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Liquid crystalline polymers: development trends and photocontrollable materials

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The results of studies on thermotropic liquid crystalline polymers containing mesogenic groups in the main chains of linear macromolecules or in pendant side-chain branches of comb-shaped polymers are analyzed and summarized. The concept for the preparation of liquid crystalline polymers *via* introduction of molecules of low-molecular-mass liquid crystals into the macromolecules is outlined. The presence of rodlike anisometric fragments of liquid crystals in the main chains of macromolecules is shown to control the high level of orientational order in melts and solutions of liquid crystalline polymers. The structure and photooptical properties of photochromic comb-shaped liquid crystalline polymers are considered. The mechanism of light-induced structural chemical transformations in photoactive liquid crystalline compounds is addressed. Examples illustrating the development of photocontrollable liquid crystalline polymers and related composites are discussed. Structural optical properties of binary and ternary liquid crystalline photochromic block copolymers with independent modulation of photoalignment of photochromic and non-photochromic subblocks are analyzed. The feasibility of preparation of light-controlled liquid crystalline gels is considered. Special attention is given to mass transfer processes in liquid crystalline polymers, which allow the development of nanostructured surfaces and formation of diffraction gratings as well as enable preparation of diverse supramolecular structures. This review covers the challenges concerning the preparation of light-controlled liquid crystalline dendrimers and holographic media as well as the problems related to the nonlinear optical properties of liquid crystalline polymers. The roadmap for the practical applications of liquid crystalline polymers and their composites as photoactive media in photonics, optics, display technology, and in the systems for data recording and storage is outlined.
The bibliography includes 240 references.

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I. Introduction

From the standpoints of production volumes and the scope of practical applications, among diverse chemical compounds and related materials, including inorganic semiconductors, ceramics, silicon-containing and other heteroorganic compounds, and supramolecular ensembles of organic compounds, a prominent role belongs to high-molecular-mass compounds, usually called polymers. Suffice to say that, according to the documents of the VII Russian Congress of Plastic Converters, the worldwide annual production of thermoplastic polymeric materials in 2013 was as high as 245 million tons with a well-pronounced growing tendency up to 250 million tons by 2015.[1]

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The materials used by the mankind have always played an important and often decisive role for the development of our civilization. They gave their names to the whole eras of the mankind development such as the Stone Age, the Bronze Age, the Iron Age ... With a certain hint of arbitrariness and personal bias, the modern age can be referred to as the Age of Polymeric Materials.

At the present time, scientific and applied studies on polymers can be conditionally divided into three mainstream trends.

The first trend is concerned with the large-scale commercial production of polymers such as polyethylene (PE), polypropylene (PP), and their related copolymers, poly(vinyl chloride) (PVC), polystyrene (PS), polyurethane, and diverse derivatives of polyesters and polyamides, synthetic rubber (SR), cellulose as well as some other polymeric materials. The general scientific challenges in this area are of the technological nature and are related to the development of new approaches providing cost effective synthesis, search for new catalysts of the synthesis, and routes for the development of cost-cutting technologies in whole. The principal demands for the above polymer materials are the following: high physicomechanical characteristics, thermal stability, and degradation resistance.

The second trend is concerned with the development of innovative polymeric materials with much lower production volumes. Specific functional characteristics of these materials made them virtually indispensible for many areas of science, technology, and medicine. Among them are well-known natural and synthetic polymers. Typical examples are the following: copolymers of acrylic monomers, which are used for the production of contact lenses in ophthalmology, artificial limbs and prosthetic devices in orthopedics and dentistry, and biodegradable organic polymers based on polyesters. In recent years, special emphasis was focused on energy-saving coatings, modified polyesters to be used in optical devices and units (in photo- and video cameras), and natural polymers (cellulose, chitin, and their composites).

The third trend is related to a new class of polymeric materials, so-called 'smart' materials. This class primarily involves electroconducting and photochromic polymers, ionogenic and ionophore polymers, polymer-based fluorescent and responsive systems and also nonlinear optical materials, pH-sensitive gels and selective nanomembranes, flexible polymeric films to be used as displays and for the development of electronic paper (e-paper).

In our opinion, among the broad scope of the above organic, inorganic, and hybrid organic – inorganic 'smart' materials, a leading position is likely to belong to organic liquid crystalline (LC) polymers, which offer a fine combination of good physicomechanical properties of high-molecular-mass compounds (the ability to produce stable films, fibres, and thin-film coatings) and unique optical characteristics of liquid crystals.[2–30] The ability of the above compounds for self-organization and formation of diverse ordered supramolecular structures, which can be easily tuned under the action of external mechanical and electromagnetic fields, thermal treatment and light irradiation, presents a great interest for the development of innovative photo-, thermo- and electrotunable materials with locally adjustable structure and optical characteristics.

At the present time, 'smart' materials have attracted a keen interest of scientists all over the world, and this aspiration has been triggered by a thriving progress in the development of information technologies, with their products (PC displays, laptops, large TV screens and small-sized screens of cell phones and video cameras) being absolutely vital to our modern life. All recent technological advances along this line rely on the results of fundamental studies on electrooptical and magnetooptical properties of low-molecular-mass liquid crystals, the structure and optical characteristics of which can be easily tuned under the action of external fields. Along with modern technical devices, which are now common in our normal daily life, the attention of scientists has been attracted to the development and characterization of new types of 'smart' materials, including LC polymers.

The authors of this review in cooperation with their coworkers from the Laboratory of Chemical Transformations of Polymers (Division of High Molecular Compounds of the Lomonosov Moscow State University) have advanced the underlying principles for the synthesis of LC polymers and have studied several hundreds of diverse LC polymers with the comb-shaped structure. The results of our works with Russian and foreign collaborators were described in numerous scientific publications, including monographs, chapters of books, collections of articles, reviews, and original scientific publications.[2, 6, 9, 11–13, 21, 31–36]

Noteworthy is that, only since 2013, more than ten collections of articles and reviews[19–30] on synthesis, characterization, and practical use of the LC polymers were published. Therefore, in this review, we tried to avoid the unnecessary citation of these well-known results in the hope that our readers will find all important and interesting information by themselves.

This review is primarily focused on the advances in the research activities of the Russian scientists within the recent $\sim$ 15 years, and these results are compared with the results obtained by our foreign colleagues on comb-shaped LC polymers and polymeric LC systems (polymer LC systems also involve LC composites and blends of LC polymers with low-molecular-mass liquid crystals).

The authors did their best in order to make this review more comprehensible to a broad audience but they also offer detailed information on the subject, which fully reflects and covers all recent advances in this fascinating scientific area of high-molecular-mass compounds.

II. Liquid crystals and liquid crystalline polymers. General concepts

II.1. Liquid crystals

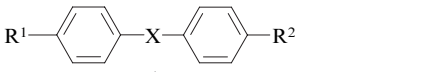
Purely academic studies of liquid crystals, which were first discovered more than 120 years ago,[37–42] were followed by a fantastic boom of their practical applications. At the present time, nobody can imagine any progress in any technical area without the use of liquid crystals, and the term 'liquid crystalline' is quite familiar (even though not well understood) to all modern people.

What are these unusual compounds? As follows from their name, liquid crystalline compounds, in astonishing ways, combine the properties of liquids and solid crystalline bodies. Like a common liquid, they can flow and take the form of a vessel into which they are placed, but, at the same time, they show anisotropic properties similar to solid crystals. In other words, their physical characteristics appear to be different in different directions; hence, they

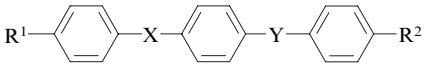
are often referred to as anisotropic liquids. Noteworthy is that the LC state is a thermodynamically stable phase state, which takes an intermediate position between an isotropic (amorphous) state and a crystalline state of a solid body; hence, this state is often referred to as the mesomorphic state or as the mesophase (from the Greek word *mesos* meaning intermediate).[22, 38–41]

The principal feature of liquid crystalline molecules is concerned with their anisometric shape and molecular rigidity. The most well-known and common representatives are so-called calamitics (from the Greek word *kalamus* meaning cane), which are composed of rodlike molecules. In most cases, these molecules contain two (or more) benzene rings, which are linked to each other either directly or *via* chemical groups. Typical examples are structures **1** and **2**, in which R^1 and R^2 are either similar or different alkyl or alkoxyl groups. Instead of benzene rings, these molecules can also contain cyclohexane and heterocyclic fragments as well as cholesterol derivatives.

Structures 1, 2



1

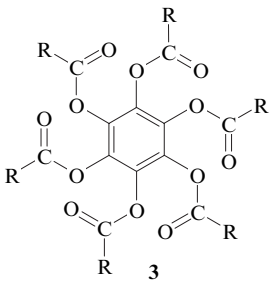


2

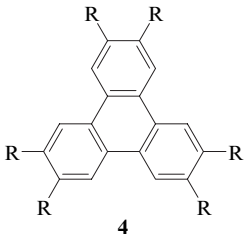
X and Y = N=N, CH=CH, CH=N, C≡C, C(O)O

In addition to calamitics, there exist some other types of liquid crystals that can have either board-like or disc-like shape. The latter usually contain several long flexible chains, which are linked to a central (rigid) part of the disc (structures **3** and **4**); they are known to produce the discotic type of the mesophase.

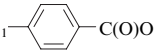
Structures 3, 4



3



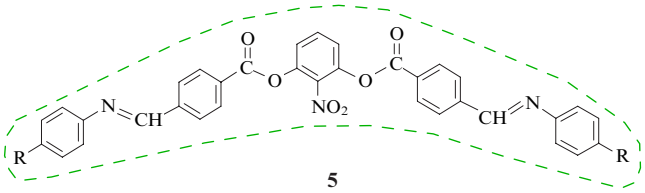
4

R = C_nH_{2n+1}, $C_nH_{2n+1}O$, $C_nH_{2n+1}C(O)O$, 

The molecules of liquid crystals are often referred to as mesogens, and rigid fragments of their molecules are called mesogenic groups.

To date, tens of thousands of organic substances are known to be able to exist in the LC state, and their number is steadily increasing. Even in the 21st century, new LC compounds with exotic molecular structures were synthesized, such as banana-shaped liquid crystals, for example, 2-nitroresorcinol derivative (structure **5**).

Structure 5



5

R = $OC_{12}H_{25}$-n

In terms of the principle of LC state formation, liquid crystals can be classified into two types:

— thermotropic liquid crystals (which are formed upon heating or cooling);

— lyotropic liquid crystals (which are formed upon dissolution of solid compounds in certain solvents).

In this review, our attention will be focused only on thermotropic liquid crystals and thermotropic LC polymers.

The key distinction of liquid crystalline molecules is their asymmetric structure, which provides polarization anisotropy and development of the orientational order. In this case, the tendency for the alignment of molecules along their long axes is particularly typical of calamitics or, in other words, of rodlike molecules; in the discotic mesophases, discs are aligned parallel to one another along their short axes.

Depending on the character of their alignment, liquid crystalline molecules can be divided into three basic types of LC structures, according to the classification suggested in 1922 by the French scientist G.Friedel: nematic (N), smectic (Sm), and cholesteric (Chol or N*) types (Fig. 1). The character of molecular packing in these structures is primarily controlled by their geometry and chemical structure (see Fig. 1). The simplest nematic type shows only unidimensional orientational order along long (in calamitics) or short (in diskotics) molecular axes. Since the centres of gravity of the molecules are randomly distributed in space, no translational order is observed.

The smectic type mostly resembles the structure of crystalline bodies, where molecules are arranged in layers and the centres of gravity are mobile in two dimensions. In each layer, the long axes of molecules are perpendicular to its plane (orthogonal smectics A and B) or inclined at a certain angle (inclined smectic C). Within the layer, the arrangement of molecules can be either chaotic (smectics A, C) or ordered (smectics B, E, F, I, J, K, *etc.*).

The disc-like molecules are also able to produce columnar phases (Fig. 1). As concerns the banana-shaped molecules, the structures of which are being intensively studied, they are able to produce either a disordered nematic phase or an ordered packing, which is similar to the smectic type.

The cholesteric type of LC structures is characteristic of chiral (optically active) compounds. In many ways, cholesterics are similar to nematics: both types show a unidimensional orientational order. However, chiral asymmetric centres of molecules or minor amounts of chiral compounds incorporated into nematics force the rotation of the layers † with respect to each other by a small angle α. After a certain number of layers, the orientation of molecules is repro-

† Note that, in reality, no cholesteric layers exist, and this concept is used here for the explanation of the structure of this mesophase.

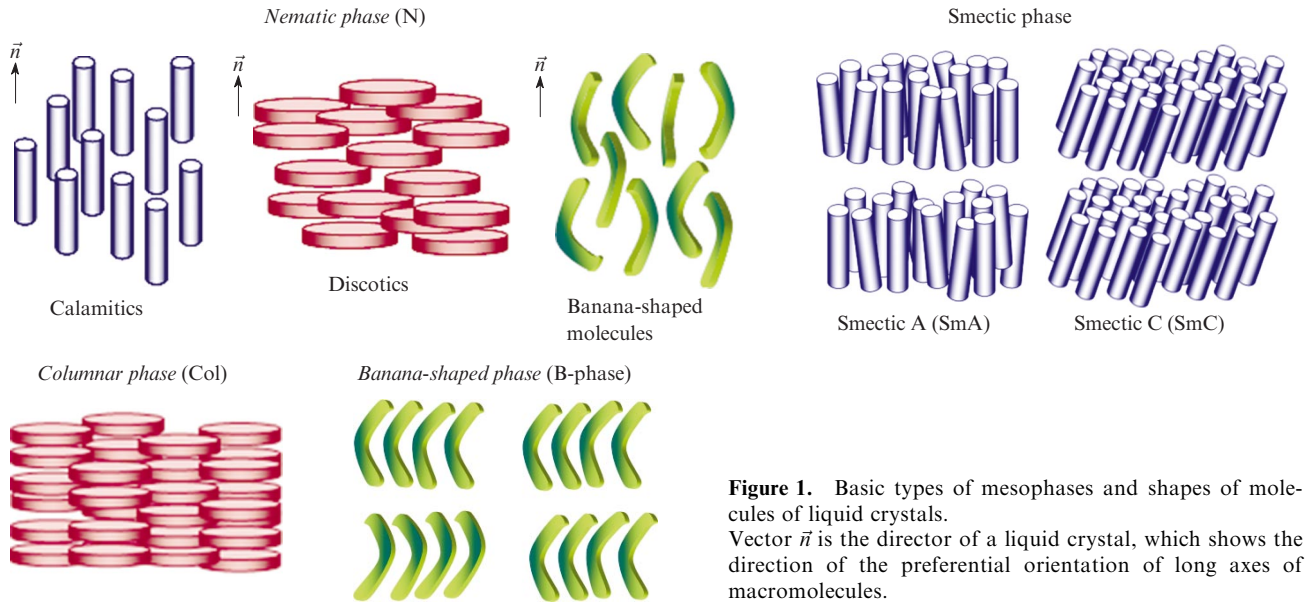


Figure 1. Basic types of mesophases and shapes of molecules of liquid crystals.
Vector $\vec{n}$ is the director of a liquid crystal, which shows the direction of the preferential orientation of long axes of macromolecules.

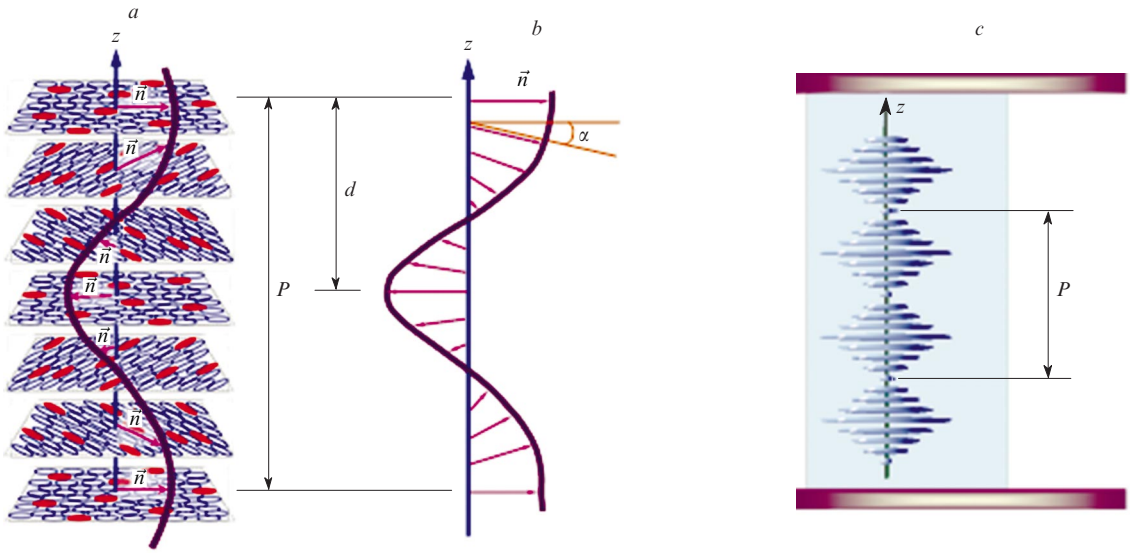


Figure 2. Packing of rodlike molecules in cholesterics (*a*), scheme illustrating the helical arrangement of the director $\vec{n}$ (*b*), and planar orientation of the cholesteric crystal (*c*);[24]
z is the helical axis, *P* is the helix pitch, *d* is the period of changes in optical properties, α is the twisting angle. The direction of the director $\vec{n}$ describes the helix.

duced. In this way, a twisted helical supramolecular structure with the helical pitch *P* is formed (Fig. 2 *a*,*b*).

$$P = 2\pi\frac{d}{\alpha} \qquad (1)$$

That is the reason why cholesterics are often referred to as twisted nematics. This structure of cholesterics is responsible for their unique optical characteristics.

When a thin layer of a liquid crystal is placed between two cover glasses (in so-called LC cell), the planar structure is formed; this means that helical axes are perpendicular to the planes of glasses, and the long axes of molecules are parallel to one another and to the surface of the LC cell (see Fig. 2 *c*). This periodic helical structure of cholesterics accounts for their unique behaviour, namely, selective reflection of incident light. When the reflection angle is fixed, the conditions of interference hold only for the rays of one colour; then, a cholesteric layer (or film) appears to be coloured by this particular colour; in other words, the phenomenon of selective light reflection for a given light wavelength (λ) takes place, and its maximum is related to the helix pitch *P* in the following way:

$$\lambda_{max} = \bar{n}P \qquad (2)$$

Here, $\bar{n}$ is the average refractive index of the cholesteric. The helix pitch depends on many factors such as the chemical nature of a cholesteric, concentration and geometric shape of chiral sites (additives or a dopant). Note-

worthy is that the spectral region of the selective light reflection (λ_{max}) can vary over a broad range spanning from the UV to IR region. The main characteristic of the chiral dopant is its twisting power (β), which is defined by the following equation

$$\beta = \frac{dP^{-1}}{dx} = \bar{n}\left(\frac{d\lambda_{max}^{-1}}{dx}\right)_{x\to 0} \quad (3)$$

where x is the concentration of the chiral dopant.

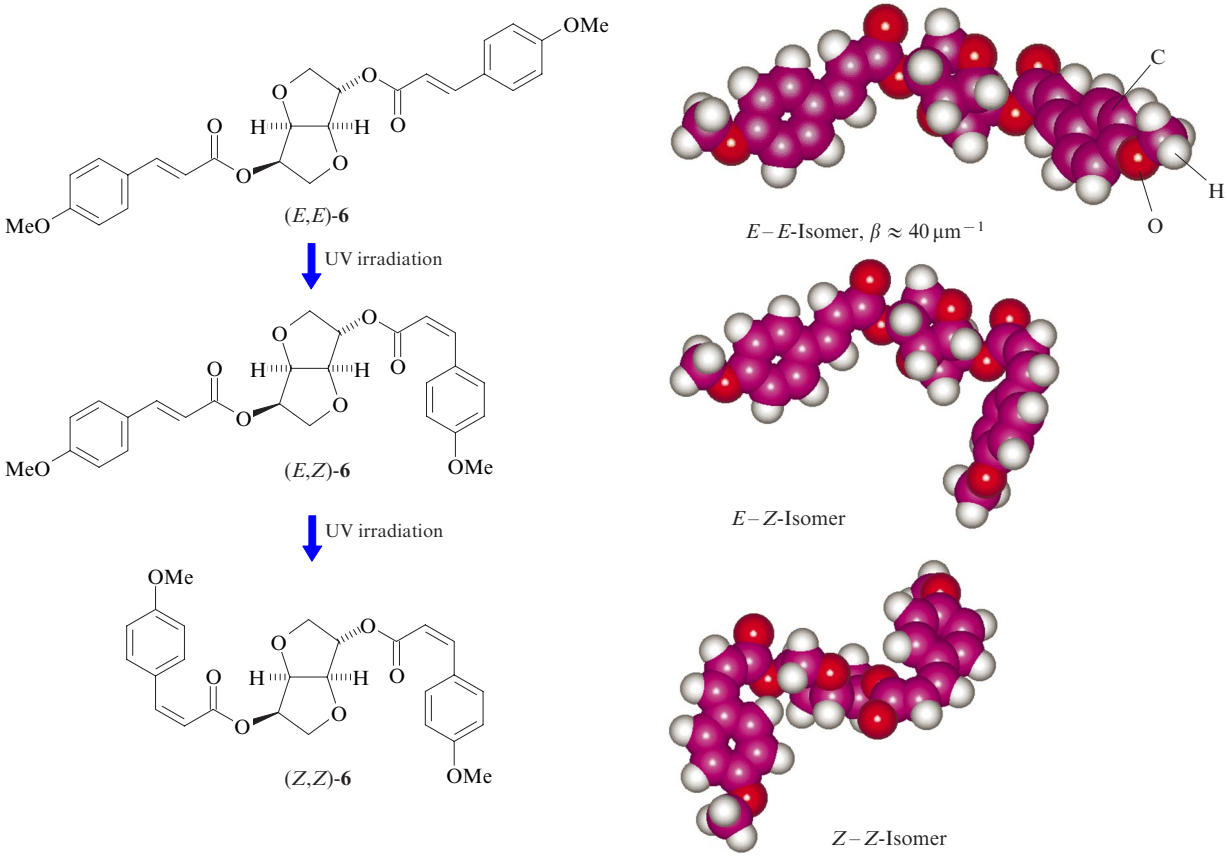
The value of β is primarily controlled by the geometric shape of the dopant molecule: more asymmetric chiral fragments are characterized by higher values of β, which vary over a broad range from several to several hundred reciprocal micrometres. Of special interest are chiral photochromic dopants; their molecules contain both chiral and photochromic groups, which are capable of light-induced isomerization and critical changes in their geometric shape. This combination makes it possible to change β upon irradiation and thus to control the cholesteric helix pitch and selective light reflection. Scheme 1 shows an example illustrating the changes in the molecular configuration of a typical chiral photochromic dopant (derivative of isosorbide **6**) under the action of the UV irradiation.[43] Photoinduced changes in the helix pitch upon irradiation are widely used in diverse technical areas for photocontrollable variation of the optical properties of cholesterics (see below).

Any type of mesophases is usually considered as a continuous anisotropic medium; within small-sized volumes of this medium ($10^4 - 10^5$ molecules), mesogens are aligned parallel to each other. The method of polarized optical microscopy (POM) is helpful for detecting the set of fine structural details in the sample; in other words, its macrostructure which is referred to as a texture. Each type of mesophase spontaneously produces its characteristic texture, which is seen in the POM images as a picturesque coloured pattern. Figure 3 shows the polarized optical microphotos of the two types of mesophases (N and N*). Similar microphotos often appear on the covers of scientific and popular science magazines. These textures are easily rearranged under a mild action of diverse external fields (mechanical, magnetic, and electric fields). It is these structural rearrangements that critically change the optical properties of liquid crystals, thus encouraging broad areas of their practical applications in all LCD indicators.

As an example, let us consider two different orientations of liquid crystals placed in an electrooptical glass cell with a current-conducting coating. As was stated above, the distinctive feature of liquid crystals is related to the combination of high molecular mobility (the hallmark of a liquid) and anisotropy of physical properties (a liquid crystal behaves as a crystalline body). The anisotropy in physical properties is defined by the degree of orientational ordering of molecules, and it is this ordering that governs birefringence (Δn) and anisotropy of dielectric permittivity ($\Delta\varepsilon$) of the LC compounds.

Birefringence of liquid crystals is usually high and varies within a broad range — from 0.1 to 0.4 (for comparison, Δn of quartz is only 0.01). The magnitude and the sign of $\Delta\varepsilon$ depend on the ratio between anisotropy of molecular polarizability and constant dipole moment (μ) as well as on the angle between its direction and the direction of the long molecular axis.

Scheme 1



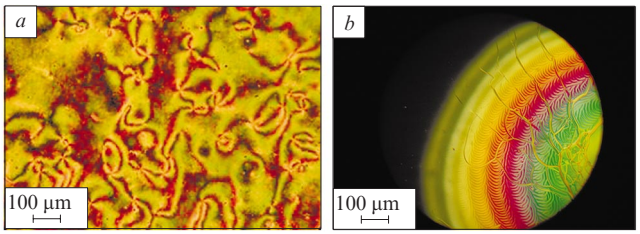


Figure 3. Polarized optical microscope images of typical structures of nematic (*a*) and cholesteric (*b*) phases of liquid crystals.

Figure 4 illustrates the different orientations under the action of electric field ($E = 1-3$ V) depending on the sign of $\Delta\varepsilon$ for two compounds. When $\Delta\varepsilon > 0$, homeotropic orientation is developed (see Fig. 4 *a*); at $\Delta\varepsilon < 0$, planar orientation is observed (see Fig. 4 *b*).[22] The sign of $\Delta\varepsilon$ is determined by the direction of the dipole moment of the molecules. The homeotropic or planar orientation can also be achieved by a special treatment of the substrates.[18,22]

Twist orientation of the molecules is also possible (see Fig. 4 *c*); in this case, the long axes of the molecules are twisted in the direction from the lower to upper glass of the electrooptical cell. This type of orientation of liquid crystals is provided by the special pretreatment of glass plates, for example, using so-called aligning compounds, which are surfactants that specify the direction of molecular orientation.

Under the action of an electric field, the cholesteric helix can be untwisted; as a result, the helix pitch is changed. By varying the helix pitch according to Eqn (2), one can tune the colour of the cholesteric sample in the electrooptical cell.

The principal element of each LCD indicator is the electrooptical cell containing a twisted nematic. Essentially, this description of LCD indicator is rather simplified; in reality, this device features a multilayered 'cake', which is composed of thin layers of polarizers, electrodes, colourants (dyes), diffusers that boost light scattering and other thin-layer coatings providing a sharp and clear coloured or WB images on the screens of TV sets, smartphones, computers, and other modern electronic devices.

II.2. Liquid crystalline polymers

The upsurge of research activities on practical applications of low-molecular-mass liquid crystals in the mid-1960s and in the early 1970s boosted new attempts aimed at the development of thermotropic LC polymers. With respect to flexibility of macromolecules, all polymers are classified into flexible-chain and rigid-chain polymers; since molecules of low-molecular-mass liquid crystals are shaped as rods, the molecular design of LC polymers can be accomplished through two alternative routes[3,6,9,21] (Fig. 5 *a*,*b*): the use of rigid-chain macromolecules, which should seemingly produce the LC phase *via* spontaneous orientational ordering of macromolecules or the use of flexible-chain macromolecules[40,44,45] and their further modification *via* incorporation of rigid rodlike mesogens like calamitics or discotics (in other words, molecules of low-molecular-mass liquid crystals) into polymer chains (see Fig. 5 *c*,*d*).

The first scenario appeared to be less beneficial, as rigid-chain polymers are characterized by exceptionally high melting temperatures, and the hypothetical temperatures corresponding to the transition from the crystalline state to the LC phase lie within the temperature range of their chemical degradation.[3,15] Nevertheless, upon dissolution in appropriate solvents, rigid-chain polymers are able to produce rather stable lyotropic liquid crystals. The use of these lyotropic systems since the 1970s has culminated in the preparation of a well-known family of high-strength and high-modulus synthetic fibres based on aromatic polyamides, which are soluble in sufficiently harsh solvents (like sulfuric acid).[46–49]

The second scenario for the development of thermotropic LC polymers appeared to be more convenient. This approach is concerned with chemical binding of flexible and rigid (mesogenic) fragments in one macromolecule (see Fig. 5 *c*,*d*). Depending on the mode in which these fragments are linked, two types of LC polymers can be formed:

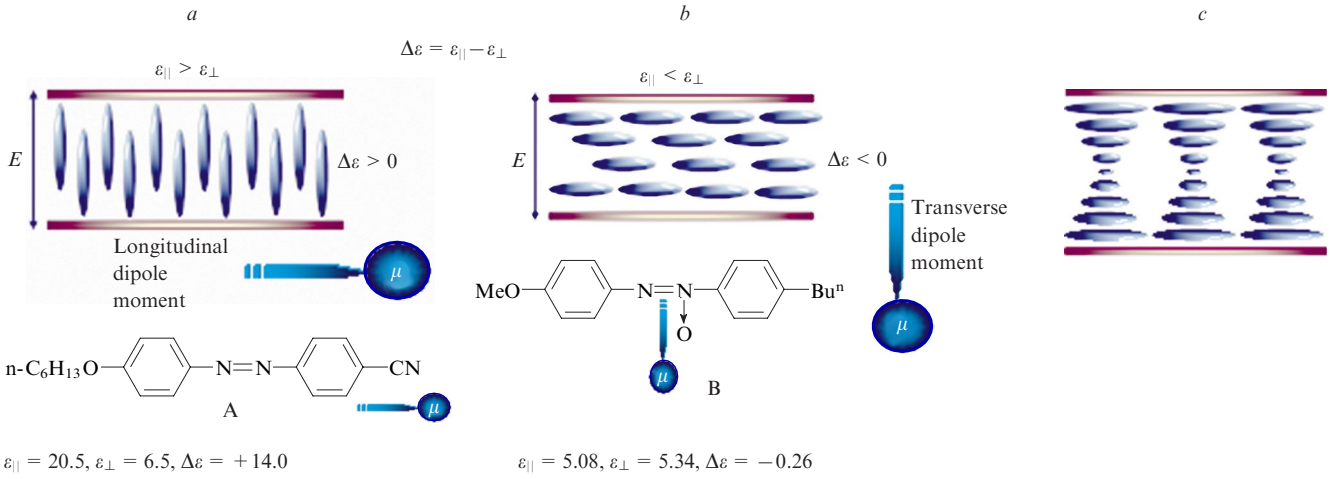


Figure 4. Examples illustrating three modes of orientation of liquid crystals (anisotropy of dielectric constant is presented for two types of molecules, A and B).[22]
Orientation: (*a*) homeotropic, (*b*) planar, (*c*) twist; $\varepsilon_{||}$, $\varepsilon_{\perp}$ are the dielectric constants corresponding to longitudinal and transverse dipole moments, respectively.

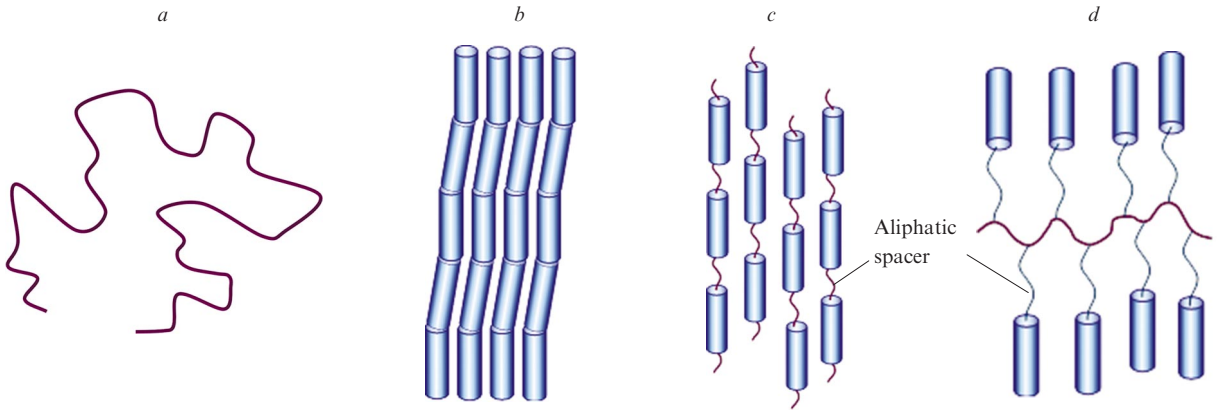


Figure 5. Schemes illustrating the structure of macromolecules with different rigidity.[24]
(*a*) Flexible-chain polymer, (*b*) rigid-chain polymer, (*c*) LC polymer with mesogens in the main chain, (*d*) LC polymer with mesogens in the side groups (comb-shaped polymer); mesogens are depicted as cylinders.

