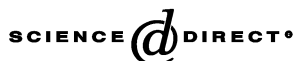




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Photoactive liquid crystalline polymer systems with light-controllable structure and optical properties

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Abstract

The state-of-the-art in the field of molecular design, synthesis, phase behaviour and photooptical properties of photochromic liquid crystalline (LC) side chain polymers, their blends with chiral and photochromic low-molar-mass dopants, hydrogen-bonded photochromic LC polymer systems, as well as photoresponsive LC dendrimers, is reviewed. The molecular architecture of the LC polymers and photochemical reactions of the main types of low-molar-mass achiral and chiral photochromes are briefly described. Recent advances in research dealing with the synthesis and study of optical and photooptical properties of a series of photochromic LC polymers bearing nematogenic and photochromic side groups forming nematic, smectic and cholesteric mesophases are considered.

Among the various types of photochromic systems used to obtain the photoresponsive LC polymers the main attention focus on the so-called combined multifunctional systems composed of nematogenic, chiral and one or two photochromic fragments incorporated in the same monomer units or entirely into the macromolecule as individual monomers. The systems of both types form chiral nematic (cholesteric) phase with helical supramolecular structure. Polymer cholesteric films with planar orientation exhibit a selective reflection of light in the visible or IR spectral range. The action of light leads to the isomerization of both chiral photochromic groups (or the photochromic group alone), which results in the variation of the helical twisting power of the chiral fragments. This process is accompanied by sharp changes in the supramolecular helical structure and the optical properties of the polymer. By properly selecting the copolymer composition and preparing blends of the LC polymers with low-molar-mass chiral and photochromic dopants, using hydrogen-bonded systems, it is possible to obtain materials with different characters of the light-induced transformations. In particular, this provides the ability of controlling the pitch of the helix, the rate of helix twisting and untwisting, the width of the selective light reflection peak, etc.

The last part of review covers a relatively new class of LC compounds—LC photochromic dendrimers, whose photochemical and photooptical properties are briefly discussed.

The photochromic LC copolymers under consideration offer new promising materials for reversible and irreversible black/white and colour data recording that can be used in optoelectronics, data storage (in optical memory systems), holography, and colour projection techniques and give rise to a new generation of video discs, flat light guides and coatings with controllable optical properties.

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Keywords: Liquid crystal polymer; Photochromic polymer; Dendrimer; Chiral polymer; Photoisomerization; Photoinduced birefringence; Selective light reflection

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1. General introduction

The macromolecular structure of high-molar-mass compounds provided by the presence of long and flexible chains is responsible for the principal features

of such compounds, and in due time this direction constituted a new branch of science referred to as Polymer Science or Macromolecular Science [1]. The chain structure of both natural and synthetic polymers offers almost unlimited options in the molecular design

when one macromolecule may contain numerous identical or different structural units (monomer units), and their arrangement presents the primary structure of high-molar-mass compounds.

This multicomponent (multilink) character of the primary structure (which may be referred to as polyfunctionality) is most pronounced in proteins, which present copolymers composed of monomer units of 20 different amino acids. Their primary structure is responsible for the development of more complex secondary, ternary, and even quaternary supramolecular structures, with their specific properties providing the functioning of living organisms.

Self-organization and genetic code transfer responsible for the self-reproduction of the complex molecular and supramolecular structures may only be achieved due to a long-lasting evolution of living systems composed of chain molecules. Knowledge of the basic principles of their development and function allowed the preparation of a number of synthetic biopolymers with a given primary structure (insulin, ribonuclease, etc.), which governs all further stages of self-organization of macromolecules that are presently synthesized via dozens or even hundreds of computer-monitored reactions [2]. Presently, this approach seems to be the best, not only for the biochemists, but also for the synthetic chemists who work on the development of new complex compounds via the multistep reactions and synthesis of the target products with desired properties.

1.1. Molecular architecture of LC polymers

A vivid example of the preparation of complex multifunctional polymers with variable molecular and supramolecular structure is provided by the synthesis of LC polymers and copolymers, capable of self-organization and the development of various thermotropic and lyotropic mesophases, with a high anisotropy of all physical properties.

Among various scientific directions that developed in the physical chemistry of high-molar-mass compounds over the last 15–20 years, most attention has been devoted to the problems aimed at the synthesis and study of LC polymers. This trend has been attested by the dozens of monographs and collections of papers of international conferences, numerous scientific communications and patents as well as

dozens of commercially produced polymer fibres (Kevlar, Terlon, Unitica, Tvaron, etc.) and plastics (Xydar, Vectra, etc.) based on LC polymers. Comprehensive information concerning LC polymers may be found in Refs. [3–16]. In this section, we would only like to demonstrate the ample advantages offered by modern organic and polymer chemistry in the synthesis of complex molecular structures with LC properties.

So far, the synthesis of several thousand LC polymers has been accomplished; macromolecules of these polymers show one specific feature: as a rule, they contain flexible and rigid (mesogenic)¹ fragments shaped as rods and disks. These fragments are connected to each other in different ways. Fig. 1 vividly demonstrates the many opportunities of the molecular design of widespread LC polymers containing mesogenic groups in main chains (main-chain polymers) and side chains (side-chain LC polymers or comb-shaped LC polymers). In addition to purely linear (Fig. 1(a)–(d)) and purely comb-shaped branched macromolecules (Fig. 1(e)–(i)), one may obtain combined macromolecules containing mesogenic groups both in the main chains and in the side groups (Fig. 1(j) and (k)). More complex LC polymers with cross-shaped mesogenic groups (Fig. 1(l)) and polymers composed of macromolecules with alternating laterally connected rod-like and disk-like groups have been synthesized (Fig. 1(m) and (n)).

The advantages of the chemical design of LC polymers may be substantially widened by the synthesis of random binary and ternary copolymers, by the preparation of polymer LC networks, as well as by LC block and graft copolymers in which a mesogenic compound is used as at least one of the components (Fig. 2).

In the above LC polymers, whether they are homopolymers or copolymers, all mesogenic groups are chemically (covalently) involved in the macromolecules. However, one should also mention an alternative type of LC polymer, in which the mesogenic groups may be attached to the polymer chain via either an ionic interaction between

¹ Mesogenic groups are the fragments with a sufficient anisotropy in both attractive and repulsive forces in a molecule or macromolecule which provide the development of LC phase in both low-molar-mass and polymeric compounds.

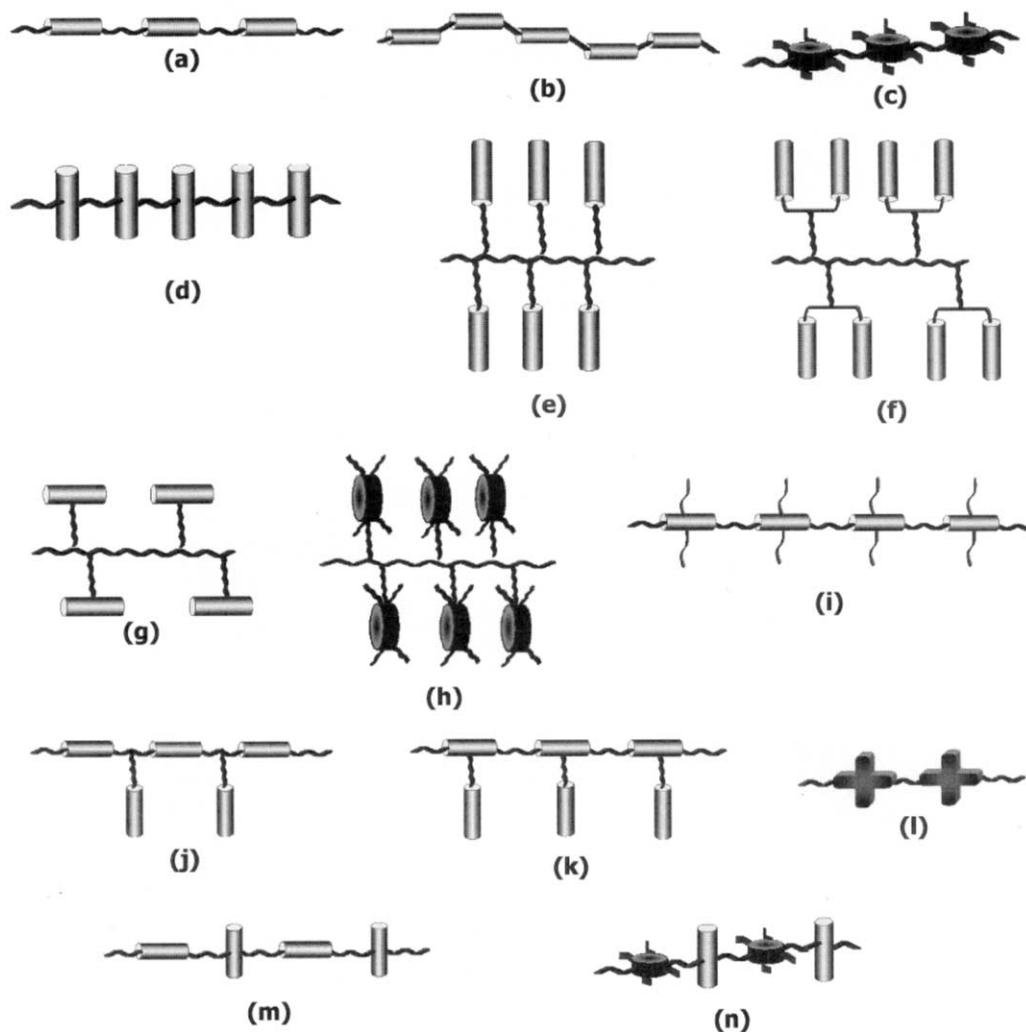


Fig. 1. Schematic representations of macromolecules of LC polymers with rod- and disk-shaped mesogenic groups.

the components or hydrogen bonding between the main chain (or side chain) and mesogenic fragments (Fig. 3(a) and (b)). In this case, the two initial components are compounds which are not mesogenic by themselves, but form mesogenic groups by their interaction due to the induced anisotropy of a new fragment (Fig. 3(c)–(e)). Different versions of such LC polymers are shown in Fig. 3(a)–(e). Fig. 3(f) demonstrates the feasibility of the preparation of cross-linked LC polymers even when a low-molar-mass bifunctional fragment, non-covalently bound to a macromolecule, is used as a chemical cross-linking agent. The development of such molecular complexes

as constructed on the basis of the molecular recognition phenomenon leads to their spontaneous organization, and a concomitant development of the supramolecular structure corresponding to a certain type of mesophase—nematic, smectic, or cholesteric [17].

Finally, we should mention one comparatively new class of LC systems: polymers with a hyperbranched molecular structure, referred to as dendrimers. These non-LC dendritic compounds were first synthesized during the early 1990s, and their exotic ball-shaped structure and unique physicochemical properties immediately attracted the attention of scientists

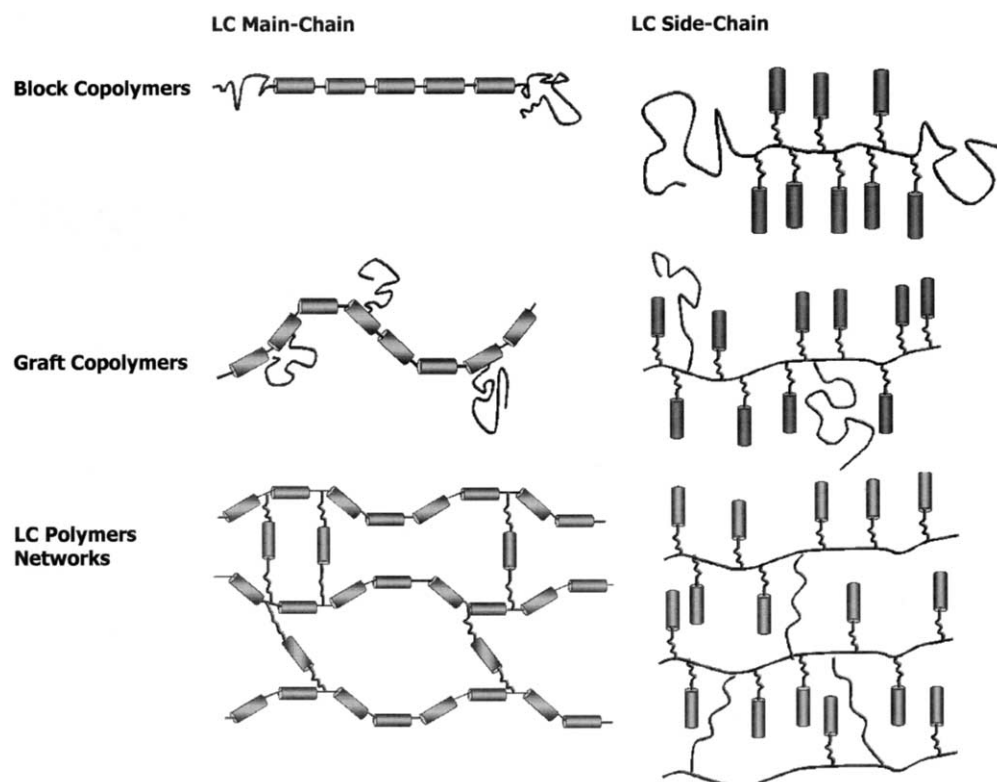


Fig. 2. Schematic structures of the block- and graft-LC copolymers and LC polymer networks.

