferential orientation of side azo-groups of the copolymer. However, after the polarized irradiation, the isotropic character of the polar diagram is sharply changed and dichroism of the absorbance bands appears. Analysis of these data gives evidence that the long axis of the photochromic fragments are oriented perpendicularly to the electric vector of the laser beam. Such kind of orientation stimulates an orientational order in an initially isotropic sample; the photoinduced order parameter equal to $s \approx 0.2$ is very close to LC order induced, for example, by an electric field.

The change of the optical axis direction of the oriented samples is also observed after irradiation of homeotropically and planary-oriented films of LC polymers. Figure 14 shows, for example the polarized UV/VIS spectra and angular dependence of the absorbance (at 380 nm) of an uniformly planary oriented film of the same copolymer X in the initial state and after polarized irradiation by laser. As can be seen

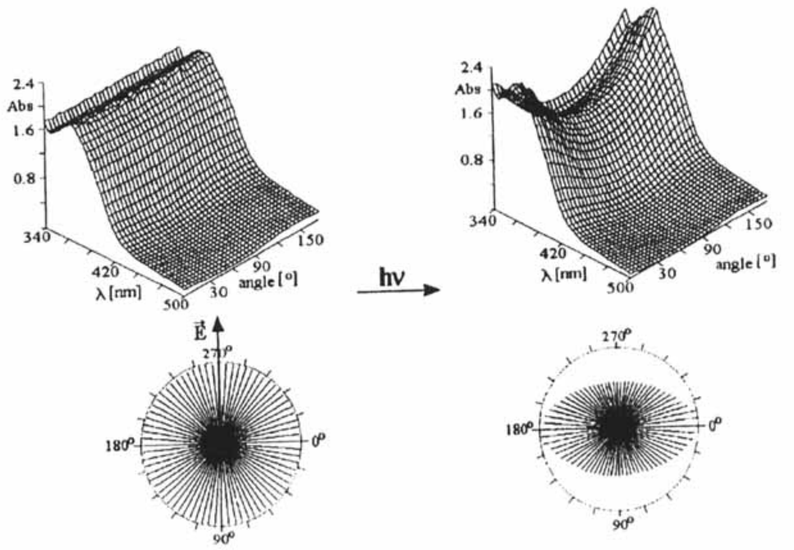


FIGURE 13 Polarized UV/V is spectra and angular dependence of the absorbance at 380 nm of copolymer X in the initial state (optically isotropic; left side) and after irradiation and relaxation (right side). (Illumination by laser beam with $\lambda = 488$ nm).

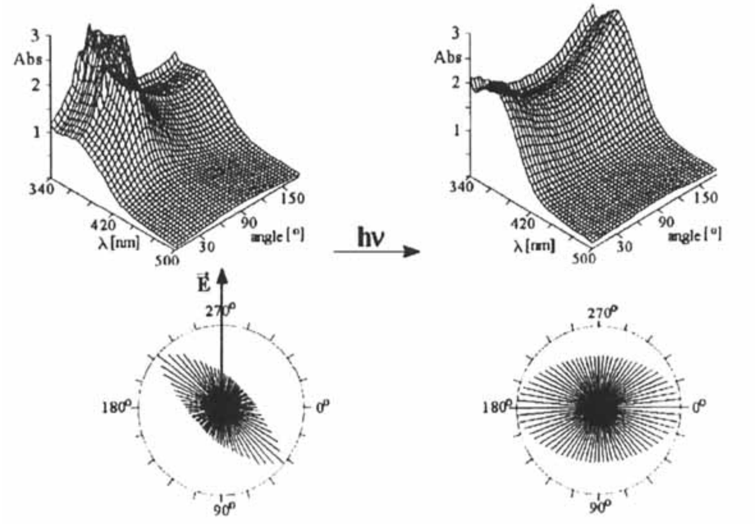


FIGURE 14 Polarized UV/V is spectra and angular dependence of the absorbance at 380 nm of an uniformly planar oriented film of copolymer X in the initial state (left side) and after polarized irradiation and relaxation (right side) [112]. (Illumination by laser beam with $\lambda = 488$ nm).

from Figure 14, in the initial state the electric vector of the actinic light forms an angle of 45° to the director orientation of the polymer film. After irradiation (and relaxation), the optical axis is rotated by 45°, *i.e.*, a reorientation of the side mesogenic groups occurs. In this case the order parameter decreases during the illumination. So if the initial order parameter of the planary-oriented film is equal to 0.4, then after the irradiation the S values decreases to 0.16 [65, 67].