— LC polymers with the linear structure, where mesogenic groups are incorporated in the main polymer chain (see Fig. 5 *c*);

— LC polymers with the branched structure, when mesogenic groups are chemically linked to the main macromolecular chain *via* flexible (usually, alkyl or alkoxyl) spacers; these LC polymers are referred to as comb-shaped polymers (see Fig. 5 *d*).

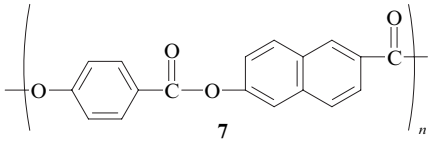
Flexible spacers also appear to be helpful for the linear structure: they decrease the rigidity of macromolecules (due to some sort of dilution), reduce melting temperatures of polymers, impart a sufficiently high autonomy to rigid mesogenic groups, which is necessary for the cooperative interaction and formation of a mesophase. The ideas concerning the vital role of a spacer in macromolecules of linear LC polymers were pioneered in 1975,[50] and the first comb-shaped LC polymers were synthesized by scientists from the Lomonosov Moscow State University (Department of Chemistry).[51 – 53] A short time later, the same concept was used by German scientists for the preparation of the comb-shaped LC polymers with a similar structure.[54] Whatsoever, noteworthy is that the proposed scientific principle on the preparation of thermotropic LC polymers has been further developed in numerous publications of foreign and Russian scientists.[22, 36, 40]

To date, tens of thousands of LC polymers have been synthesized and, with each passing day, their number is constantly increasing. Polymers with mesogens in main chains[55] (see Fig. 5 *a*,*b*) have already found their wide practical application. Fundamental scientific studies in Russia and abroad have led to the development and commercial production of high-strength high-modulus fibres based on lyotropic solutions of aromatic LC polyamides such as Kevlar (USA), Twaron (the Netherlands), Terlon and Vnivlon (Russia).[22, 38, 49]

The strength of these fibres is 2 – 2.5 times higher and the elastic modulus is 10 – 20 times higher than the corresponding characteristics of high-strength yarns based on aliphatic polyamides. Along with low density, their specific strength is 2 – 4 times higher than that of steel and glass fibres. The enhanced mechanical characteristics of these materials are provided by a more perfect packing of macromolecules in the LC phase due to the formation of ordered regions with parallel alignment of macromolecules upon spinning and drawing of fibres.

Among LC polymer plastics, aromatic polyesters like Xydar and Vectra (USA) have found the widest practical application. Owing to their high mechanical characteristics, they are referred to as self-reinforced plastics. This unusual name is associated with their structural organization, which is built up at the stage of melt spinning. As a result of extrusion of anisotropic melts through spinnerets (with calibrated holes), anisotropic structures are formed, and they serve as a certain reinforcing material. In this case, composition of the matrix is identical to that of the reinforcing material (an LC polymer). So-called 'disrupting units', which contain phenyl rings preventing the coplanarity of neighbouring moieties, are used as spacers that disrupt the rigid linear structure of macromolecules. The example is the LC polymer Vectra, which contains the units of hydroxybenzoic and hydroxynaphthoic acids[15, 26, 55] (structure **7**). This polymer with excellent mechanical characteristics is manufactured according to the process licensed by the Celanese Corporation (USA) and is widely used for the production of diverse components for telecommunication, microelectronics, aerospace industry and in fibre-optic systems.

Structure 7



7

Modern plastics based on LC polyesters (often referred to as 'superplastics') are manufactured by the convenient injection moulding technology (melt extrusion). The above self-reinforced plastics are characterized by high elastic modulus (60 – 70 GPa) and strength (up to 700 MPa) and by a low elongation at break (1.5% – 2%). An important feature of the LC polyesters is concerned with low thermal expansion coefficients ($\leqslant 10^{-6}$ K^{-1}), which are comparable with thermal expansion coefficients of inorganic glasses (5×10^{-7} K^{-1}), but are appreciably lower than those of conventional non-liquid crystalline polymers (10^{-4} K^{-1}).

In the case of thermotropic LC polymers with mesogens in the main chain, their excellent mechanical characteristics, good thermal resistance and convenient processability allow their practical use as construction and reinforcing materials in electronic and aviation industries, space-related technology, spacecraft industry and for the production of bullet-proof materials (bullet-proof vests). According to the recent data (March 2017) published in the Market Research Reports (BCC Research), in 2016, the worldwide market of thermotropic LC polymers was 1.2 billion US dollars; by 2021, this market is supposed to achieve 1.5 billion US dollars.

II.3. Comb-shaped liquid crystalline polymers

While LC polymers containing mesogenic groups in their main chains have gained their strong position for many practical applications, the researchers engaged in the studies on comb-shaped LC polymers are at the very beginning of the road leading to practical solutions and implementation.

Comb-shaped LC polymers constitute a unique class of hybrid materials, which miraculously combine the 'material' characteristics of macromolecular compounds with optical and other properties of liquid crystals. It is this unique combination of diverse properties in one material that may present fundamental scientific attraction. Many scientists working in the area of chemistry and physics of polymers, solids, materials science, and biology are involved in the comprehensive studies of these compounds. Liquid crystalline polymers are essentially typical representatives of so-called soft matter and exhibit rather peculiar structural organization, which is intermediate between solids and disordered phases.

Figure 6 illustrates the unique properties of these compounds. As follows from Fig. 6, the LC state of polymers is realized in the temperature range between the glass transition temperature (T_g) (or melting temperature if a polymer is able to crystallize) and isotropization temperature (T_{iso}), above which the polymer loses its LC properties and is transformed into an isotropic melt. Within this temperature range ($T_g - T_{iso}$), the LC polymer behaves similarly to low-molecular-mass liquid crystals, produces nematic, smectic, or cholesteric phases and can be easily subjected to the action of external fields [mechanical (σ), electric (E) or magnetic (H)]. A unique feature of LC polymers is that, after cooling below T_g, they preserve the 'frozen' structure, which is inherent in the above-mentioned phases, together with the anisotropic properties, which are either characteristic of the initial structure of the mesophase or are induced by the action of an external field.

Therefore, the possibility to fix down the anisotropic structure of the mesophase in a solid while preserving unique optical properties of LC polymers offers great and fascinating opportunities for the development of new innovative materials with unique adjustable optical as well as other physicochemical and mechanical properties.[9, 21, 24]

To date, diverse methods have been proposed for the preparation of not only trivial types of the comb-shaped LC polymers (see Fig. 5*d*), but also polymer systems with far more complicated structural architecture. New approaches have been advanced for the preparation of comb-shaped LC copolymers containing diverse mesogenic and non-mesogenic groups with functional properties [40, 55] as well as dendrimers.[56]

Figure 7 presents the hypothetical structure of a macromolecule of the multifunctional LC copolymer containing mesogenic (*1*), chiral (*2*), photochromic (*3*), electroactive (*4*), and reactive (*5*) functional groups, which are capable of complexation or hydrogen bonding. The key structural element of this macromolecule is the quantitatively dominating mesogenic groups, which govern the capability of the polymer for self-organization and formation of the LC phase. Each of other molecular groups (taken either alone

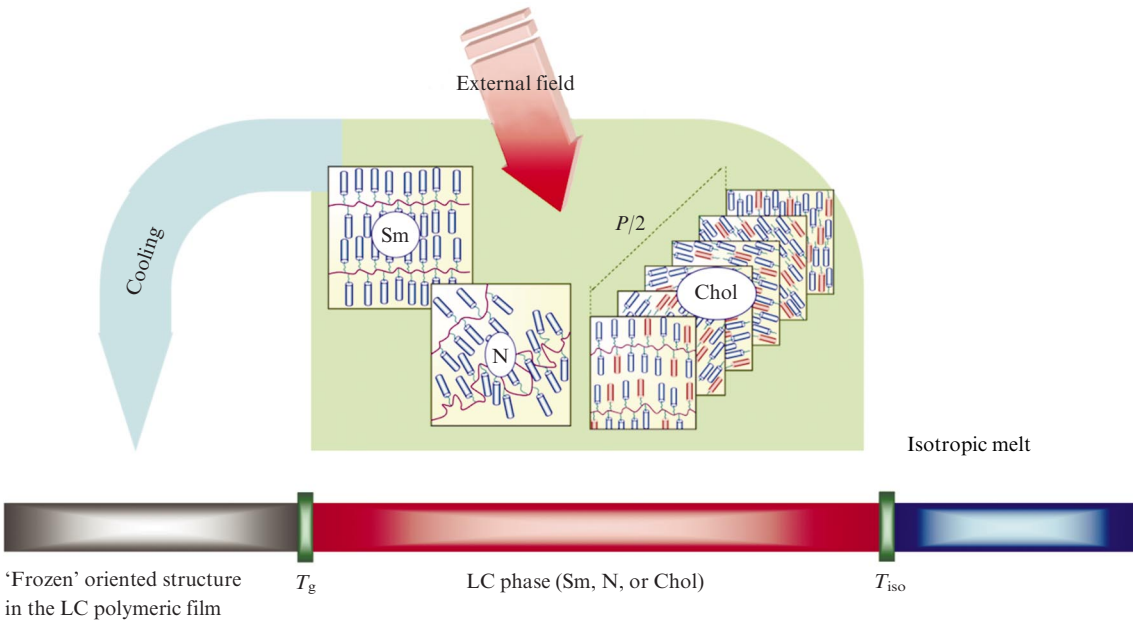


Figure 6. Scheme illustrating the existence regions of various types of mesophases in the LC polymer and their possible stabilization (freezing) with a given molecular orientation upon cooling or under the action of external fields.[24]

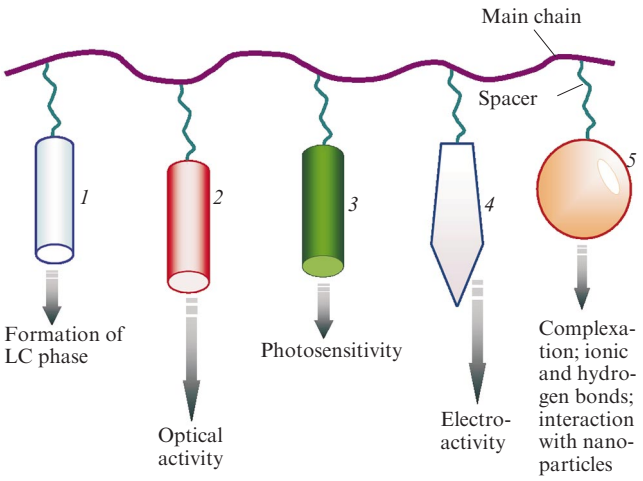


Figure 7. Schematic of a macromolecule of the multifunctional comb-shaped LC polymer.[36, 55]
(*1* – *5*) See text.

or together with others) provides desired functional properties (photochromic, electrical, chiral, ionophore, *etc.*) of the LC polymer.

These polymers are usually prepared by copolymerization of monofunctional nanoscale monomers; in other words, this approach is based on the bottom-up method of the assembly of nanomaterials.[56] Here, we would like to mention that the similar principle of self-assembling operates in living organisms where complex (multifunctional) protein macromolecules are assembled from twenty amino acids. This primary structure of the protein molecules controls further more complex processes providing the development of secondary and tertiary structures.

In this case, monomers containing functional groups with dimensions of about several nanometres are assembled into complex structurally organized and functionally integrated multifunctional LC polymeric systems.

III. Photochromic comb-shaped liquid crystalline polymers

We would like to remind (see Introduction) that this review primarily addresses the description and analysis of the studies on photoorientational processes taking place in photochromic LC polymeric systems with diverse molecular structures. The problems related to purely chemical approaches for the preparation of these compounds are beyond the scope of this review; this information can be found in numerous domestic and foreign publications. This review is mainly focused on the analysis of physicochemical processes taking place in photochromic polymeric systems under the action of external fields, which are accompanied by changes in their molecular and supramolecular structure and lead to the development of the desired optical properties. Depending on the molecular structure, these photochromic LC systems can be divided into several groups.

The first group involves polymers, copolymers, and dendrimers, and their schematic images are shown in Fig. 8. All presented types of homo- and copolymers contain mesogenic and photochromic groups. Photochromic groups can be either mesogenic and favour the development of LC phases or non-mesogenic; in the latter case, their concentration should be moderate (at least, not more than 50%) as not to prevent the formation of LC phases.

Moreover, in addition to mesogenic and photochromic moieties (see Fig. 8 *a*,*b*), LC copolymers may contain chiral side groups incorporated in the copolymer as individual monomeric units (see Fig. 8 *c*); chiral and photochromic moieties can also be integrated in one monomer unit (see Fig. 8 *d*). Liquid crystalline copolymers may also contain photochromic banana-shaped and ionophore groups; the latter are capable of complexation with metal species (see Fig. 8 *e* – *g*). Special type of LC compounds are binary and ternary block copolymers with different subblocks (see Fig. 8 *h*,*i*). In recent years, of special interest have been cross-linked LC polymeric networks (see Fig. 8 *l*).[25]

The second group involves LC composites, which are photopolymerizable blends based on mono- and bifunctional monomers. In the course of polymerization, polymer-stabilized cross-linked LC composites are formed, containing molecules of low-molecular-mass liquid crystals (see Fig. 8 *l* and Fig. 9). As monomers and low-molecular-mass liquid crystals chiral compounds can be used, and this approach offers wide opportunities for the development of chiral LC networks and composites.

The third group includes a rather exotic type of LC compounds, namely, hyperbranched homo- and copolymers with the dendrite structure. Depending on the generation number, they may contain from 8 (the first generation) to 128 (the fifth generation) mesogenic and photochromic terminal groups (see Fig. 8 *j*,*k*), which, like comb-shaped polymers, are characterized by the presence of spacers linked to the main carbosilane (or some other) matrix *via* methylene chains of different lengths.

A special type of photochromic LC composites features microporous oriented films of polyolefins (PE and PP), which are used as nanocontainers; their asymmetric pores are loaded with the molecules of low-molecular-mass liquid crystals. When the above LC blends include dichroic dyes and photochromic molecules, which are spontaneously oriented by the pore walls (together with the LC molecules), this approach offers unique opportunities for the development of polymeric photo- and thermotunable photochromic polyethylene and polypropylene film materials for diverse practical applications.

Since all of the above systems are characterized by the presence of different types of mesophases, which are primarily responsible for their specific optical properties, our attention is focused on the photooptical behaviour of each of the above groups of compounds. Special emphasis is placed on common and specific features of photooptical properties of the compounds with the account for the types of related mesophases (nematic, smectic, or cholesteric).

The above-mentioned 'liquid crystalline boom' in the area of polymeric compounds observed in the 1970s – 1990s was related to the works of chemical nature focused on the development of new methods for the synthesis of these 'polymeric centaurs of Nature' as well as to theoretical and purely physical studies, especially devoted to the comparison of their optical parameters with the corresponding characteristics of low-molecular-mass liquid crystals.

Regarding the number and quality of studies of LC polymers, we would like to emphasize the studies of their optical, photooptical, and electrooptical properties. Optical

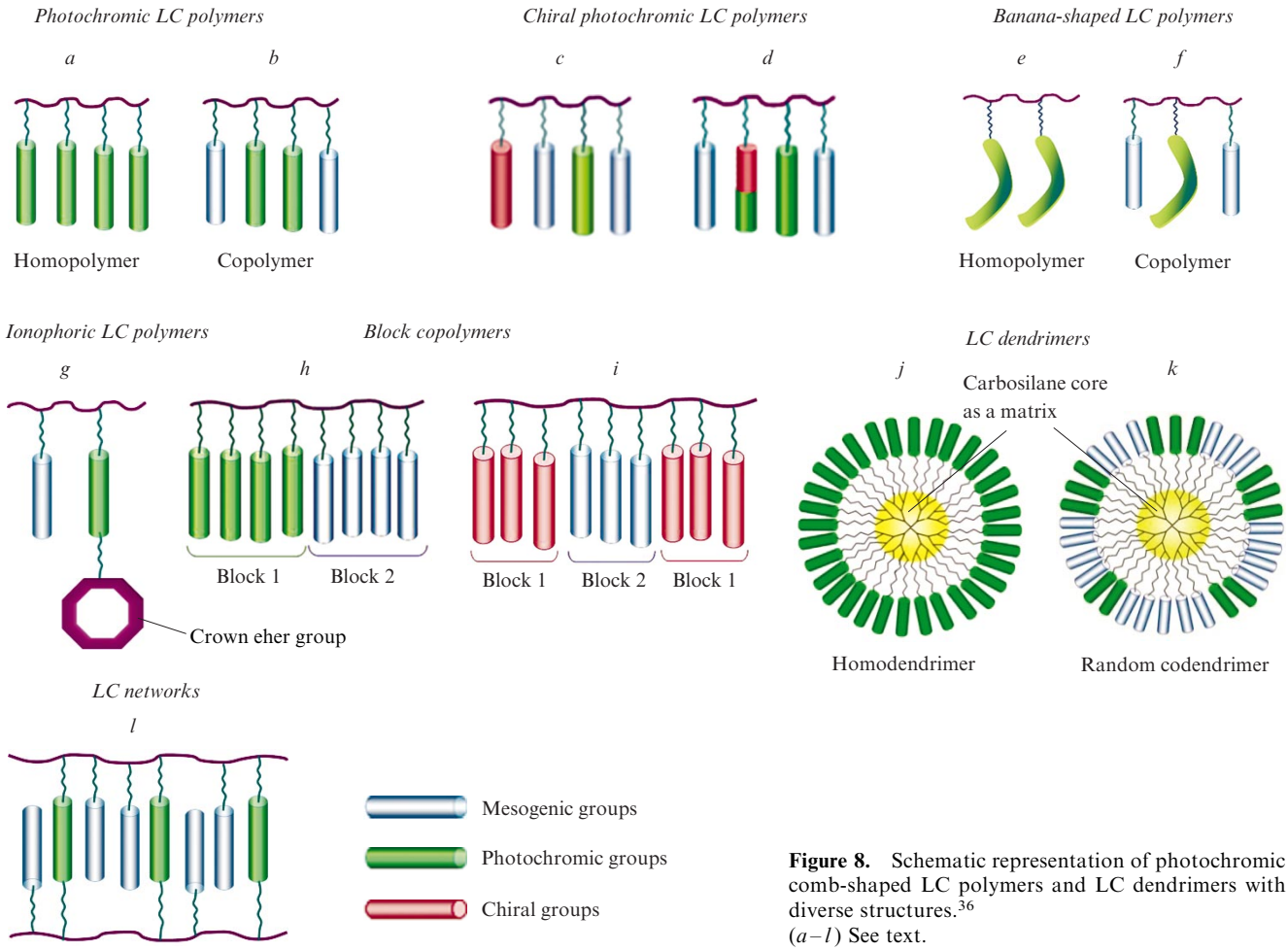


Figure 8. Schematic representation of photochromic comb-shaped LC polymers and LC dendrimers with diverse structures.[36]
(*a* – *l*) See text.

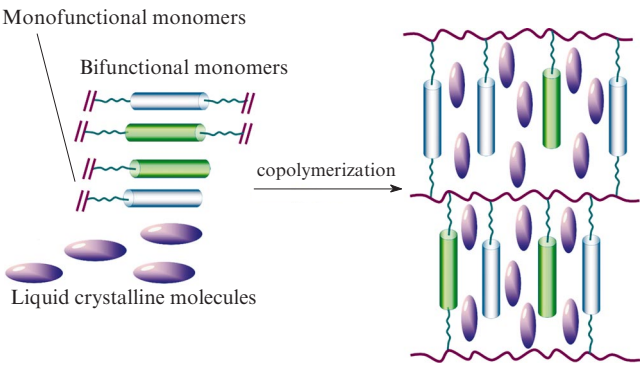


Figure 9. Scheme illustrating the pathways to photochromic LC polymer networks and the related composites by copolymerization of mono- and bifunctional monomers in the presence of liquid crystals.[36]

and electrooptical properties were discussed in detail in the publications of Russian [13, 35, 36] and foreign [27 – 30] researchers. In this part of the review, our attention is concentrated on the analysis of the properties of photochromic LC polymers and their composites.

III.1. Photoorientational processes in liquid crystalline polymers

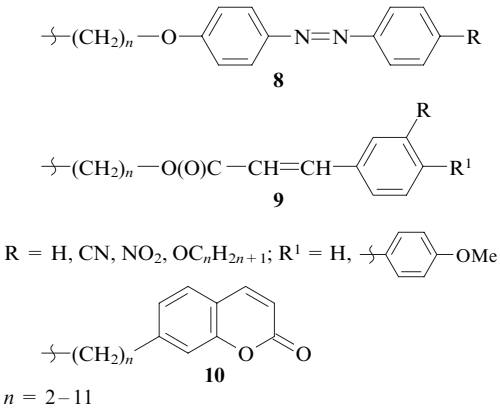
Pioneering works on the synthesis and characterization of photochromic comb-shaped LC polymers with widely used photochromic azobenzene groups date back to the end of the 1980s and the beginning of the 1990s. These studies were largely based on the works of Bulgarian scientists who discovered that, under the action of UV irradiation inducing the $E-Z$-isomerization of photochromes, low-molecular-mass derivatives of azobenzene mechanically incorporated into the matrices of some conventional polymers [gelatin, poly(methyl methacrylate)] are able to be aligned, thus giving rise to dichroism.[57]

The discovery of photoalignment of chromophores in polymeric films has triggered the chain of studies in Japan,[58, 59] Germany [60 – 62], and Canada [63, 64] on the mechanism, dynamics, and kinetics of photochemical and photoalignment processes. Further progress along this line has been achieved due to the scientific cooperation between the scientists from the Lomonosov Moscow State University and the Humboldt University of Berlin,[65, 66] and, later, from the Fraunhofer Institute for Applied Polymer Research (Potsdam). The results of these studies performed in various periods of time were discussed in detail in several reviews [31, 35, 36, 40] and in the monograph.[3]

In this Section, the attention is focused on a brief description of photoinduced processes and (mainly) photoalignment in the LC polymeric systems containing photo-

chromic groups in their macromolecules. The operation principle of these systems under the light irradiation is based on the photochemical transformations of photochromic moieties which are covalently or non-covalently linked to macromolecules. Depending on the chemical structure of photoactive moieties, these transformations may involve *E*–*Z*-isomerization, cyclization, dimerization, cross-linking, and polymerization. Various derivatives of azobenzene (moiety **8**), cinnamic acid (**9**), and coumarin (**10**), which are incorporated into LC polymers as side groups linked to the main chain *via* methylene spacers with different lengths, are widely used as photoactive moieties.

Structures 8 – 10



Photochromic moieties **8** – **10** are characterized by two specific features. For example, under the action of light irradiation, azobenzene-containing polymers with N=N bonds and cinnamoyl polymers with C=C bonds undergo the reversible *E*–*Z*-isomerization. Moreover, the derivatives of cinnamic acid and coumarin are capable of {2 + 2}-photocycloaddition. Photochromism is known to be the light-induced reversible transformation of substance A (photochrome) into substance B, with A and B differing in the absorbance spectra.

$$A(\lambda_1) \underset{h\nu_2, \Delta T}{\overset{h\nu_1}{\rightleftharpoons}} B(\lambda_2) \qquad (4)$$

Figure 10 presents an example of photochemical transformation of the azobenzene derivative and the corresponding absorbance spectra of its *Z*- and *E*-isomers.

Irrespective of the type and structure of photochromic compounds, light irradiation triggers the chemical reactions in the photoactive groups **8** – **10**, which serve as peculiar 'molecular switches' and turn on the whole cycle of further structure chemical transformations. However, the difference in the structure of photoactive moieties influences their further post-isomerization. For example, photoalignment processes play crucial role for azo, coumarin, and cinnamoyl derivatives; these processes were described in detail for the azobenzene-containing LC polymers (see below).

The irradiation of amorphized films of LC polymers induces, first of all, the *E*–*Z*-isomerization of azobenzene-containing units (Fig. 11). In this case, as the probability of the absorption of a photon (*p*) by azobenzene groups is directly proportional to the squared cosine of the angle between the electric field vector and the long axes of

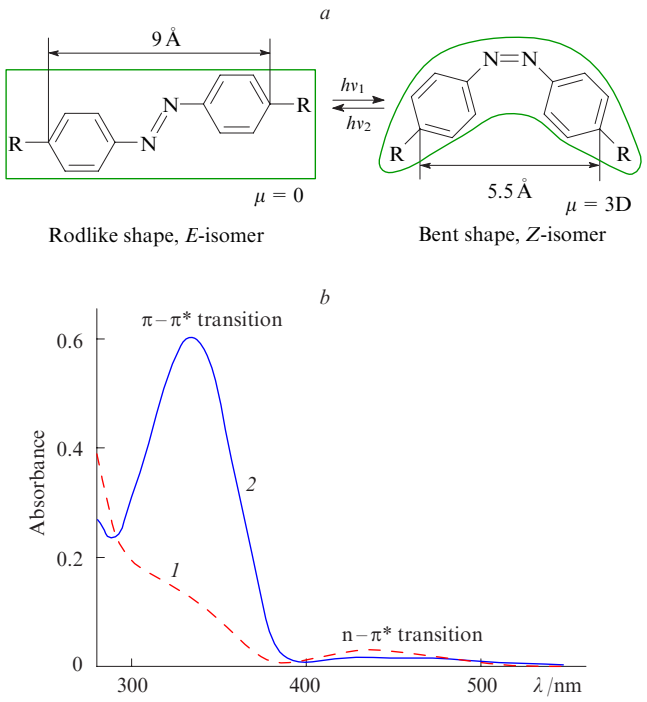


Figure 10. Photochemical transformations of azobenzene derivative (*a*) and the absorbance spectra of *Z*- (*1*) and *E*-isomers (*2*) (*b*).[21]

mesogenic photochromic groups (α), photoselection is first observed. In other words, azo groups whose long axes are perpendicular to the plane of light polarization do not isomerize, while the isomerizing azo groups are converted to the *Z*-form in a twisted (folded) conformation, which is appreciably different from the conformation of the rodlike azobenzene substituent. This is followed by photoalignment of the photochromes whose long axes are perpendicular to the plane of light polarization. The successive stages of direct and back isomerization engage the neighbouring non-photochromic groups into the photoalignment process, which becomes cooperative. This process leads to the local photoinduced orientation of all side groups of the polymer, which is accompanied by the development of a well-pronounced dichroism and by induced birefringence (Δn_{ind}), the value of which depends on the structure and the initial phase state of the polymer and can vary from 0.15 to 0.30.[67]

Figure 12 depicts the kinetic curve illustrating the growth of photoinduced birefringence upon irradiation of the LC polymer film by the polarized light. When irradiation is switched off, Δn_{ind} slightly decreases; stable birefringence (Δn_{stab}) can be preserved in the polymer films for a long period of time (for years), and this phenomenon can be used for data and image recording due to the difference in the birefringence of virgin (non-irradiated) and irradiated regions of one and the same sample. In other words, this phenomenon offers unique benefits for the local recording of latent images upon irradiation.

Figure 13 shows examples of this scenario of image recording: the image of a test grating and the image of a cat recorded on the LC acrylic films containing azobenzene moieties with cyanobiphenyl side groups. Three principal features of the above photoinduced processes should be emphasized. **First**, this polarized image recording is rever-

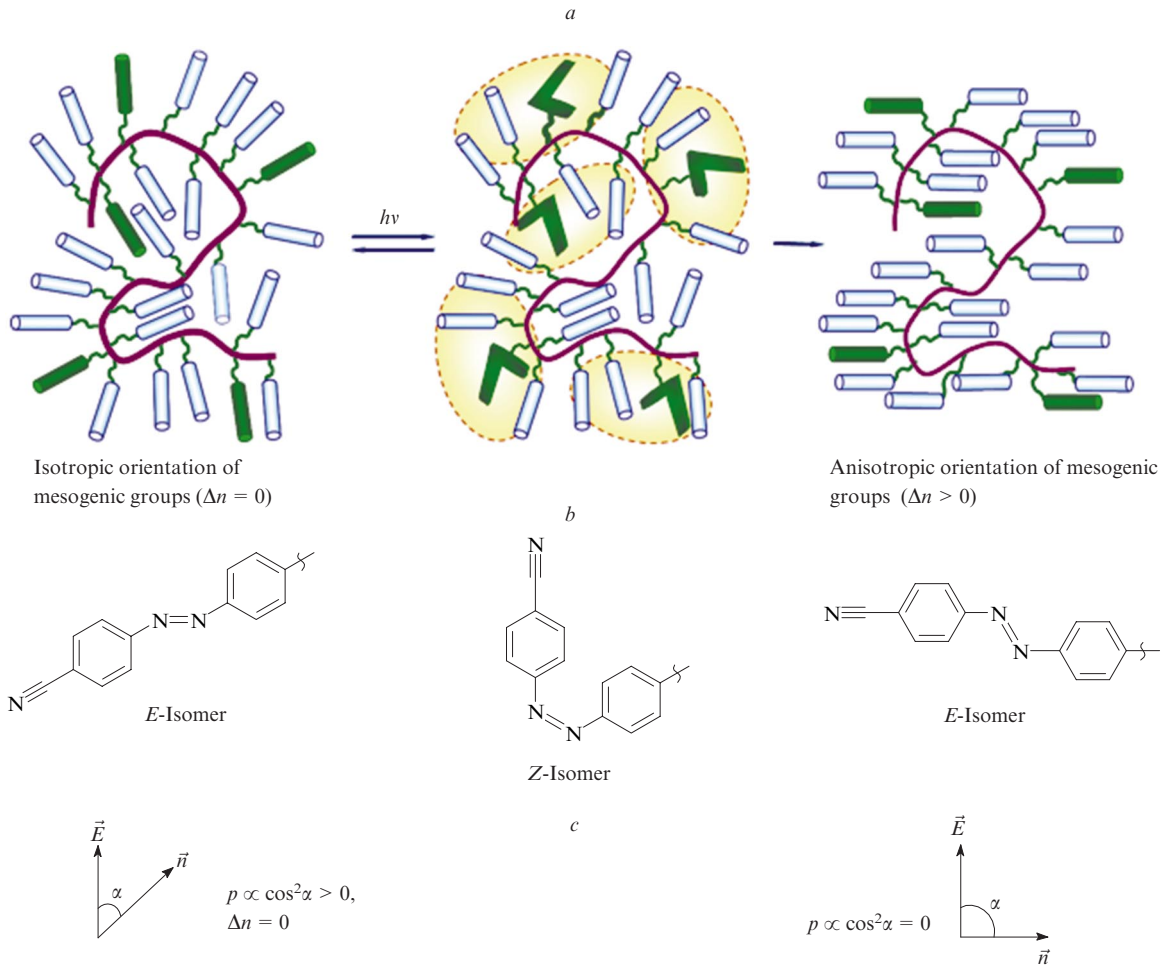


Figure 11. Schemes illustrating the development of photoinduced anisotropy in the films of azobenzene-containing polymers.[21] (*a*) Changes in the orientation of photochromic and mesogenic groups, (*b*) *E*–*Z*–*E*-isomerization of benzene groups, (*c*) change in the direction of the director $\vec{n}$ with respect to the electric vector of the light wave $\vec{E}$ upon photoorientation; Δn is birefringence.

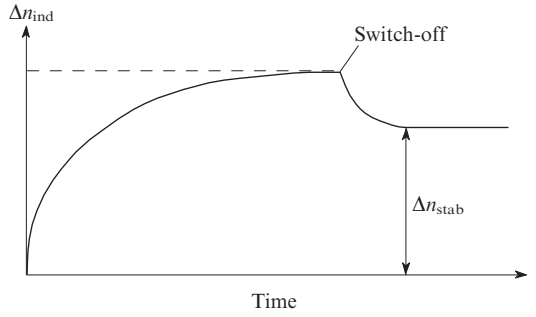


Figure 12. Typical curve illustrating the growth of photoinduced birefringence upon laser beam irradiation of the polymer film. Due to relaxation of Δn_{ind} , Δn_{stab} retains its stable value once irradiation is switched off.