[18–33]. However, the first LC dendrimers were prepared somewhat later by several independent groups working in Germany [21–23,25], Russia [24, 26–28], and USA [29–32]. Presently, depending on the arrangement of mesogenic fragments, the as-synthesized systems (probably more than 100) may be classified into at least two groups.² The first consists of LC dendrimers with mesogenic groups distributed over the whole volume of macromolecules; the second group involves LC dendrimers where mesogenic groups exist as the terminal groups at the periphery of dendrite matrix (Fig. 4). The first review devoted to LC dendrimers was recently published by Russian authors [33].

A potential synthesis of LC polymers constructed of macromolecules with different combinations of mesogenic and non-mesogenic fragments offers

ample opportunities for the molecular design of new polymer LC compounds.

On one hand, such compounds provide new and rather complex objects for scientific cognition where their synthesis and characterization present an evident academic interest. On the other hand, there exists the problem concerning their practical application and potential areas of utilization.

Synthesis of new lyotropic LC systems based on aromatic polyamides in the early 1970s, and the further development of the industrial production of Kevlar fibres, triggered an intensive development in scientific activities, primarily focused on the synthesis of main-chain and side-chain thermotropic polymers [34–36].

The results of these research activities allowed one to approach the industrial production of new high-strength and high-modulus fibres and high-strength plastics, some of which were mentioned above. All of these commercial polymers were based on linear main-chain copolyesters and polyamides, which

² Here, we do not consider the LC dendrimers without mesogenic groups when the development of LC phase is controlled by microphase separation. For example, see Refs. [31,32].

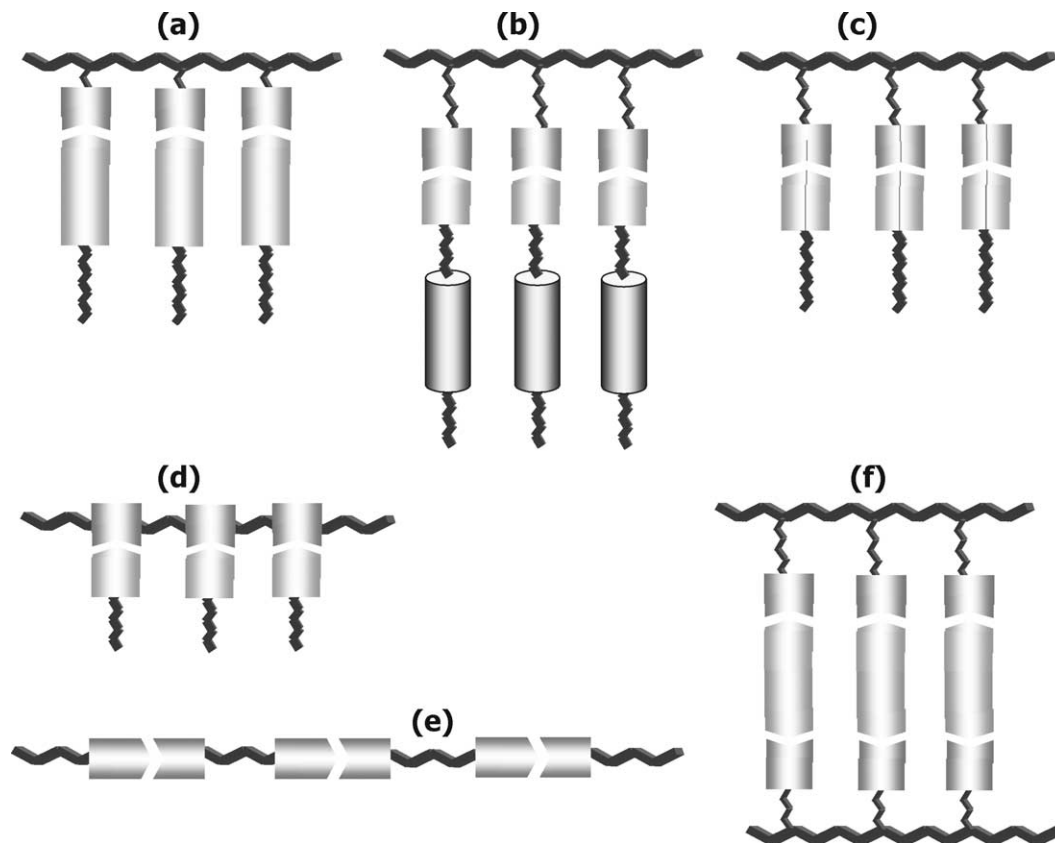


Fig. 3. Principles of molecular construction of LC polymers by self-assembly induced by hydrogen or ionic bonding.

present an evident interest as engineering materials: fibre-forming polymers and self-reinforced plastics [7,8,34].

In the case of the synthesis of comb-shaped LC polymers, scientific and practical interest in this area

is primarily controlled by the feasible development of new functional polymer materials referred to as smart or intelligent materials. In this respect, one should mention LC cholesteric materials, LC ferro-electrics, LC polymers sensitive to the action of

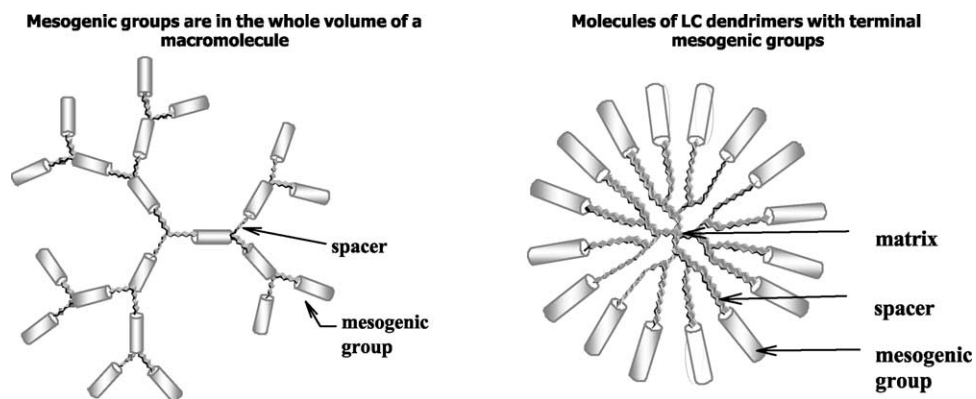


Fig. 4. Two types of LC dendrimers.

external electric and magnetic fields (so-called electroactive polymers), LC ionogenic and metal-containing polymers, photochromic LC polymers, and LC dendrimers.

Some of the above types of LC polymers, such as cholesterics [35,37–40] and electroactive LC systems [13,41–44], were considered in monographs and reviews. In recent years special attention was given to the synthesis, characterization, and practical application of photoactive LC polymer systems that offer exceptionally fascinating advantages in molecular and supramolecular design as well as in the photocontrolled changes in optical properties [13,44–50].

In this work, the authors attempted critical analysis of exceptionally scattered but rather abundant data on the development of photochromic LC polymer systems, investigation of their phase behaviour, and characterization of their photochemical and photooptical properties. It seems important to mention that, even though their principal attention was focused on their work performed during the recent 5–6 years, all important and valuable works of other authors were also reviewed. Primarily, they focused on the photochemical and photooptical properties of comb-shaped LC polymers containing photochromic side groups which form nematic, smectic, or chiral nematic N^* (cholesteric) mesophases with helical supramolecular structure.

The second group of the photosensitive LC polymer systems as discussed in the review is presented by compositions of two types: mixtures of photochromic LC polymers with low-molar-mass photochromic or chiral dopants, and mixtures of functionalized mesogenic polymers with photochromic low-molar-mass dopants stabilized by ionic or hydrogen bonds.³

The last section is focused on a new class of compounds referred to as hyperbranched dendritic polymers that also contain photochromic groups (photochromic dendrimers).

1.2. Preparation of photochromic LC polymers

Rapid development of various modern systems for data recording, transfer, processing, and visualization of images, as well as the miniaturization of optical devices, requires the solution of many technological problems and preparation of new responsive materials capable of rapid and reliable response to the control signals transmitted by electromagnetic fields, particularly by light and laser irradiation.

Among various inorganic and organic photoreponsive materials (usually referred to as ‘smart’ or ‘intelligent’ materials) the most important role obviously belongs to polymers. As shown above, a significant advantage of macromolecular systems concerns the ability of combining various functional groups and fragments, as well as the ability of polymers to form stable films, fibres, and coatings that can be readily applied onto various substrates (metals, plastics, ceramics) by simple methods such as spin coating, dipping, lamination, etc.

LC photochromic polymers occupy a special place among high-molar-mass photoreponsive materials. Note that any LC polymer shown in Figs. 1–3 may be considered as a photochromic polymer when its macromolecules contain photochromic groups. This statement concerns LC photochromic homopolymers and copolymers (the latter are most often synthesized and studied) containing photochromic and mesogenic groups providing the development of an LC phase. Examples of such compounds will be presented below.

These polymers successfully combine the physicochemical properties of macromolecular compounds (with their ability to form plastics, elastomers, films, and fibres) with the mesomorphic properties of liquid crystals and the photosensitivity of chromophores chemically or non-covalently included in LC polymers. The binary nature of photochromic LC polymers offers great advantages with respect to processing properties, photoactivity, stability of the stored information, and possible data recording on the thin polymer films. The pronounced ability of the above compounds for self-organization and formation of various ordered supramolecular structures under the action of external fields creates interest in the development of new materials with local properties controlled by optical methods. These materials could

³ The results on studying the photochromic compositions will be considered together with the data on the photochemical study of photochromic copolymers in Section 3.4, while the hydrogen-bounded photochromic systems are discussed in Section 3.5.

be used as new effective media for waveguides, laser disks, light-switched triggers, and optical storage devices for electronics, electrooptics, and holography [6,13,51–54].

How we can incorporate photochromic fragments into LC polymer matrix? There are at least three principal methods that allow us to obtain photosensitive LC polymers.

The first approach involves the preparation of polymer mixtures with specific compounds containing photoresponsive groups (photochromic dopants). In this case, the polymer serves as matrix, or ‘host’ and the additive (photochromic dopant) as ‘guest’. Such mixtures allow us to control the properties of the guest component by light irradiation without any changes in the matrix itself. In such systems, the polymer acts as a passive host giving ‘cart blanche’ to guest molecules.

The second method seems to be more complicated but is more efficient. In this case, photoactive molecules or their fragments are chemically ‘incorporated’ into macromolecules. In this case, the polymer matrix is no longer indifferent to the guest and may exert an influence on its behaviour or, in contrast, may feel a certain perturbing effect due to the guest.

And finally, there is the third method, when photochromic dopants are weakly attached to the polymer matrix via non-covalent interactions, H-bonding, or ionic bonding (Fig. 3). In this case, the photochromic complexes are derived from molecular recognition processes between structurally different or closed molecular species.

In all cases, photochromic fragments control the optical properties of the three groups of polymers, including LC photochromic dendrimers. The presence of photochromic groups in the macromolecules of LC polymers or in the mixtures of dopants with polymers accounts for their sensitivity with respect to light or laser irradiation, which induces certain photochemical transformations. The photochromic groups play the role of effective ‘switchers’ capable of sharply changing their configuration and conformation upon photoisomerization, photocyclization, keto-enol tautomerism, and other reactions. Any change in shape of the photochromic guest molecules necessarily leads to the distortion of the local packing of the mesogenic groups, determining the type of the LC phase.