The detailed study of orientation process showed that not only photochromic but non-photochromic groups also are included in the photoorientational process, which can be considered as cooperative one [65–68].

5.3. Photoinduced Birefringence and Information Recording

Now let us consider how the optical properties of polymer films are changed after the illumination by laser.

Figure 15 shows the electrooptical cell containing an homeotropically oriented sample of LC photochromic copolymer. This cell is irradiated

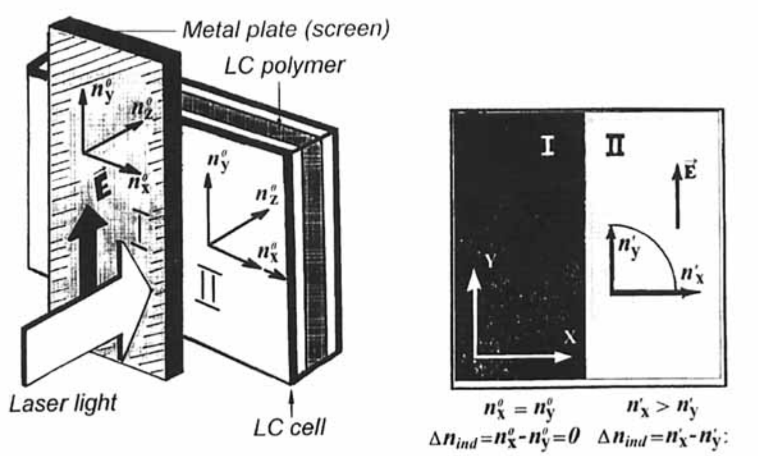


FIGURE 15 Schematic illustration of the optical recording on the homeotropically oriented LC film. On the left the electrooptical cell is shown. On the right the microphotos of the homeotropically oriented film before and after laser-beam irradiation in crossed-polarizers are shown. The left part of the cell was not irradiated.

by a vertically polarized laser beam. The electric vector of the incident laser beam coincides with the *Y*-direction; the *Z*-direction corresponds to the long axis of the mesogen. The left part of the cell is covered by a metal plate; in other words this part of the cell is not illuminated. On the right, the microphotos of polymeric films, recorded in the crossed polarizers of an optical microscope before and after irradiation are shown.

Before irradiation, refractive indices n° in the *X*- and the *Y*-directions are equal. It means that birefringence Δn_{ind} is equal to zero. That is why the left part of the cell looks like as a dark one in crossed polarizers.

After illumination the values of n_x become greater than n_y; that is, the biaxiality and birefringence $\Delta n_{\text{ind}} = n'_x - n'_y$ appear. It is clearly manifested in the microphoto on the right side of the cell, which becomes practically light after irradiation [42].

If now we place a test-pattern on the LC cell surface and illuminate this sandwich construction with a laser one can obtain the image of this test pattern (Fig. 16) [69].

It should be emphasized that the stored image is invisible to the naked eye and can be "read" only in polarized light. The optimum visibility of the irradiated regions was attained when the cell was situated so that

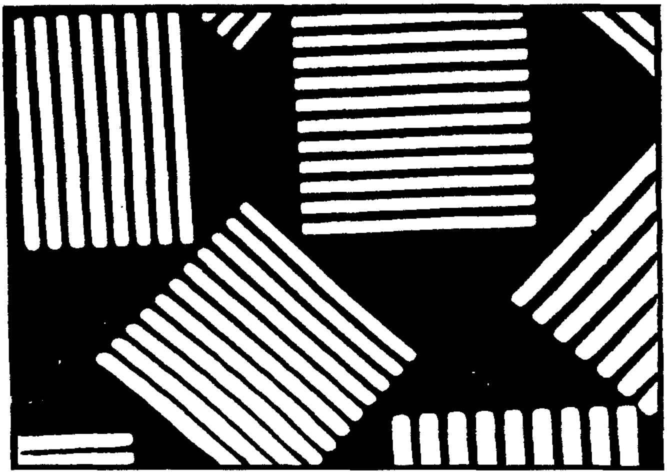


FIGURE 16 Photomicrograph of a film of LC copolymer obtained with use of the test pattern after illumination by laser. (Film thickness 20 μm, distances between strips 3 μm).