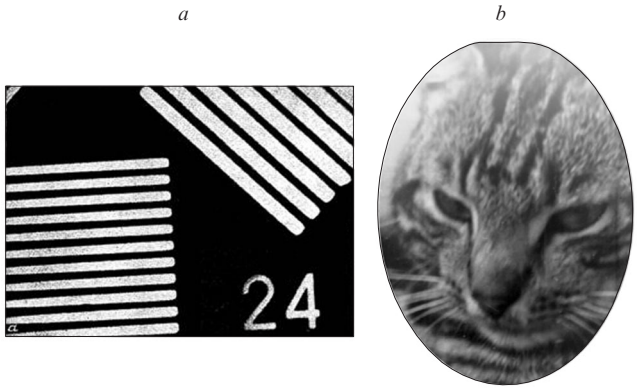


Figure 13. Example of recording of a test grating (*a*) and the image of a cat (*b*) on azobenzene-containing polymers.[21]

sible. By varying the polarization of a writing beam, information can be either recorded or erased; hence, these polymers can be used as photoreversible tunable optical materials for the recording of graphical symbols (see Fig. 13 *a*) and images (see Fig. 13 *b*, images with different grey tone gradation).

The second distinctive feature of all azobenzene-containing polymers under study is related to the possibility of smooth control of photoinduced birefringence (the value of

Δn_{ind}, see Fig. 12). In other words, during recording, one can control the grey tone scale, record and erase the recorded images only as a result of controlled changes in the directions of polarization planes of writing and erasing beams. In this case, noteworthy is that the amorphized films of LC polymers are characterized by the highest values of Δn_{ind}, which lie within the range of 0.25 – 0.30; at the same time, for the nematic polymers with the planar structure, Δn_{ind} varies from 0.15 to 0.20. Of special interest is the substantial increase in Δn_{ind} (up to 30%) for pre-irradiated quenched (rapidly cooled) samples of LC polymers after their subsequent heating above the glass transition temperature.[67] This effect referred to as the 'gain phenomenon' was also observed by Bieringer *et al.*;[68] this behaviour can be explained by the additional self-organization of the pre-irradiated initial film of the LC polymer due to the orientation of mesogenic groups at temperatures above T_g.

Finally, the third important feature of photoinduced processes and properties of photochromic LC polymers is the following: the recorded image is invisible (latent) for the naked eye and can be visualized only in the polarized light (for example, using the crossed polarizers).

The advanced materials with their photooptical properties were licensed by the researchers from the Bayer company, the Humboldt University together with us (Moscow State University);[69] this knowledge serves as the basis for the development of polymeric films for diverse systems with optical memory, which can be used in map-making, for the preparation of microfiches, IDs, *etc*. The German company Certego GmbH has worked out a process for the preparation of such films. Noteworthy is that, at the present time, early fundamental studies[65 – 67] appeared to be highly demanded for cryptography for the protection against forgery and authentication of securities, bank records, and ID cards.[70]

III.2. Photoaligning compounds and command surfaces

The phenomenon of photoalignment (photoorientation) of LC polymers described in the preceding Section serves as the basis of so-called command surfaces and photoaligning compounds for low-molecular-mass liquid crystals used in the LCD technology.

Practical application of liquid crystals is feasible only when the LC material can be well oriented or, in other words, when the molecules of the LC compounds or their fragments can be strictly aligned with respect to the confining surfaces. The action of external electromagnetic or electric fields allows the control over the orientation of the molecules of liquid crystals and changes their optical characteristics. This principle serves as the basis for all modern electrooptical LC devices, including TV sets, laptops, mobile phones, *etc*.

The alignment of liquid crystals in the LC cells is primarily achieved by the classical method of surface finish (or mechanical rubbing) of a thin polyimide layer as well as metal sputtering and deposition of surfactants as substrates for further deposition of a thin layer of LC material.[71] This simple method is widely used in the LCD technology despite its evident drawbacks such as the development of electrostatic charge on the surface of the substrate and its contamination with the abrasive material used for the surface finish, formation of defects and imperfections in the coating, *etc*.

In recent years, the most promising method for the preparation of the oriented layers for the LC displays has been concerned with the development of photoaligning surfaces based on diverse polymeric compounds and dyes.[17, 18] The basic principle of this approach is based on the use of the low-molecular-mass photochromic substances or photochromic polymers, which are deposited onto glass substrates and subjected to the action of the polarized light at a given wavelength. Under the action of light, uniaxial planar orientation of photochromic molecules of low-molecular-mass substances or side photochromic groups of polymers is induced.

This contact-free method of polarized light irradiation triggering the development of photoinduced optical anisotropy and dichroism in thin polymeric films, for example, *via* reversible *E* – *Z*-isomerization of azobenzene-containing layers on solid substrates is widely used for the preparation of command surfaces, which provide control over the optical properties of the deposited low-molecular-mass liquid crystals. This method referred to as photoalignment has been widely used by Japanese researchers, who employed diverse photochromic low-molecular-mass azobenzene and stilbene derivatives as photoaligning compounds.[17, 18] Irradiation of these compounds (usually supported on glass) with the polarized light leads to modification of the surface properties of the substrate due to the alignment of photochromes, so that subsquent deposition of liquid crystals provides their planar orientation.

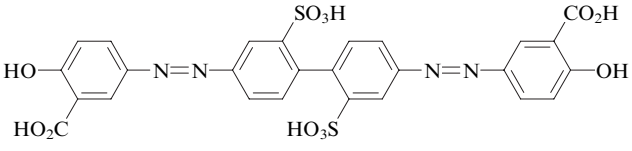
The fundamental research performed in various countries resulted in the preparation of numerous photochromic compounds that can serve as command surfaces. However, despite the synthesis of a huge number of low-molecular-mass photoaligning compounds based on azo derivatives, cinnamoyl derivatives, fulgides, and other substances, there arise challenging problems concerning thermal resistance, cyclicity of orientation, and fair miscibility with liquid crystals (liquid crystals appear to be partially dissolved in the surface layer and deteriorate its orientation).

Among numerous photoaligning compounds, most promising is a compound with the complex structure, namely, 4,4′-bis(4-hydroxy-3-carboxyphenylazo)-2,2′-disulfobiphenyl (**11**). This compound has been successfully used for the orientation of low-molecular-mass liquid crystals[18] and LC polymers.[72] However, despite evident benefits of this compound, photochromic films of the LC polymers seem to be a better choice.

Taking into account the modern tendency for miniaturization of most technical devices and household appliances (LCD equipment, mobile and telecommunication systems), we set ourselves the task to prepare photoaligning polymers using the above-cited approaches. As the key objects of our studies, polyacrylic azobenzene-containing polymers were synthesized.[72, 73]

Figure 14 depicts the design of the experiments. Polymer solutions were cast onto a glass substrate by the spin-coating method and illuminated with linearly polarized light (*1*), which induced the orientation of photochromic mesogenic groups of the LC polymer (*2*). Then, the LC cell

Structure 11



11

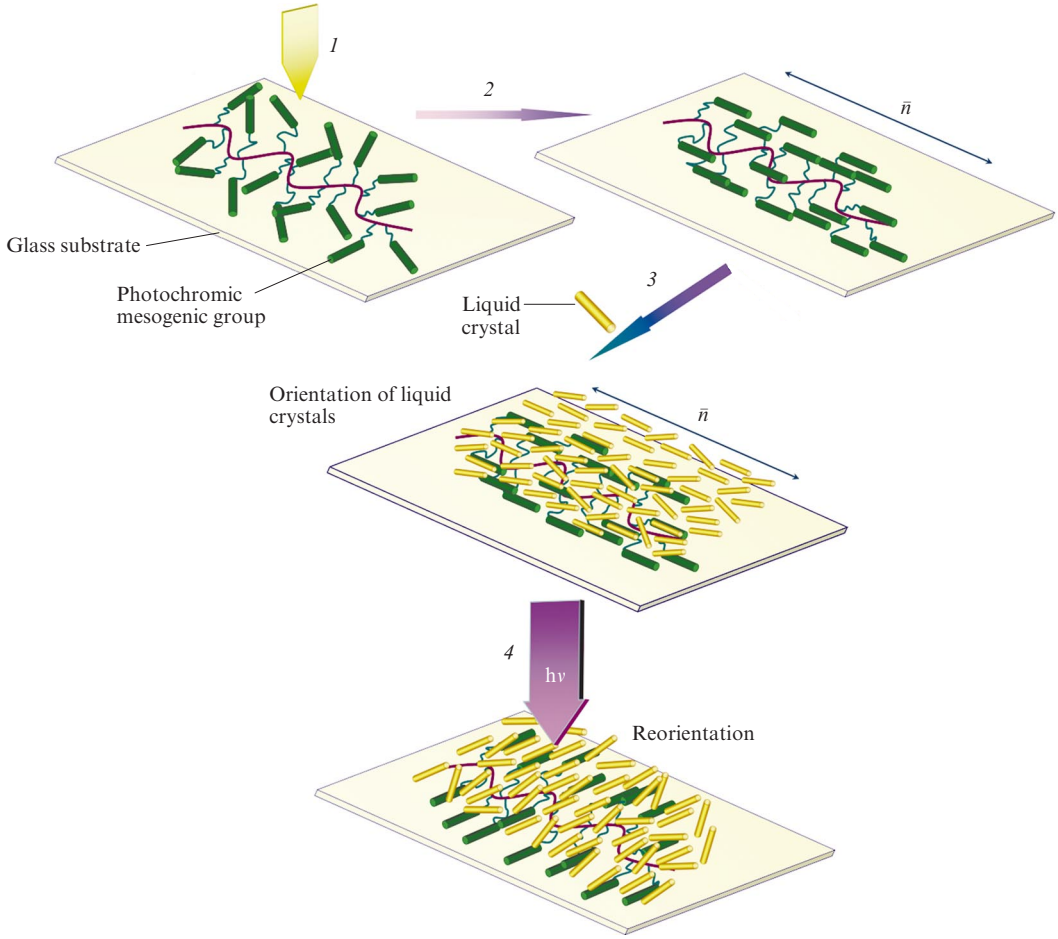


Figure 14. Scheme illustrating orientation of mesogenic groups under the action of polarized light, introduction of liquid crystals into the cell, and reorientation of photochromic groups of the LC polymer and liquid crystalline molecules.[72]
(*1* – *4*) See text.

was assembled from two glasses with an aligning coatings, and the liquid crystal was introduced (*3*); the liquid crystal molecules were aligned along long axes of side mesogenic groups. Noteworthy is that changes in the direction of UV light polarization (*4*) resulted in reorientation of both the side groups of the polymer and the molecules of the liquid crystal.

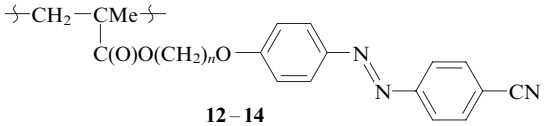
The introduction of minor concentrations (usually < 0.5 mass % – 1 mass %) of dichroic dyes into this system makes it possible to calculate the induced dichroism (*D*), and the corresponding *D* values for the series of polymethacrylic esters **12** – **14** are listed in Table 1. For comparison, the values of dichroism of the same polymeric films oriented by surface finish are presented. As follows from Table 1, these films are characterized by much lower values of dichroism. Note that the maximum values of *D* are typical of the LC polymers with the shortest spacers.

Figure 15 illustrates the possibility of repeated reproduction of orientation and reorientation processes upon cyclic irradiation with different directions of light polarization: positive and negative values of dichroism appear to be close in their absolute values, and this behaviour offers fascinating opportunities for practical use of the above advantages of photochromic LC polymers.

Table 1. Dichroism of LC polymers **12** – **14** after illumination and rubbing of the LC cell.[72]

Polymer	After illumination	After reorientation	After cell rubbing
12	0.72	−0.70	0.40
13	0.69	−0.64	0.55
14	0.71	−0.42	0.65

Structures 12 – 14



12 – **14**

12: $n = 4$ (G 58, N 159, I) (see ‡); **13**: $n = 6$ (G 48, SmA 135, I); **14**: $n = 10$ (G 58, SmA 165, I)

‡ Here and for other structures, phases are indicated: G is glass state, N is nematic, SmA is smectic phase A, I is isotropic; the numbers stand for temperature /°C.

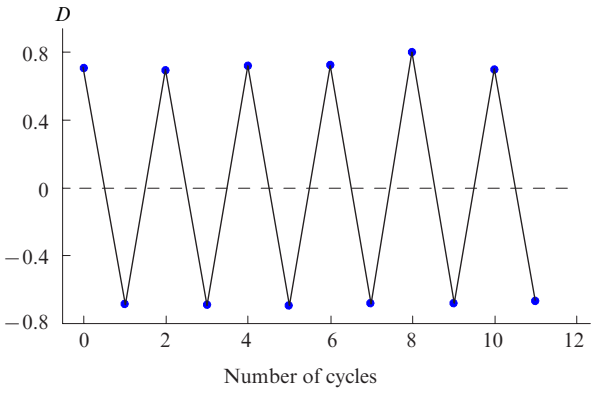


Figure 15. Changes in the dichroism of the LC cell (λ = 610 nm) upon cyclic illumination with varying directions of polarization.[72] Prior to illumination in each cycle, the direction of polarization was changed by 90°.

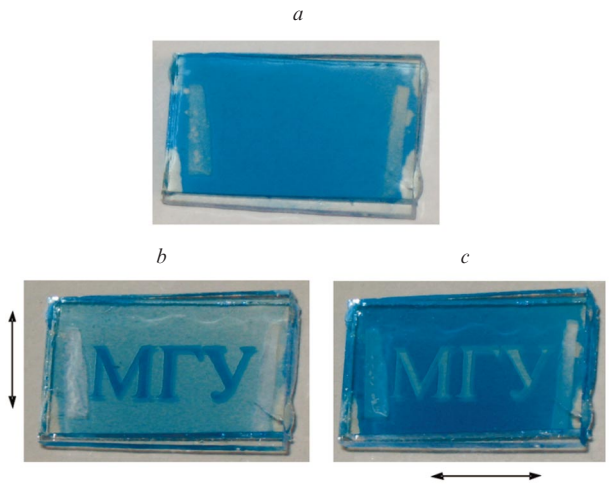


Figure 16. Micrographs of the LC cell filled with a nematic LC mixture based on polymer **12** under non-polarized (*a*) and polarized light (*b*, *c*).[73]
The arrows show the directions of light polarization.

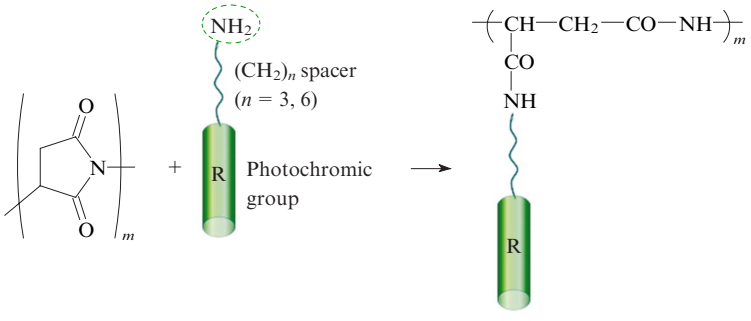
A possible application of the above systems is concerned with the recording of latent information (see the preceding Section). The most promising for this purpose is methacrylic polymer **12** containing a spacer with four methylene groups. An LC cell was assembled [73] and illuminated for 10 min with the polarized polychromatic light of the mercury lamp with a certain direction of polarization. Then, the direction of the polarization plane was changed, and the cell was illuminated through a mask. After that, the cell was filled with a nematic LC mixture containing 0.1 mass % of a merocyanine dye.

Figure 16 presents the micrographs of the LC cell after its irradiation with the polarized light. In the absence of polarizers, the abbreviation 'МГУ' is invisible to the naked eye; however, in the polarized light (in other words, visualization through polarizers), this word becomes visible; moreover, by varying the direction of polarizers, either negative or positive images can be obtained. These photoaligning coatings present a certain interest for their use in optoelectronics, photonics, and LCD technology.

The above data on photoalignment were obtained using LC polymethacrylates.[72] Unfortunately, the application of these coatings is limited by their insufficiently high glass transition temperatures (~50 – 60 °C) as well as by their good solubility in low-molecular-mass liquid crystals. For the preparation of photoaligning compounds with higher glass transition temperatures (at least, above 100 – 120 °C) insoluble in liquid crystals, the procedure for the synthesis of photochromic polyamides with a higher thermal resistance (Scheme 2) has been worked out.

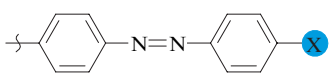
The preparation of about ten new polyamides containing the above types of photoactive groups with different substituents has been described in detail in papers [72 – 74] and

Scheme 2



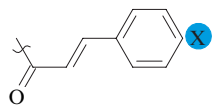
Photochromic group R:

Azobenzene derivatives

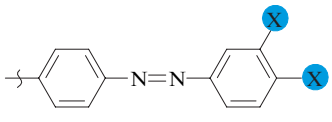


X = F, CN, NO_2

Cinnamic acid derivatives

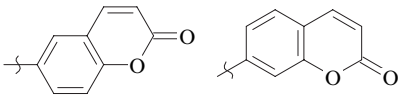


X = H, F



X = F, CN

Coumarin derivatives



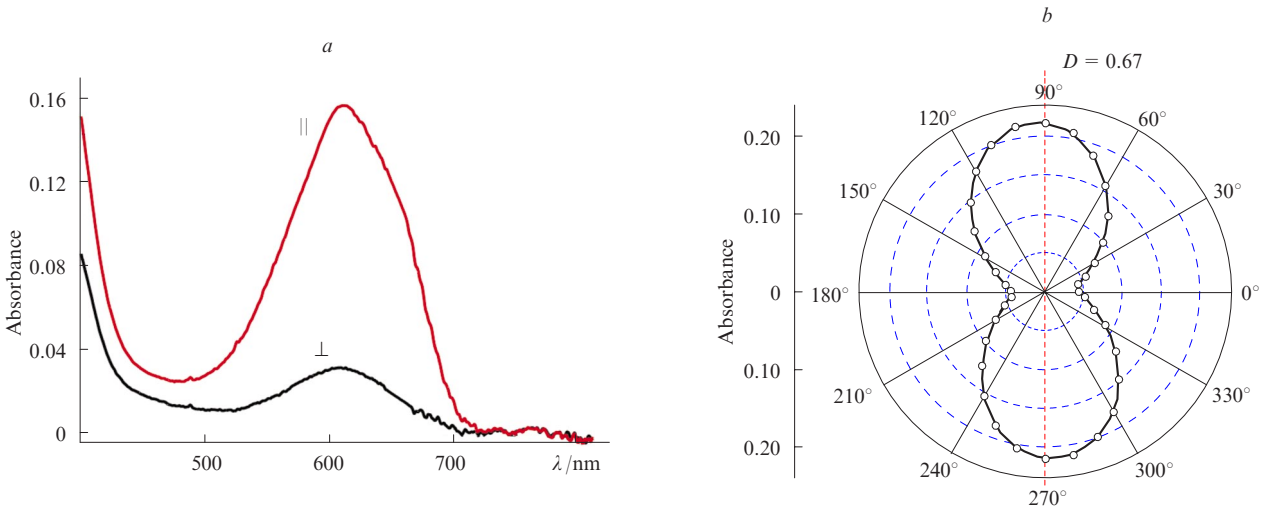


Figure 17. Polarized absorption spectrum (*a*) and polar absorption diagram (*b*) for the LC cell with a sample of uniaxially oriented comb-shaped polyamide containing an LC mixture and 0.5 mass % of a dichroic merocyanine-based dye.[73]

a patent.[75] All these polymers are characterized by high glass transition temperatures (150 to 170 °C), and the temperature range of thermal stability of their mesophase is 250 – 260 °C. The advantages of photochromic comb-shaped polyamides are concerned with their high solubility in many organic solvents and ability to produce thin polymeric coatings.

Polyamide coatings were prepared by spin coating of dilute solutions of polyamides. Figure 17 presents the polarized absorption spectrum and the polar diagram for the LC cell with the sample based on one of the polyamides with cyanoazobenzene photochromic groups, which contains a low-molecular-mass mixture of the liquid crystal and 0.5 mass % of a dichroic dye.

Comparative analysis of the data on dichroism and other characteristics shows that polyamides can compete with commercial polyimides used in the LCD devices.[75] The benefits of the synthesized compounds include high glass transition temperatures and thermal resistance.

As follows from Fig. 17, the dye molecules and the molecules of the low-molecular-mass liquid crystal are characterized by a well-pronounced uniaxial orientation ($D = 0.67$); this orientation is directed perpendicular to the polarization plane of the UV light used to illuminate the LC cell. For polyamides studied in the research laboratory of the LG-Chem company (South Korea), two following parameters crucial for the LCD industry were evaluated: Voltage Holding Ratio (VHR) and black level (BL) luminance. For the synthesized polyamides, VHR is equal to 96.8% – 98.2%, while BL is characterized by the maximum level of 5 points, which corresponds to the exceptionally high degree of orientation of liquid crystalline molecules.[75]

As shown above, azobenzene-containing polymers offer a unique opportunity for repeated changes in the directions of the orientational action of the aligning coating *via* the UV irradiation with different polarization directions. This suggests that the comb-shaped photochromic polyamides with azobenzene groups can be used for the reversible recording of latent images. Figure 18 shows the micrographs of the LC cell with the command (aligning) coating based on photochromic polyamide.

Prior to the loading of the liquid crystal, the LC cell was illuminated with the UV light with some polarization direction and, next, the cell was illuminated through a mask with the light of the perpendicular polarization. After irradiation, the cell was loaded with the low-molecular-mass liquid crystal containing a fluorescent dye. In the normal light, the image escapes any visualization with the naked eye (see Fig. 18 *a*); when the polarizer is used, the written letters are clearly seen. Noteworthy is that the image of the letters 'LG' is characterized by the high contrast. This mode of recording can be used for imaging in the modern displays for the 3D TV sets. The synthesized photoactive polyamides seem to be very promising compounds for the development of a new generation of thermally resistant highly effective photoaligning compounds.

As mentioned above, the number of photooptical studies on LC polymers with photochromic groups in the main chain is rather limited. Among them, of special interest is the original work [76] of German scientists devoted to the synthesis and characterization of a rigid-chain polymer, poly(*p*-phenylene), containing an azobenzene group in the main chain and the adjacent benzene moiety with two long n-dodecyl side groups (compound **15**). Inherently, this is a typical comb-shaped polymer in which side aliphatic chains produce a hexagonal packing similar to classical comb-shaped polymers.[3]

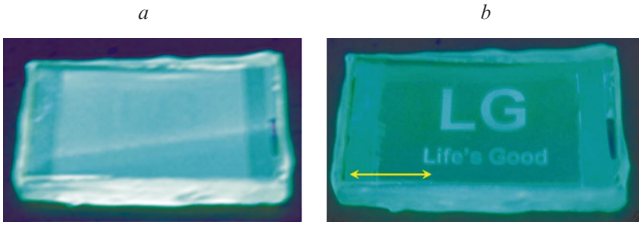
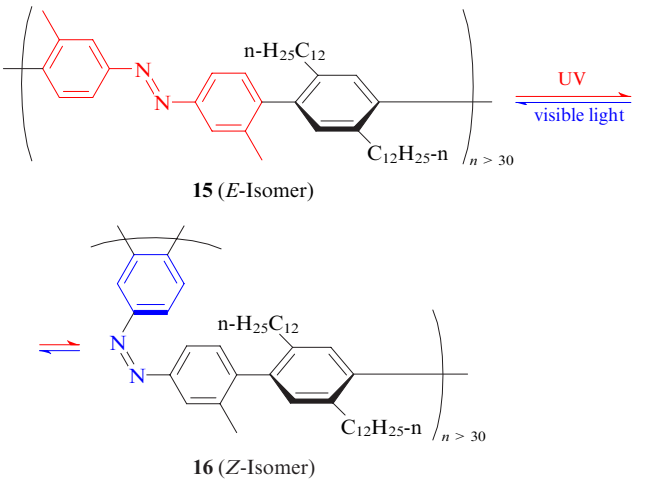


Figure 18. Snapshots of an LC cell with a photoaligned polyamide coating in the native (*a*) and polarized (*b*) light.[74]
The arrow shows the direction of light polarization.

The polymer film is characterized by the layered hexagonal (seemingly, smectic) packing of the side groups. Under the action of the UV irradiation, the *E*–*Z*-isomerization of azobenzene groups takes place (Scheme 3); in this case, the linear configuration of the main chain is distorted (structure **15** is transformed into isomer **16**) very quickly (within ~5 s). In turn, this leads to violation in the coplanar packing of the side chains of dodecyl groups. Upon further irradiation, the film is amorphized due to the cooperative effect of photoalignment induced by the *E*–*Z*-isomerization. The subsequent visible light irradiation restores the initial state of the film. The authors revealed an analogy between this process and a zipper; as a result, this process has been referred to as 'molecular zipper', which can be either unzipped or zipped under the action of light (Fig. 19). Noteworthy is that, in the presence of only 20% of the formed *Z*-isomers, disorder of the side groups (in other words, unzipping) is critically boosted; this observation clearly attests to the cooperative character of this phenomenon.

Scheme 3



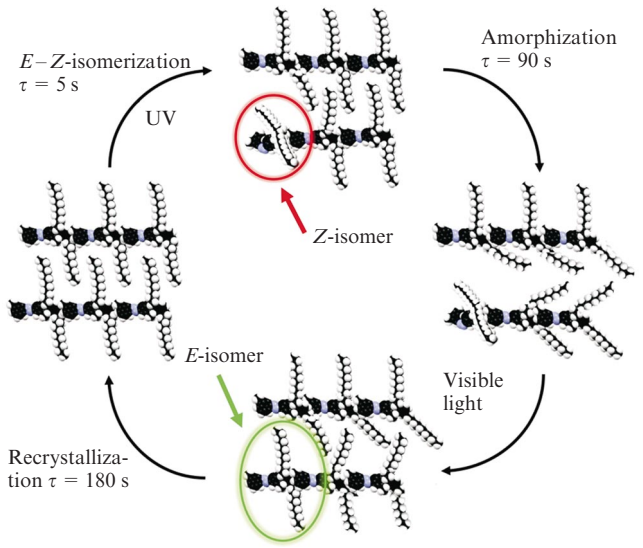


Figure 19. Scheme illustrating the operation of the 'molecular zipper': the *E*–*Z*-isomerization zipping and unzipping of azobenzene groups, that is, destruction and recovery of the packing of dodecyl groups under the action of the UV and visible light.[76]

The proposed mechanism of the molecular zipper is largely similar to the processes involved in the design of molecular machines that operate by harnessing the light energy.

Therefore, the above cooperative photoalignment processes taking place upon irradiation of azobenzene-containing LC copolymers have found their unorthodox application for the control over structuring in the comb-shaped polymers containing azobenzene groups not in the side chains but in the main chains of macromolecules.[76]

III.3. The principle of photoinduced control over helix pitch of cholesteric polymer systems

In the preceding Sections, we considered the principles of photomodulation of optical properties of polymeric nematic systems, which allow the development of photoactive materials for the WB data storage and recording. However, the use of the LC polymers that produce the cholesteric mesophase seems to be more promising. The cholesteric mesophase with its helical supramolecular structure offers unique advantages for the control of not only optical properties (transparency, light scattering) but also the colour of polymeric films. According to Eqns (2) and (3), the action of light on cholesteric films can change the helix pitch and the selective light reflection wavelength (λ_{max}) due to the variation, first, of the concentration of the incorporated optically active dopant and, second, the twisting force β [see Eqn (3)]. The second case offers evident advantages for the recording of coloured images on the coloured background.

As was convincingly shown in the publications by Bobrovsky and co-workers,[77–84] the principle of variation of the helix pitch is valid for copolymers containing chiral photochromic moieties in the side groups of macromolecules (see Fig. 8 *c*,*d*) as well as for the blends of nematic polymers doped with chiral photochromic molecules. Irradiation of the cholesteric polymer film (Fig. 20 *a*) leads to photoinduced isomerization of chiral photochromic units upon their covalent bonding to the main chain (see Fig. 20 *b*); the same tendency is observed for the mechanical blend of the nematic polymer doped with chiral photochromic compounds (see Fig. 20 *c*). As a result of photoinduced isomerization of photochromic groups, β decreases ($\beta_2 < \beta_1$) due to the reduced anisotropy of *Z*-isomeric fragments. The helical structure of the cholesteric LC is untwisted; according to Eqn (2), the helix pitch increases ($P_2 > P_1$), and λ_{max} is shifted to higher wavelengths. Scheme 4 illustrates the changes in the configuration and geometric shape of the chiral photochromic moiety in the copolymer under the action of the UV light. Under UV irradiation, the film changes its initial colour from green (λ_1 = 550 nm) to red (λ_2 = 630 nm) due to helix untwisting.

The proposed approach providing changes in the parameter β was used for the data recording *via* local UV irradiation of the cholesteric polymer films through the mask (Fig. 21).

For the derivatives of benzylidenementhanone presented in Scheme 4, helix untwisting is irreversible; however, copolymers with azobenzene-containing chiral photochromic groups where this process is reversible have been later synthesized.[82, 83]

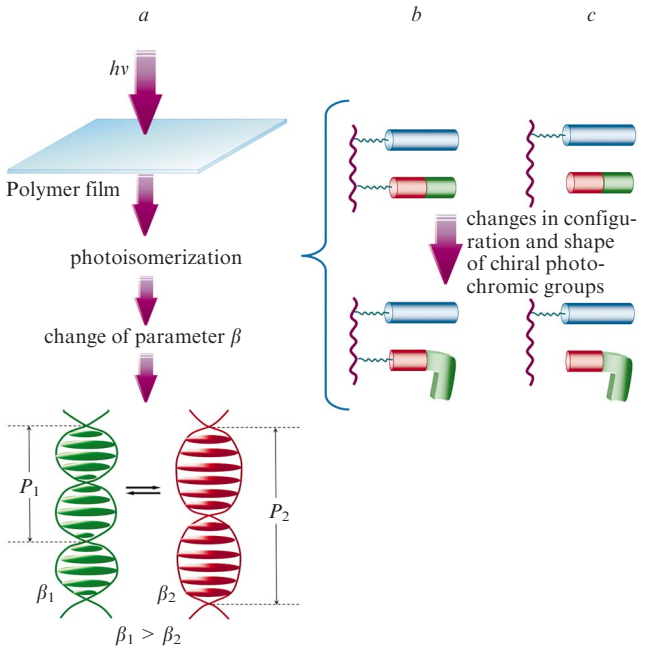
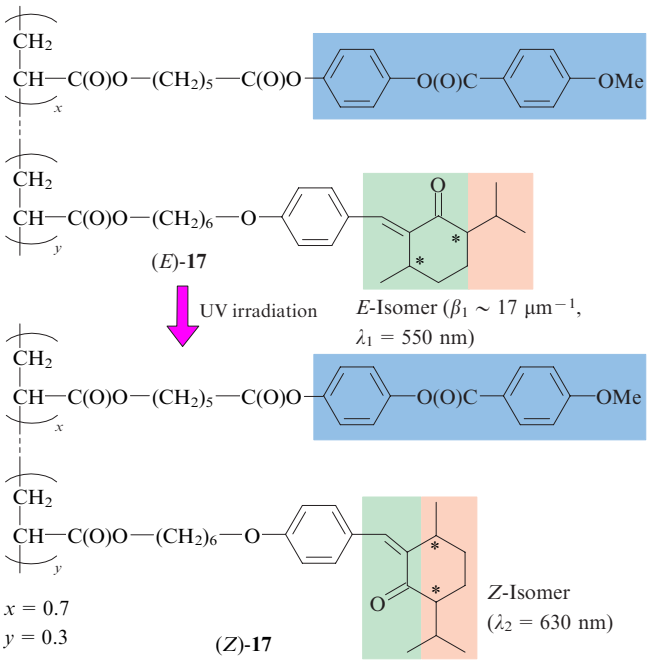


Figure 20. Scheme illustrating the untwisting of the cholesteric helix upon irradiation of the polymer film *via* photoisomerization of the dopant and change of the parameter β (*a*) for the cholesteric copolymer (*b*) and for a blend of the nematic polymer with the chiral photochromic dopant (*c*).[36]

Analysis of the literature data highlights a marked interest of scientists in cholesteric polymers, which is concerned with the possibility of preparing thin polymeric films, which are suitable for at least two applications. First of all, they can be used as polarization and multispectral light filters, deflectors and light reflecting coatings in a broad spectral range (in the entire visible and IR

Scheme 4



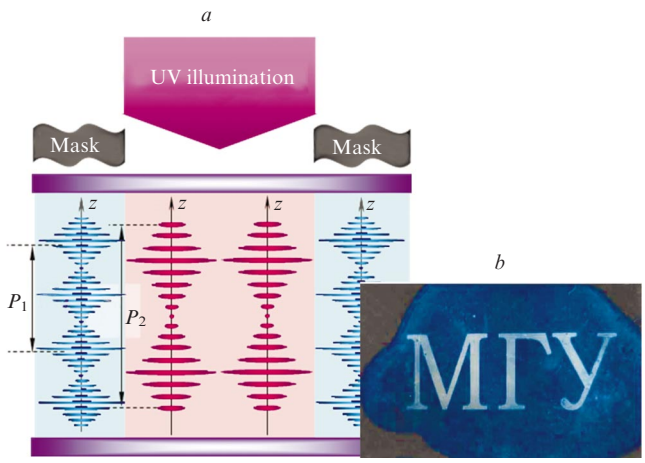


Figure 21. Scheme illustrating the recording (*a*) of the image (*b*) on the cholesteric polymer film based on copolymer **17**.[81]

regions).[11, 21, 55] The second application is related to the possibility of using photochromic cholesteric polymers for the coloured image recording against a coloured background (see above).