This process naturally poses important questions concerning the relationship between the molecular structure of the photomodified monomer units and the supramolecular structure of the initial LC matrix: (1) what is the ‘response’ of a polymer matrix to the photoinduced changes of molecules chemically (or non-covalently) bound to this matrix; (2) whether the photoinduced structure transformations are restricted to changes in local order in the vicinity of photochanged molecules or include large-scale rearrangements involving their neighbouring non-photochromic units; (3) what is the role of the structural organization of the LC matrix (nematic, smectic, or cholesteric) in the light-induced rearrangements; (4) how the possible local or large-scale changes in the supramolecular structure can be used for the controlled modification of the optical properties of polymer films?

These questions are directly related to the global task of creating new photochromic materials with desired locally controlled optical properties for the optical memory systems and for both reversible (read/write) and irreversible data recording (storage), transfer, and display imaging.

In this work, all the above problems present the subject of a deliberate analysis. However, prior to the analysis of the results obtained for photochromic LC polymers, let us consider in brief some general concepts concerning the low-molar-mass liquid crystals and photochromism phenomena.

1.3. A brief description of LC structures

In this short section, we will introduce some general concepts used for the description of liquid crystals and LC polymers.

Notwithstanding the wide diversity of the molecular structures of LC polymers containing mesogenic groups, the structural types of mesophases are similar to those of low-molar-mass liquid crystals: nematics, smectics, and cholesterics.⁴ Actually, the number of the known structural types of low-molar-mass liquid crystals is several dozen; for LC polymers, the number of known and well-defined structural modifications is

⁴ A detailed structural classification of LC polymers is beyond the consideration of this work and may be found, for example, in Ref. [15].

much less. Nevertheless, it is possible that among the structures shown in Fig. 1, new structural modifications rather than those known for low-molar-mass liquid crystals might appear.

In this work, the structural features of photochromic LC polymers will not be discussed; only a short description of the classical structural types of mesophases that are developed both in low-molar-mass and polymer liquid crystals is presented.

A nematic mesophase is characterized by the parallel alignment of long axes of the molecules, whose centres of mass are devoid of long-range positional order. The molecules are, on average, orientationally ordered about a common axis defined as the director and represented by the unit vector \vec{n} (Fig. 5(a)).

The long-range orientation order relative to the director is characterized by the order parameter S which is defined as

$$S = \langle 3 \cos^2 \theta - 1 \rangle / 2 \quad (1)$$

where θ is the angle between the molecular symmetry axis and the director \vec{n} ; $\langle \rangle$ denotes an ensemble average.

For rod-like molecules the order parameter at the nematic-isotropic transition is about 0.3 and can increase to about 0.7 deep in the nematic mesophase.

A smectic mesophase is the closest to natural crystalline substances (Fig. 5(b)). The molecules are arranged in disordered or ordered layers, and their centres of gravity are usually mobile in two dimensions (in the smectic plane). There are various types of smectic phases, characterized by a variety of molecular arrangements within the layers. For instance, a type of structure called smectic A (SmA) indicates that the molecules are arranged parallel to each other within the layers, in which the long axes of the molecules tend to be perpendicular to the layer planes and the molecular centres of mass have no long-range positional order. This type of mesophase is shown in Fig. 5(b). If the molecular axes are tilted with respect to the layers, the structure is called smectic C (SmC).

A cholesteric or chiral nematic mesophase is a mesophase with a helical supramolecular structure formed by chiral molecules or by doping the nematic host with chiral guest molecules in which the local director \vec{n} precesses around a single axis (Fig. 5(c)). For the normal incidences of a light beam upon

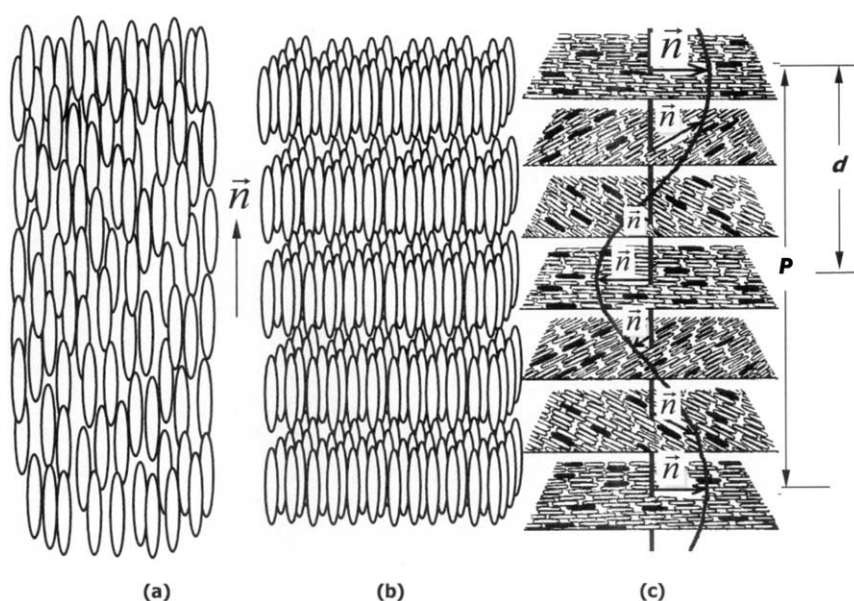


Fig. 5. The main types of LC phases: (a) nematic, (b) smectic and (c) cholesteric. \vec{n} is the director of liquid crystal; P is the pitch of the helix; chiral molecules are shaded.

a planar-oriented cholesteric texture (with the helix axis perpendicular to the layer), the helix pitch is related to the wavelength λ_{\max} of the maximum selective light reflection by a simple formula

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

where \bar{n} is the mean refractive index of the LC polymer. Thus, a unique feature of the LC polymers forming chiral nematic phases is the ability to selectively reflect light in the UV, visible, or IR spectral ranges in accordance with the helix pitch.

The main parameter determining the helix pitch is called the helical twisting power β of an optically active dopant, introduced either by mechanically mixing with the LC matrix composition or by chemically binding to the polymer macromolecule. The β value is inversely proportional to the helix pitch and is related to the chiral dopant concentration X by the formula:

$$\beta = (dP^{-1}/dX)_{X=0} = \bar{n}(d\lambda_{\max}^{-1}/dX)_{X=0} \quad (3)$$

The helical twisting power β of a chiral dopant depends on number of factors, including the interaction with the LC matrix, the temperature, and the molecular structure and shape of the dopant molecule (or fragment in the case of macromolecule).

It should be emphasized that the mesogens arrangement of LC polymers in the above-mentioned classical phases is very similar to the molecular packing of mesogens in low-molar-mass liquid crystals. As a rule, the polymer chains are arranged into LC phase and adopt the anisotropic oblate or plolate conformation in depending on mesophase type [55].

1.4. Photochromism and photoinduced reactions

Photochromism is usually defined as a reversible transformation of a chemical species, induced in one or both directions by electromagnetic radiation, between two states A and B giving observable light absorptions in different regions of the spectrum— λ_1 and λ_2 , respectively [53]



Radiation hv_1 , acting on species A , generates species B until a photostationary state is reached. Normally,

species B has at least one absorption band appearing at a longer wavelength than the absorption band of species A . The most prevalent photochromic systems are based on unimolecular reactions ($A \rightarrow B$), which mainly will be considered in this review. It should be noted that species B can be transformed to species A spontaneously (due to heating) or under the action of light energy hv_2 .

It is very remarkable that such photochemical reactions are accompanied by a rapid and reversible change of colour. This phenomenon already has several real and many potential applications, such as the photochromic glasses which darken in sunlight (protecting our eyes from excessive light intensity) and lighten in dim light. These glasses are now a part of our everyday life.

The photochromic properties of such compounds, often called photochromes, are due to their capability to exist in two different states having different molecular or electronic configurations. Generally speaking, all photochromic compounds can be roughly divided into groups according to the nature of the photoinduced transformation, which can have a photophysical or photochemical mechanism [56].

Photophysical optical active media are characterized by quick photoinduced changes in the electron density, namely, by the occupation of the excited electron states of molecules. Under the action of laser irradiation, one may observe the appearance of an additional absorption as provided by triplet–triplet transitions. However, due to a short-term absorption in photophysical media (up to 5 s), their application in informatics is rather limited; they are primarily used for the recording of dynamic holograms.

Serious attention has been focused on the investigation of *photochemical photochromic media*, which are capable of dramatic light-induced intra- and intermolecular rearrangements leading to the formation of new stable or unstable chemical compounds. The character of the above reactions and thermodynamical stability (or instability) of photoinduced products determines their possible application as reversible or irreversible photochromic materials.

Among the reversible photochemical reactions of organic compounds, one should mention

the *cis*–*trans*-isomerization as provided by the hindered rotation of the fragments about the double bond (azo compounds, olefins), valence isomerization provided by redistribution of π - and σ -electrons in molecules (fulgides, fulgimides), photoinduced hetero- and homolytic ruptures of valence bonds (spiropyrans), photodimerization, photocyclization, etc.

However, a detailed consideration of the molecular mechanism of the above photochemical reactions is beyond the consideration of this review. The related information has been repeatedly discussed in literature [13,51–54,56–59]. In this section, we will only consider the photoinduced reactions for some of the most extensively studied photochromic compounds (photochromes), which are widely used in the synthesis of photochromic LC polymers.

2. Low-molar-mass organic photochromic compounds

The selected photochromic compounds may be conditionally classified into two groups: achiral and chiral systems. This classification is dictated by the fact that chiral type photochromic fragments will be treated as the components for the preparation of LC polymers that form chiral nematic (cholesteric) mesophase with a helical supramolecular structure. At the same time, achiral photochromic compounds are used for the synthesis of photochromic LC polymers with a simplest nematic (and sometimes smectic) type of mesophase. Photoinduced structural transformations in these two types of liquid crystals provide a marked difference in their optical properties. That fact predetermined the subdividing photochromic compounds into two groups.

More complicated multifunctional photochromes combining chiral and photochromic fragments in the same molecules are presented in Section 2.3.

2.1. Achiral photochromes

The subdivision of photochromic compounds into two classes—achiral and chiral—is substantially a matter of convention because some achiral photochromes become chiral ones (for example, fulgide

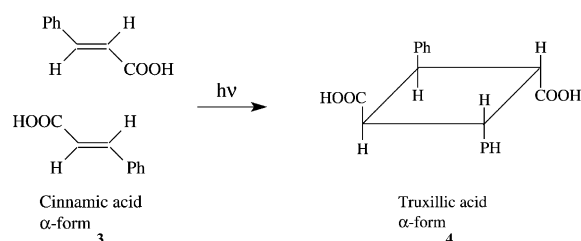
derivatives) during the photochemical reactions. In this connection, only azo-containing and olefin-type compounds were assigned to the achiral photochromes.

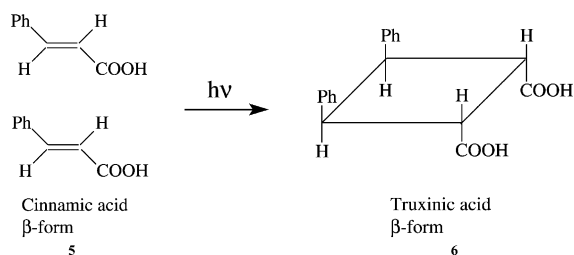
2.1.1. Olefin-type compounds

Stilbene is the best-studied example of an olefin-type chromophore. In general, the *trans*-isomer is thermodynamically more stable, and the *trans*–*cis* isomerization takes place upon the UV-irradiation according to the scheme shown in Table 1 [53, 56–60]. The reaction mechanism is excited state twisting about the $\text{C}=\text{C}$ double bond. The thermal back *cis*–*trans* reaction can be slow or fast, depending on the experimental conditions. Unfortunately, the number of publications concerning the photochromic properties of olefin derivatives containing strongly polarized substituents (such as CN , NO_2) is rather limited, even though such compounds are of considerable interest as photooptical and electrooptical media as well as non-linear optical materials.