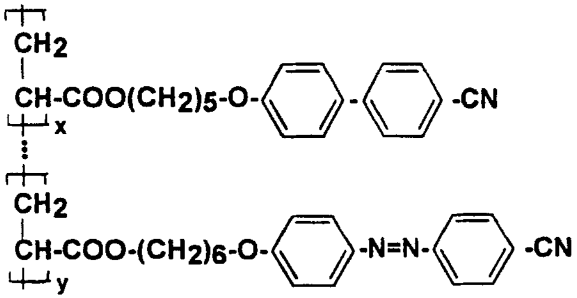
the angle between the direction of the polarization plane of the recording ("writing") beam and the polarizer axis was ± 45°; when the angle was 0 or + 90°, the image was no longer visible [70].

The similar photooptical behaviour is also characteristic for amorphous polymers containing azobenzene mesogenic groups [66, 67].

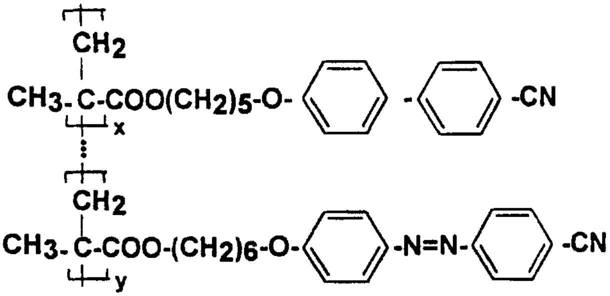
Thus, one can affirm that the polarized irradiation of the amorphous comb-shaped polymers containing mesogenic photochromic (azobenzene) side groups leads to considerable changes of their optical properties in the solid.

It is manifested in the increase of the refractive index of the amorphous and LC films in the direction perpendicular to the electric vector of the laser beam; in other words the irradiation process is accompanied by a change in the direction of the optical axis of homeotropically and planary oriented LC films or the appearance of the orientational order in the initially amorphous samples.

However, the difference between LC and amorphous comb-shaped photochromic polymers is clearly manifested in the values of photoinduced birefringence. Figures 17a and b illustrate the typical kinetic curves showing the photinduced birefringence (to be more precise-phase shift) as a function of time for photochromic LC (polymers XI) and amorphous copolymers (polymers XII) containing different concentration of one and the same cyanoazobenzene groups.



(XI)



(XII)

We would like to draw attention to the following points:

1. It is clearly seen that the higher concentration of dye molecules, the higher birefringence independently on the phase state of polymers.
2. The values of birefringence in amorphous polymers are one order of magnitude higher as compared to the PLCs. That means the photoinduced process is much more effective in amorphous than in the LC state. In other words, the less-ordered structure of comb-shaped polymers favors higher values of Δn_{ind}. As for the mesophase type influence on Δn_{ind} values one can assume that a more-ordered type of mesophase, probably greatly prevents the reorientation of mesogenic groups, thus showing low values of birefringence.
3. After switching the illumination off, a small decrease of primary induced birefringence Δn_{ind} takes place and stable values of Δn are preserved.