IV. Liquid crystalline photoactive block copolymers

Among numerous publications on the characterization of the synthesized block copolymers with different structures, only few works were devoted to the liquid crystalline block copolymers. Apparently, this situation can be explained not only by the difficulties related to the synthesis of well-characterized samples by using special protocols of anionic and free-radical living polymerization, but also by the lack of an adequate set of structural and physical methods for their characterization for specialists involved in the synthesis of these fascinating compounds.

Liquid crystalline diblock copolymers can be classified into several types. First of all, these are liquid crystalline block copolymers of linear and comb-shaped structure, which are composed of linear amorphous (A) and liquid crystalline (B) subblocks or two blocks as the combination of linear and branched segments of the macromolecule (Fig. 22).

The number of the known copolymers of the first type (see Fig. 22 *a*) is rather limited, and their characteristics have been surveyed.[85, 86]

We failed to find any publications on linear liquid crystalline block copolymers composed of two linear LC subblocks, A and B. Most of the literature data is devoted to the second type of the LC copolymers (see Fig. 22 *b*). Finally, only a few publications are devoted to the third type of polymers (see Fig. 22 *c*) composed of two LC comb-shaped subblocks.

In addition to the above diblock LC copolymers, there are triblock LC copolymers like A_n-b-B_m-b-A_n as well as more complex triblock molecular structures such as A_n–[statAB]–A_n, where the central block is a random copolymer composed of units A and B, and the decorating subblocks correspond to fragments A_n or B_m.

The heightened interest of scientists in the development and characterization of liquid crystalline block copolymers

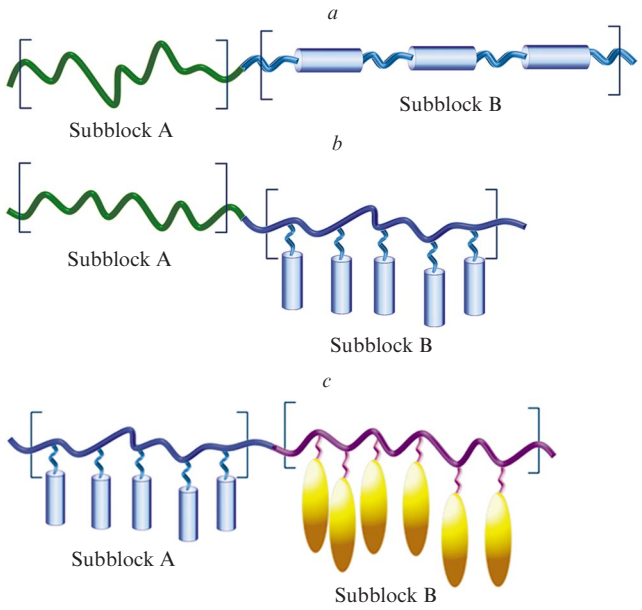


Figure 22. Various options for the molecular structure of liquid crystalline block copolymers.
(*a* – *c*) See text.

has been triggered by their unique ability to produce microsegregated systems, which can experience spontaneous self-assembly of the LC subblocks. As was reported,[87] in diblock and triblock copolymers, periodic ordered nanostructures can be formed; their dimensions and morphology are controlled by the chemical nature, concentration, and mutual arrangement of their subblocks and types of the LC phases.

Usually, liquid crystalline block copolymers shown in Fig. 22 *c*, are characterized by the two-level self-organization and microphase separation on the scale of about tens of nanometres, which is provided by immiscibility of separate blocks and anisotropic ordering of side mesogenic groups in the LC block on a somewhat smaller scale.

Examples of certain types of diblock LC copolymers, which are constructed according to the above principle, are provided by compounds **18** – **20** (the phase transitions of polymers are shown: SmA, SmC are smectic phases A and C, respectively; SmX is a non-identified smectic phase).[87 – 89] These are LC copolymers composed of subblocks of amorphous polymers and LC subblocks with the comb-shaped structure.

As an amorphous subblock, these diblock copolymers usually contain polystyrene, poly(methyl methacrylate) and the most common polyethylene glycol (PEG) segments (compound **20**), whose length can be easily varied. As the second LC block, 'purely mesogenic' subblocks (compound **18**) and photochromic segments (compounds **19**, **20**) are used.

Figure 23 shows the schematic structures of diblock copolymers based on the second type of polymers (see Fig. 22 *b*), which are composed of LC and amorphous subblocks with different compositions. According to the Japanese authors,[87 – 89] their structure is approximately similar to the structural hierarchy observed for common diblock copolymers without any photochromic group rather than for photoactive liquid crystalline block copolymers. When the concentration of photochromic LC subblocks in these systems is low, amorphous subblocks serve as a parent matrix. As the concentration of the LC subblocks increases, typical LC entities are formed; they can be organized into lamellar and cylindrical structures and, finally, when the content of the LC component is high, the LC subblocks serve as the matrix (see Fig. 23).

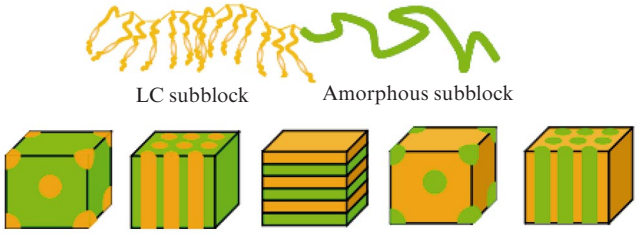
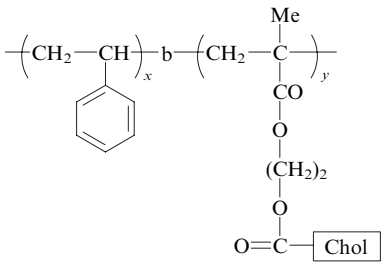


Figure 23. Schemes illustrating the structure of the second-type diblock copolymers (see Fig. 22 *b*) with the microphase separated structure (the fraction of the LC block increases from left to right).[29]

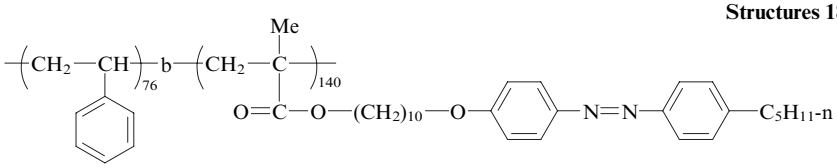
The hypothetical images of the structural entities shown in Fig. 23 constructed on the basis of theoretical speculations are not always supported by experimental evidence.

Analysis of the microsegregated structure of amorphous non-LC block copolymers and construction of the corresponding phase diagrams are usually performed according to the self-consistent mean field (SCMF) theory with the

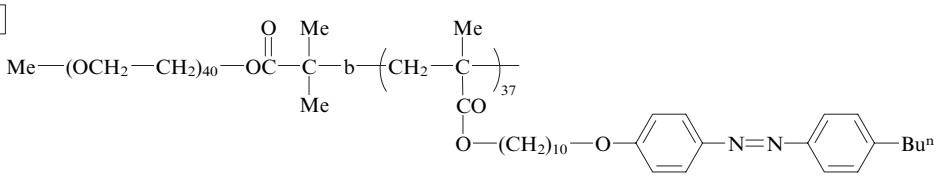
Structures 18 – 20



18 (G 126, SmA 187, I)



19 (G 43, SmX 90, SmA 118, I)



20 (SmX 65.2, SmC 94.9, SmA 114.1, I)

account for the Flory – Huggins parameter and the degree of polymerization or, in other words, the length and the volume fraction of of subblocks. Unfortunately, the number of these theoretical studies on liquid crystalline block copolymers is very low,[90] even though the theoretical approach based on the analysis of the given molecular structure parameters can be exceptionally helpful for the interpretation of structural data and photooptical behaviour of these systems. In this connection, note the works by Potemkin and Bodrova (*e.g.*, Ref. 91), where the theoretical and experimental results were compared.

All photooptical and photoalignment processes discussed in this review are primarily based on the strict analysis of the initial structure of photochromic liquid crystalline block copolymers, which can be altered under the light irradiation and controls the resulting supramolecular structure induced by this action.

The application of photochromic liquid crystalline block copolymers offers more promising (as compared with conventional block copolymers) opportunities not only for the control over their optical and photooptical properties. The point is that light irradiation or thermal action on the liquid crystalline block copolymers can trigger phase separation processes; in this case, suitable prerequisites are attained that provide the development of new structural organization of individual subblocks, which, under certain annealing (or cooling) conditions, can be preserved in the solid phase — in a polymer block or in a polymer film (coating).

When considering photoactive and photoalignment properties of liquid crystalline block copolymers composed of amorphous and LC subblocks, the key problem is concerned with the characterization and study of relations between the character of photoinduced alignment of photoactive subblocks and its effect on inert (not photoactive) subblocks. Since the photoinduced transformations proceeds under the conditions of phase-separated segregation of individual domains formed by subblocks (often, of different size), the study of the resulting structure of these systems with the complex phase state presents a challenging task.

In this work, we will not dwell on the known experimental data but we will consider more general problems related to the study of liquid crystalline block copolymers and discuss new approaches to the possible application of these fascinating hybrid systems.

Analysis of the results of most experimental works shows that the key feature of all block copolymers, including liquid crystalline block copolymers, is related to the development of the microphase separated structure, which controls all their physicochemical properties. However, when studying the effect of light irradiation and electric field on the above system, several problems arise, as the LC subblocks are involved not only in the photochemical processes but also experience critical structural rearrangements, which cover both photochromic and non-photochromic amorphous LC and even crystalline phases, which comprise the subblocks of binary and ternary block copolymers. Structural rearrangements under the action of the external impact markedly depend not only on the initial molecular structure of liquid crystalline block copolymers (concentration and molecular mass of LC subblocks), but also on the structure of block copolymers, which is changed in response to the external action. In this case, of special importance are the experimental conditions (temperature, irradiation dose, intensity of the electric field, *etc.*), which often control the dynamics of current processes as well as the mechanism and direction of chemical and structural transformations.

An important factor in considering the processes taking place in the LC subblock is to take into account the changes at interfaces of the sample, which often alter the orientation of LC fragments due to the appearance of intrablock interfaces, *etc.* These problems are of crucial importance for the analysis of experimental results on the effect of electromagnetic radiation on liquid crystalline block copolymers. The crucial stage of these studies is concerned with the detailed experimental examination of molecular and supramolecular structure of block copolymers under targeted variations in their molecular parameters — length, concentration, and distribution of subblocks in macromolecules.

However, currently, the number of experimental works devoted to the influence of the composition of liquid crystalline block copolymers on changes in the concentration of each individual component (subblock) is rather limited. Hence, it is impossible to discuss the validity of certain experimental relationships concerning their structural and photooptical properties. To confirm the foregoing, we will discuss several experimental results.

Let us consider the process of so-called 3D-orientational control[92] (named by the authors) for liquid crystalline diblock copolymer **19** composed of polystyrene and azobenzene-containing subblocks. Analysis of spectral data and AFM images makes it possible to advance the following scheme[93] illustrating the structure of the initial block copolymer **19** and the related samples upon irradiation with polarized and non-polarized light (Fig. 24). According to the authors, the initial film after annealing is characterized by the alignment of cylindrical domains of both subblocks perpendicular to the substrate. After irradiation with the plane polarized light ($\lambda = 436$ nm) and subsequent annealing, cylindrical domains are realigned; upon subsequent irradiation with orthogonal polarization, cylindrical domains change their arrangement, and the calculated photoinduced dichroism of mesogenic groups appears to be equal to 0.68.

Somewhat different situation was observed for the liquid crystalline block copolymer **21** containing a long polyethylene glycol tail, which is chemically linked to the mesogenic cyano-containing subblock.[94]

The initial liquid crystalline block copolymer is characterized by the hexagonal packing of cylindrical domains based on subblocks of poly(ethylene oxide) (PEO), which are located perpendicular to the surface of the glass substrate due to the homeotropic orientation of azobenzene mesogens in the smectic layered structures. However, upon irradiation at room temperature ($\lambda = 488$ nm) and subsequent annealing at temperatures somewhat lower than the isotropization temperature, mesogens are reoriented, and a perfect planar packing of poly(ethylene oxide) domains elongated in the direction perpendicular to the laser beam polarization is developed. This character of reorientation of domains is explained by the cooperative process, which leads to the formation of the perfect perpendicular and parallel orientation of nanocylinders composed of different subblocks in one and the same sample (Fig. 25).

In further studies,[95] the molecular structure of the liquid crystalline block copolymer was modified by the introduc-

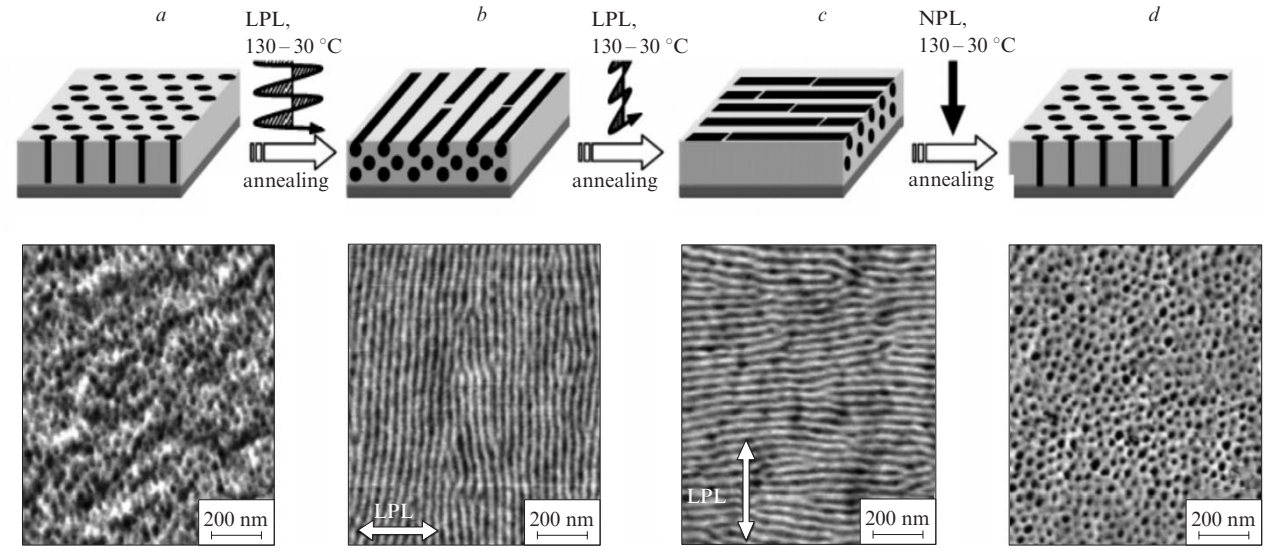
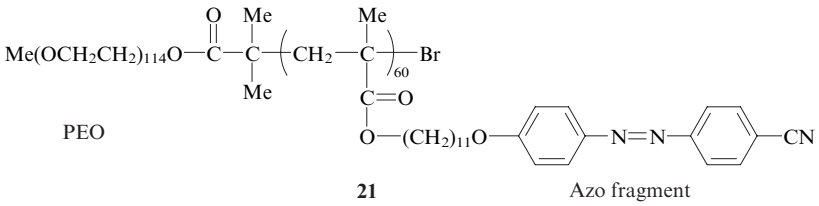


Figure 24. Initial structure of the liquid crystalline block copolymer **19** (*a*) and its changes under the action of linearly polarized light (LPL) (*b*, *c*) and non-polarized light (NPL) (*d*).[93]

Structure 21



tion of another mesogenic moiety with the cyanobiphenyl group. Scheme 5 depicts the molecular and supramolecular cooperative action of the polarized light on the sample of liquid crystalline block copolymer. Under the action of the polarized light, the *E*–*Z*-isomerization of azobenzene groups takes place, inducing the cooperative motion of neighbouring inert mesogenic groups and their joint photo-induced orientation (the right-hand part in Scheme 5), which, according to the authors, triggers the supramolecular impact on the poly(ethylene glycol) moiety of the block copolymer. The result of this impact is the self-assembly of the PEO subblocks. Upon irradiation, the resulting film of the liquid crystalline block copolymer appears to be transparent and can be used for the recording of test gratings and images. Noteworthy is the fact that this orientation of the whole sample of the triblock copolymer can be achieved by the introduction of only 5% of azobenzene units to the copolymer!

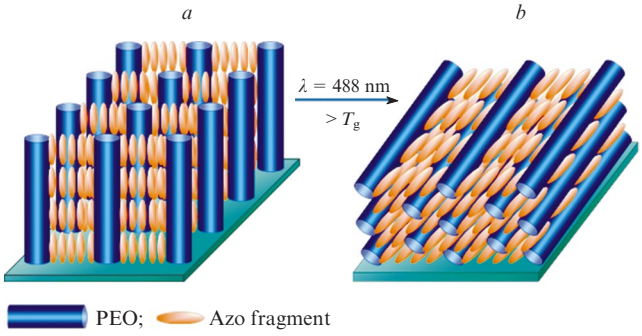
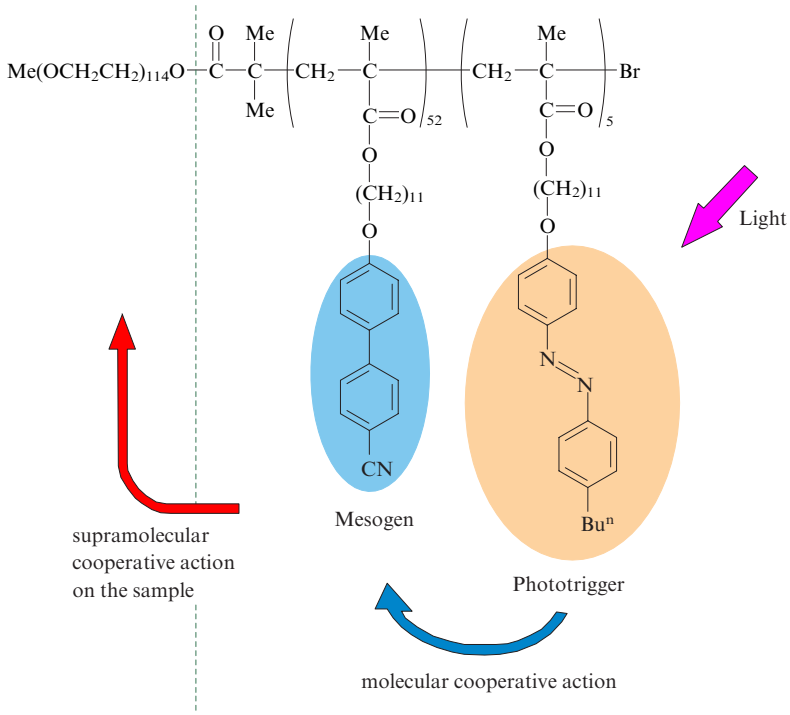


Figure 25. Perpendicular (*a*) and parallel (*b*) orientations of nanocylinders for the same sample of the block copolymer **21** after annealing and laser irradiation.[94]

The PEO-based triblock liquid crystalline copolymers with different concentrations of LC blocks of cholesterol framing crystallizable blocks of PEO macromolecules was synthesized[96] (Fig. 26). Even though macromolecules of this block copolymer are free of photochromic groups, this study[96] is of evident importance as it demonstrates the possibility of sharp changes in the supramolecular structure of block copolymers as a result of varying the composition of the components (see Fig. 26 *b*,*c*). By varying the concentration of the cholesterol LC subblocks from 30 mass % to 80 mass %, the authors elucidated the changes in the supramolecular structure of the block copolymer: at low concentrations of mesogenic groups (below 50 mass %), the structure called 'LC lamellae in PEO lamellae' is formed (see Fig. 26 *b*); as the concentration of the LC blocks increases (> 60 mass %), the formation of the lamellae composed of PEO blocks is suppressed, and these blocks are separated from the lamellar LC phase as amorphous cylindrical domains (see Fig. 26 *c*).

According to the publication cited,[96] depending on the number and length of subblocks, the development of diverse hierarchical structures is directly related to the formation of isolated nanoscale microphases, which exert a certain effect on the forming supramolecular structural elements. The

Scheme 5



whole structural pattern of similar triblock LC copolymers becomes more complex due to the incorporation of photochromic fragments.

Among recent publications devoted to the synthesis of diblock and triblock photochromic LC copolymers composed of only LC subblocks,[97–99] let us consider the studies on photooptical properties of photochromic diblock LC copolymers containing photochromic azobenzene moieties (Fig. 27). X-Ray diffraction studies of both block copolymers revealed the existence of the microphase-separated lamellar structure, which is schematically depicted in Fig. 28.

According to this model, alternation of smectic [composed of subblocks $(Azo)_{25}$] and nematic [composed of subblocks $(MPhB)_{53}$] mesophases is anticipated. In the shorter block copolymer, $(MPhB)_{26}$-b-$(Azo)_{12}$, at the same ratio (2 : 1) of phenyl benzoate and azobenzene mesogenic groups in the macromolecule, short subblocks appear to be mixed, and a common nematic phase containing elements of smectic order is formed.[98]

To study the possibility of the control over optical characteristics of the above diblock copolymers, their samples as amorphized films (prepared by spin coating) as well as the samples of azobenzene-containing homopolymer were illuminated by the linearly polarized light, and the photoinduced dichroism was calculated.

Figure 29 presents the kinetic curves of the induced dichroism for the samples under study. As the exposure time increases, linear dichroism markedly increases for both the homopolymer and the diblock copolymer. For the homopolymer, the maximum value $D \approx 0.7$ is quickly achieved; then, this value slightly decreases whereas the dichroism increases for both block copolymer samples; this fact attests to enhanced orientational capacity of side azobenzene

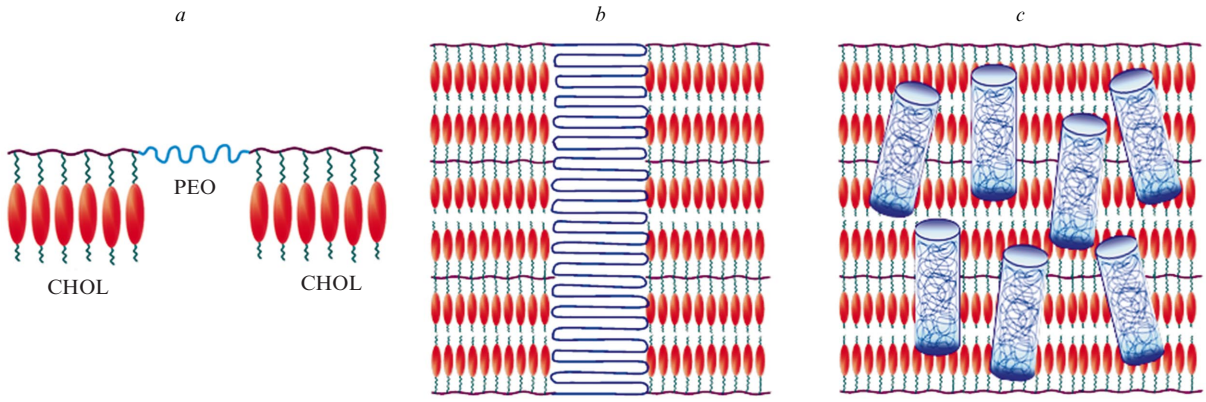


Figure 26. Schemes illustrating the structure of a macromolecule of the liquid crystalline block copolymer (*a*) and arrangement of individual subblocks of PEO and mesogenic moieties (CHOL) in this copolymer at low (*b*) and high (*c*) concentrations of mesogenic groups.[96]

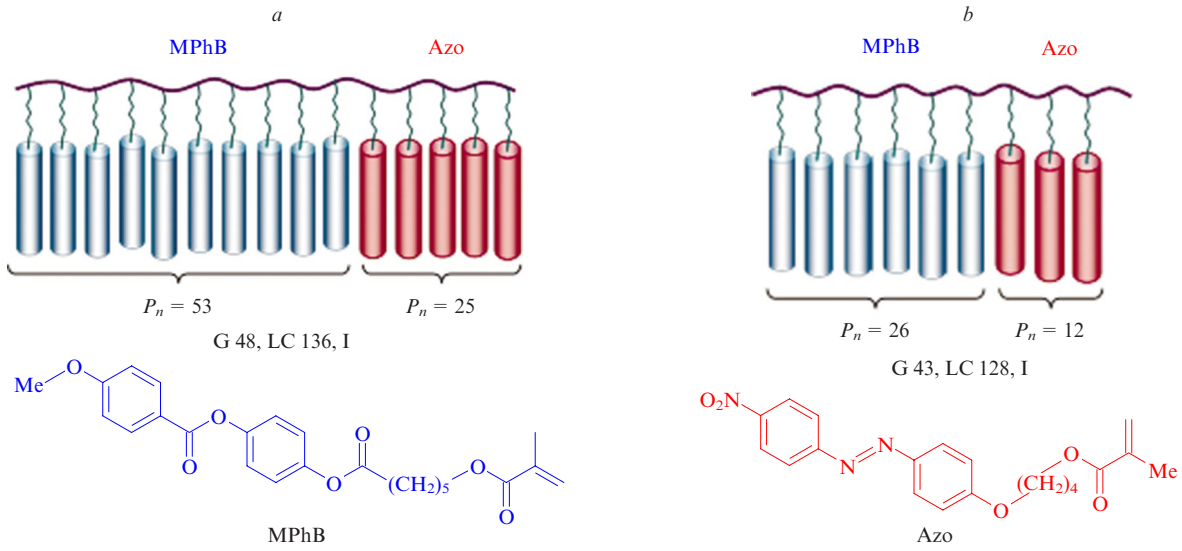


Figure 27. Scheme illustrating the structure of liquid crystalline di- and triblock acrylic copolymers with varying length of methoxyphenyl benzoate (MPhB) and azobenzene-containing (Azo) subblocks.
P_n is the degree of polymerization. This figure also shows the phase transitions of block copolymers; LC is the LC phase with unknown structure.

groups, which also assist the cooperative orientation of non-photochromic fragments. Due to the subsequent annealing of polymeric samples above their glass transition temperature, the induced dichroism increases (D_{Azo} = 0.7) for both types of block copolymers, and this behaviour suggests the absence of any effect of the molecular structure of block copolymers on their orientation.

For the ternary block copolymer composed of only LC blocks, the situation is somewhat different. For example, for the liquid crystalline triblock copolymer $(Azo)_4$-b-$(MPhB)_{80}$-b-$(Azo)_4$ with a common nematic phase, virtually no orientation of chromophores is observed (D_{Azo} = 0.08), and the values of dichroism are independent of the the phase state of the film (amorphized or liquid crystalline). This is likely to be related to the low content of chromophoric groups in the block copolymer (the degree of polymerization is 4).

A different character of orientational processes is observed for a fully liquid crystalline triblock copolymer with longer photosensitive subblocks (the degree of polymerization is 10). In the amorphized films of the triblock copolymer $(Azo)_{10}$-b-$(MPhB)_{80}$-b-$(Azo)_{10}$ (Fig. 30), the azobenzene groups are aligned upon irradiation (D_{Azo} = 0.23), irrespective of the presence of non-photosensitive phenyl benzoate units (see Fig. 30 *a*,*b*). In this case, photoalignment of azobenzene groups is not accompanied by the cooperative rearrangements of phenyl benzoate groups (see Fig. 30 *b*, D_{MPhB} = 0.05). However,

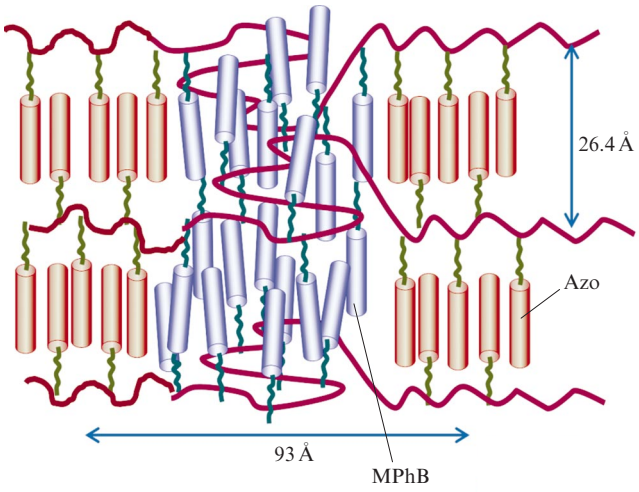


Figure 28. Presumed packing of side groups of the macromolecules of diblock copolymer $(MPhB)_{53}$-b-$(Azo)_{25}$ in the microsegregated lamellar structure.[98]

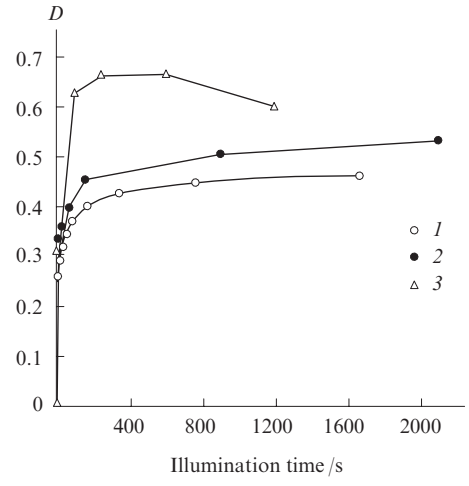


Figure 29. Kinetic dependences of the induced dichroism in the amorphized films of diblock copolymers $(MPhB)_{53}$-b-$(Azo)_{25}$ (*1*), $(MPhB)_{26}$-b-$(Azo)_{12}$ (*2*) and azobenzene homopolymer $(Azo)_{25}$ (*3*).[98]

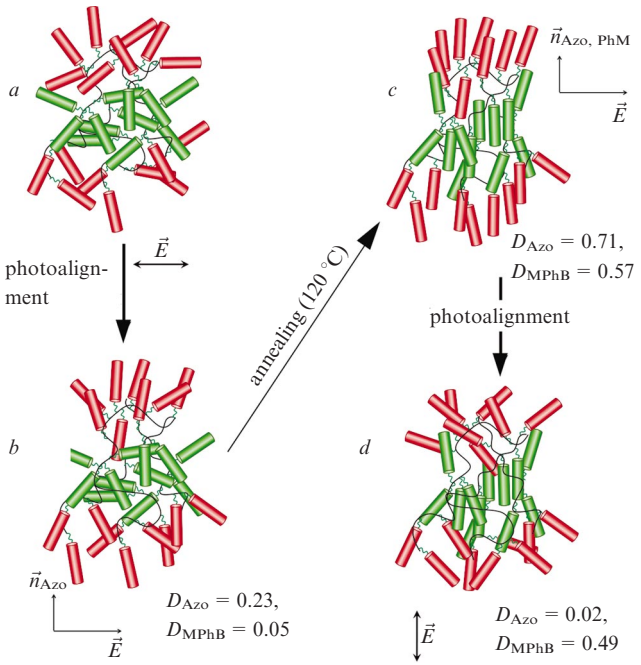


Figure 30. Scheme illustrating the alignment processes in the initial film of block copolymer $(Azo)_{10}$-b-$(MPhB)_{80}$-b-$(Azo)_{10}$ (*a*) and after illumination (*b*), annealing (*c*), and subsequent reorientation (*d*).[99]

subsequent annealing of this polymer film at high temperature (~120 °C) favours the alignment of non-photochromic MPhB groups caused by the induced cooperative effect, which is simultaneously growth due to the gain effect [68] (see Section III.1). As a result of these processes, dichroism of both photochromic moieties in the individual subblocks is markedly improved ($D_{Azo} = 0.71$ and $D_{MPhB} = 0.57$, see Fig. 30 *c*). However, upon further irradiation of this organized polymeric film, alignment of both photochromic and non-photochromic groups is violated, and the dichroism sharply decreases ($D_{Azo} = 0.02$ and $D_{MPhB} = 0.49$, see Fig. 30 *d*).