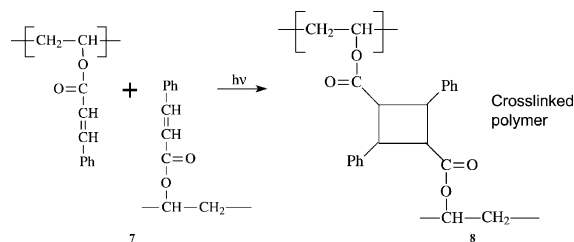
In addition to the *trans*–*cis* isomerization of stilbene, photocyclization may take place, giving dihydrophenantren under irradiation (Table 1, compound C). This reaction is realized through the excited singlet state with a rather high quantum yield of about 0.1. The back reaction is also run in the excited singlet state with a higher quantum yield of 0.3.

However, one of the most important photochemical reactions of olefin derivatives is the photodimerization of cinnamic acid derivatives, which leads to the formation of cyclobutane derivatives. It is interesting to note that photodimerization may proceed in a solid phase of any isomeric modification of *trans*-cinnamic acid (α or β) and, as is shown below, α -truxillic β -isotruxillic acids are formed [61]:





Usually, the above reactions proceed in polymers containing the cinnamic acid fragments. The latter fragments are often introduced to poly(vinyl alcohol), and this approach allows the preparation of polymer films which can experience photoinduced cross-linking under UV-irradiation. This cross-linking occurs via the formation of cyclodimers between cinnamate groups of neighbouring macromolecules (for details, see Section 3.3.2):



2.1.2. Azobenzene derivatives

Azobenzene and most substituted derivatives constitute a family of dye molecules known since the middle of the last century [53,54,56–62]. These compounds are characterized by intensive colour, high thermal stability (up to 350 °C) and the possibility of photochemically induced *trans*–*cis* isomerization. Azobenzene and nearly all its monosubstituted derivatives in the *trans*-form show a strong band in the UV-region (~320 nm), attributed to the $\pi \rightarrow \pi^*$ -transition, and a weak band in the visible region (450 nm), due to the $n \rightarrow \pi^*$ -transition (Fig. 6). The *trans*-form is generally more stable than the *cis*-form, but each isomer can be easily converted into the other by light irradiation of the appropriate wavelength (Table 1). However, the *cis*–*trans* isomerization is thermally stimulated; on conversion to the *cis*-isomer, the ($\pi\pi^*$) band shifts to shorter wavelengths, and the intensity of the ($n\pi^*$) absorption increases (Fig. 6).

Usually, the two mechanisms for the *trans*–*cis* reaction are considered. The first mechanism is known as the rotation mechanism, in which the N=N double bond is opened and allows the free rotation of one of the phenyl rings around the N–N axis. The second mechanism is the inversion mechanism, in which all

Table 1
Photochromism of olefin-type compounds

A	B	λ_1^{\max} (A), nm	λ_2^{\max} (B), nm	Compound
		295	280	1
		λ^{\max} (C) = 450		
		320	450	2

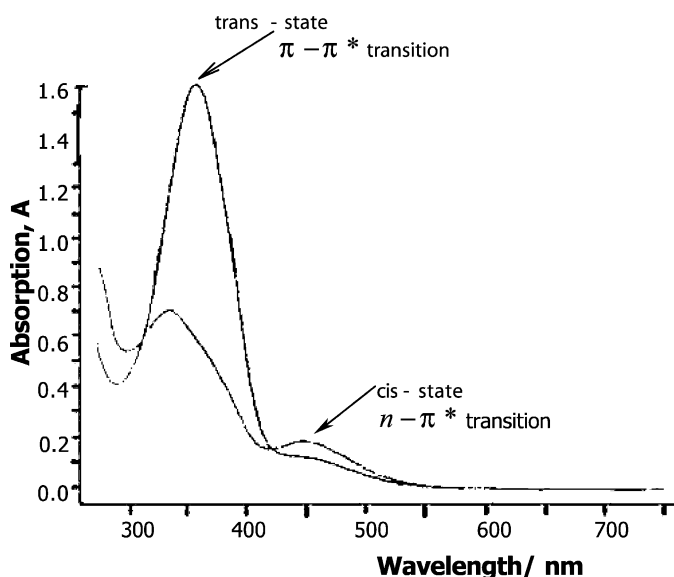


Fig. 6. Absorption spectra of *trans*- and *cis*-isomers of azobenzene.

atoms remain in one plane and the transition takes place over an *sp*-hybridized N-atom. The mechanism used depends on the exact surroundings of the azo group. Photoinduced isomerization of azobenzene involves dramatic structural rearrangements: the distance between the *para* carbon atoms in the molecule (Table 1) decreases from about 9.0 Å in the *trans*-form to 5.5 Å in the *cis*-form. The change in the configuration leads to a high increase in the dipole moment. The *trans*-form is planar and has no dipole moment, whereas the *cis*-form is non-planar and exhibits a dipole moment of 3.0 D.

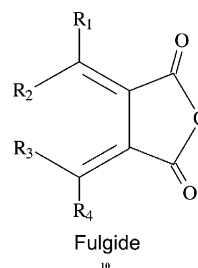
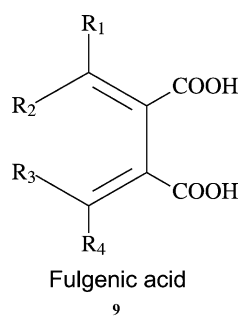
As it will be shown below later (Section 3.3.1), such changes may strongly affect the structural transformations in azobenzene-containing polymeric films under irradiation; hence, azobenzenes are good candidates as constituents of molecular switches, image storage devices, and materials with photomodulable optical and other physical properties [13,54,62,63].

2.2. Chiral photochromes

2.2.1. Fulgides

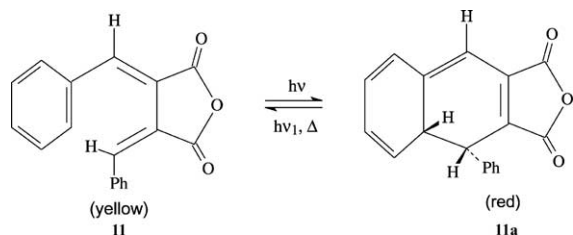
Photochromism of arylfulgides was discovered by Stobbe at the end of the XIX century [64]. The derivatives of 1,3-butadien-2,3-dicarboxylic acid

and its acid anhydride are referred to as ‘fulgenic acid’ and ‘fulgide’, respectively:



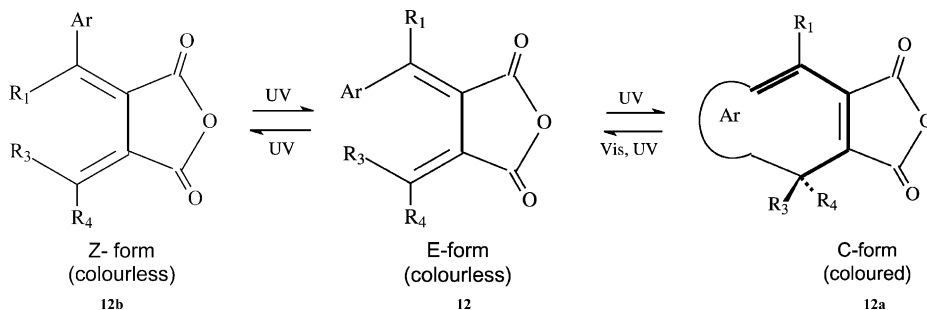
These names came from the Latin word ‘fulgere’ which means ‘to glisten’ and ‘to shine’ as they are often crystallized as bright and shiny crystals. Some fulgides are normally yellow/orange crystalline

compounds that can change their colour to a deep orange or red upon exposure to UV-light.



The colour change can be reversed either thermally or with white light. From the chemical point of view, according to the IUPAC nomenclature, these compounds should be named as derivatives of furan-2,5-dione; however, they are normally named as substituted bis-methylsuccinic anhydrides or fulgides [65].

To be photochromic, fulgides should have at least one aromatic ring on the *exo*-methylene carbon atom, so that they form a 1,3,5-hexatriene structure that may undergo cyclization. Fulgides have an intrinsic chiral nature in the hexatriene moiety that undergoes cyclization upon photo-irradiation to yield a cyclohexadiene derivative. The photochromism of fulgides occurs between one of the colourless open forms (abbreviated as the *E*-form because the geometry of the double bond connecting the aromatic ring and the succinic anhydride is usually shown as *E*-) and the photocyclized coloured form (abbreviated as the *C*-form) [65]:

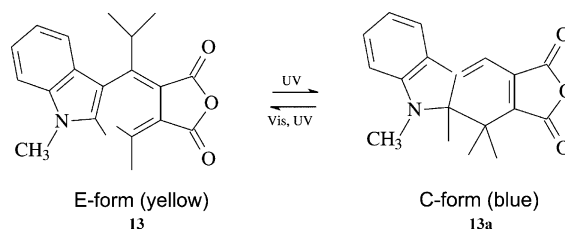


However, there is an additional photochemical *E*–*Z* isomerization pathway. The *Z*-form, the geometrical isomer of the *E*-form, is not considered as an important member of the photochromic system. There have been no reports that the *Z*-form cyclizes directly by adsorbing one proton to give the *C*-form.

Therefore, the *E* → *Z* photoisomerization, competing with the photochromic *E* → *C* isomerization, is an energy-wasting as well as system-complicating process in terms of the ‘photochromism of fulgides’.

Among a number of synthesized sterically overcrowded fulgides, indolyfulgide and its derivatives present a considerable interest as chiroptical molecular switches [65–67].

The photochromic reaction of indolyfulgide involves the open-colourless and conformationally mobile *E*-form (often in equilibrium with the *Z*-form) and the closed and rigid *C*-form:



Authors [67] reported that optically active fulgides **13** can work as chiral dopants to induce a cholesteric phase in the nematic liquid crystals, and the cholesteric pitch values can be reversibly controlled by photoirradiation.

Although mechanisms of the photochemical processes induced by irradiation of fulgides and their derivatives are complex, the number of the communications devoted to their synthesis and characterization gradually increases. At the present time,

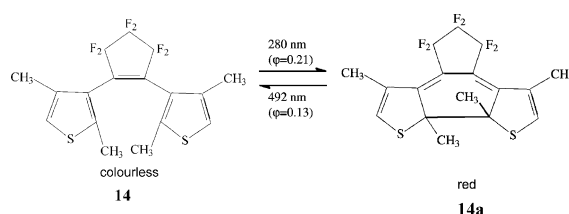
many fulgides containing heterocyclic furan and indole fragments were obtained, and the synthesis of pyrrole, oxazolyl, thiazolyl, and pyrazolyl derivatives was accomplished. The above compounds are characterized by a highly reversible character of the photochromic cycle, high thermal resistance of the photoinduced

group, and high quantum yield. They also show a high fatigue resistance (about 100 000 cycles) which allows one to treat these materials as promising candidates for new advanced technologies [65].

Current studies focus on the synthesis of indole fulgides with fluorescent properties [68]. The interest in such compounds is dictated by their possible application in the preparation of photochromic materials which, under the action of laser irradiation, are able to exhibit fluorescent properties. In other words, when the sample (for example, as a layer deposited onto a disc) is irradiated with an activated laser irradiation, the fulgide-based compound does not reflect light (as in traditional data carriers such as CD, DVD, etc.) but emits light with a certain wavelength. In this case, the fluorescent emission of a given element freely penetrates the layer on the disc, and this trend allows one to perform the recording through the whole thickness of the deposited layer. This finding gave rise to the term ‘three-dimensional 3D disk’. The Constellation 3D company pioneered the concept of volumetric storage of information by recording data on multiple layers located inside a disk or card, as opposed to the single or double layer method available in compact disks and DVDs. The absence of multiple interferences (which are typical of CD and DVD technologies) is a principal advantage of this method, because the as-induced fluorescent emission is not coherent. Constellation 3D Inc. announced the development of Fluorescent Multi-layer Disks (FMD) with a capacity up to 140 GB and a read rate of 1 GB per second. As compared with the existing DVD discs with a capacity up to 10 GB, the FMD statistics look rather impressive. Early applications for this exciting new product include digital cinema and digital players, Internet content streaming, and data warehousing [69].

2.2.2. Diarylethenes

In a certain sense, this family of photochromic compounds can be assigned to the olefin-type photochrome group. However, since their molecules comprise heterocyclic aryl groups, they normally are separately classified. Table 2 shows the most common photochromic diarylethenes, which can be considered the most promising photoswitches known today [70]. Photochemical switching of a perfluoro-substituted diarylethene is shown below:



Upon irradiation with UV-light, the colourless (non-conjugated) open-ring form transforms to the close-ring (coloured) form, which can again undergo ring-opening under visible light. The quantum yield (ϕ) of the direct reaction is much higher than the quantum yield of the back reaction.