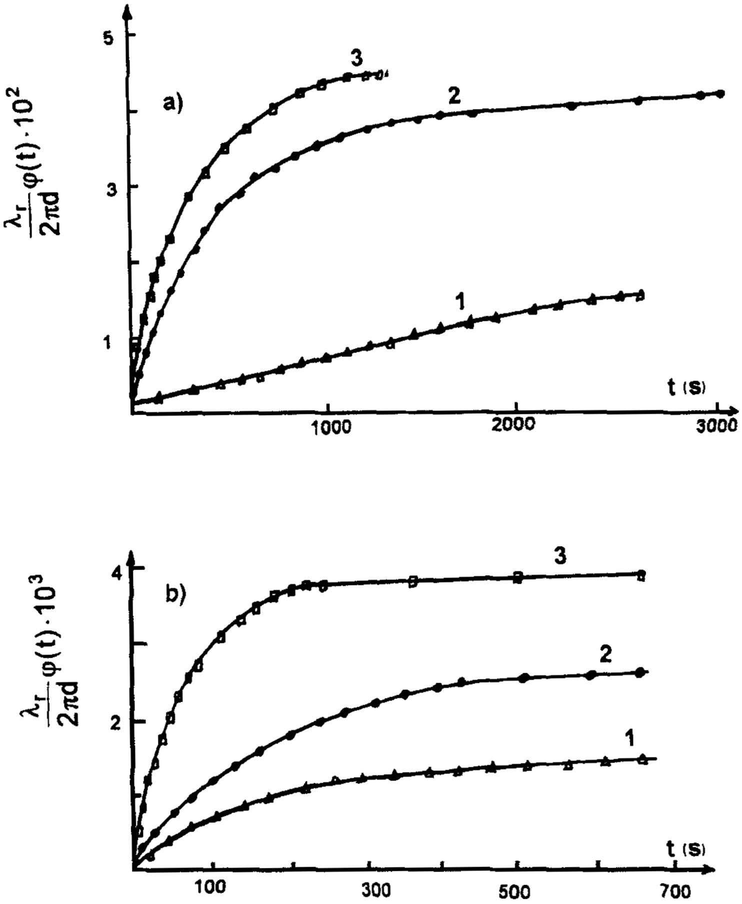


FIGURE 17 Time dependence of laser-induced birefringence Δn_{ind} in planar-oriented films of (a) LC copolymers XI and (b) amorphous copolymers XII, containing (1) 10 mol%, (2) 20 mol% and (3) 40 mol% of photochromic units; power density: 0.2 W cm^{-2} (The thickness of the film was varied from 10 μm till 100 μm); (The phase shift, which is proportional to Δn_{ind}, is plotted on the vertical axis).

Analysis of the kinetic curves of photoinduced birefringence [71, 72] has shown that the kinetics of Δn_{ind} can be described at least by a superposition of two processes corresponding to the fast and the slow birefringence increase- $\Delta n^{f}_{\text{ind}}$ and $\Delta n^{s}_{\text{ind}}$, respectively. In this case the general expression for the photoinduced birefringence can be described as follows (Fig. 18):

$$\Delta n_{\text{ind}}(t) = \Delta n^{f}_{\text{ind}} + \Delta n^{s}_{\text{ind}} \tag{5}$$

The fast process, whose contribution to the common value of Δn_{ind} is around 5–10% for amorphous polymers and 10–20% for LC polymers proceeds for a few seconds after switching the laser on. This fast process doesn't make the long-term recording. Switching the light off after a short time exposure leads to decrease $\Delta n_{\text{ind}} = 0$ (Fig. 17).

The slow process is responsible for the recording and can be well described by a monoexponental equation [71, 72]:

$$\Delta n^{s}_{\text{ind}}(t) = \left(\Delta n^{s}_{\text{ind}}\right)_{\max} \cdot \left[1 - \exp\left(-t \cdot \tau_s^{-1}(I)\right)\right] \tag{6}$$

where I – is the "writing" beam intensity; $\left(\Delta n^{s}_{\text{ind}}\right)_{\max}$ is the maximum value of Δn_{ind} at $t \to \infty$ and τ_s is the characteristic time for which the photoinduced birefringence Δn_{ind} reaches the value of $(1 - e^{-1})\left(\Delta n^{s}_{\text{ind}}\right)_{\max}$. It should be noted that the values of the photoinduced birefringence practically do not depend on the "writing" beam intensity at $t \to \infty$ *i.e.* $\left(\Delta n^{s}_{\text{ind}}\right)_{\max} \approx$ const.

Using Eq. (6), one can calculate the maximum values of Δn_{ind} which are directly associated with the stable Δn_{ind} (Fig. 18). As mentioned above, the more ordered phase hinders a reorientation of the mesogenic side groups with the result that the stable photoinduced birefringence Δn_{ind} for amorphous polymers has a higher value. The comparative analysis of experimental data concerning the numerical

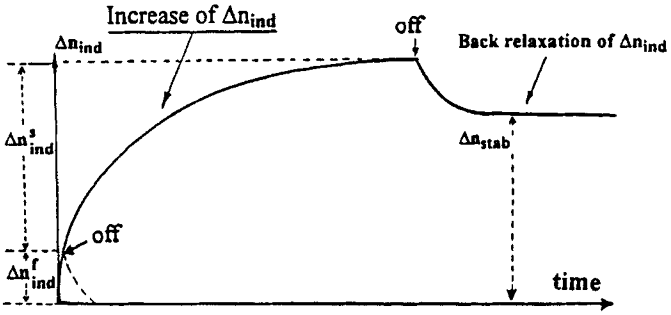


FIGURE 18 Generalized diagram of increase of photoinduced birefringence Δn_{ind} as a function of time.

values of Δn_{ind} shows that maximum values of Δn_{ind} for amorphous mesogenic side chain polymers may be as much as 0.20. These values for LC polymers usually vary between 0.05 and 0.15 depending on orientation type of the mesogenic groups.