This evidence highlights the fascinating opportunities for the control over the alignment of the side groups in different subblocks of the fully liquid crystalline triblock copolymers under the action of linearly polarized light and subsequent thermal treatment. Controlled variations in the local properties of individual subblocks give grounds to consider the above triblock copolymers as the basis for the development of innovative advanced materials for photonics and holography.

V. Photochromic liquid crystalline dendrimers

Among photochromic LC polymers with a complex architecture, of special interest are LC dendrimers.[100] Despite a spherical shape of their molecules, the presence of anisometric mesogenic groups in dendrimers assists the development of different types of LC phases. To date, several hundreds of diverse LC dendrimers containing classical mesogenic groups have been synthesized; as in the case of the comb-shaped polymers, the LC dendrimers are linked to the basic spherical matrix *via* aliphatic spacers of different lengths. As a polymeric matrix, polysiloxane, polypropylene, carbosilane, phosphazene, and other derivatives are used.

Let us consider in brief only photoactive azobenzene-containing carbosilane LC dendrimers and the behaviour of these exotic molecules under the action of irradiation. Five generations of carbosilane dendrimers containing 8, 16, 32, 64 and 128 mesogenic photochromic groups were synthesized and characterized.[100] Figure 31 shows the molecular structures of the LC dendrimers of three generations.

First, noted the detailed study of the structure and character of the molecular packing reveals a marked difference between the dendrimers of lower (first to third) and higher (fourth and fifth) generations. The dendrimers of lower generations are usually characterized by the layered (as a rule, smectic) structure with the antiparallel packing of mesogenic groups and by the formation of so-called H-aggregates (Fig. 32 *a*,*c*). For the dendrimers of higher generations, this aggregation is absent due to the large number of peripheral mesogenic groups (see Fig. 32 *b*). Liquid crystalline dendrimers of higher generations produce columnar phases due to the packing of disklike dendritic molecules as cylindrical columns (see Fig. 32 *d*).[100]

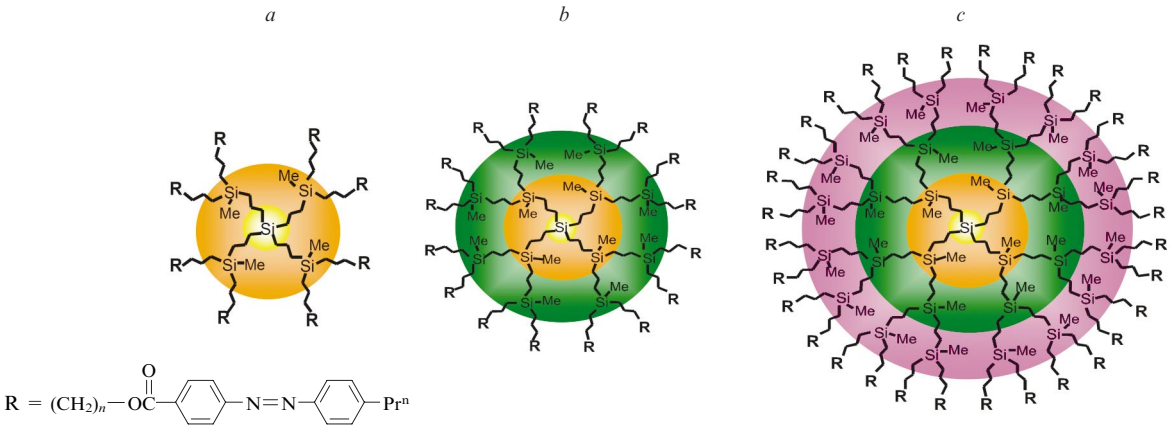


Figure 31. Carbosilane dendrimers of the first (*a*), second (*b*), and third generations (*c*) with mesogenic photochromic groups R.[100]

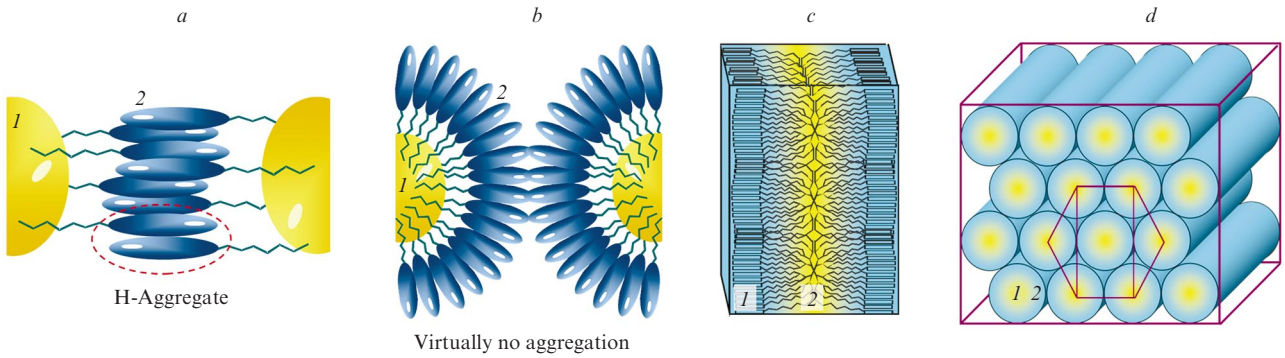


Figure 32. Schemes illustrating the local packing of photoactive mesogenic groups (*a*, *b*) and molecules (*c*, *d*) in the samples of LC dendrimers.[100, 101]
(*a*, *c*) Samples of lower generations; (*b*, *d*) samples of higher generations; (*1*) dendrite matrix, (*2*) mesogenic groups.

Analysis of the results of photooptical studies and kinetics of dichroism growth reveals a marked difference between the behaviours of LC dendrimers of different generations (Fig. 33). For the dendrimers of lower generations, as the generation number increases, the efficiency of orientation strongly decreases. This behaviour can be explained by a partial destruction of the smectic structure with increasing dimensions of the matrix. At the same time, the dendrimers of the fourth and fifth generations demonstrate high photoinduced dichroism: *D* reaches 0.6 for the dendrimer of the fifth generation, and this is likely to be related to the specific features of the orientation of columns along the light polarization vector.

Therefore, the branched centrosymmetric structure of dendrimers controls their fascinating photooptical properties, which are appreciably different from those of the comb-shaped polymers.

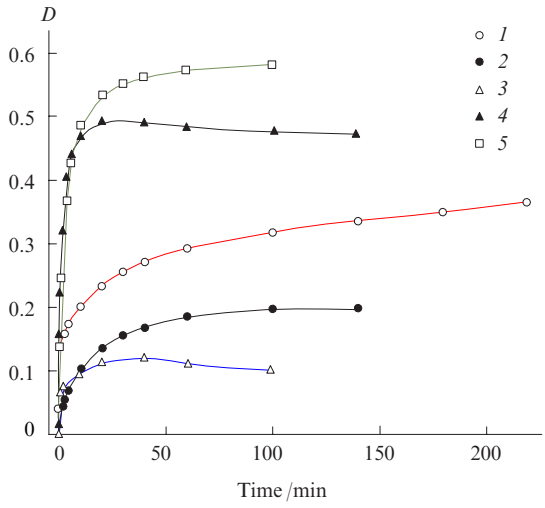


Figure 33. Kinetic dependences of dichroism for the dendrimers of the first (*1*), second (*2*), third (*3*), fourth (*4*), and fifth generations (*5*).[102] Dendrimer films were irradiated with polarized light of blue laser (473 nm).

VI. Photoinduced mass transfer in polymeric and oligomeric liquid crystalline systems

The preceding Sections address photo- and electroinduced phenomena, which are primarily provided by the rotational diffusion of chromophores under irradiation and the concomitant isomerization processes. Another interesting process induced by the irradiation is the phenomenon of mass transfer, which has been revealed in the middle of the 1990s.[103 – 107] Since then, this phenomenon has attracted a marked interest as it allows the design of a complex surface pattern at the nanoscale level.[108] This design seems to be promising from the viewpoint of the development of complex optical devices for photonics and surfaces with the photoadjustible wettability.

VI.1. Formation of periodic gratings *via* photoinduced mass transfer

Most publications on periodic gratings are devoted to the development of a regular periodic relief in the films of amorphous azobenzene-containing polymers (see Section III). To date, this subject has been discussed in numerous publications,[103 – 130] including reviews and monographs (for example, Refs 56, 116 and 117). Within the first approximation, the development of a regular periodic relief is related to the translational macroscopic displacement of chromophores (together with polymeric chains) from the regions with a higher light intensity to the regions with a lower light intensity. However, this mechanism fails to explain the cases when the surface pattern is produced upon irradiation of the films with light of a spatially uniform intensity and a periodically modulated polarization. Even though several theoretical works [104, 123 – 130] on photofluidization (marked reduction in viscosity) or photodeformation are available, at the present time, an unambiguous interpretation of the mass transfer mechanism is missing.

From the viewpoint of the development of the regular periodic relief, polymeric LC systems are known to be even less studied.[119 – 122] In this respect, it is necessary to mention the works [119, 120] that showed that, the preliminary irradiation of the films based on the smectic azobenzene-containing polymers, for example, compound **22**, appears to markedly enhance the development of the surface relief (Fig. 34 *a*). When films of these copolymers are exposed to

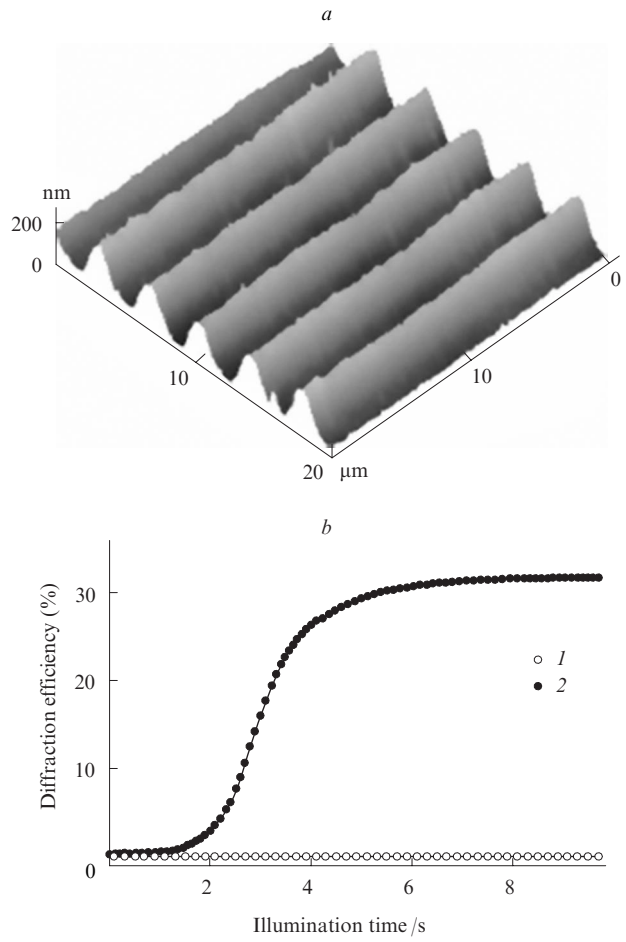


Figure 34. AFM scan of the regular periodic relief (*a*) and kinetics of the growth of the first-order diffraction efficiency (*b*) upon irradiation with argon laser interfering beams of a freshly prepared film of azobenzene-containing polymer (*1*) and UV illuminated film (*2*).[119]

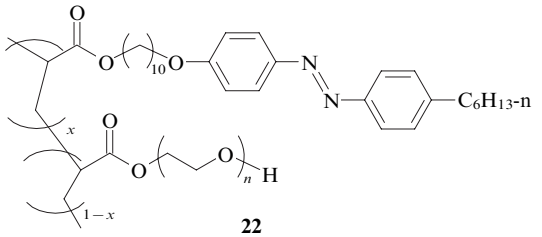
formaldehyde vapour, their chemical cross-linking proceeds *via* hydroxyl groups, and the photoinduced surface relief appears to be additionally stabilized.

Bearing in mind numerous publications on the periodic relief, we will consider less studied but still intriguing phenomena related to variations in surface morphology induced by irradiation with a single focused laser beam [131 – 138] as well as the spontaneous development of the periodic relief and the pathways allowing its controlled modulations in cholesteric oligomers.[139 – 144]

As was shown in several publications, irradiation of the films of amorphous azobenzene-containing polymers with the focused laser beam can lead to the formation of uniform cavities (depressions), so-called craters. In these films, the direction of the preferential mass transfer coincides with the direction of light polarization.[131 – 133] Moreover, in some cases, irradiation with a spot beam provides a spontaneous development of a periodic relief;[134 – 137] in this case, orientation of the photoinduced grating and the flow direction of the material are controlled by the direction of light polarization.

Under the action of the well-focused beam, craters are formed in the LC polymers. For the comb-shaped nematic LC polymer with the side azobenzene groups **23** and for the cholesteric mixture of this polymer containing minor amounts of the chiral dopant **6**, mass transfer processes were studied.[138]

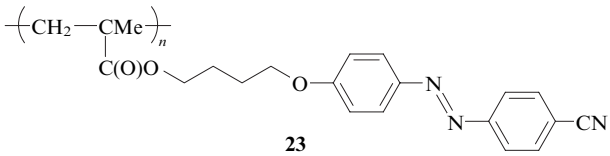
Structure 22



22

$x = 50$, $n = 4.5$

Structure 23

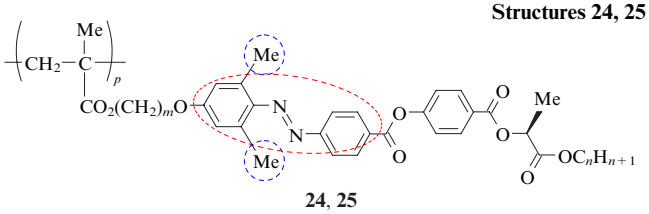


23

The depth of the formed craters was shown to be tens of nanometres and to depend on the exposure time (Fig. 35 *a*). One of the principal results of the studies on the polymer **23** and cholesteric mixture containing this polymer is the fact that the presence of the chiral dopant and helical supramolecular structure exert no effect on the crater diameter, depth, and formation kinetics (see Fig. 35 *b*). The studies of the uniaxially oriented films of nematic LC polymer show that its properties are critically different from the properties of the amorphous films of azobenzene-containing polymers. As shown above, in the case of the amorphous polymers, mass transfer always proceeds along the light polarization direction. Somewhat different situation is observed for the oriented films of the nematic polymer: the direction of mass transfer coincides with the direction of the initial orientation of chromophores in the films and is independent of the polarization direction (Fig. 36).

The photooptical properties of two photochromic polymers (**24**, **25**) containing azobenzene groups with lateral substituents in the *ortho*-position were studied.[143] Both polymers have similar azobenzene photochromic moieties and main chains but different lengths of spacers and terminal aliphatic groups (6 or 10 methylene units). Lateral methyl substituents in the azobenzene chromophores markedly enhance photosensitivity of these systems (as compared with that of unsubstituted analogues). The photosensitivity of these polymers is so high that, under the action of the red

Structures 24, 25



24, **25**

24: $m = 6$, $n = 10$ (G 20, N* 72, I);
25: $m = 10$, $n = 6$ (G 20, SmA_1* 82, I)

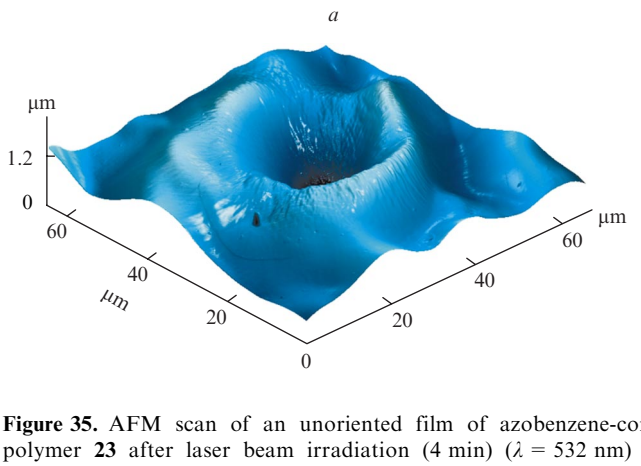


Figure 35. AFM scan of an unoriented film of azobenzene-containing polymer **23** after laser beam irradiation (4 min) (λ = 532 nm) (*a*) and kinetics of the crater deepening (*b*) upon illumination of nematic polymer **23** (*1*) and a cholesteric mixture with this polymer (*2*).[138]

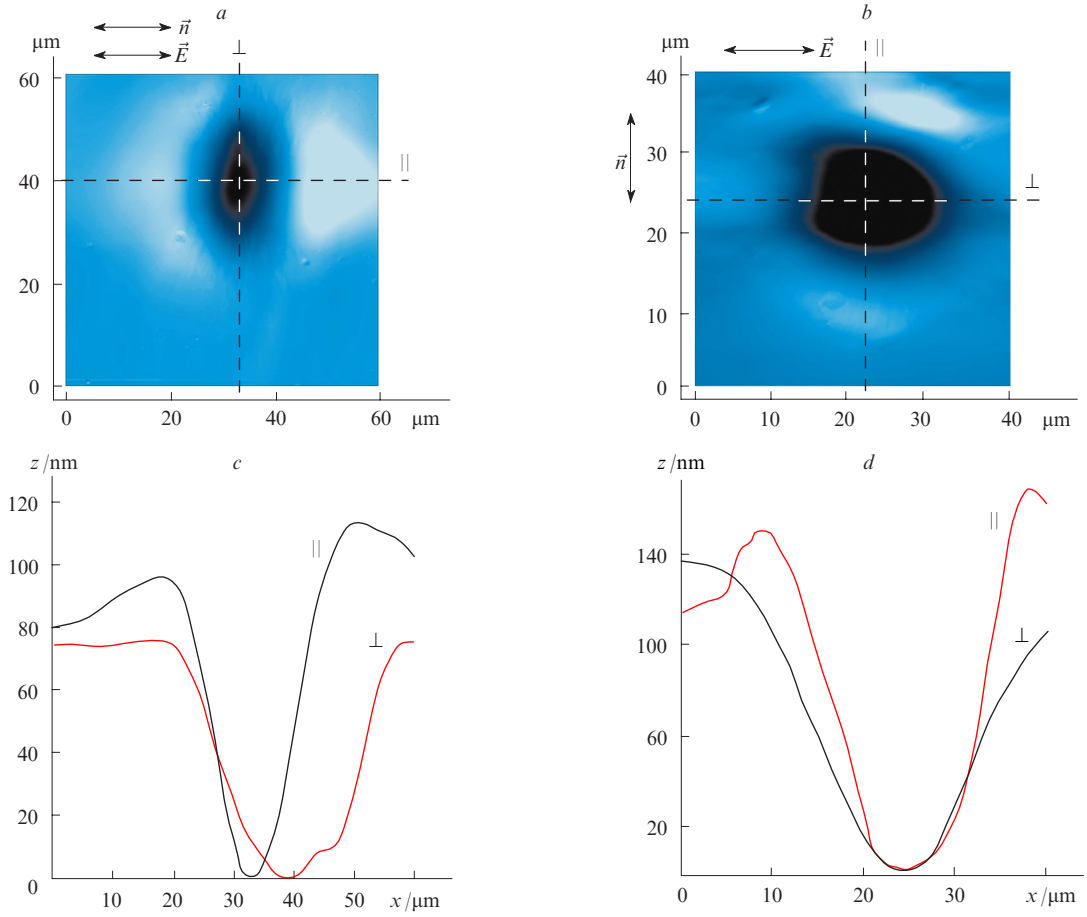


Figure 36. AFM scans of the oriented film of polymer **23** after laser illumination with light polarization along (*a*) and across (*b*) the LC director and corresponding profiles of the crater cross section in the above directions (*c*, *d*).[138]

helium – neon low-intensity laser irradiation (λ = 633 nm), effective photoorientation takes place.[143]

Of special interest are the results of studies on the effect of highly focused beams of green (λ = 532 nm) and red light (λ = 633 nm) on the surface topography of the films of the above polymers using the custom-made setup that combines polarized optical microscopy and atomic force microscopy.[144] Under the action of the well-focused green beam (with a diameter of 30 μm), anisotropic clusters are formed in both polymers (Fig. 37 *a*) or, in other words, in the case of the green light irradiation, the behaviour of these polymers is nearly identical to the behaviour of the earlier studied azobenzene-containing polymers. The predominant direction of mass transfer coincides with the direction of

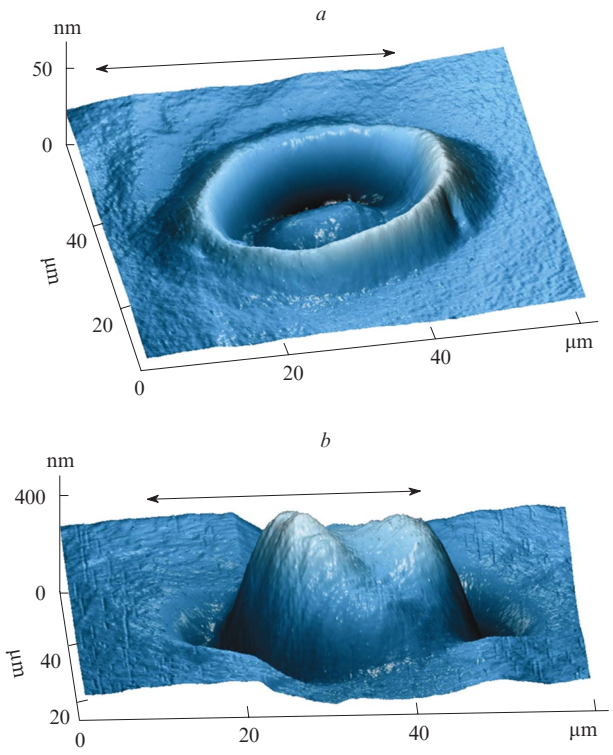


Figure 37. Surface structures produced under the action of a well-focused green (*a*) and red light (*b*) on the film of polymer **24**.[144] The arrows show the direction of light polarization.

light polarization. However, under the red light irradiation, quite the opposite scenario is observed: 'hills' are formed (see Fig. 37 *b*).

Evidently, the observed phenomena are provided by the photoinduced diffusion of chromophores upon the repeated cycles of $E-Z-E$-photoisomerization (see Section III.1); however, the reasons behind this marked effect of the light wavelength are still unclear. Nevertheless, the experimental evidence highlights a great potential for the use of well-focused laser beams for the development of diverse surface structures in photochromic comb-shaped polymers.

The intriguing photomechanical effect arises upon irradiation of micronic particles of amorphous [115, 145–147] and liquid crystalline azobenzene-containing polymers [148] involved in various non-photosensitive matrices (such as gels, elastomers); in other words, the particles are deformed along the direction of light polarization. Figure 38 illustrates this phenomenon for the particles of LC polymer **26**. Experimental evidence shows that, upon deformation, the azobenzene chromophores are oriented perpendicular to the light polarization plane, but the correlation between the processes of photodeformation and photoorientation is still unclear. This deformation is thermally and photochemically reversible: upon irradiation with non-polarized light or heating of the particles at temperatures above glass transition temperature, the initial spherical shape is recovered.

VI.2. Photocontrol of surface topography of oligomers

The preceding Section addresses the photochromic LC systems, in which the periodic surface relief is formed under the action of irradiation. However, there is a class

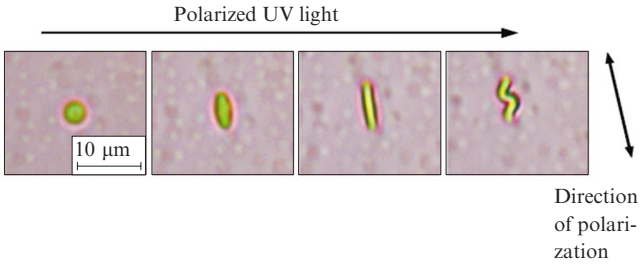
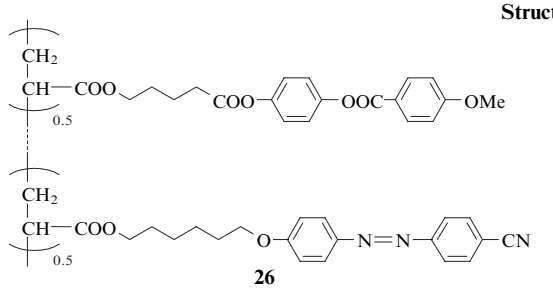


Figure 38. Micrographs of a particle of LC polymer **26** upon deformation under the action of polarized UV light (overall exposure time is 3 min).[148]

Structure 26



26

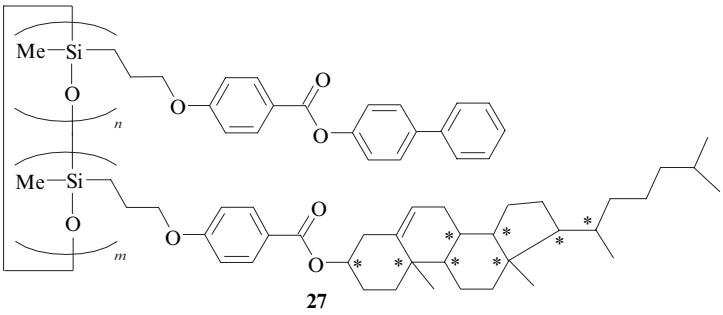
of liquid crystalline oligomers and polymers, in which this relief arises spontaneously. These systems are characterized by the helical supramolecular structure or, in other words, they produce a cholesteric phase (see Section II). Spontaneous development of helical periodic structures was revealed back in the mid-1990s;[149, 150] however, only recently, new approaches to the controlled tailoring of the surface morphology in these systems have been advanced. To this end, the topography of cholesteric films based on the left-handed (LH) cyclosiloxane oligomers **27** with the incorporated right-handed photochromic additive based on isosorbide **6** (3 mass % – 4 mass %) [43, 139–141] or azobenzene dopant **28** (10 mass %)[142] was studied.

On the surface of these systems, a double helix is formed, and this helix is untwisted to the right in the clockwise direction (Fig. 39). The UV irradiation of the films containing dopant **6** leads to the $E-Z$-isomerization of the dopant, and the twisting power decreases. Oligocyclosiloxane is characterized by the left-twisted helical supramolecular structure, and the chiral photochromic dopant **6** triggers the formation of the right-handed cholesteric structure. Introduction of the dopant leads to a partial untwisting of the cholesteric helix and, upon the subsequent UV irradiation, the $E-Z$-isomerization of the dopant molecules takes place; as a result, the twisting power is reduced and, as a consequence, the helix is twisted, and the selective light reflection is shifted to the shorter-wavelength region (see Fig. 39).

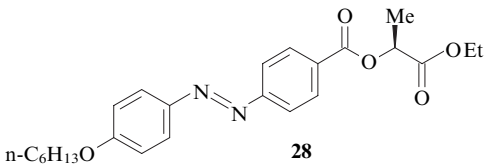
The possibility of the fine tuning of the helix pitch allows one to reveal the correlation between the helix pitch and the period of surface helical structures. This period is shown to depend on the helix pitch in a nearly linear fashion; however, for the mixtures with a large helix pitch ($\sim$700 nm), the 'fingerprint morphology' is formed.[139]

Direct observations of the rearrangements of the surface topology in the films after UV irradiation within a broad temperature range (from 50 to 100 °C) have been repor-

Structures 27, 28



27



28

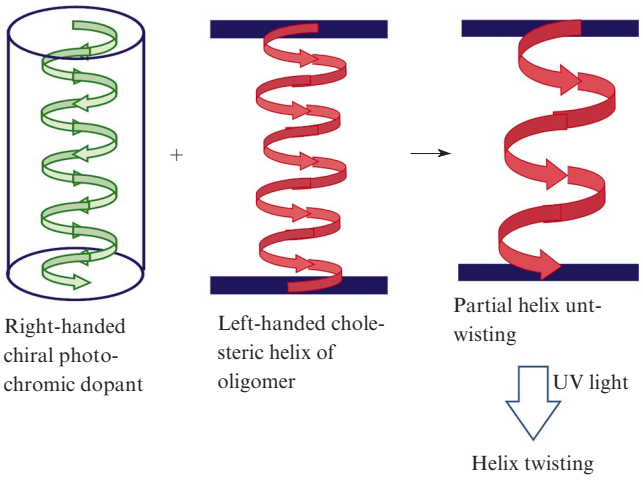


Figure 39. Scheme illustrating partial untwisting of the cholesteric helix upon introduction of dopant **6** into oligomer **27** and subsequent helix twisting upon UV illumination and photoisomerization of the dopant.[12]

ted.[151] Figure 40 presents the examples of changes in the surface topology of the films upon twisting of the cholesteric helix. All principal changes in the films were observed within the first two hours.

At room temperature, the cholesteric blend exists in the glassy state; to untwist the helix, the sample is heated above the glass transition temperature. As a result of UV irradiation and subsequent annealing, the mean period of the surface relief decreases from 576 to 356 nm. In this case, the double helices rotate in the anticlockwise manner at the centre of the confocal domains, and the surface area occupied by the defective regions between the domains increases. In the case of the tetragonal packing of domains (see positions *1*–*4* in Fig. 40), the double helix is formed in the space between them, and untwisting of this helix proceeds in the anticlockwise manner. In less symmetric cases, new disclinations are produced in the defect regions. This experimental evidence makes it possible to advance the scenario of reorientation and displacement of cholesteric layers near the film surface as a result of a decrease in the cholesteric helix pitch.

Mixtures of cyclosiloxane **27** with the azobenzene dopant **28** have been studied.[142] Two types of samples were prepared, namely slowly (1 K min^{-1}) and quickly cooled (quenched) films after annealing at 140 °C. The slowly cooled films contain the depressions (cavities) with the helical structure (Fig. 41), whereas the quenched films are seen to be covered by 'hills' (Fig. 42 *a*). For both films, irradiation with the focused polarized light at $\lambda = 532$ nm leads to the formation of anisometric hills (see Figs 41 and 42 *b*,*c*). This process is accompanied by the uniaxial photoorientation of chromophores and mesogenic groups perpendicular to the light polarization plane and by the deformation of hills in the same direction (see Fig. 42 *b*). The observed changes in surface topography are provided by the occurrence of several processes, including photoinduced heating of the film and concomitant changes in the cholesteric helix pitch, photoorientation of chromophores

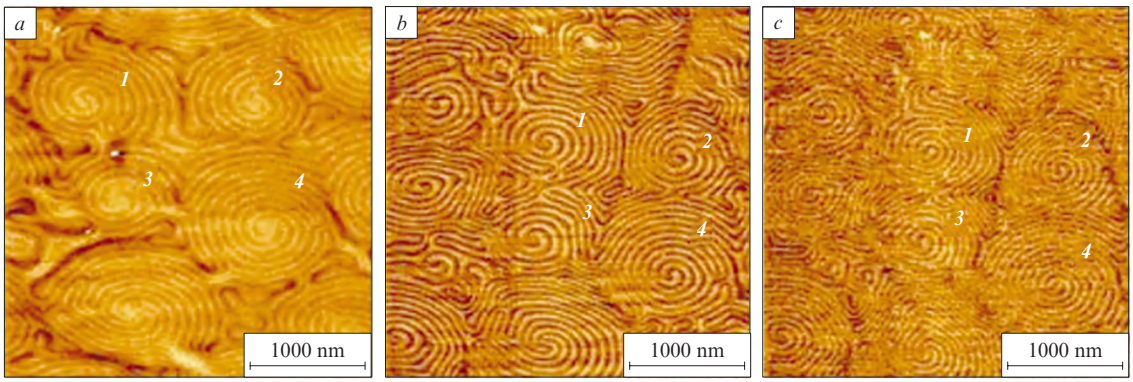


Figure 40. Micrographs of the surface of the cholesteric film of a blend of oligomer **27** with dopant **6** after UV illumination at room temperature.[151]
Surface before heating (*a*), after keeping at 70 °C for 41 (*b*) and 141 min (*c*). Size of the image is 20×20 μm ^{2}.
(*1*–*4*) Selected domains.