First of all, it is necessary to note that all of the diarylethenes reported so far have not shown any thermochromism. The open-ring isomers are thermally stable, and the thermal stability of the coloured closed-ring isomers is dependent on the type of aryl groups. If the aryl groups are furan, thiophene, selenophene, or thiazole rings, which have low aromatic stabilization energies, the closed-ring isomers are thermally stable and do not return to the open-ring form isomers even at 80 °C (Table 2).

However, the most striking feature of these compounds is their high fatigue resistance. The colouration–decolouration cycle could be repeated more than 10^3 – 10^4 times in keeping with the photochromic performance. The absorption spectra of diarylethenes are dependent on the types of aryl groups, the substitution positions of aryl groups to ethane moiety, and upper cycloalkene structures. The open-ring isomers synthesized so far show absorption maxima ranging from 230 to 460 nm, and the closed-ring isomers show adsorption maxima from 425 to 830 nm. The cyclization and cycloreversion quantum yields were moderate, ranging from 0.01 to 0.86. The above-mentioned characteristics of diarylethenes satisfy the main requirements for their applications to optoelectronic devices, such as optical memories and switches [71–73].

An unusual and very interesting phenomenon concerning the reversible surface morphology changes of a single photochromic diarylethene crystal under irradiation was recently described by Irie et al. [74]. The crystal of diarylethene IV (Table 2) underwent a thermally irreversible but photochemically reversible colour change (from colourless to blue) upon an alternating irradiation with UV ($\lambda = 366$ nm) and

Table 2
Thermal stability and fatigue-resistant property of some diarylethenes [70]

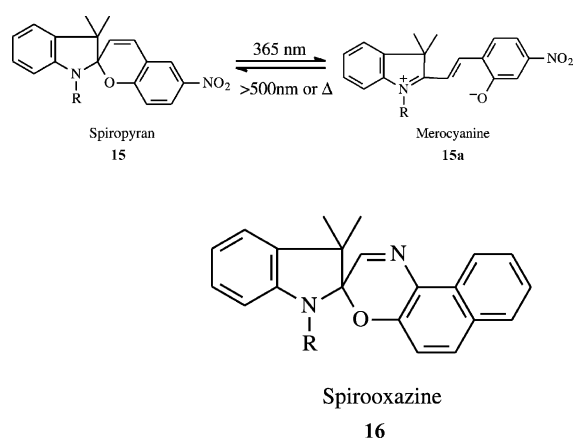
N	Isomerization		Thermal stability	Repeatable isomerization, cycles number	
	Open-ring form	Closed-ring form		In air	Under vacuum
I			> 500 h at 70 °C	–	–
II			Stable	3.7×10^3	1.0×10^4
III			Stable	–	$> 1.1 \cdot 10^4$
IV			Stable	80 (in hexane)	200 (in hexane) $> 10^4$ (in crystal)

visible ($\lambda > 500$ nm) light that induced reversible photocyclization reactions. Upon irradiation with UV-light, some steps appeared on the (100) single-crystalline surface that disappeared upon irradiation with visible light. The step height (about 1 nm) corresponds to one molecular layer. UV-irradiation formed valleys on the (010) surface that also disappeared by bleaching upon irradiation with visible light. One can suggest that the reversible change in the shapes of single crystals could potentially be used for the creation of photodriven nanometer-scale actuators.

As was reported in recent publications, optically active (chiral) fragments can be incorporated into the diarylethylene molecules. This allows one to prepare new diastereoisomers and to utilize these new compounds as effective chiral photochromic dopants. Once these dopants are incorporated into the liquid crystals it is possible to control their optical properties via light irradiation with a certain wavelength corresponding to the absorption of the chromophore groups. This will be considered in more detail in Section 2.3.

2.2.3. Spiropyrans and related compounds

The term ‘spiropyran’ is very generally used to denote a molecule containing a 2H-pyran ring in which the number-2 carbon atom of the ring is involved in a spiro linkage (see compound **15**). Spiropyran **15** and spiroxazine **16** are the most widely used spiroorganic photochromes [62,67].



Both compounds can exist in two basic forms (as is shown above)—the colourless parent spiro structures **15** and **16**, and the intensely coloured merocyanine

structures **15a** and **16a**. The photochromic (and thermochromic) behaviour is due to the interconversion of the closed spiropyran form and open merocyanine form. UV-irradiation leads to the open form, which reverts to the closed form either thermally or by irradiation with visible light. The spiro carbon atom is a stereogenic centre in spiropyrans, but due to the achiral nature of the merocyanine form, the photochromic process always leads to racemization. Introduction of different substituents (aryl and alkyl groups) in the left and right parts of spiropyrane and spiroxazine molecules allows one to change the spectral regions of photochromic transitions and the ‘lifetime’ of the photoinduced forms.

Let us consider some features of spiropyran photochromism. The coloured merocyanine form of the spiropyrans and spirooxazines have a very strong tendency to associate into aggregates with a stack-like arrangement of merocyanine molecules. When the molecular dipoles are arranged in a parallel (head-to-head) structure (the so-called J-aggregates), their absorption spectra are shifted to the red region as compared with the isolated merocyanine molecules. In the case of the antiparallel (head-to-tail) dipole arrangement (H-aggregates), the spectra are shifted to the blue region. The tendency for merocyanine aggregation is so strong that they form in solutions and polymer films under irradiation. The detailed information relating to J-aggregates and their use in wavelength-multiplexed memory systems may be found in Ref. [75].

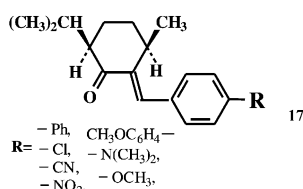
Because of their photochromic and thermochromic properties, spiropyrans and spirooxazines have been the object of extensive academic and applied interest. A number of the excellent reviews relating to spiropyrans

is available [53,76–79]. Moreover, the discovery of the photochromic reactions of spiropyrans in 1952 [80] initiated an active research on photochromism

application: self-developing photography, actinometry, displays, filters and lenses of variable optical density, including eye-protective glasses, etc.

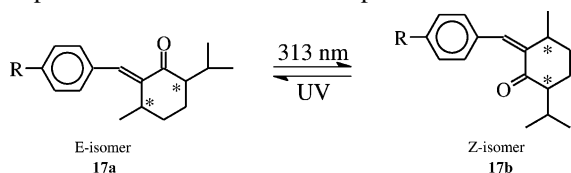
2.2.4. Arylidene menthanone derivatives

This type of compounds has been intensively studied by Ukrainian scientists [81–83] who synthesized a number of arylidene menthanone derivatives of the general formula:



These compounds, combining photochromic and chiral properties, are known as effective chiral dopants used for the induction of chiral nematic phase by introduction into the nematic phase. The majority of arylidene-*p*-menthanone-3-one derivatives possesses high helical twisting power (Section 1.3) in the range from 20 to 50 μm^{-1} , depending on the chemical structure of substituent.

As is seen in formula 17 1,2-arylidene-*p*-menthanone-3-ones have an *exo*-cyclic double bond fixed in an *s-cis* disposition and capable of *E-Z* isomerization. Analysis of electronic and UR-spectra as well as NMR data of arylidene-menthanone derivatives in different solvents before and after UV-irradiation strongly intimated that *E-Z*-isomerization with respect to the double bond takes place:



The back reaction is also induced by UV-irradiation. The ratio of quantum yields of the forward (φ_E) and back (φ_Z) reactions is equal to 3–4; this is testimony to the higher efficiency of *E* → *Z* isomerization ($\varphi_{E>} \sim 0.32\text{--}0.37$) as compared with the back reaction ($\varphi_{Z>} \sim 0.08\text{--}0.13$).

The uses of arylidene-*p*-menthanones for cholesteric phase inducing in nematic liquid crystals are described in detail by the Ukrainian authors who greatly contributed to the synthesis and study

of these fascinating chiral-photochromic dopants [84,85].

2.3. Other chiral-photochromic and multifunctional switches

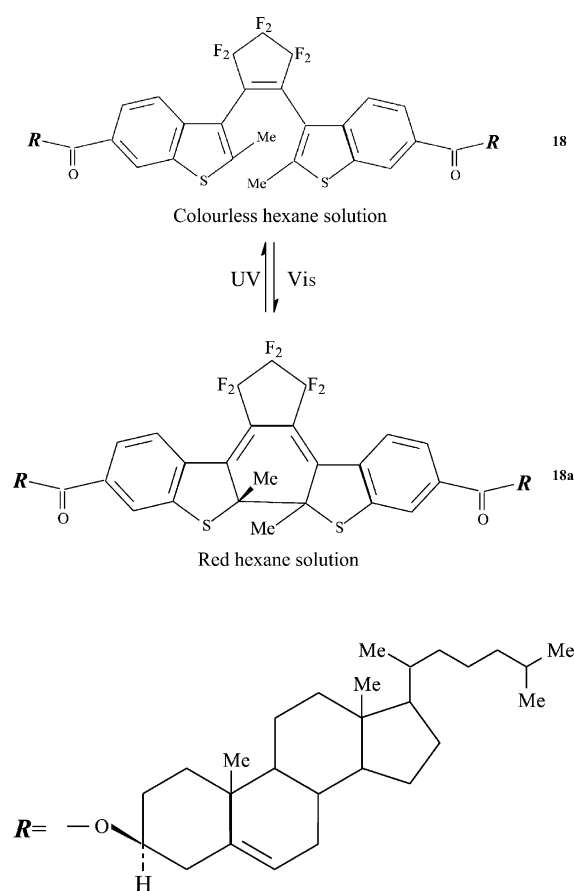
The above photochromic systems belong to the best studied families of chemical compounds, which have already found or are just starting their practical application in information technologies. In addition to these compounds, such compounds as salicylideneimines, viologens, azulenes, etc. offer substantial advantages. These topics are beyond the scope of this review, but the related information may be found in a special issue of ‘Chemical Review’ [86] devoted to photochromism and photochromic compounds.

In this section, we would like to focus our attention on more complex photochromic compounds that were synthesized quite recently. A controlled preparation of the compounds (and materials) combined both photochromic and optically active (chiral) groups, fragments of photochromic groups and LC compounds, photoluminescent and chiral fragments, etc. In this respect, spiropyranes and menthanones offer excellent examples as they show a dual functionality: their molecules are both photochromic and chiral. However, the number of such hybrid systems is rather limited, and new approaches for the preparation of such compounds are wanted. Such combined or multifunctional compounds are interesting from at least two standpoints.

First, the development of chiral photochromic systems is closely related to the problems of stereochemistry and stereoselectivity of the reactions. Hence, the research activities in this direction show a purely scientific interest.

Second, the presence of photochromic fragments and chiral groups in the same molecule allows one to use these compounds as dopants incorporated into the liquid crystals. These dopants, under the action of light irradiation, are able to change their LC structure and optical properties [67,87]. Some examples of such compounds are discussed below.

For example, one such chiral-photochromic hybrids, a diarylethene with the two cholesterol units, was described in Refs. [70,88].

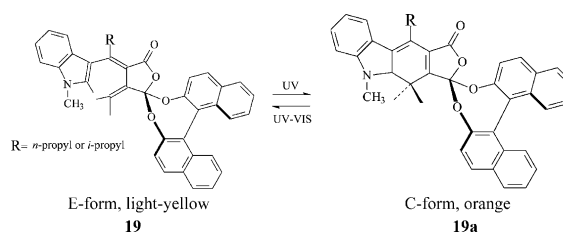


where $\text{Me} = -\text{CH}_3$

The hexane solution of **18** was colourless and the absorption maximum was observed at 318 nm. Upon irradiation with UV-light, the hexane solution turned red-purple, producing the closed-ring isomer **18a** as shown above. The coloured isomer showed an absorption maximum at 543 nm and was stable at 70 °C, not returning to the colourless isomer **18** in the dark. Upon irradiation with visible light ($\lambda > 480 \text{ nm}$) the colour disappeared and the colourless **18a** was regenerated.

The initial cholesterol-containing derivative of diarylethene **18** (1–2 wt%) was doped into a nematic liquid crystal to form a stable cholesteric (chiral nematic) phase. After UV-irradiation of the mixture (254 nm) for 60 s, the chiral nematic phase disappeared, and a nematic texture was observed. The cycle could be repeated more than 50 times without any deterioration of the LC phase.