Figure 19 shows the isotropic arrangement of the side mesogenic and photochromic groups in the amorphous state and the planar orientation of the photochromic copolymer. (The main chains are omitted for simplicity). On the left, the disposition of individual dye

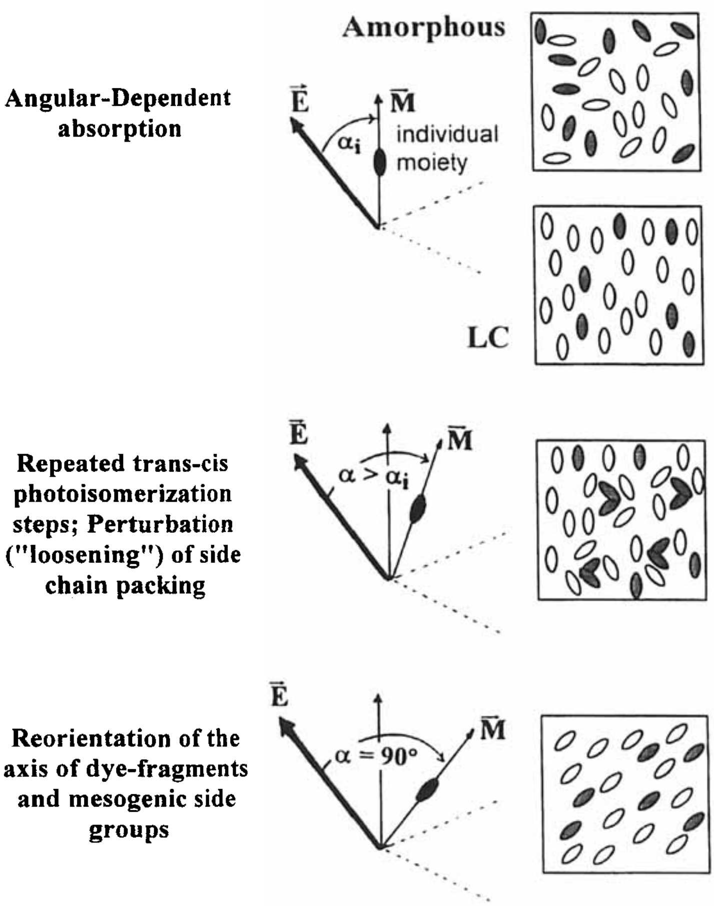


FIGURE 19 Schematic representation of reorientation of mesogenic groups in the amorphous and planar oriented polymer films.

fragments is shown. Its transition moment $\vec{M}$ coincides with the long axis of the azobenzene fragments; α-is the angle between the electric vector of laser beam $\vec{E}$ and the long axis of the mesogen. The first step is the absorption of linearly polarized light by azo dye fragments. This absorption is proportional to the square of the cosine of the angle α. The smaller the angle α, the greater the probability that the appropriate photochromic group will be excited. It is clear that planar orientation is the most favourable one for absorption of the light (in this case the angle α tends to 0). Thus, this step may be designated as the angular-dependent absorption.

The second step corresponds to the repeated *trans-cis* and *cis-trans* isomerization processes. As mentioned above, the geometry of the dye molecules is changed due to the *trans-cis* isomerization and the rod-like *trans*-isomers are transformed into the bent-shaped *cis*-isomers. Such transformations lead to the local changes of an orientation of neighboring non-photochromic side groups. In other words, the perturbation ("loosening") of side group packing takes place. This process is probably more effective in the less ordered medium, that is in the amorphous state. The orientational order in the LC state restricts the reorientation of dye fragments. Nevertheless, a certain additional free volume for reorientation appears.

The final stage of the photooptical effect is the reorientation of the photochromic moieties, which cause a continuous reorientation of non-photochromic but rod-like side gorups. The azo fragments are reoriented in such a way that the long axis of the dye fragments are perpendicular to the electric vector $\vec{E}$. The probability that an individual azobenzene unit exists will decrease again if the angle α becomes greater and *vice versa*.

Thus, this process results in the orientation of the mesogenic side groups in the amorphous polymer and reorientation of the mesogenic side groups in the LC polymer, accompanied by a drastically change of the optical properties of the solid polymer films. The key condition of such photooptical reorientation is the existence of strongly anisodimetric mesogenic fragments as the side branches of comb-shaped polymers.