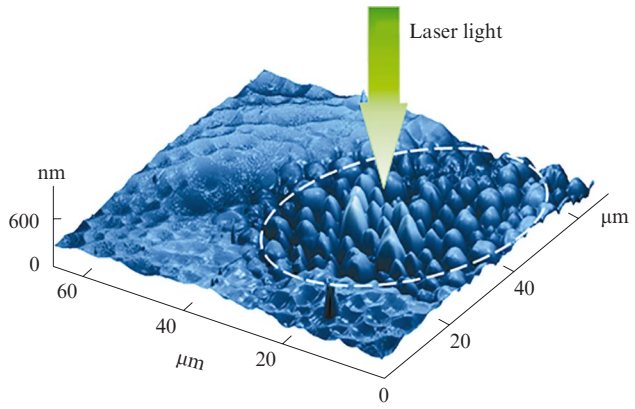


Figure 41. AFM images of a slowly cooled film of cyclosiloxane **27** doped with compound **28** after local laser light irradiation (λ = 532 nm).[142]
The irradiated region is shown by the dashed line.

and mesogenic groups as well as their cooperative mass transfer.

Therefore, the obtained data on the specific features of changes in the surface relief of cholesteric films makes it possible to gain a deeper insight into the processes underlying the development of nanostructured elements such as domain entities, which primarily control the optical properties of cholesterics.

VII. Polymeric liquid crystalline photoactuators

Photoactuators are materials capable of converting light energy into mechanical work. In other words, irradiation of the samples based on these materials triggers their motion — bending, changes in the linear dimensions, *etc*. The pioneering idea of polymer-based photoactuators has been advanced in 1967 by Lovrien,[152] who assumed that light irradiation may trigger conformational changes in the polymer chain, when isomerizable chromophores are incorporated into macromolecules. However, several decades have passed until this concept has been implemented. One of pioneering works on these systems was published only in 2001.[153] The authors succeeded to achieve a 20% contraction of the film based on photochromic LC elastomer, which was synthesized by the hydrosilylation of poly(methyl hydrosiloxane) **29** with a mixture of compounds **30** – **34**.

The phenomenon of contraction and changes in the linear dimensions of the film is provided by reversible *E* – *Z*-isomerization of photochromic azobenzene groups and by the transition of the oriented LC elastomer into the isotropic state due to the low anisometry of the *Z*-form, which breaks down the mesophase. However, for a given system, the rates of photoinduced deformation and relaxation appear to be exceptionally low: at room temperature, the time constant of contraction is 14 min, and the relaxation time constant is 230 min.

The problem related to the increased response rate has been solved nine years later[154] for the polymer networks based on azobenzene-containing mono- and diacrylates. The authors show that the films of these samples can oscillate with a high amplitude (Fig. 43) under the laser irradiation with varying wavelength (λ = 457, 488 and 514 nm) and even under the action of the focused sunlight. The frequency of oscillations was shown to depend on the light intensity and linear dimensions of the film and can reach 270 Hz. In our opinion, the cited publication[154] is the first proof-of-the-concept work that offers an effective photoactuator, which can be easily tuned by the light irradiation of a relatively low intensity.

To date, numerous publications, including several comprehensive reviews, have been devoted to polymeric LC photoactuators (*e.g.*, Refs 145 – 163) and several international conferences on this topical subject have been held. Therefore, in this review, we will consider only a few publications with the most interesting, in our opinion, results in this area.

Lee *et al.*[158] have shown the possibility of the control over the bending direction of the photoactuator film due to changes in the direction of light polarization. This approach was helpful for the development of the 'shape memory' materials based on the above systems. The films of photoactuators were prepared by the radical copolymerization of diacrylates **35** and **36**.

Linearly polarized light (λ = 442 nm) was applied for the photoinduced stabilization of the film geometry. Figure 44 presents the direction of bending plotted against the polarization direction. When the polarization direction coincides with the long axis of the film, the film is bent towards the irradiation source, and *vice versa*. Evidently,

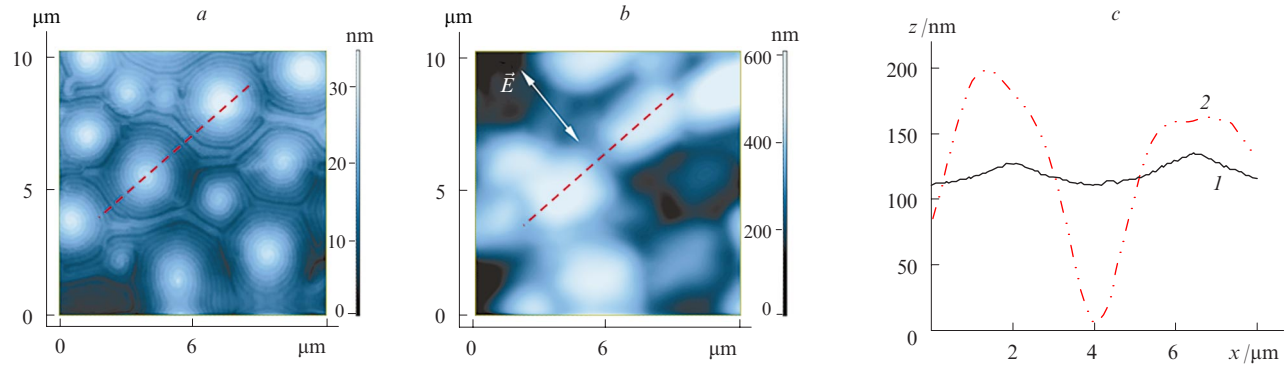
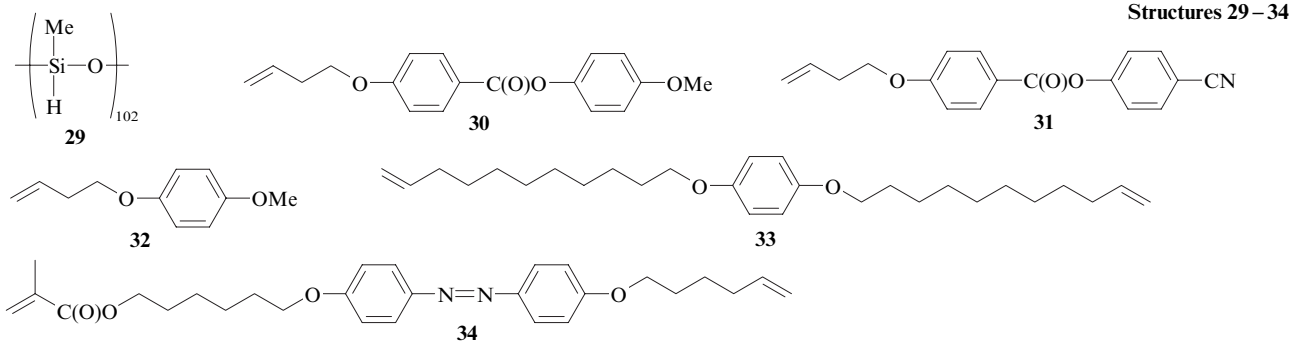


Figure 42. AFM scans of a quickly cooled (quenched) film of cyclosiloxane **27** doped with compound **28** before (*a*) and after illumination (*b*) with the green light and cross section profiles of the surface relief before (*1*) and after (*2*) the illumination (*c*).[142]
The dashed lines show the positions where the surface relief is sectioned.

Structures 29 – 34



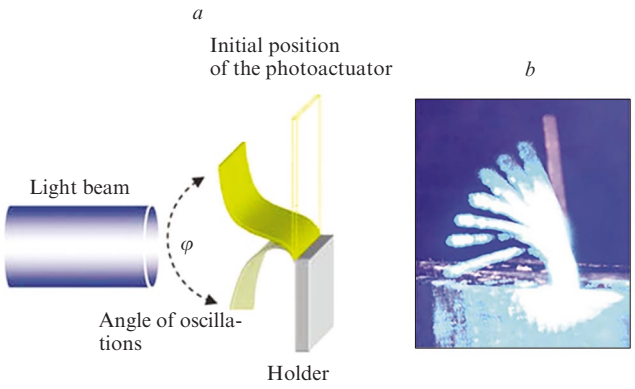


Figure 43. Scheme of the experiment demonstrating fast oscillations of the polymer film (*a*) and snapshot of the film upon its deformation under the action of a laser beam (*b*).[154, 155]
(*a*) The polymer film is positioned vertically and oscillates with respect to the horizontal plane of the laser beam incidence with the full angle of oscillations φ.

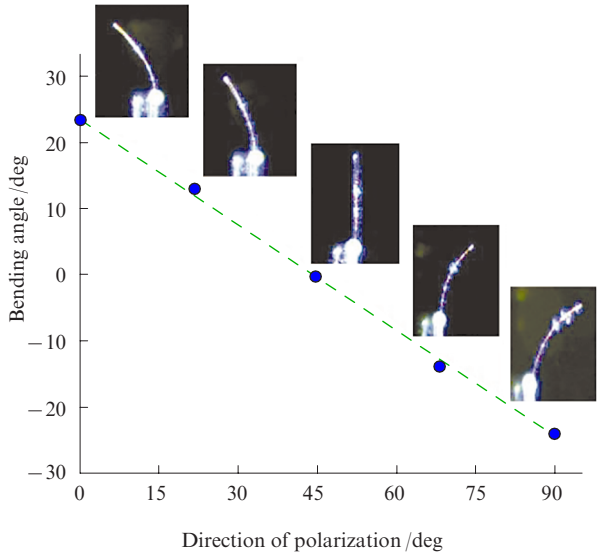


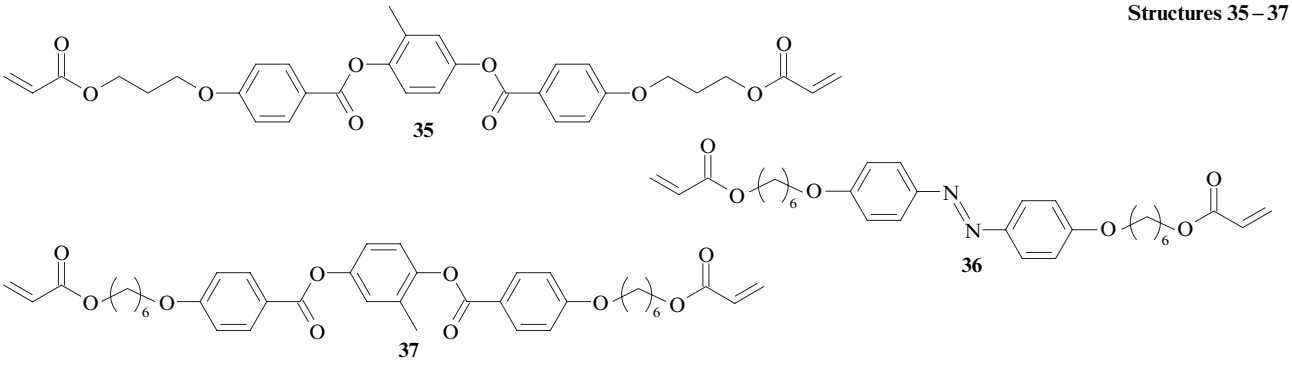
Figure 44. Bending angle of the film prepared by copolymerization of compounds **35** and **36** plotted *vs.* the angle between its long axis and the direction of blue light polarization (λ = 442 nm).[158]
The inset shows the snapshots of the film: light falls from the left.

this difference is provided by the process of cooperative photoorientation of azobenzene and benzene groups of the elastomer; however, the adequate mechanism of bending is still unclear. Combination of thermo- and photo-induced shape stabilization [158] substantially extends the functional resources of photoactuators.

In most publications on photoactuators, LC elastomers are prepared by the radical polymerization of LC monomers in a glass cell (with or without an aligning coating); to remove the free-standing film, the cell is disassembled.

In our recent works,[159] an alternative approach to the fabrication of photoactuators has been advanced. This approach involves polymerization of mesogenic and photochromic mono- and diacrylates within the matrix of the porous polyethylene. The porous oriented films of polyolefins can serve as suitable nanocontainers for the incorporation of low-molecular-mass liquid crystals; the pore walls are able to align the LC director strictly along the direction of tensile drawing of the film. The proposed approach allows the development of a photochromic polymer-stabilized weblike structure containing azobenzene moieties, which are able to undergo light-induced *E*–*Z*-isomeriza-

Structures 35 – 37



tion, within the PE pores. The composition of the photochromic polymerizable mixture involves azobenzene-containing diacrylate **36** (50%), nematogenic diacrylates **35** (12%) and **37** (36%) as well as the thermoinitiator; the mixture was loaded into the porous PE films at 95 °C; then, the thermal polymerization was performed.

Polymerization of mono- and bifunctional monomers is accompanied by the formation of a network throughout the whole volume of the polymer film. The resultant cross-linked, but rather flexible films of photoactuators are sensitive to the action of the UV (λ = 365 nm) and visible (λ = 457 nm) light. Under the action of the UV irradiation, the $E-Z$-isomerization of photochromic azobenzene groups takes place, and this process is accompanied by the decrease in their anisotropy and triggers the mechanical deformation of the polymer film: the polymer film is seen to bend (Figs. 45 and 46 *a*); once irradiation is switched off, the film experiences unbending (relaxation). The scheme shown in Fig. 47 demonstrates the mechanism of bending under the action of the UV irradiation.

Noteworthy is that, in the case of the visible light, bending of the film proceeds in the opposite direction as compared with the bending upon the UV irradiation (see Fig. 45 *b*); in other words, the mechanism of this process seems to be far more complicated and to involve photoorientation of photochromic groups and also, most likely, photoinduced heating of the film.

Note also the high rate of the reversible processes of the photoinduced bending and relaxation in the case of the visible light irradiation: both processes are accomplished within 2 s. The phenomenon of bending is related to $E-Z$-photoisomerization of azobenzene chromophores, their photoorientation under the action of the polarized light as well as the thermoinduced heating of the film.

Further progress along this line has led to the development of photomechanical devices, which resemble diverse biological objects.[160–163] A new approach [160] was proposed for the design of an array of small-sized parallel fibres,

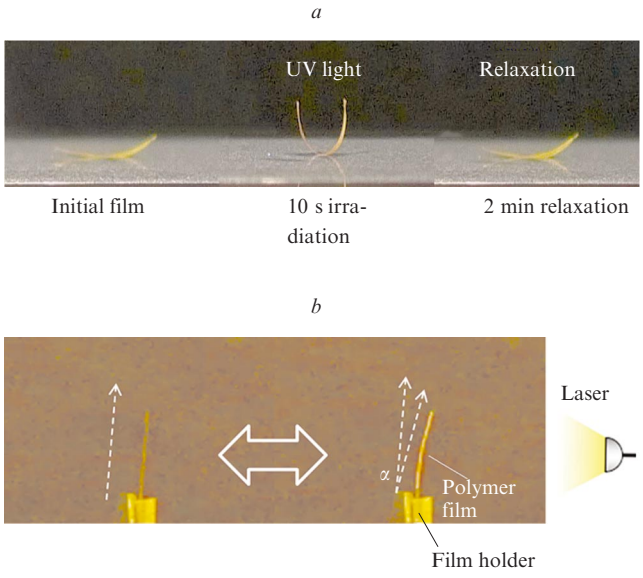


Figure 45. Snapshots of the photoactuator film prepared by copolymerization of monomers **35**–**37** during bending under the action of the UV (λ = 364 nm, 100 °C) (*a*) and visible light (λ = 457 nm, room temperature) (*b*).[159]

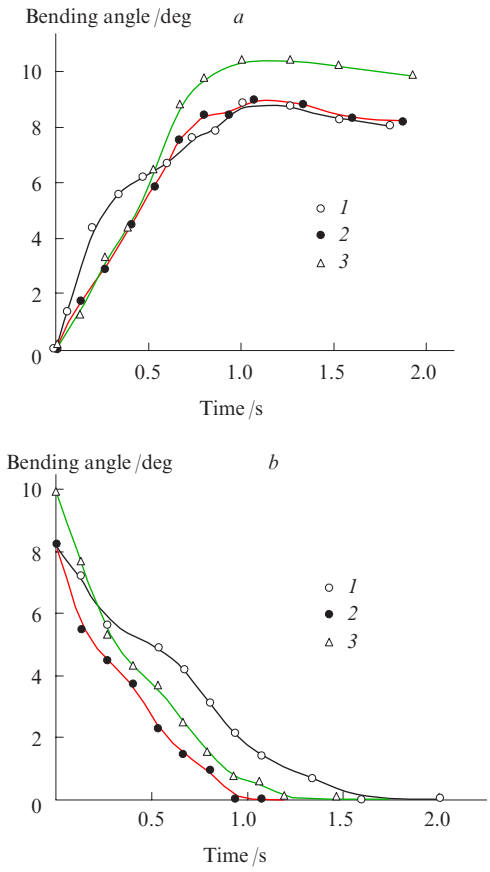


Figure 46. Kinetic dependences of the bending angle of the photoactuator film prepared by the copolymerization of monomers **35**–**37** upon illumination with visible light of varying intensity (*a*) and upon relaxation (*b*). (The figure is taken from the collection of experimental materials used for the preparation of Ref. 159 for publication.)
Intensity /mW cm^{-2}: (*1*) 380, (*2*) 444, (*3*) 520.

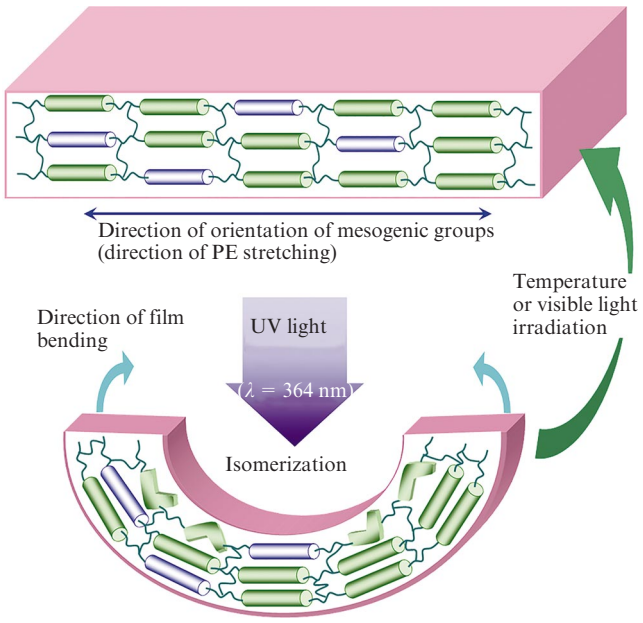
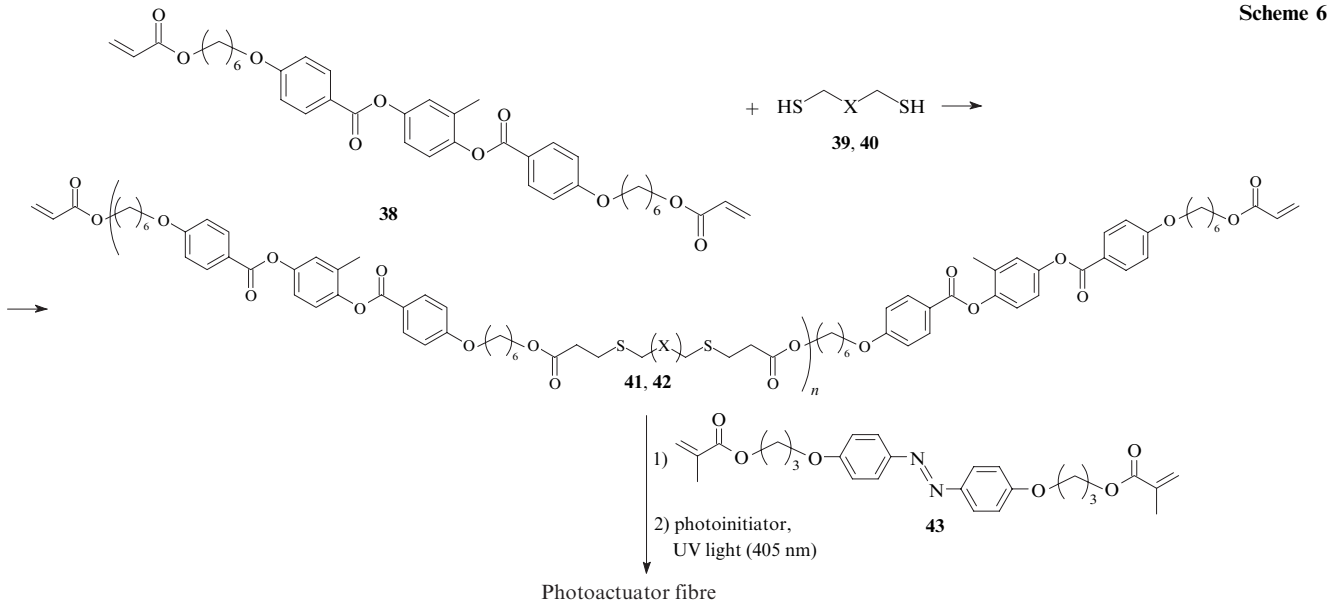


Figure 47. Operation principle of LC photoactuators based on the LC polymer network produced by polymerization of monomers **35**–**37** in a porous polyethylene matrix.[159]

Scheme 6



X = CH_2 (**39**, **41**), $CH_2OCH_2CH_2OCH_2$ (**40**, **42**)

which operate as specific 'ciliae' providing the motion of the liquid flow. The fibres are composed of the cross-linked comb-shaped LC polymer prepared by two-stage polymerization. At the first stage, reagents **38**–**40** undergo the Michael addition reaction (Scheme 6) to give oligomers **41** and **42**; next, the resultant oligomers are cross-linked *via* photopolymerization in the presence of azobenzene-containing diacrylate **43** and the photoinitiator.

The procedure for the preparation of fibres is illustrated in Fig. 48 *a*, and the corresponding snapshot is presented in Fig. 48 *b*.[160]

Under the action of UV radiation, the as-prepared fibres experience a cooperative bending towards the UV light source (Fig. 49). Mechanical deformation of the fibres is provided by the *E*–*Z*-photoisomerization of azobenzene groups (as in the above-cited work [153]). Due to the high optical density of fibres, this process primarily proceeds on one side of the fibre (which is closer to the light source), thus leading to bending.

When the fibres are immersed into a liquid, their cooperative bending generates the flow, which is able to move small-sized objects (see Fig. 49). The average rate of displacement is 0.56 mm s^{-1} at 80 °C.

Optically induced reversible development of complex topographic structures in the elastic films of azobenzene-containing LC polymers was studied by Ahn *et al.*[161] Surface alignment allows the preparation of complex structures with different local orientation of the LC director. The UV irradiation (λ = 365 nm) of the films leads to their photomechanical deformation and reversible 2D – 3D transformation of the film shape. When the UV irradiation is switched off, the shape of the film is metastable but its 2D shape can be easily recovered under the action of the visible light (λ = 532 nm). The authors believe that these materials are

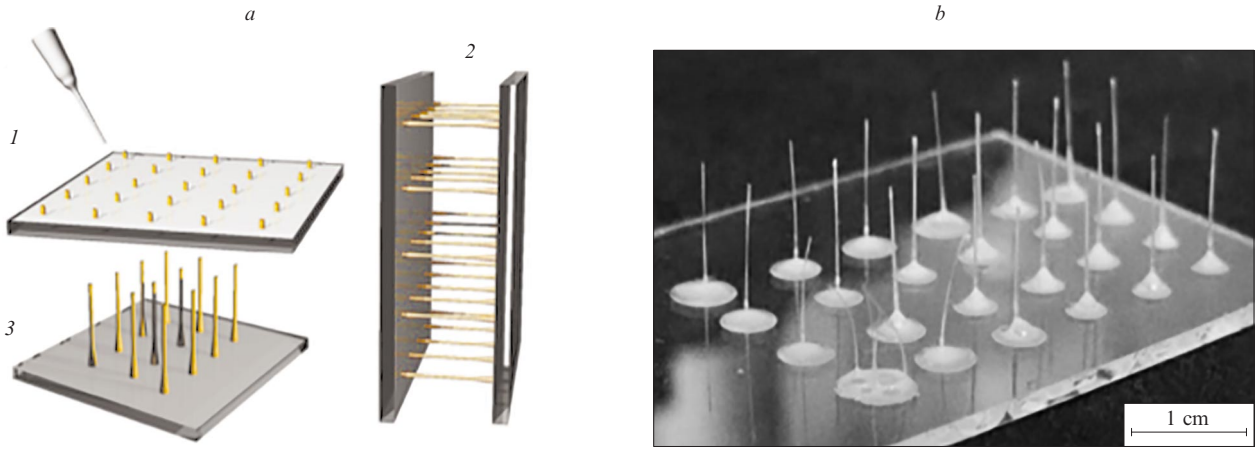


Figure 48. Scheme (*a*) and snapshot of the prepared fibres (*b*).[160]
(*a*) Droplets of the polymerizing blend **41** (**42**) + **43** are placed onto a glass substrate in a definite order (*1*); the separation of the plates gives fibres (*2*); array of fibres is formed after polymerization and one-side cutting of fibres (*3*).

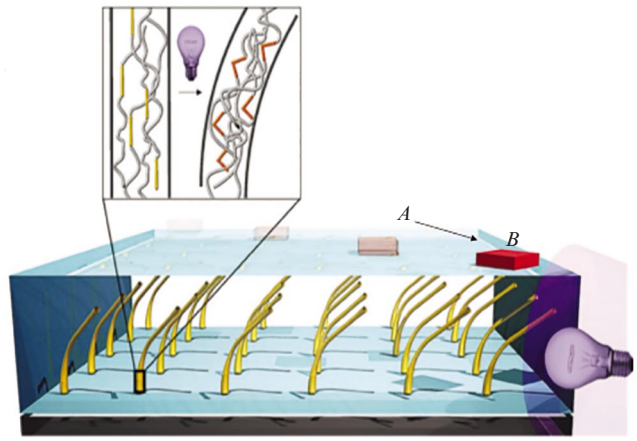


Figure 49. Scheme illustrating the cooperative bending of photoresponsive fibres, which forces moving of a floating subject from position *A* to position *B*.[160]

promising for their diverse applications in optics and medicine.

A fascinating version of photoactuators which mimic the motion of seedpod opening driven by elastomeric 'springs' prepared by photopolymerization has been advanced by Aßhoff *et al.*[162] The propagation of many plants occurs *via* violent explosion of seedpods. Plant pods typically feature a flat hull comprising two narrow fibrous layers oriented at angles of $+45^\circ$ and -45° with respect to the longitudinal axis of the pod (Fig. 50 *a*). When the pod dries, each fibrous layer shrinks perpendicularly to its orientation (shown by arrows), inducing mirror-image saddle-like curvatures and eventually a dramatic opening of the seedpod. Following this analogy, the authors prepared the LC networks featuring periodically alternating bars. One set of bars is polymerized in the state of lowered LC order (see Fig. 50 *b*); as a result, elongation of these bars upon further UV irradiation is negligibly small. Other bars are polymerized while retaining a high LC order state and, upon further stimulation, they exhibit an anisotropic shape transformation (see Fig. 50 *c*). The difference in the level of LC ordering was provided by the polymerization under the action of light of different wavelengths: in the case of the UV irradiation, polymerization is coupled to the *E*–*Z*-isomerization (see Fig. 50 *c*), and the degree of LC order is reduced. Upon irradiation with the visible light, the degree of the LC order is appreciably higher.

Figure 51 illustrates the mechanism of opening of an artificial pod. Two mirror-image ribbons (*1*) were cut from the film and assembled into an artificial seedpod (*2*). Under the UV light irradiation, the valves initially bend along their long axes (*3*) and, next, they bend along the short axes to form a hollow cavity at their centre (*4*) until the valves suddenly detach from each other and twist into springs, and the pod opens.

Therefore, this work demonstrates the design of photomechanical devices based on the LC polymers where the potential energy is stored as the elastic energy and can be released under the light stimulus.

Liquid crystalline photoactuators can find their practical application in the areas related to the design of diverse light-controlled mechanical devices, microrobots, valves, pumps for microfluidics, *etc.*

VIII. Photochromic liquid crystalline gels

In the colloid chemistry, gels are systems with a liquid dispersion phase, where the gel-forming particles produce a three-dimensional network. In the case of the high-molecular-mass compounds, a polymeric framework is stabilized by intermolecular contacts and entanglements; voids of the as-formed network are filled with a solvent, in which the polymer is usually insoluble but can swell, thus markedly increasing the dimensions of the sample. Due to the presence of the three-dimensional network, the gels acquire the mechanical properties of a solid: the absence of

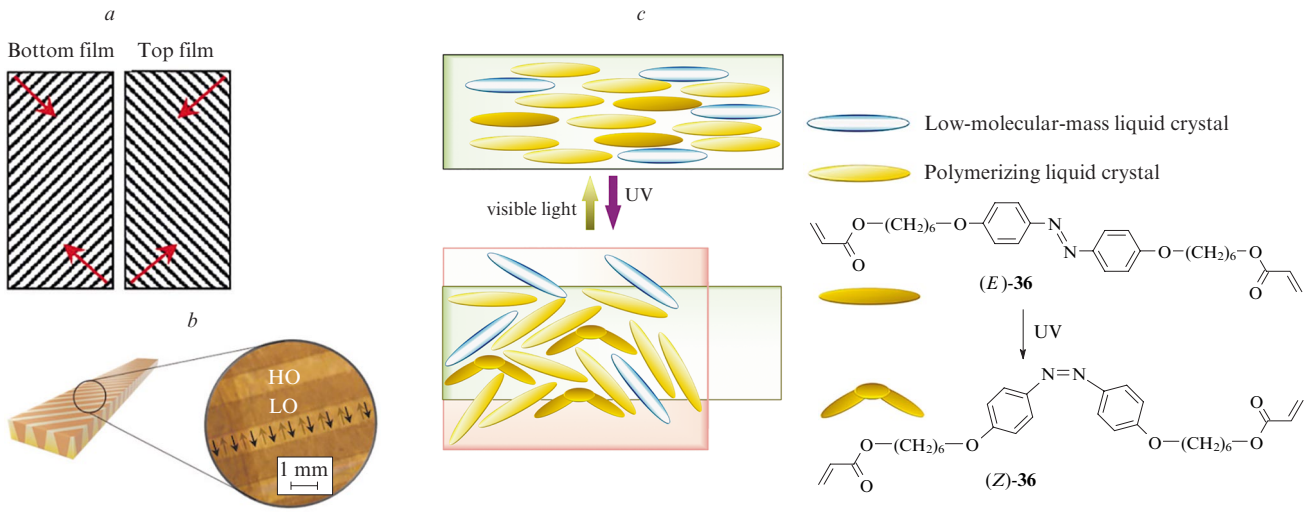


Figure 50. Scheme illustrating the molecular design of photoactuators mimicking the operation of seedpods.[162]
(*a*) Rigid fibres are oriented perpendicular to each other in each of two valves in a seedpod; the arrows show the direction of the contraction upon drying; (*b*) the LC network with periodically alternating layers with higher (HO) and lower (LO) LC order; (*c*) scheme illustrating the photoinduced isomerization of diacrylate **36** leading to disordering of the LC network and film deformation.

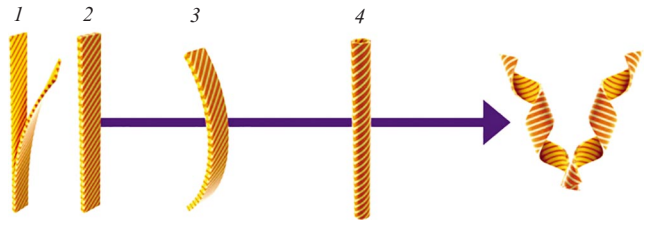


Figure 51. Mechanism of artificial seedpod valve actuation.[162] (*1* – *4*) See text.

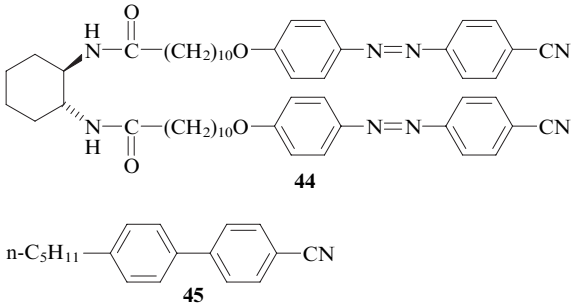
fluidity, strength, ductility, and elasticity. The substances, including polymers, that are able to produce a three-dimensional network, are referred to as gelators.

Gels occupy a special place among diverse smart materials. The interest in these systems has been primarily inspired by their ability to experience rapid and, in some cases, reversible changes in mechanical properties and linear dimensions (due to shrinkage or swelling) under the action of external stimuli (light irradiation, changes in pH, temperature, mechanical strain, *etc.*). Most promising are photoresponsive gels, as light is a powerful and convenient tool providing a fast, remote, and local impact on the mechanical characteristics of materials, including gels.[164 – 176]

This review primarily addresses the LC gels, which combine unique optical characteristics of liquid crystals and gel-forming properties due to the introduction of low-molecular-mass or polymeric gelators.[174 – 187] This review is focused on the description of photosensitive LC gels, which are capable of marked light-induced structural changes and photoinduced gel – sol transition.