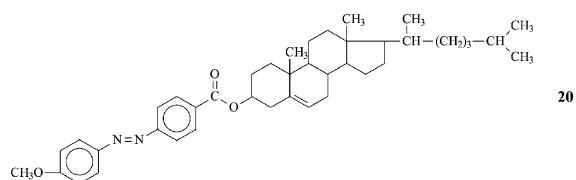
Another interesting example is connected with the creation of chiral fulgide derivatives via the modification of indolylfulgides with (**R**)-binaphthol [89]. As it was shown above, fulgides have an intrinsic chiral nature in the hexatriene moiety that undergoes cyclization upon photoirradiation to yield a cyclohexadiene derivative (Section 2.2.1) having a stereogenic quaternary carbon atom on the cyclohexadiene moiety. Another way to obtain an optically active photochromic fulgide is the incorporation of a chiral auxiliary to its molecule. Japanese authors [89] have introduced **R**-binaphthol to indolylfulgide molecule and obtained the new compound **19** combining these two fragments:



Authors reported that the modified indolylfulgides with (**R**)-binaphthol showed diastereoselective photochromic behaviour ascribed to the highly biased diastereomer ratio of the *E*-forms (see compound **13** in Section 2.2.1) with regard to the helicity of their hexatriene moiety. The compound **19**, similar to non-modified indolylfulgide **13** (Section 2.2.1), generated the cholesteric phase when added to nematic cyanobiphenyl liquid crystal (4-cyano-4'-pentylbiphenyl).

In both cases, the cholesteric pitches were reversibly changed by photoirradiation according to the above-mentioned schemes. However, the helical twisting power β was higher for the light-coloured form **13** (Section 2.2.1) than for the deep-coloured form **13a**, whereas the β value was higher for the deep-coloured form **19a** than for the light-coloured form of **19**. In addition, the β value of **13** is generally smaller than that of **19** and **19a**. These very interesting phenomena were explained in terms of the helical conformation of the hexatriene moiety of fulgides and the chirality of the binaphthol moiety.

Ikeda et al. [90] described reversible gel formation by using cholesterol functionalized with a photo-reversible azobenzene fragment:



It was shown that *trans*-isomer of this compound (with respect to the azo-group) forms a gel in *n*-butanol with $T_g \sim 15$ °C. Gel formation was effected by photoisomerization (330–380 nm) and afforded a photostationary state with 38% of *cis* isomer and $T_g = 2$ °C. The thermal reisomerization to the *trans*-form took place upon irradiation at $\lambda > 460$ nm. The *trans* isomer of **20** showed a CD effect because it formed helical aggregates due to chirality of the cholesterol moiety. In contrast, the *cis*-isomer did not show a CD effect; hence, the sol–gel phase transition can be controlled by light with non-destructive read out by CD.

A large number of chiral photochromic liquid crystals containing azobenzene fragments chemically linked to chiral groups have been synthesized and studied by different research groups [90–92]. These compounds are of significant interest because they can be used both as individual substances and in mixtures with liquid crystals as optical switching materials whose optical properties can be changed selectively and reversibly by light.

3. Photochromic LC polymer systems

Notwithstanding evident advantages of the possible practical utilization of photochromic low-molar-mass organic compounds, their application as individual compounds (without any substrates) is rather limited. Usually, polymer compounds are used as substrates. The substrates are prepared by the introduction of chromophores to the polymer matrix via mixing and a subsequent formation of a film or coating. This approach has been widely used, for example, for the preparation of photoresists and in lithography [56,59]. As was shown above, an alternative approach involves the chemical binding of photochromic groups with the macromolecules of high-molar-mass compounds; in other words, the preparation of photochromic copolymers.

In this section, we will consider in brief the specific photooptical behaviour of the blended photochromic systems and will discuss in more detail the problems related to the preparation of photochromic LC polymers and specific characteristics of such compounds.

3.1. Mixtures consisting of polymers and photochromic compounds

Systems in which the dye molecules are dispersed in the polymer matrix (so-called blends or composites) rather than bound to it have been studied since the classical paper by Weigert and Nakashima [93]. They observed optical anisotropy induced by polarized light in solid due solutions in gelatin. The birefringence photoinduced in the films prepared from the solutions of pure dyes and mixtures with different polymers was studied rather extensively [51,56,61,94–99].

Aromatic azo dyes are the most frequently used dyes. The reversible photoinduced anisotropy and dichroism of azo dyes (guests) in an amorphous polymer matrix (host), such as poly(vinyl alcohol) or poly(methyl methacrylate), was studied in detail by Todorov et al. [100,101]. More recently, a few groups have investigated the photoinduced anisotropy phenomena in polymers doped with spiropyrans [86].

Let us consider what is happening with azo dye molecules incorporated into an amorphous polymeric matrix under polarized light irradiation. The molecules of aromatic azo dye located in parallel (and almost parallel) directions to the electric field vector of the light (Fig. 7(a)) are transformed into an excited state (Fig. 7(b)) and undergo a *trans*- (or E) \rightarrow *cis*- (or Z) \rightarrow *trans* photoisomerization (Section 2.1.2, Table 1) that changes their orientation. The photochromic molecules tend to line up in a direction perpendicular to the direction of polarization of the electric field vector of incident light (Fig. 7(c)). As a result, the intensity of transmitted light T in the direction parallel to the electric field vector T_{\parallel} (i.e. in the direction of polarization of the ‘writing’ beam) increases whereas that in the direction perpendicular to the electric field vector T_{\perp} decreases (Fig. 8).

This implies that the different molecules of the initially disordered set of dye molecules absorb light with a different probability. The maximum probability

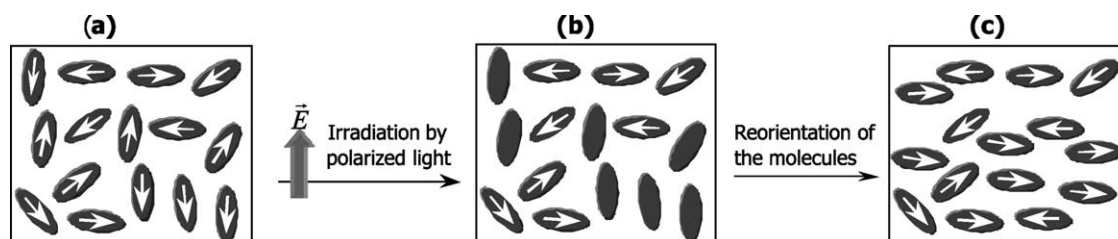


Fig. 7. Generation of optical anisotropy by polarized light irradiation in the amorphous polymer film containing photochromes. Direction of dipole moment of photochromic molecules is shown by arrows. The excited photochromic molecules are shown without arrows. \vec{E} is the electric vector of polarized light. (a) Initial (unoriented) state; (b) excited state; (c) oriented state.

for the resonance light absorption is characteristic of molecules for which the dipole moment of the transition coincides with the direction of the electric field vector of the light. When these vectors are aligned perpendicularly to each other, the probability of light absorption is equal to zero. Thus, light seems to ‘select’ the molecules according to their orientation; this process was called photoselection [54,59, 102].

Photoselection was studied in solid solutions of azobenzene dyes (methyl orange, methyl red) in poly(vinyl alcohol), polymethyl methacrylate (PMMA), and poly(vinyl acetate) films using laser irradiation ($\lambda = 488$ nm) [100,101]. However, the light-induced dichroism and birefringence (about 10^{-3}) were preserved for only a limited period of time and then disappeared (Fig. 8).

A similar phenomenon was reported by Williams and co-workers [103,104] for PMMA blends with photochromic fulgides. Substantial photoinduced optical anisotropy ($\Delta n = 0.2$ – 0.3) was also observed in the Langmuir–Blodgett (LB) films of azobenzene dyes [105,106] and, later on, in a number of polymers containing chemically linked azobenzene derivatives.

In general terms, the photoinduced anisotropy can be quantitatively defined by two parameters. The first parameter is the photoinduced birefringence Δn

$$\Delta n = n_{\parallel} - n_{\perp} \quad (5)$$

where n_{\parallel} and n_{\perp} are refractive indices for polarizations parallel and perpendicular to the polarization of the excitation, respectively.

The second parameter is the macroscopic order parameter S

$$S = (A_{\parallel} - A_{\perp}) / (A_{\parallel} + 2A_{\perp}) \quad (6)$$

where A_{\parallel} and A_{\perp} represent the absorbance with a polarization parallel and perpendicular to the polarization of the excitation, respectively.

The use of polymer-dye blends and composites as materials with controllable optical properties (in particular, for data storage) is characterized by a number of important drawbacks. As a rule, because of poor solubility, the content of dye in the polymer matrix is between 1 and 5%. Incorporation of greater amounts of photochromic compounds or dyes is usually accompanied by phase separation. In addition, such blends are extremely susceptible to temperature; temperature variations promote phase separation. Ultimately, the stability of such systems and their ability for repeated performance

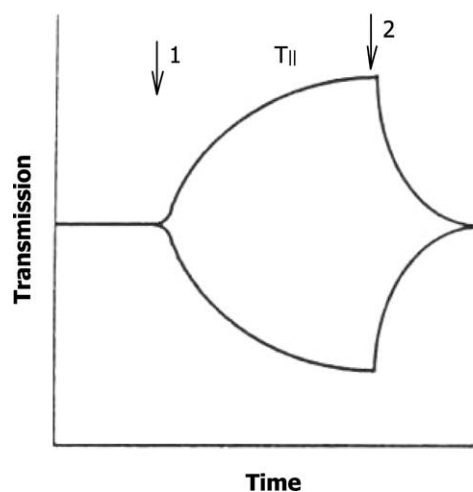


Fig. 8. Scheme of the variation of optical transmission of light by the polymer film containing a small amount of the dissolved azobenzene dye with time: (1) the light is switched on; (2) the light is switched off.

are also low; the relaxation of photoinduced dichroism and birefringence, which are controlled by the diffusion of low-molar-mass photochromic compounds or dye molecules, takes place rather rapidly, significantly altering the optical characteristics of the mixtures.

Despite the disadvantages of polymer compositions with organic photochromic compounds, such systems offer evident advantages over the individual organic photochromes. First, this reasoning is related to the possible processing of photochromic materials as polymer films or as coatings on different substrates. A simple preparation of such materials (for example, via centrifuging, evaporation of the solvent from the solution) and easy handling present a special attraction for technologists and engineers. To improve the miscibility, various additives are introduced into the compositions to serve as plasticizing agents and compatibilizers. However, the optimum preparation of polymer photochromic materials is presented by the development of copolymers where the monomer units contain photochromic or dye fragments as one of the components. Many scientific publications devoted to the synthesis and characterization of photochromic polymers are available [6,13,42,44–47,51–54,56–63,76,86,98,99].

In the present review, we consider only photochromic LC (or amorphizable liquid-crystalline) polymers and photochromic LC mixtures.

3.2. Principles of molecular design of photochromic LC polymers

It might seem that radical homopolymerization of monomers containing photochromic groups leading to the formation of the corresponding photochromic LC polymers provides the best way for their synthesis. However, this approach is evident only when photochromic groups are also mesogenic. In this case, polymerization of such monomers provides the formation of LC photochromic polymers. In practice, this approach was used for monomer derivatives of azobenzene with a high anisotropy of molecules and photochromic N=N fragments. In this case, polymerization yielded photochromic LC polymers. In most other cases, bulky (non-mesogenic) photochromic groups (spiropyranes, fulgides, etc. see Section 2.2)

dramatically hinder the development of the LC phase. As a result, homopolymerization of such monomers leads to the formation of amorphous polymers with photochromic properties. These systems are beyond the scope of this review. At the same time, monomers with bulky groups may participate in copolymerization with other mesogenic monomers and produce photochromic LC copolymers.

Radical copolymerization of mesogenic and photochromic monomers provides a convenient method for the synthesis of photochromic LC polymers (Fig. 9). This simple procedure makes it possible to control the concentration of both components; the knowledge of the reactivity ratios for both components allows one to judge the compositional inhomogeneity of the as-formed copolymers. In this case, it seems important to note that the concentration interval of the existence of the mesophase is markedly controlled by the presence (or absence) of spacers between the photochromic fragments and the polymer backbone. The longer the spacer between the photochromic group and the main chain, the higher the concentration of photochromes that may be introduced with no disruption of mesophase, independently of its structure (nematic, smectic, or cholesteric). However, mesogenic photochromic groups as well as non-mesogenic photochromic groups can be incorporated into the macromolecules.