The above-mentioned process leading to the appearance of photoinduced birefringence may be used for recording information and optical data storage. In this case the question about the possibility of reversible erasure of the recorded information naturally arises. There exist at least two methods of erasure.

As can be seen from Figure 18, the stable fixed birefringence Δn_{stab} practically does not change in the polymer films in the glassy state below T_g. The increase of the temperature above T_g leads to the falling of birefringence practically to 0. This character of birefringence changing "prompts" the erasure method of the recorded information, which lies in the heating of the polymer film above the glass transition temperature. Further, in the case of LC polymers repeated orientation is necessary for successive recording; in the case of amorphousable polymers heating the sample above T_{cl} and the successive quenching is also necessary for repeated recording.

However, as shown by us in [42] more convenient and prospective method of erasure exists. This method consists of the irradiation of LC film with recorded information by a laser beam with its polarization plane opposite to the initial polarization plane of the writing beam. This very simple method permits us to influence effectively the ratio of the values of birefringence in three directions-X, Y and Z (see Fig. 15).

Analysis of the optical data has allowed us to suggest the following generalized diagram of the cyclic process of the information reversible recording on the homeotropically-oriented polymer film (Fig. 20).

Curve OA shows the photoinduced birefringence increase during the irradiation process, *i.e.*, in the recording process. When the polarization plane of the "writing" beam is parallel to Y-coordinate, it means that the refractive index, n'_x, becomes greater than the refractive index,

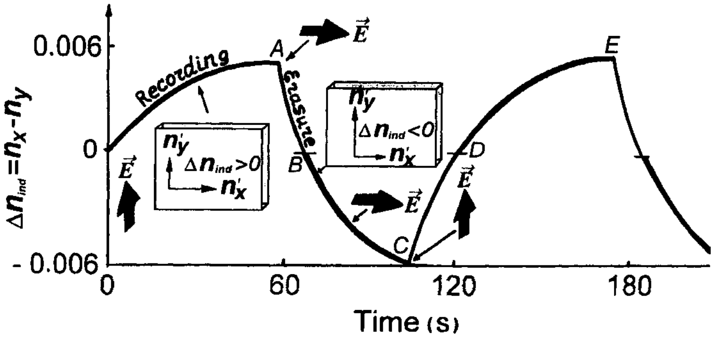


FIGURE 20 Scheme of reversible optical photorecording showing the photoinduced birefringence as a function of time.

TABLE IV Comparison of some important characteristics of acrylic PLCs containing cyanobiphenyl side mesogenic groups for thermooptical and photooptical recording

Parameter	*Thermooptical recording (Homopolymer + 2% dye)*	*Photooptical recording. Dye-containing copolymer*
Power density of laser beam, W/cm^2	10^2-10^3	$10^{-1}-10^{-2}$
Resolution, lines/mm	200	1000
Storage capability, bit/cm^2	$5 \cdot 10^6$	10^9
Write/erase cycles	tested to 10^3	tested to $4 \cdot 10^2$
Bit stability	> 7 years	tested to 4 years

n'_y. (It is shown by the coordinate arrows). When at point A a maximum value of $\Delta n_{\text{ind}} = n'_x - n'_y$ is reached a polarization plane (*i.e.*, electric vector $\vec{E}$ of the laser beam) is turned at 90°. After that the erasure process proceeds. At point B the image is completely erased ($\Delta n_{\text{ind}} = 0$). However, if the laser illumination of the film is continued (with the same direction of the polarization plane) the rise in Δn_{ind} (curve BC) is observed again (in this case $n'_y > n'_x$) and recording of information takes place; however the value of birefringence changes sign ($n'_x - n'_y < 0$).

By changing the direction of the polarization plane of the laser beam again (point C) one can repeat the recording process. It is important to emphasize that in this way one may obtain any values of birefringence lying in the range from $\Delta n_{\max}$ to $\Delta n_{\min}$ which allows the whole "scale of greyness" to be realized.

In conclude this article some comparative characteristics of LC materials used for thermooptical and photooptical recording are listed in Table IV.

As is seen from the Table, the photooptical recording is characterized by a higher storage capability and higher spatial resolution than thermooptical recording. In addition, the possibility of reversible recording and a very simple method of erasure in combination with high cyclicity of the photochromic PLCs permits us to consider these systems as rather promising ones for practical applications.

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