The work by Moriyama *et al.*[176] is one of the pioneering studies on these systems. This work is concerned with the photoinduced melting of the gel containing hydrogen-bonded chiral gelator **44** in the dispersion medium of the nematic **45**.

Structures 44, 45



44

45

This mixture is characterized by several structural states, and the transition between these states proceeds upon temperature variations or UV irradiation (Fig. 52). Upon heating above the isotropization and melting temperatures of the gel, an ordinary homogeneous solution without any anisotropic properties is formed (see Fig. 52 *a*). Upon cooling, the nematic gel is produced due to the formation of hydrogen bonds between the gelator molecules (see Fig. 52 *b*). Upon the UV irradiation, the gel melts down and the molecules **44** are dissolved in the nematic (see Fig. 52 *c*). This behaviour is provided by the *E* – *Z*-isomerization of azobenzene groups; the *Z*-form of compound **44** is unable to produce a gel because of the low anisometry of the molecules. Due to the chirality of molecules **44**, the nematic phase transforms to the cholesteric phase, as can be seen from the characteristic texture. When the illuminated mixture is allowed to stand at room temperature for a week, the back *Z* – *E*-isomerization and stabilization of the cholesteric phase take place (see Fig. 52 *d*). Upon further heating of the cholesteric gel to 120 °C, the LC phase and the gel

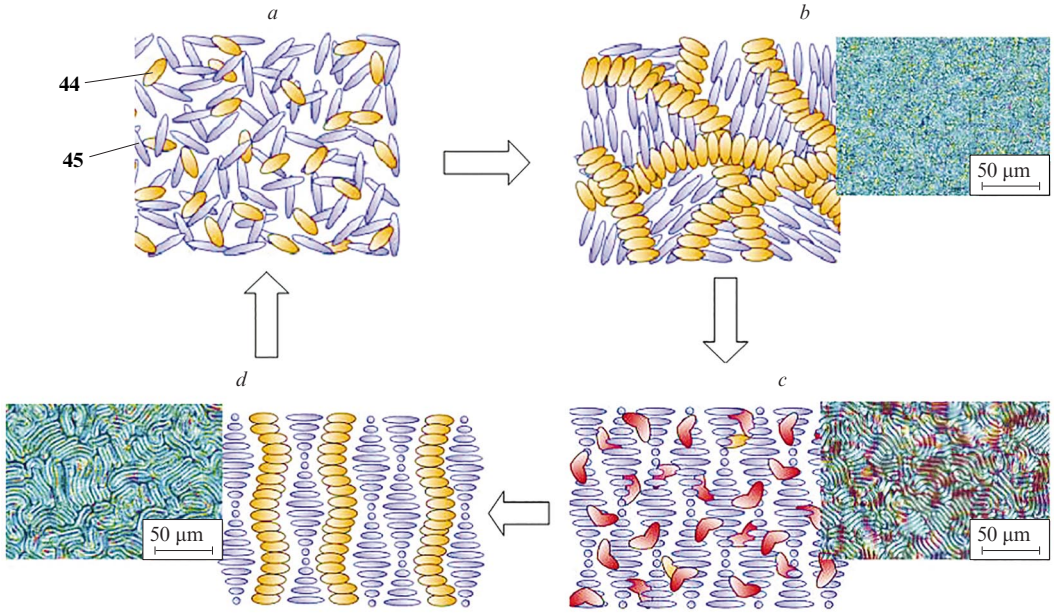


Figure 52. Schemes of structural transformation of the blend of nematic components with 3 mass % of a gelator and POM images of the textures.[176]
(*a*) Initial homogeneous solution of compound **44** in nematic **45**; (*b*) gel produced upon cooling of the solution at room temperature; (*c*) formation of the cholesteric phase after UV irradiation; (*d*) formation of hydrogen bonds and the cholesteric gel when the irradiated blend is allowed to stand at room temperature.

melt down (see Fig. 52 *a*). This material[176] presents an evident interest from the viewpoint of the optical data recording (Fig. 53).

An interesting example concerning the development of electroswitchable diffraction gratings based on cholesteric gels, which, in addition to the gelator **46**, contain the nematic mixture of cyanobiphenyl derivatives doped with chiral compound **47**, was reported by Zhao and Tong.[177] The UV irradiation of the initial gel (Fig. 54 *a*) through the periodic mask affords diffraction gratings due to the local photoinduced gel melting (see Fig. 54 *b* – *d*).

The illuminated gratings can be tuned by an external electric field. Under the applied electric field, the diffraction efficiency is quickly changed, and the scenario of this process with increasing the intensity of the external impact is far from being trivial: in the course of the first cycle (curve *1* in Fig. 55), the diffraction efficiency initially decreases but then increases. This initial downturn at low field intensity is related to the transition of the planar texture to the unoriented confocal texture, which is capable of pronounced light scattering. As a result, the diffraction efficiency decreases. Next, the confocal texture is transformed into a transparent homeotropic texture, and the diffraction efficiency increases. Upon further repeated cycles of the external field variations (curves *2* and *3* in Fig. 55), the diffraction efficiency increases with increasing field intensity. For the diffraction grating, switch-on and switch-off times are equal to 65 and 50 ms, respectively; these values are seen to exceed the characteristic times of the Fredericks transition for a pure liquid crystal (units of milliseconds).[188]

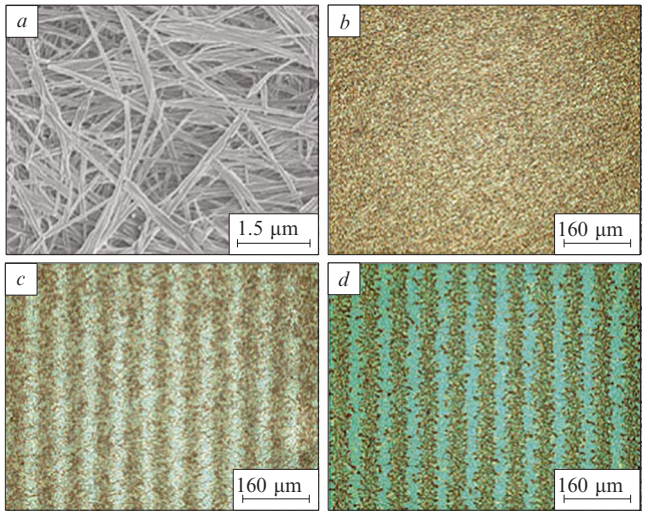
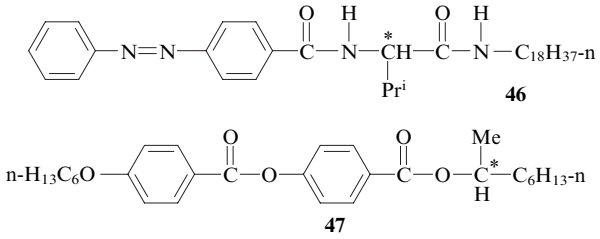


Figure 54. SEM images of the fibrous aggregates produced by the gel based on a mixture of a nematic, gelator **46** (1%), and chiral dopant **47** (5%) (*a*) and POM images of the LC gel upon the UV light irradiation (*b* – *d*).[177]
Duration of the UV irradiation /min: (*b*) 0, (*c*) 5, (*d*) 10.

Structures 46, 47



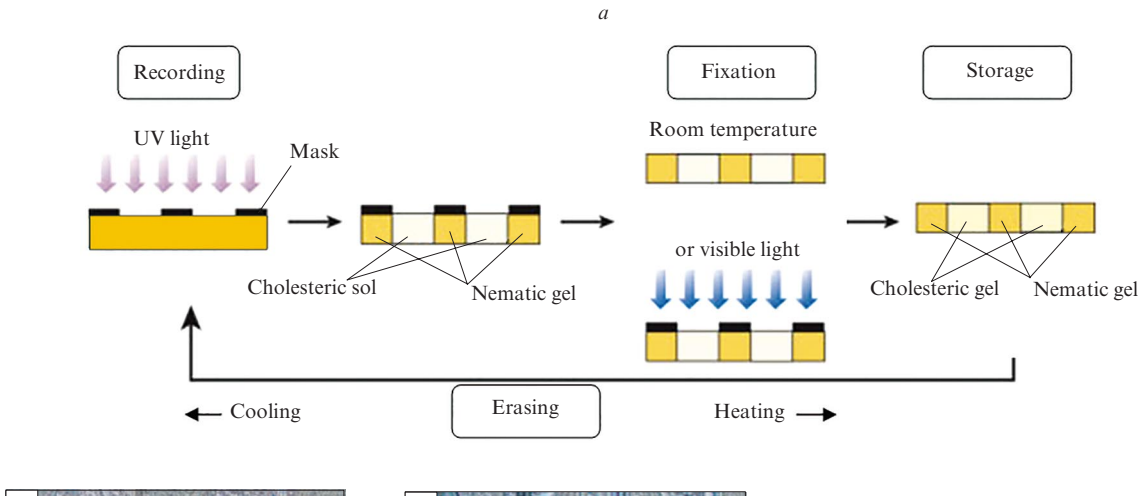


Figure 53. Scheme illustrating the principle of image recording on photochromic LC gels (*a*) and POM images of the structures recorded on the gel under the action of UV irradiation through different masks (*b*, *c*).[176]

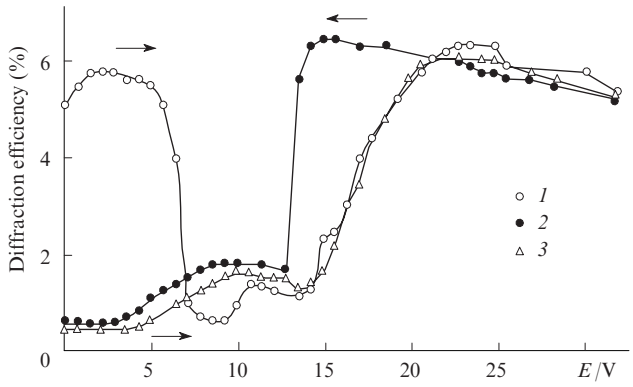


Figure 55. Diffraction efficiency of the first-order photoinduced grating based on photochromic LC gel *vs.* the applied electric field.[177]
(*1* – *3*) See text. The arrows show the direction of changes in electric field intensity: ⟶ is increase and ⟵ is decrease.

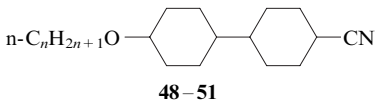
Therefore, the use of photochromic gelators allows the preparation of photochromic LC gels with fascinating optical properties and offers the pathways for the control over these properties by variation of the external electric field. However, noteworthy is that, despite evident progress along this line, there are no studies on the phenomenon of changes in the mechanical properties of the LC gels (flowability) under the light stimulus.

The possible use of polymeric and low-molecular-mass photochromic compounds as gelators for low-molecular-mass nematic and cholesteric liquid crystals has been studied.[186, 187] As photochromic gelators, azobenzene derivatives were synthesized and characterized; these compounds are able to produce ordered phases at room temperature. Systematic search for efficient gelators (such as low-molecular-mass and polymeric azobenzene and cinnamoyl derivatives) has been performed for different low-molecular-mass liquid crystals (derivatives of cyanobiphenyl, cyclohexane, *etc.*)

For the nematic LC mixture of compounds **48** – **51** (commercial mixture of cyanobicyclohexane derivatives), two efficient photochromic gelators were selected: polymer **52** and banana-shaped photochromic compound (*E*)-**53**. When the LC mixture doped with 1 mass % – 3 mass % of the gelator **52** is heated up to 120 °C (isotropic melt), the components are fully dissolved, and a homogeneous transparent melt is formed. However, upon cooling to room temperature, a strong clouding is observed, and a solid gel is formed (Fig. 56 *a*).

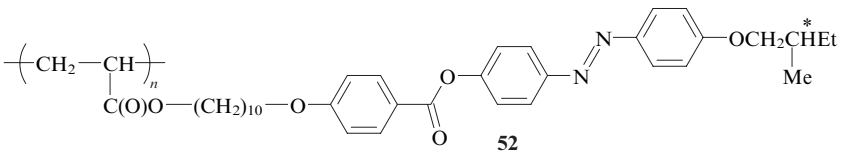
Upon UV irradiation of the gel based on the low-molecular-mass gelator (*E*)-**53**, the gel melts down (see Fig. 56 *b*). This melting is related to the *E* – *Z*-isomerization

Structures 48 – 52



48 – **51**

n = 2 (**48**), 3 (**49**), 4 (**50**), 7 (**51**)



52

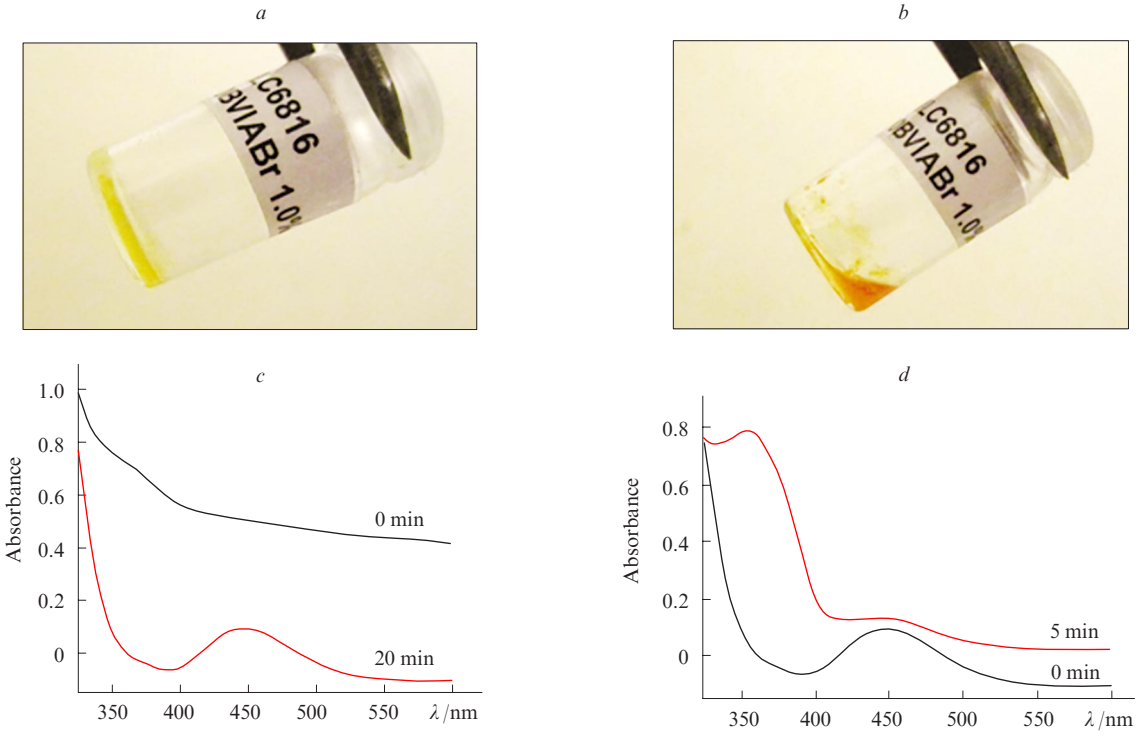
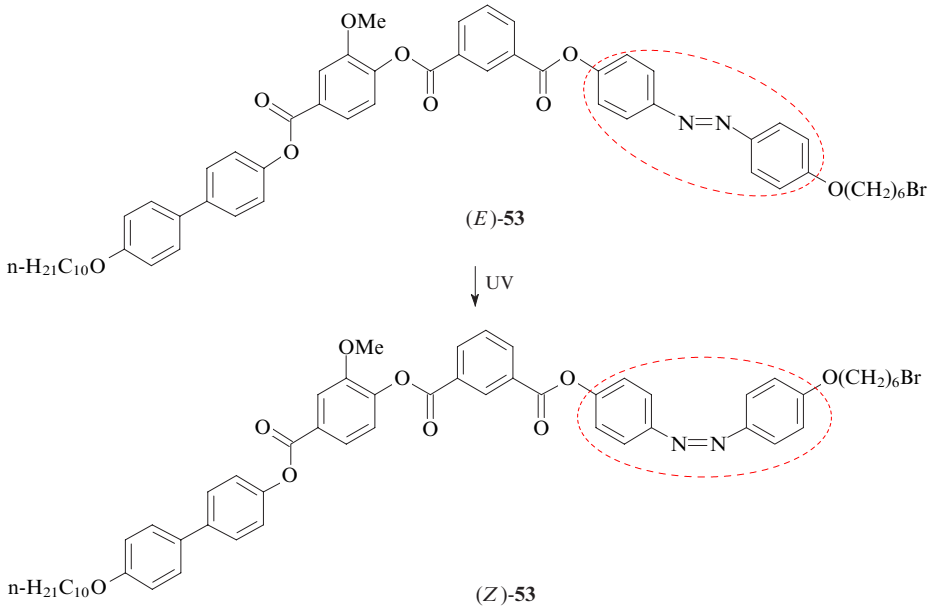


Figure 56. Snapshots of a nematic mixture of compounds **48** – **51** and banana-shaped gelator **53** (1.0%) before (*a*) and after (*b*) UV-irradiation (λ = 380 nm) and absorbance spectra of the gel containing 2.6 mass % of photochrome **53** upon the UV light irradiation (*c*) and subsequent visible light irradiation (λ = 436 nm) (*d*).[187]

Scheme 7



of the photochromic compound (Scheme 7); as a result, the dopant crystals melt down, and the formed Z-isomer **53** is dissolved in the liquid crystal (see also Fig. 57).

Figure 56 *c*,*d* presents the data on photooptical characteristics of photochromic gels. As follows from Fig. 55 *c*, the gel is characterized by low light transmittance and absorbs the light over the entire spectral range, and this behaviour is provided by light scattering due to the presence of two phases, nematic and crystalline. The slight shoulder in the spectrum at a wavelength of ~360 nm is related to the electronic π – π*-transition of azobenzene chromophores in the *E*-form. Upon the UV irradiation, the absorbance goes down due to the melting of the gel. In the photostationary state, the spectra clearly show the peak with a maximum at about 450 nm, which corresponds to the electronic n – π*-transition of the azobenzene chromophore to the *E*- and *Z*-form. Due to the subsequent irradiation with the visible light, the intensity of the electronic n – π*-transition decreases, and the absorbance markedly increases in the region of the electronic π – π*-transition of azobenzene chromophores in the *E*-form (see Fig. 56 *d*). This process is accompanied by the simultaneous upturn of the absorbance over the entire spectral region due to the back process of crystallization of the *E*-isomer in the course of the *Z* – *E*-isomerization and gelation.

For the first time, photochromic LC gels were prepared and feasibility of their reversible melting under the action of UV irradiation was proved in joint studies of Russian and Czech researchers.[187] This presents a considerable interest from the viewpoint of practical application of the phenomenon of photoinduced melting of gel systems.

Therefore, photochromic LC gels feature a new class of smart materials, which can experience several interesting photoinduced transformations such as photoisomerization and isothermal melting under the light irradiation. These phenomena were applied for the photooptical image recording and development of photo- and electrotunable diffraction gratings.[176, 177] The evidence available to date allows the conclusion concerning good prospects for their further study and use.

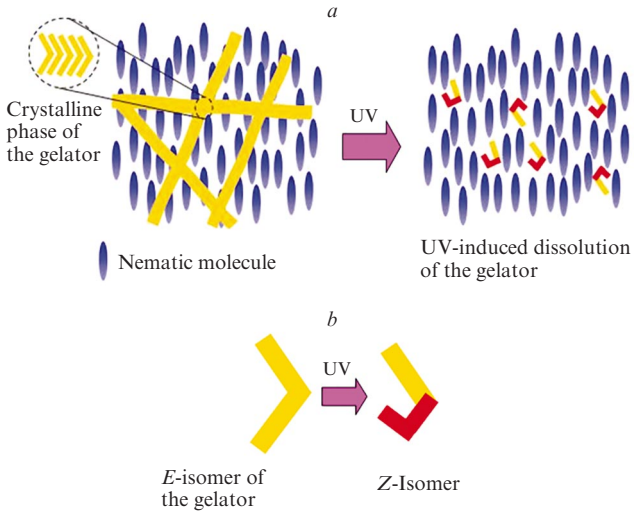


Figure 57. Schemes illustrating structural transformations (*a*) and melting (*b*) of the gel based on banana-shaped compound (*E*)-**53** under the UV irradiation.[187]

IX. Photocontrollable liquid crystalline composites

Since long ago, the attention of scientists has been attracted to the methods for the design of the LC composites by the preparation of mixtures of liquid crystals with inorganic materials (silica, porous glasses) and polymers. From the practical viewpoint, the advantages of these systems are evident: they successfully combine the properties of polymers (the ability to form films, fibres, and coatings) and nematic and cholesteric liquid crystals (the ability to experience orientational transformations under the action of external fields and changes in optical characteristics such as transparency, light scattering, colour, *etc*.). Examples of the above well-known materials are provided by polymer-dispersed liquid crystals and thermoresponsive films based on cholesterics.[189 – 192]

Note an alternative approach to this problem, which has been advanced by the researchers from the Lomonosov Moscow State University (Department of Chemistry, Division of High Molecular Compounds). This approach involves the introduction of diverse low-molecular-mass compounds, including dyes and liquid crystals, into so-called crazed polymeric films. These porous films are usually prepared by tensile drawing of solid polymers in the presence of adsorptionally active liquid environments (low-molecular-mass compounds are dissolved in these solvents, which are later sorbed at the pore walls and at the solid/liquid interfaces). More information on this subject can be found in the publications by Bakeev and Volynskii (for example, see monograph [193]).

A new approach for the development of polymer-based LC composites was based on the use of highly oriented porous films of widely used commercial polymers such as polyethylene and polypropylene, when their pores are loaded with liquid crystals and photochromic compounds.[194 – 200]

Microporous PE films with a thickness of 10 – 25 μm were first prepared by the researchers from the Institute of Macromolecular Compounds (Russian Academy of Sciences) by the extrusion of polymer melts followed by annealing, tensile drawing, and thermal stabilization.[194] As a result of this treatment, polymer films become opaque and milky white (due to the highly porous oriented structure). The overall porosity of these films is 40% – 50%. Electron microscopic examination prove the existence of the highly porous structure with numerous fibrils oriented along the direction of tensile drawing (Fig. 58 *a*). In this work, the samples prepared at the laboratory of the Institute of Macromolecular Compounds (Russian Academy of Sciences) and commercial porous PP films (Celgard) were used.[194 – 201]

The PE-based composites containing liquid crystals (commercial nematic mixtures of different compositions) were prepared by the method of dip coating when the layer of the liquid crystal (the excess was removed) was deposited onto the surface of the PE film. The nematics were selected so that the mean refractive indices of the LC mixture and PE were the same. After the introduction of the LC mixture into the sample, the PE film becomes transparent (see Fig. 58 *b*), whereas in the crossed polarizers, bright colouring is observed, and this observation suggests a strong birefringence (see Fig. 58 *c*), and the direction of the optical axis coincides with the direction of the tensile drawing of the PE film. This fact implies that the liquid crystalline molecules are oriented strictly along the direction of preliminary stretching.

This direction of orientation was proved when minor amounts of dichroic dyes (azobenzene, merocyanine, stilbene, *etc*.) were introduced into the LC matrix. In these systems, dichroic ratio is only ~20% lower than that in the standard glass cell with the aligning polyimide coating.[198] Therefore, the degree of orientation of the LC molecules in the composites is fairly high and can be compared with the degree of orientation achieved by standard methods using aligning substrates or under the action of external fields.

The strong aligning effect of the pore walls enables photooptical recording on the composites that contain high concentrations of the chiral photochromic dopant **6**, which is dissolved in the nematic matrix. For the LC composite with a negligibly small helix pitch (< 200 nm), a partial helix formation is observed. Under the action of UV irradiation, the *E* – *Z*-isomerization of the dopant provides a complete helical untwisting within the pores of the composite. As a result, birefringence and dichroism of the incorporated dye markedly increase.[195] When the above composite samples were illuminated through the mask, the feasibility of the recording of the reference grating was proved (see Fig. 58 *c*).

However, essential drawback of the above PE-based composites is related to the possible diffusion of the components of the low-molecular-mass LC additive. To prevent this, the LC mixtures containing monoacrylates **54**, **55** and diacrylate **37** with a photoinitiator were used. The UV irradiation of these systems triggers photopolymerization, formation of the three-dimensional network pro-

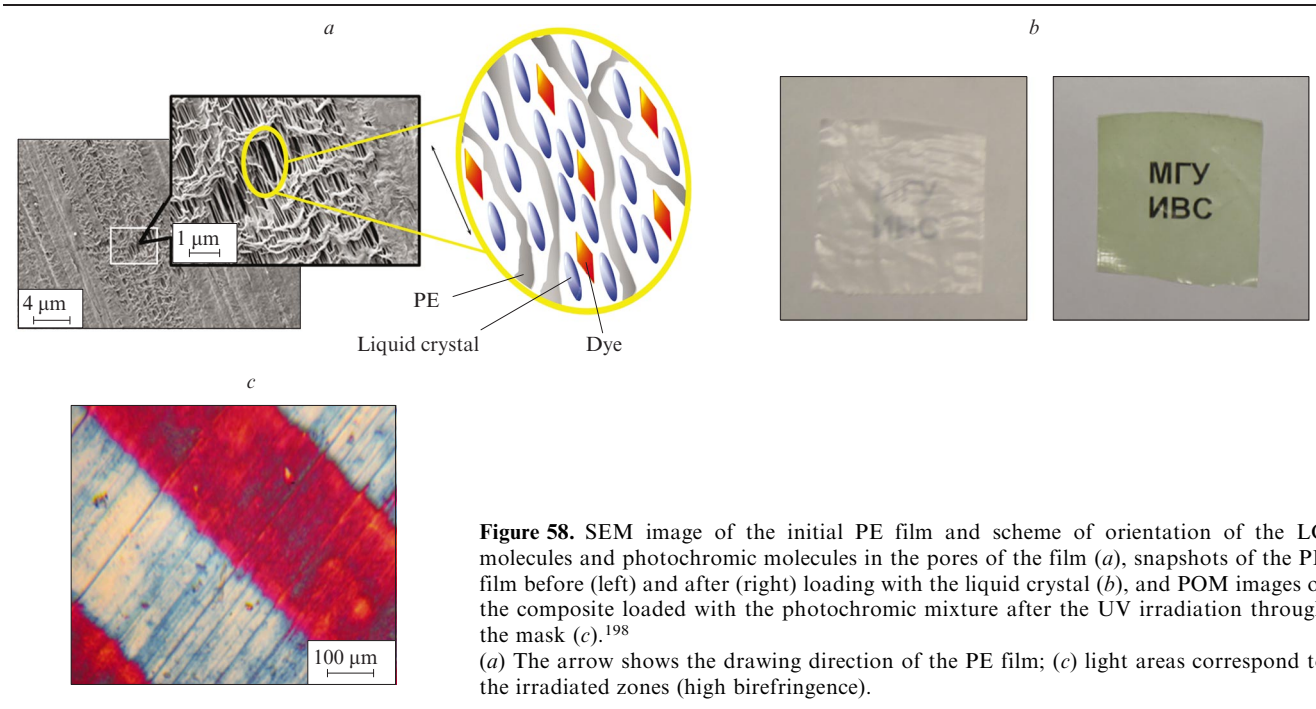


Figure 58. SEM image of the initial PE film and scheme of orientation of the LC molecules and photochromic molecules in the pores of the film (*a*), snapshots of the PE film before (left) and after (right) loading with the liquid crystal (*b*), and POM images of the composite loaded with the photochromic mixture after the UV irradiation through the mask (*c*).[198]
(*a*) The arrow shows the drawing direction of the PE film; (*c*) light areas correspond to the irradiated zones (high birefringence).

viding structural stabilization, and improvement of the mechanical properties of the composite.

This method of stabilization served for the preparation of a series of photochromic films containing photoactive components based on spiropyran **56**, **57**, diarylethylene **58**, **59** (Fig. 59 *a*,*b*) as well as films containing fluorescent perylene moiety **55**. Spiropyran and diarylethylene derivatives are characterized by a clear-cut photochromism and are able to isomerize under the action of UV irradiation, resulting in the formation of a coloured photoreaction product (Scheme 8).[198]

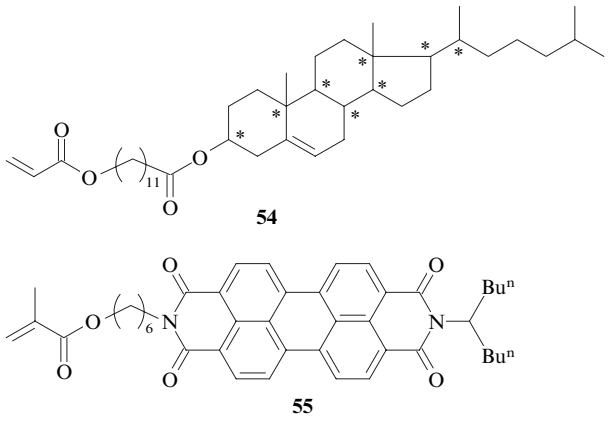
Figure 59 *a* shows the micrograph of the film of the photochromic liquid crystalline PE-based composite where the dark regions of the film with a width of 0.5 mm correspond to the LC network containing the photochrome in the merocyanine (coloured) form. Figure 59 *b* presents the POM image of this composite: bright bands correspond to the LC polymer which, as compared with the PE matrix, is characterized by a higher birefringence. Both films were exposed to the UV irradiation (λ = 365 nm) through the mask; then, the non-polymerized fraction of the LC mixture was removed by being dissolved in acetone.

Liquid crystalline PE-based composites with perylene fluorophores **55** are characterized by a linearly polarized emission (see Fig. 59 *c*), which is related to their high orientation in the matrix of the LC polymer within the porous PE film.

Another approach providing the photocontrol over the optical properties of liquid crystalline PE-based composites involves incorporation of azobenzene dopants[197] or azobenzene-containing copolymers into the pores of the polyolefin films.[200] In this case, the UV irradiation triggers isomerization of the azo compound, which is accompanied by the transition from the nematic to isotropic phase and leads to the reduction of birefringence. This approach allows reversible recording of optical images. The image of the copolymer at room temperature was stable for not less than 15 days, and this phenomenon was provided by the copolymerization of the components within the porous PE matrix and the lateral methyl substituents of the azobenzene chromophore, which stabilized the photoinduced *Z*-form of azobenzene groups.

Unfortunately, small pore dimensions preclude the Fredericks transition of the nematics involved in the above composites. The applied electric field with an intensity of

Structures 54, 55



300 – 350 V is unable to trigger the reorientation of LC molecules and, as the field intensity increases, the breakdown of the films takes place. However, it has been demonstrated[201] that electrooptical switching of the ferroelectric LC mixture (which produces the SmC* phase) within the PE pores is feasible. The switch-on/switch-off time of these composites was ~30 ms at a saturation voltage of about 2×10^7 V m^{-1}. A simple theoretical model explaining the reorientation of molecules of ferroelectric liquid crystals within the PE pores has been advanced, and this model agrees with the experimental data.[201]

The above new approaches to the preparation of photochromic and fluorescent liquid crystalline PE- and PP-based composites offer promising routes for the development of multifunctional materials based on widely used polymers such as polyolefins and also highlight the roadmap for the preparation of phototunable LC composites based on diverse porous polymeric materials.