Polymer analogous reactions are the second synthesis method for LC photochromic copolymers, involving the addition of photochromic and mesogenic groups to a polymer chain containing functional groups (Fig. 9).

It should be noted that a partial conversion of polymer analogous reaction leads to the preparation of so-called functionalized photochromic LC polymers containing mesogenic photochrome and functional groups. Such copolymers can also be obtained by copolymerization of mesogenic photochromes with functional monomers containing carboxylic groups. Functionalized LC copolymers are important for the synthesis of ionogenic and metal-containing LC polymers, which are presently under study [107–109] (Section 3.5).

And, finally, the polycondensation of photochromic fragments with other blocks bearing the functional groups is chosen much more rarely (Fig. 9).

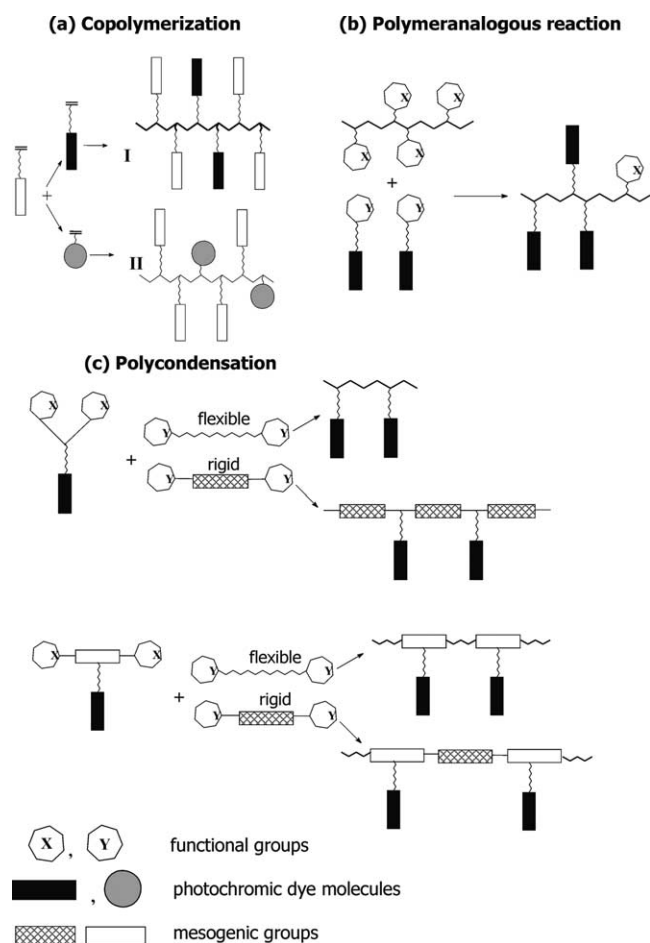


Fig. 9. Different approaches to the synthesis of photochromic LC polymers and schemes of their molecular structures.

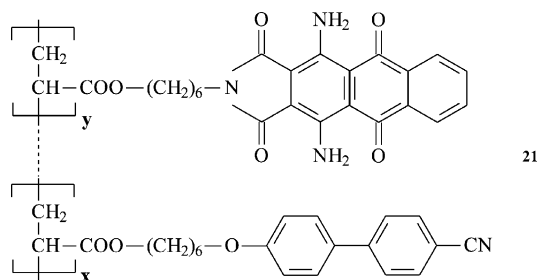
This method leads to the formation of polymers containing mesogenic groups in the main and/or side branches.

Using all of these methods, one can ‘chemically incorporate’ the dye-containing fragments in the polymeric chains. As can be seen from Fig. 9(a)–(c), one can vary the connection type of dye-containing fragments by including them in the main and side chains as well as by changing their distribution in the macromolecule. In general, any type of molecular structure (shown in Fig. 1) containing photochromic moieties can be obtained by using one of the above-mentioned methods. Polymers with covalently connected dye molecules have essential advantages over polymer-dye mixtures.

The photochrome-containing copolymers are more stable due to the covalent bonds of dyes with the LC ‘mother-matrix’. The content of photochromic monomer units with mesogenic shape fragments in copolymers may reach 60–70 mol% without distortion of the LC phase.

On the other hand, the incorporation of bulky photochromes such as anthraquinone or spiropyran into the side chain of macromolecules generally destroys the mesophase at high dye concentration. For example, the acrylic copolymer **21** containing 36 wt% of bulky anthraquinone groups is still liquid crystalline but, at a higher concentration of dye, the LC phase disappears [110]. It should be mentioned that, in general, similar anthraquinone dyes in

low-molar-mass nematic hosts have poor solubilities (usually below 0.5 wt%).



In whole, the mesophases produced by the LC polymer are stable relative to the ‘chemical incorporation’ of bulky photochromic groups to macromolecules.

When analyzing the literature on this particular problem, one should note that the number of the photochromic compounds or dyes used for the preparation of LC photochromic polymers is rather limited. There are various azobenzene derivatives that are able to interact with a polymer matrix and produce rather interesting photocontrolled LC systems, which have found their practical application in optical memory devices [13,44,46,50,54], holography [111–114], and recording systems for the preparation of so-called ‘command surfaces’ that control the properties of low-molar-mass liquid crystals. One of the challenging directions developed by Italian scientists is related to the preparation of photochromic azobenzene-containing polypeptides. Presently, research work in this direction is focused on examining the behaviour of such compounds in dilute solutions [115]. Azobenzene derivatives also present an evident interest for scientists involved in study of lyotropic and thermotropic liquid crystals; research work related to the investigation of the structure of the above compounds in concentrated solutions and in a solid phase may offer new fascinating results.

Cinnamic acid derivatives and spiropyran are among other photochromic compounds used for the synthesis of LC photochromic polymers. However, the number of related works for these compounds is much smaller than the number of communications devoted to the azo-containing polymers. As for other photochromic compounds (in particular, those considered in Section 2.3), only a few publications on their use in the preparation of photochromic LC polymers are available.

Taking into account the extent of the existing review publications devoted to the azo-containing LC polymer systems, we will pay less attention to such systems in this review, but will consider some other photochromic LC systems. The principal emphasis is the generalization and analysis of the results for photochromic LC polymers producing the cholesteric type of mesophase, which is characterized by the development of a helical supramolecular structure.

3.3. Photochromic LC polymers with nematic and smectic structures

Despite a great variety of low-molar-mass organic photochromic compounds, the number of photochromic polymers and, in particular, photochromic LC polymers is rather limited. This situation is likely to be related to the difficulties of their synthesis and possibly to an evident lack of close cooperation between scientists working in photochemistry and polymer science. As a rule, efficient cooperation between the specialists working in various scientific areas may be considered a principal factor in the solution of many challenging problems. This is especially true when dealing with research in the adjacent areas of science, such as the photochemistry of macromolecular compounds.

In spite of a great number of chromophores, the macromolecules of most amorphous and LC polymers involve photoactive groups such as the derivatives of azobenzene, spiropyran, and cinnamate fragments. Less publications were devoted to the synthesis and characterization of LC polymers containing other achiral and chiral fragments such as the derivatives of fulgides, diarylethylene, binaphthol, etc. (those considered in Section 2). Independently of the type of photochromic groups involved in the macromolecules, all photochromic LC polymers may be conditionally classified into two groups depending on the type of the induced mesophase.

The first group of these compounds includes the binary nematic and smectic LC copolymers containing nematogenic (or smectogenic) and photochromic fragments, which can be mesogenic or non-mesogenic. For instance, this group includes azobenzene and spiropyran derivatives, respectively. It should be emphasized that some copolymers can be supercooled to form amorphizable films, the optical properties of

which differ from those of the LC films. These systems are considered in detail below.

The second group of the compounds includes cholesteric (chiral nematic) copolymers with chiral and photochromic groups that can be chemically linked together in the same monomer unit or can be incorporated into the polymer chain as individual monomeric units. In turn, they can be subdivided into several groups (Section 3.4).

Investigations of the optical properties of the substances belonging to the first group of photochromic LC polymers were performed for poly(acrylic) and poly(methacrylic) homopolymers and copolymers containing azobenzene photochromes.

3.3.1. Azobenzene-containing LC polymers

Among photochromic LC polymers, azobenzene binary LC copolymers (see scheme in Fig. 9(a), I) are the most common compounds. They have been studied in detail, and their optical properties were reported in our works [35,44,116–121], in our joint publications with German scientists [122–125] as well as in the numerous papers of many researchers from Germany [114,126–128], Japan [129–132], Canada [133–136], Denmark [137–140], and other countries [141–143].

Taking into account that investigations devoted to azo-containing LC polymers were considered in detail in several reviews and generalized papers [13,14,42–47,54,113,114], we will restrict the analysis of these systems to the most general conclusions.

3.3.1.1. Photoorientation and kinetics of photoinduced process. A wide series of azo containing fragments have been used for the synthesis of acrylic

and methacrylic homopolymers and copolymers. In the latter case, the second monomer is usually the nematogenic-fragment-containing polar or non-polar terminal group that allows one to control the temperature interval of the existence of LC phase. Chemically bound to the macromolecules and exposed to the light with an appropriate wavelength λ , the azobenzene fragments exhibit sequential photochemical configuration transformations significantly affecting the shape of the photochromic monomer units. The rigid rod azobenzene groups are transformed from *trans*- to *cis*-isomers with a non-mesogenic bent shape (Table 1 and Fig. 10).

Fig. 11 shows the absorption spectra for the film of azo-containing copolymer **22b** containing 40 mol% of azobenzene groups as irradiated by a mercury lamp for over different time periods [44]

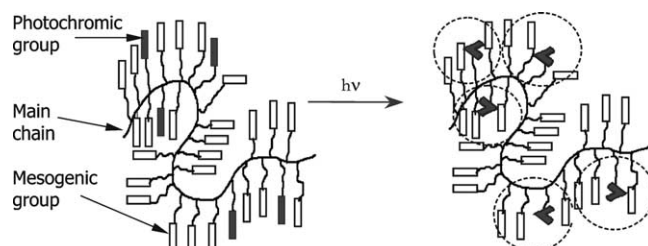
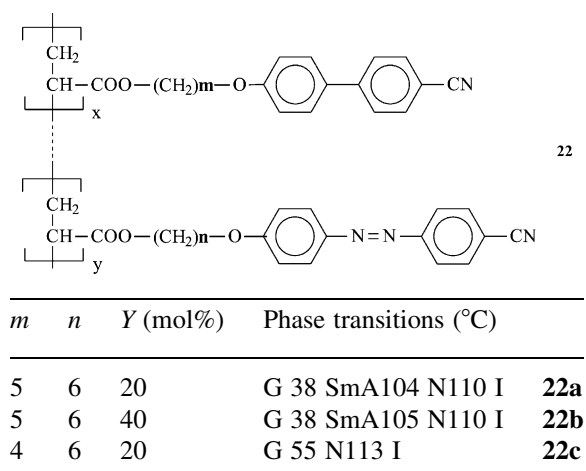


Fig. 10. Schematic representation of structural transformations in shape of the photochromic azo-containing side groups in the course of the light-induced *trans*–*cis* isomerization [44].

As the duration of irradiation increases, the concentration of *trans* isomers (the peak at 367 nm) rapidly decreases. As the irradiation is ceased, the reverse process of *cis*–*trans* isomerization takes

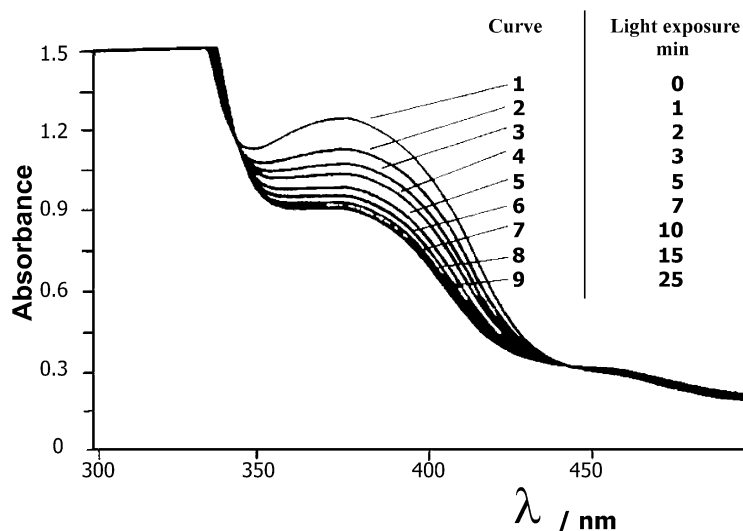


Fig. 11. Absorption spectra of a film of acrylic copolymer **22b** containing 40 mol% of azo dye during irradiation by UV-light ($\lambda = 365$ nm, $P = 1.7$ mW/cm²). Light exposure time is indicated in the figure [44].

place. The rate of this reverse process is slow (tens of hours); hence, a certain stationary state, controlled by the intensity and duration of the irradiation, is established between *trans* and *cis* isomers.