X. Photoinduced diffraction gratings based on polymeric cholesterics

In optics and spectroscopy, main elements of devices are diffraction gratings, and their operation is based on the phenomenon of light diffraction. Usually, these gratings feature an array of multiple regularly arranged bars (slits,

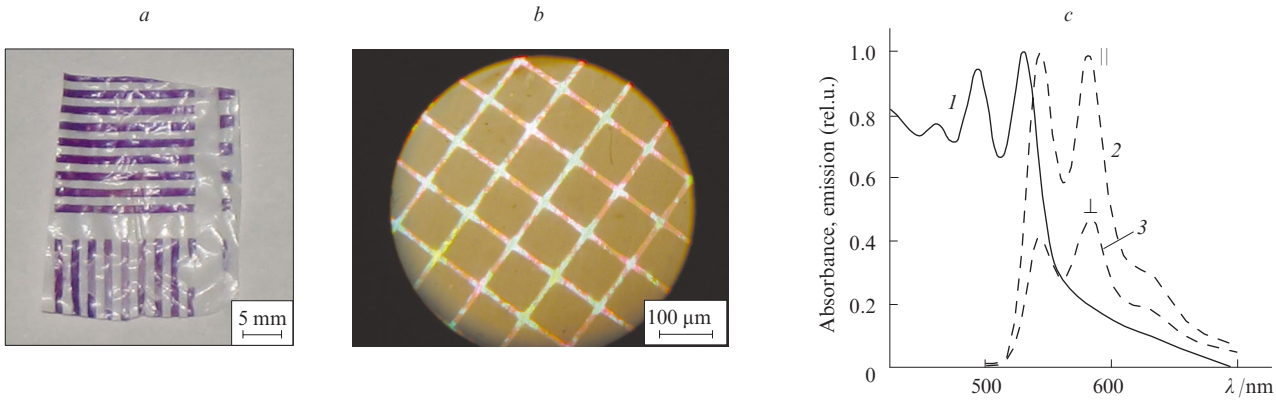
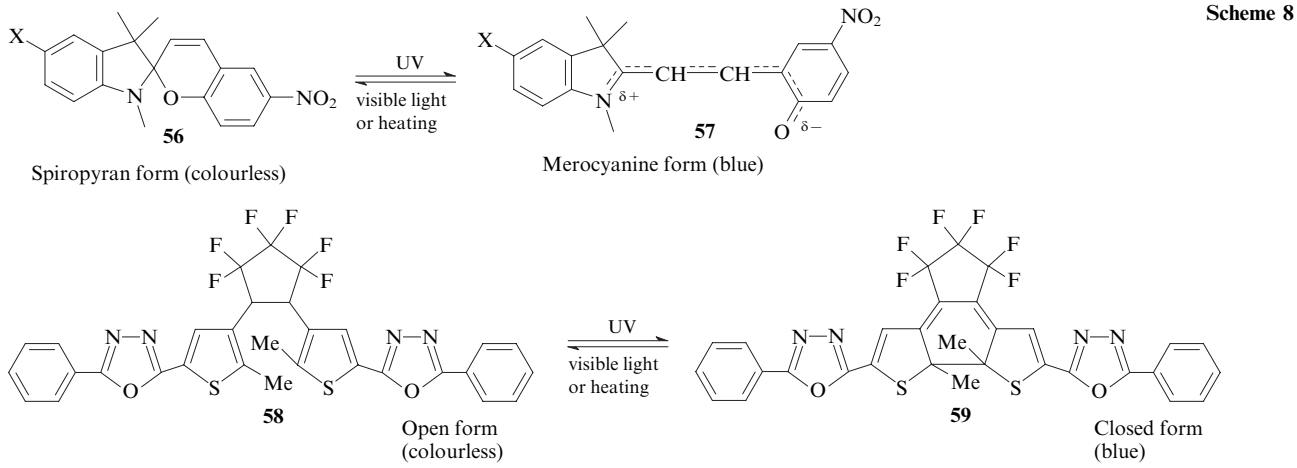


Figure 59. Snapshot of the liquid crystalline PE-composite film based on the cross-linked polymer network containing spiropyran photochrome **57** (*a*),[198] POM image of the PE composite prepared by polymerization of a mixture of mono- and diacrylates using the mask (*b*), and absorbance (*1*) and polarized fluorescence (*2*, *3*) spectra of the PE composite containing perylene fluorophores **55** (*c*).[196]

Scheme 8



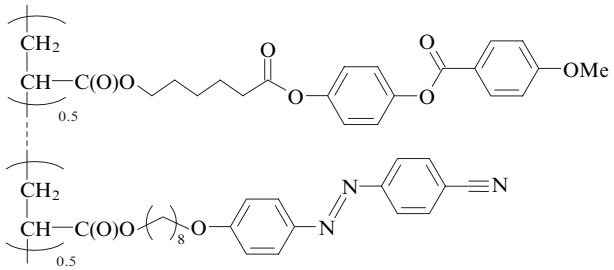
bulges) deposited onto an appropriate surface or layers (films) with alternating absorbance or refractive index. Due to their fast response to the action of weak external fields and unique optical properties, liquid crystals seem to be promising for the development of photo- and electrotunable gratings. The most used routes providing the development of these gratings in the LC systems include the controlled periodic changes in the orientation of the LC director upon a special treatment of the substrates [202 – 207] or variation of the external electric field, which generates periodic modulations of the orientation of the LC director.[208 – 215]

Polymer-based LC systems seem to have no future from the standpoint of the preparation of quickly switchable optical media, but they offer great opportunities for the fabrication of passive optical elements whose parameters can be controlled by different modes of orientation and deformation of the LC director field, including light irradiation or the action of electric field.[17, 20]

The best studied method for the development of periodic structures in the polymeric systems is the holographic recording. Back in the mid-1980s, a group of German scientists [216, 217] succeeded to perform the holographic recording of the diffraction gratings and images for the films of azobenzene-containing polymers. To date, recording of various gratings for amorphous and nematic polymer films due to photoalignment processes (see Section III) or due to the development of the periodic surface pattern have been reported in numerous publications.[218 – 223] Noteworthy is that, viewed from this angle, smectic and cholesteric polymer systems remain largely unexplored. Usually, the smectic phase is known to strongly suppress photoalignment and mass transfer processes and, in its unoriented form, it shows an intense light scattering. The cholesteric phase is characterized by an immense optical activity, and this fact strongly complicates the recording of gratings and evaluation of their optical (polarization) characteristics.

Nevertheless, the development of periodic diffraction gratings on polymer cholesterics upon photoalignment processes was studied in several works.[224 – 229] Of special interest is our work published together with German scientists [227] where the dual image recording was accomplished for the cholesteric blend of the nematic copolymer **60** with the chiral photochromic dopant **6** (Fig. 60). The first image was recorded due to photoinduced modulations of the helix pitch (upon photoisomerization of the chiral dopant), and the second image (on the top of the already recorded image) was fabricated *via* the holographic recording of gratings (due to photoalignment of azobenzene groups).

Structure 60



60

The films of the above blend were cast onto a glass substrate covered with a rubbed polyimide aligning coating in order to provide the development of the planar orientation (see Fig. 60). Then the film was exposed to UV light (stage *1*), which triggered the irreversible *E*–*Z*-isomerization of the dopant; this process was accompanied by a marked decrease in its twisting power due the reduced anisometry of molecules. When the film was annealed (stage *2*), the cholesteric helix was untwisted, and the selective light reflection peak was shifted to longer wavelength. Next, the sample was exposed to two interfering argon laser beams with the orthogonal polarization (stage *3*).

Figure 61 presents the snapshot of the diffraction grating recorded over a long period of time, which can be easily erased by thermal annealing (stages *1*, *2*) and the snapshot of the diffraction grating recorded on the top of the abbreviation IAP (Fraunhofer-Institut für Angewandte Polymerforschung) (stage *3*). Photoinduced changes in the helix pitch can be used for the recording of the polarization-responsive diffraction gratings. This concept has been proved by Russian and German scientists [228] for the ordinary blend of the nematic copolymer **61** doped with chiral photochromic dopant **6** (3.6 mass %). Irradiation of these films based on the above blends through a periodic mask template (Fig. 62) yielded gratings, which exhibited not only high efficiency (up to 40%) but also appeared to be responsive to a stimulus in a particular spectral range and to the direction of the circular polarization of the probe beam.[228]

Earlier, we discussed the pathway to periodic spatial modulations of the optical properties consisting in the

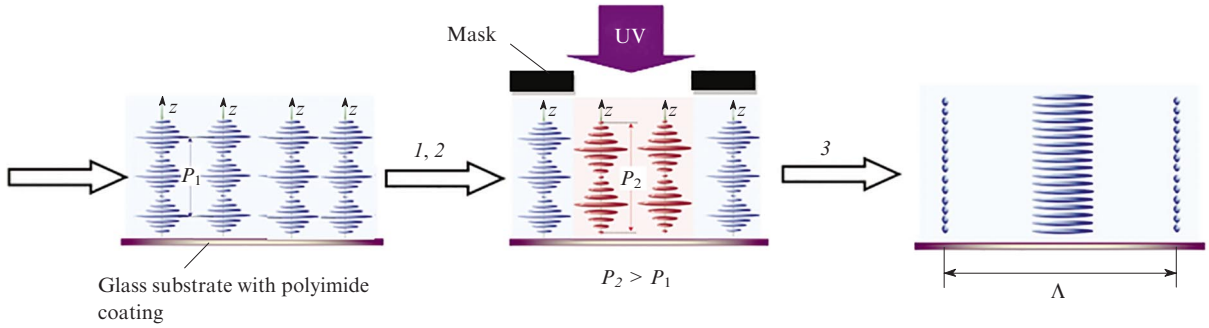
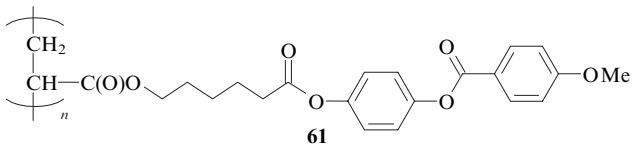


Figure 60. Scheme illustrating the dual recording on the films of photoresponsive azobenzene polymer **60** doped with chiral photochromic dopant **6**.[227]
(*1* – *3*) See text; *P* is the helix pitch; *z* is the axis of the cholesteric helix, Λ is the period of the formed grating (only mesogenic groups are shown; see the description of the experimental protocol in the text; the figure shows the limiting case when the holographic recording leads to a complete disruption of the cholesteric structure).

Structure 61



61

action of external magnetic or electric fields. Phototunable modulation of the parameters of the electroinduced diffraction grating in the polymeric cholesterics was studied by Ryabchun *et al.*[229] In this work, the cholesteric mixture consisted of nematic homopolymer **61** and chiral photo-

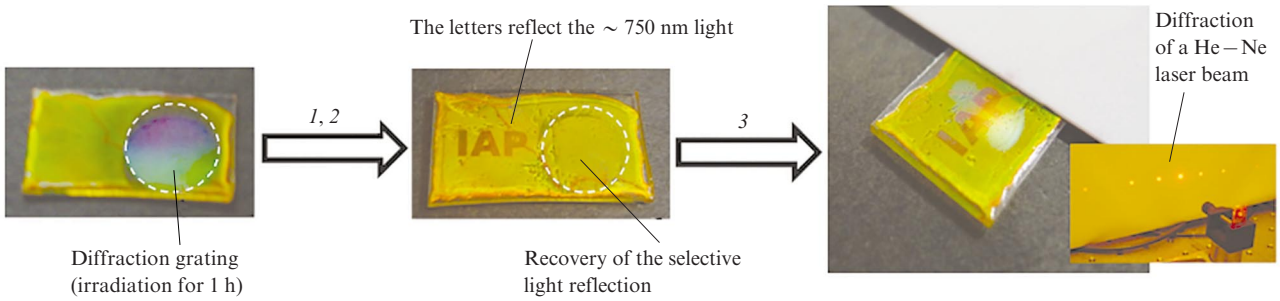


Figure 61. Dual image recording on the film of a cholesteric polymer blend.[227]
(*1*) Irradiation through the mask, (*2*) annealing, (*3*) recording of the diffraction grating (1 min). The diffraction pattern of a helium neon laser beam on the grating recorded on the top of the coloured abbreviation IAP (Fraunhofer-Institut für Angewandte Polymerforschung) is shown in the right-hand bottom corner.

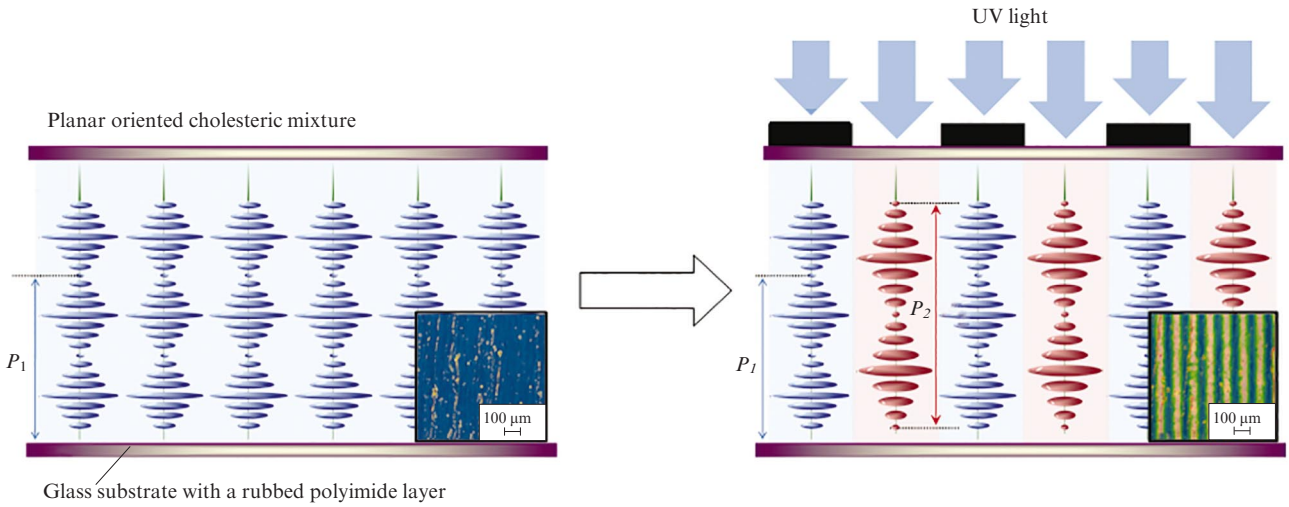


Figure 62. Scheme illustrating the recording of the diffraction grating due to the photoinduced untwisting of the cholesteric helix in a **61** + **6** mixture.[228]
The insets show the POM images of the observed textures.

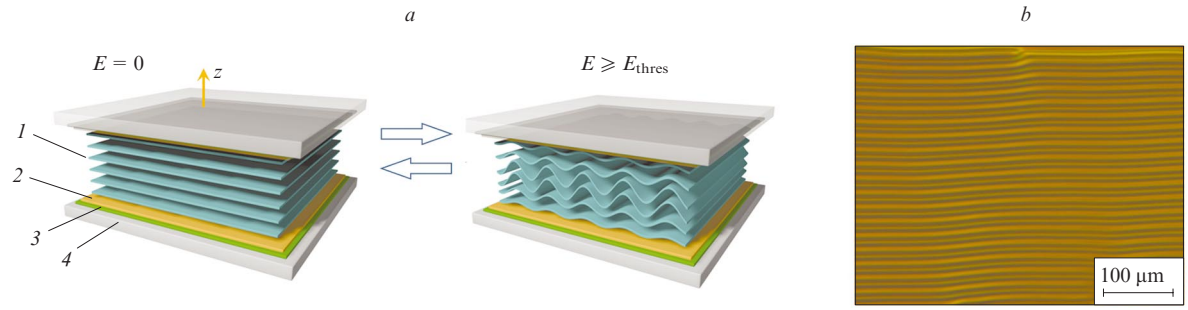


Figure 63. Basic scheme for the fabrication of diffraction gratings based on cholesteric materials (*a*) and POM image of the modulated structure (*b*).[229]
(*1*) Cholesteric layer, (*2*) polyimide aligning layer, (*3*) transparent electrodes, (*4*) glass substrate; E_{thres} is the threshold voltage providing deformation of the texture.

chromic dopant **6** (0.6 mass %), which allowed irreversible modulation of the cholesteric helix pitch.

The basic concept underlying the development of the diffraction gratings for the cholesteric mesophase is concerned with the application of weak external electric fields to planar oriented cholesteric layers (Fig. 63 *a*) or, in other words, along the direction parallel to the helical axis (*z*). At certain values of the helix pitch, when the ratio d/P (d is the layer thickness) varies from 0.25 to 2 and the electric field exceeds the critical level, periodic sinusoidal distortion of the field of the director of the cholesteric layer takes place. In this case, the modulated texture is developed, and this texture can be visualized by polarized microscopy (see Fig. 63 *c*). The above textures feature the phase diffraction gratings, which arise due to periodic modulations in the refractive index of the medium. The properties of these gratings are directly controlled by the parameters of the cholesteric mesophase such as the helix pitch, the layer thickness, and the constant of elasticity. This evidence highlights an ample potential for the development of tunable diffraction gratings based on the advanced cholesteric materials by modulations in the helix pitch.

Specific features of the generation of the diffraction gratings in the above blend were studied in detail. By properly selecting the parameters, the sequence of all possible types of cholesteric gratings was achieved in one and the same sample. Figure 64 *a* shows the kinetic curve illustrating the changes in the grating parameters of the polymer blend under the action of UV irradiation. Noteworthy is that, in this system, the gratings are formed under the application of the external field at elevated temperatures (above T_g of the polymer). Depending on the helix pitch, two types of gratings are produced in the blend: developable modulation (DM) gratings, which arise throughout the entire sample quickly and simultaneously, and growing modulation (GM) gratings, which grow from the defects

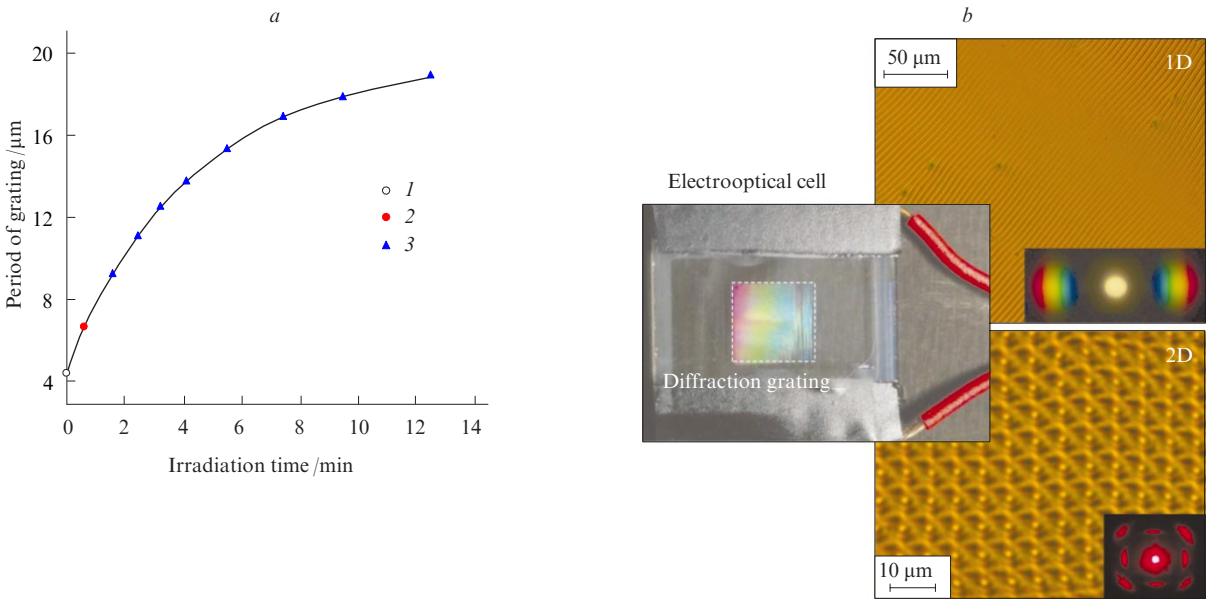


Figure 64. Changes in the period and type of the electroinduced diffraction gratings in the polymer blend **61** + **6** under the action of UV illumination (*a*), snapshot of the diffraction grating stabilized in the glassy state of the polymer, and POM image of the textures of one- (1D) and two-dimensional (2D) electroinduced gratings (*b*).[229]
(*a*) Alternating electric field with an intensity of 3.8 V is applied to the cell; (*1*) GM, (*2*) DM (⊥), (*3*) DM (||); ||, is the direction of gratings, parallel or perpendicular to the direction of rubbing of the polyimide aligning layer;
(*b*) the light diffraction patterns are shown in the bottom right-handed corner of the micrographs.

and gradually occupy the cell. When the sample is quenched down to room temperature (below T_g of the polymer), the formed grating is stabilized even in the absence of the external electric field. Undoubtedly, this behaviour demonstrates significant advantages of the above blends over conventional low-molecular-mass cholesteric liquid crystals, in which the gratings quickly disappear when the external field is switched off. Noteworthy is that by varying the parameters of the electrooptical cell, not only unidimensional but also two-dimensional diffraction gratings can be obtained, and the corresponding textures are shown in Fig. 64 *b*.

Therefore, innovative polymer cholesteric materials with the phototunable helix pitch seem to be promising for the development of advanced optical elements, including diverse diffraction gratings with tunable parameters. These advanced materials can be successfully applied in optics, optoelectronics, and spectroscopy. Their benefits are related to their unique optical properties, which provide the desired response of the gratings to different spectral regions and circular light polarization.

XI. Liquid crystalline polymers as nonlinear optical media

Photonics is one of the most rapidly developing areas of research activities focused on the development and characterization of polymeric materials. Photonics is based on the use of laser irradiation for the modification of polymers, which, in turn, change the properties of the incident light. Due to the unique combination of orientational order and high responsiveness to the action of external fields, liquid crystals and LC polymers seem to be exceptionally mesmerizing objects for their nonlinear optical properties. Upon the action of the light wave on the LC dipoles, the director of the liquid crystal is reoriented, and this process is accompanied by changes in the refractive index of the extraordinary wave. The induced gigantic orientational optical nonlinearity exceeds the Kerr nonlinearity of common liquids by nine orders of magnitude, and this observation can be explained by the occurrence of cooperative processes induced in liquid crystals containing ensembles of anisotropically oriented rigid molecules.

Pioneering experiments on characterization of nonlinear optical phenomena in the nematic liquid crystals were described in detail in the monograph by Aradelyan *et al.*[230] and in the early works by Kitaeva and Zolot'ko [231] and Zel'dovich and Tabiryan.[232]

Joint collaboration [233, 234] of the researchers from the M.V.Lomonosov Moscow State University and P.N.Lebedev Physical Institute (the Russian Academy of Sciences) was the first study of the interaction of light with nematic liquid crystals containing minor amounts (0.1 mass % – 0.5 mass %) of the comb-shaped copolymer **62** with side azobenzene groups. Upon light irradiation of these samples, the director is reoriented to become perpendicular to the electric field. When the planar oriented samples are illuminated by the light beam, the aberration pattern is formed in the cross-section of the sample, and this pattern is characterized by a certain number of aberration rings (Fig. 65). Upon both normal and inclined light incidence, the time required for the development of the pattern varies from 20 s to 1 min (depending on the intensity of laser irradiation and the laser beam tilt angle). The characteristic time of relaxation of the photoinduced refractive index is $\sim$15 s.

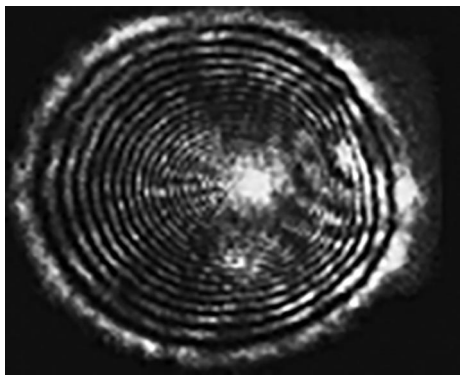
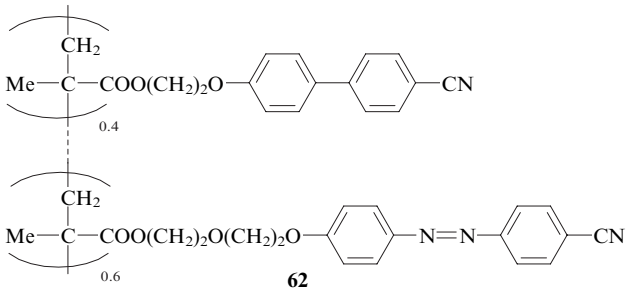


Figure 65. Pattern of aberration rings formed upon the laser beam passing (λ = 476 nm) through a planar oriented sample of the liquid crystal containing copolymer **62** (0.5 mass %).[233]

Structure 62



62

When the sample is cooled down below the glass transition temperature, the pattern of the aberration rings is preserved. It is important to mention that, upon introduction of only 0.5 mass % of the comb-shaped copolymer **62** into the nematic matrix, its coefficient of nonlinearity increases by a factor of 60. Earlier achievements in this area are related to the study of the effect of one incident beam on the samples of liquid crystals. The results have been described in terms of the photoinduced Fréedericksz effects, which are accompanied by self-focusing and self-defocusing phenomena.[232, 235] Lately, significant attention has been concentrated on the processes of reorientation of mesophases under the action of several incident waves, in particular, under the action of the interference fields.

Considering the nonlinear optical phenomena in the LC compounds with photochromic groups, one should take into account all processes of interaction of several waves, including those with different polarization and different directions of distribution. In particular, within the confined light beams, light self-focusing can take place, and the quantitative characteristics of the Fréedericksz transition may be changed.

As was shown in experiments [236] performed for the above copolymer, irradiation with left-handed or right-handed circularly polarized light triggers the development of the photoinduced chirality, and the light becomes elliptically polarized. This evidence suggests the development of a certain photoinduced chiral structure in the polymer film. Figure 66 shows the micrograph of the helical structures produced upon the irradiation of the films of copolymer **62** with the right-handed and left-handed circularly polarized light.

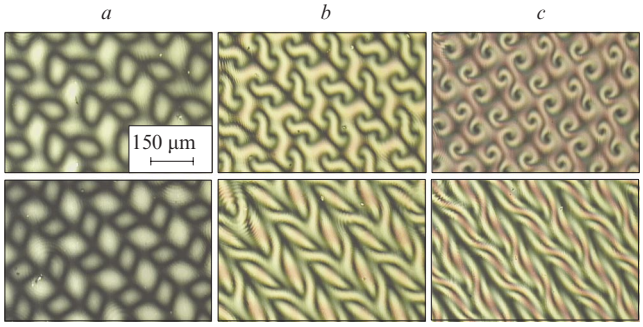


Figure 66. Micrographs of characteristic periodic structures induced by the laser beams in the sample of LC copolymer **62**.[236] Irradiation dose /J cm^{-2}: (*a*) 0.7, (*b*) 7.0, (*c*) 40.
The micrographs of the holograms (in the polarized light) were collected using orthogonal beams of linearly (upper row) and circularly polarized (bottom row) light.

Varying the geometry of the arrangement, number, intensity of the interfering laser beams and their direction (left-handed or right-handed) as well as the incidence angles, rather complex types of chiral supramolecular structures are developed.

Even though the mechanism behind the formation of these structures is still unclear, these systems have attracted a considerable interest. Essentially, this evidence offers new routes for the development of innovative types of gyrotropic media with photoinduced chirality and three-dimensional modulation of the refractive index. In this direction, new fascinating opportunities for the development of the theory explaining the formation of this type of structures are opened. These polymers may serve as a platform for the design of optically active 'light structures' with unique geometry and for the fabrication of the materials with a desired periodic surface topography.

XII. Conclusion

The photoindiced processes in photoactive polymer LC systems summarized in this review do not address all diversity of the phenomena taking place under the action of external eletromagnetic field on the LC objects with different structures and compositions. As compared with the 1970s – 1980s, the interest in the synthesis and studies of LC polymers has somewhat declined; nevertheless, only within the recent five years, not less than ten seminal collections of works and handbooks were published (see, for example, the following publications [19, 20, 22, 23, 25, 26, 38, 49]), each containing more than 600 – 700 pages, as well as several fundamental articles (see, for example, the following articles [21, 29, 30, 40, 55, 87, 117, 163, 178]), which cover the most topical challenges of chemistry and physics of LC polymers and the related composites.

As was shown in Section II, the LC polymers with mesogenic groups in their main chains can serve as the basis for the fabrication of polymeric materials, primarily, for engineering purposes such as high-strength and high-modulus fibres used as reinforcing materials as well as the plastics which are widely used for the preparation of big-sized articles for diverse purposes and applications in automotive, aviation, and space industries. On a somewhat smaller scale, these materials can be used for the fabrication of high-precision parts for electronic, radiotechnical, and telecommunication equipment.

In the first case, the key benefits are related to high orientational order, which can be readily achieved upon melt or wet spinning of LC fibres and preserved in the as-spun articles (solid fibres). **In the second case**, fabrication of parts with complex geometry requires high thermal stability and low temperature thermal expansion coefficients (10^{-6} cm^{-1}), which are characteristic of most LC polymers. These properties allow substantial improvement of the quality of scientific equipment and modern mobile electronic devices, which often operate over broad temperature ranges.

Liquid crystalline comb-shaped polymers with mesogenic groups in their side chains can be promising materials for some alternative purposes. These polymers feature functional materials, which, depending on the presence of diverse mesogenic or other functional groups, can be treated as smart materials, which can readily respond to the external impact and change their molecular and supramolecular structure and, as a consequence, physicochemical properties. The above stimulus-responsive LC polymers offer an illustrative and vivid example of self-organized thermo-, photo-, and electrotunable polymer materials, and their unique properties can be used in diverse areas such as photonics, optoelectronics, display systems, holography, development of data recording and storage systems and sensor devices.

In our opinion, the mainstream direction in the studies of the stimulus-responsive LC polymers is concerned with the development of phototunable photoactive LC polymeric systems and LC composites. Upon the contact-free irradiation of the polymer films, chromophoric molecules change their configuration and conformation. Being parts of macromolecules or dopants in the LC polymers, chromophores operate as specific switches, thus triggering further structural transformations of the LC material.

This knowledge serves as the platform underlying the operation of photomechanical actuators, which can be used not only as molecular machines,[56, 237] but also for the development of biomimetic systems similar to artificial muscles. In this respect, note the original publication [238] in which the authors designed the prototype of artificial muscles: they synthesized the cross-linked LC copolymer (in this case, the azobenzene cross-linking agent serves as a switch), and this approach allows the preparation of mechanically robust samples which experience a reversible deformation under irradiation and are characterized by short turn-on and relaxation times.

At the present time, the development of new methods for preparation and characterization of the cross-linked LC polymers is of a great fundamental and applied interest. Various aspects of the above problems have been discussed in detail in the collective monograph [25] published by the leading scientists in the area of LC systems.

The data summarized in this review address the LC polymers, where photochromic groups are covalently linked to macromolecules, or photochromic compounds are used as dopants, which are mechanically incorporated into the LC polymers. However, in many publications, the photochromic groups were linked to the polymeric matrix *via* hydrogen bonds.[239] Unfortunately, the lack of systematic studies on photooptical processes does not make it possible to highlight their principal features and to reveal the correlation with the covalently linked LC polymers.

In our opinion, of considerable interest are the works on photofluidization and photodeformation or, in other words, on the mass transfer in the LC polymer systems under irradiation and development of the surface micro- and macrorelief. According to the recent works,[141, 151] this approach reveals fascinating resources for the development of unique nanostructured surfaces with phototunable relief.

Another promising area of research offers a great potential for practical applications and addresses the development of phototunable diffraction gratings[227 – 229] as well as the use of interfering laser beams for holographic recording of data and high-volume images on the LC polymers. All these research areas are directly related to the studies in the field of photonics, telecommunication, and information technologies.[235, 236]

Of special interest are the works on the development of hybrid systems based on LC polymers and LC composites doped with nanoparticles. At the early stages of these works (about twenty years ago), the principal attention has been focused on the methods providing the introduction of nanoscale objects into liquid crystals and LC polymers.[23, 56] The basic underlying idea of these studies has been directed towards the development of hybrid materials, which combine the anisotropy of the LC phase and fluorescence of nanoparticles. Despite evident difficulties concerning the preparation of such hybrid compounds, a protocol of synthesis of the LC composites based on cholesteric networks[240] and semiconducting nanoparticles of cadmium selenide and zinc sulfide has been proposed. The as-prepared transparent films contain up to $\sim$6% of quantum dots and are characterized by a bright circularly polarized fluorescence. Unfortunately, despite numerous publications on this subject, difficulties in the fabrication of quantum dots modified by liquid crystals (for better compatibility with the LC polymers) prevent the detailed studies on such polymer-based hybrids. At the same time, the development of phototunable systems can provide the preparation of the materials with controlled fluorescence for high-performance light guides, which improve the brightness of displays of modern TV sets, smartphones, and other electronic devices.

Undoubtedly, the realm of big molecules offers unlimited possibilities for the development of innovative functional materials. The chain structure of molecules containing anisometric mesogenic and photochromic groups allows their further modification by introduction of diverse (by the wish of the researcher) molecular functional fragments, and this roadmap procures resourceful and long life of LC polymers.

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