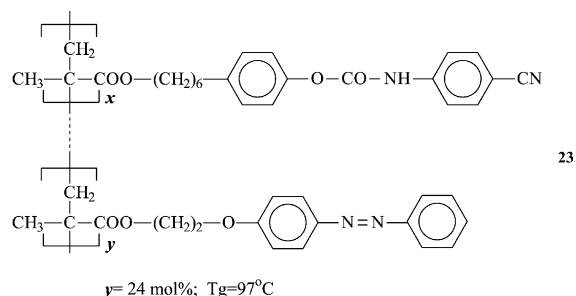
Any change in the shape of the photochromic azo dye guest molecules necessarily leads to the disruption of the local packing of the neighbouring structural and optical properties of polymer films (Fig. 10). By what means do these photochemical transformations affect the orientation of photochromic and mesogenic groups in the copolymers?

The most complete information about the orientation of side fragments in the films of comb-shaped macromolecules irradiated by polarized and non-polarized light was derived from the analysis of polarization UV/Vis spectra, FTIR data, and the angular dependence of certain absorption bands of photochromic copolymers [116,122–124]. As the probability of light absorption by photochromic fragments is different due to photoselection (Section 3.1), photochromic side branches acquire a certain preferential orientation. The photochemical transformations that take place in photochromic fragments cause deterioration in the local arrangement of the neighbouring mesogenic side groups (as shown by dashed lines in Fig. 10). In other words, the supramolecular structure changes significantly. The types of structural changes are significantly

controlled by the initial degree of order (or disorder) of the entire polymer matrix, the free volume of the polymer, the degree of ‘connection’ (spacer length) of side branches and main chain, and the kinetic flexibility of the macromolecule. Obviously, structural rearrangements, which are primarily induced by photochemical transformations of photochromic groups, are rather complex processes involving both the direct and reverse photoisomerization and structural transformations that may occur simultaneously with the photochemical process.

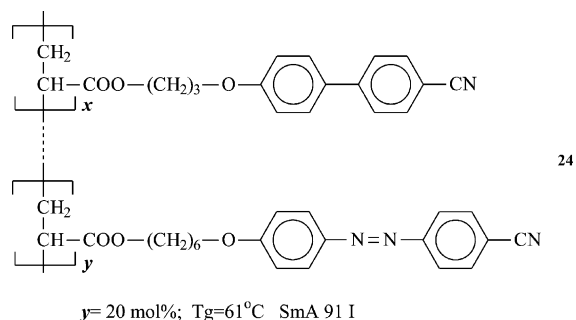
The above general scheme of photooptical transformations in photochromic copolymers leads to the natural question: can light be used to control the structure of polymers and generate an appropriate orientation of mesogenic groups in the polymer film? In other words, can light be used as an active factor to control the optical properties of photochromic comb-shaped polymers? It is absolutely clear that these questions are closely related to the general problem of designing photochromic materials with the required locally controlled optical properties for optical memory systems and reversible data recording, transmission, and imaging. Detailed investigations by different research groups into the photochemical transformation mechanisms of photochromic groups and the related structural changes in the neighbouring (non-photosensitive) fragments showed that irradiat-

ing thin polymer films of these copolymers resulted in the orientation of both photochromic and mesogenic groups. Therefore, the process of photostimulated orientation exhibits a pronounced cooperative character,⁵ clearly demonstrated in the studies of methacrylic copolymers that contain nitrile groups in the side mesogenic fragment and not in the photochromic fragments [132–134].



As is seen in Fig. 12, the initial isotropic angular distribution of absorption intensity corresponding to the vibration of nitrile groups changes for the asymmetric pattern, and photoinduced birefringence appears [122]. It means that photochromic and non-photochromic fragments of the comb-shaped macromolecules undergo the coordinated orientation induced by the light irradiation.

A similar situation takes place during the irradiation of LC polymers with a preliminary orientation of mesogenic fragments [123]. Fig. 13 shows the same dependence for the film of copolymer 24 characterized by planar orientation. In the initial state, the electric field vector forms an angle of 45° with the director, that is, with the



⁵ Degree of such cooperative motion depends on a number of factors and, in particular, on polarity of mesogenic and photochromic fragments [133–136].

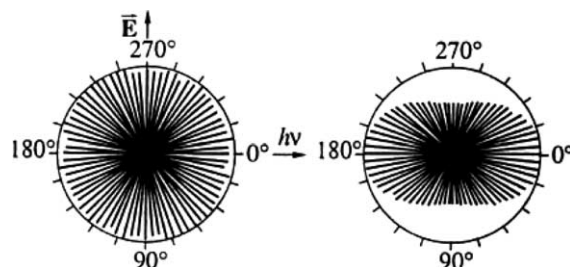


Fig. 12. Angular distribution of integrated absorption areas corresponding to the vibration of nitrile groups in the copolymers. (a) 23 before and (b) after irradiation with a laser ($\lambda = 488 \text{ nm}$, $P = 40 \text{ W/cm}^2$) [44].

orientation axis; initially, the order parameter S is equal to 0.4. After irradiation and relaxation, the optical axis rotates by 45° , and the order parameter S is reduced to 0.16. The decrease in the order parameter indicates that the reorientation of mesogenic groups deteriorates the LC order. However, the existence of order in the initial sample imposes certain constraints on the process of reorientation.

Fig. 14 shows the scheme of orientation (and reorientation) of the side fragments in unoriented (amorphous or amorphizable) and planar-oriented LC polymer films under laser irradiation. As shown, the photochromic groups and mesogenic fragments orient so that their long axes are perpendicular to the electric field vector direction of the laser beam. In other words, the laser irradiation effectively selects molecules by orienting them in a preset direction. This photoselection, or photostimulated orientation, takes place in solid polymer films at usual temperatures and leads to the appearance of induced birefringence Δn_{stab} , sharply changing the optical properties of irradiated films. The analysis of data on the optical properties of amorphous and LC polymer films before and after laser irradiation showed that the photoinduced birefringence appears as a result of an increase in the n_x value relative to n_y , where

$$\Delta n_{\text{ind}} = n_x - n_y \quad (7)$$

Fig. 15 shows the variation in the refractive indices and birefringence for a homeotropically oriented film of a photochromic copolymer (2) placed in an electrooptical cell (1) illuminated by a laser beam. In essence, this system can be used for data recording. The left-hand part of cell I is shielded by a metallic plate and not

illuminated, whereas the right-hand part II is illuminated by the writing laser beam. The right part of Fig. 15 shows the microscopic photograph of the cell taken in the crossed polarizers before and after irradiation. The non-irradiated left-hand part of the microphotograph appears dark in the crossed polarizers because it corresponds to the uniaxial nematic monocrystal, for which the refractive indices n in directions x and y are equal $n_x = n_y$, and birefringence $\Delta n = n_{\parallel} - n_{\perp} = 0$. After the irradiation of the right-hand part of the cell with a vertically polarized laser beam, the optical properties of the film dramatically change. According to the above concepts, the side fragments of macromolecules are aligned in the direction perpendicular to the electric field vector of the light beam $n-\pi^*$. As a result, n_x increases, as compared with n_y , photoinduced birefringence Δn_{slab} appears, and the right-hand part of the cell becomes bright in the crossed polarizers.

A generalized typical kinetic curve for variations in the photoinduced birefringence Δn_{stab} in the polymer film under laser irradiation is shown in Fig. 16. Analysis of the photochemical and photooptical studies of LC azo-containing polymers showed that the kinetics of photoinduced birefringence may be described as a superposition of slow and fast processes.

$$\Delta n_{\text{ind}} = \Delta n_{\text{ind}}^{\text{f}} + \Delta n_{\text{ind}}^{\text{s}} \quad (8)$$

Curve 1 in Fig. 16 can be described in terms of the fast and slow components. Usually the contribution of the fast process to the overall photoinduced birefringence is 5–10% or 10–20% for the amorphous and LC polymers, respectively. The fast process proceeds from milliseconds up to several seconds depending on chemical structure and degree of polymerization of copolymers and temperature. It is important that the fast

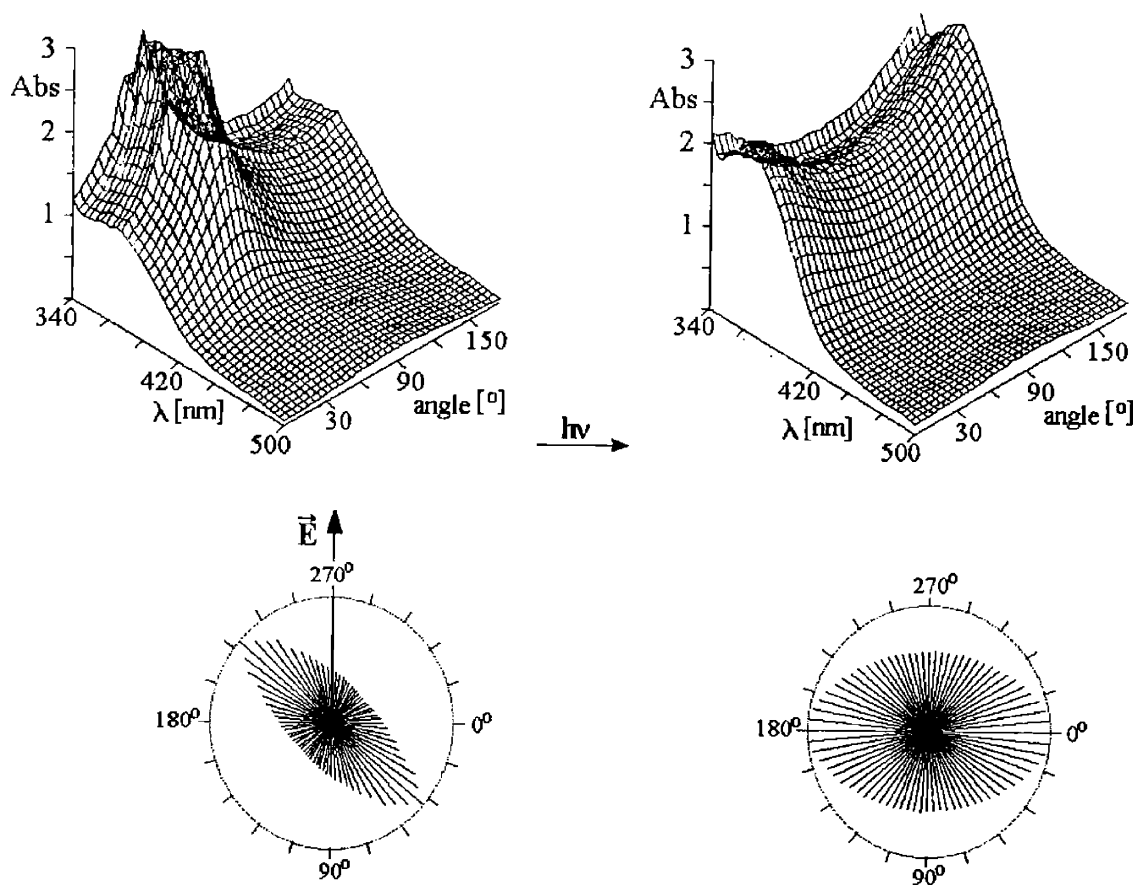


Fig. 13. UV polarization spectra ((a) and (c)) and angular dependences ((b) and (d)) of the absorption bands at 380 nm of the planarly oriented films of copolymer **24** ((a) and (b)) before and ((c) and (d)) after irradiation with a laser ($\lambda = 488$ nm) [44].

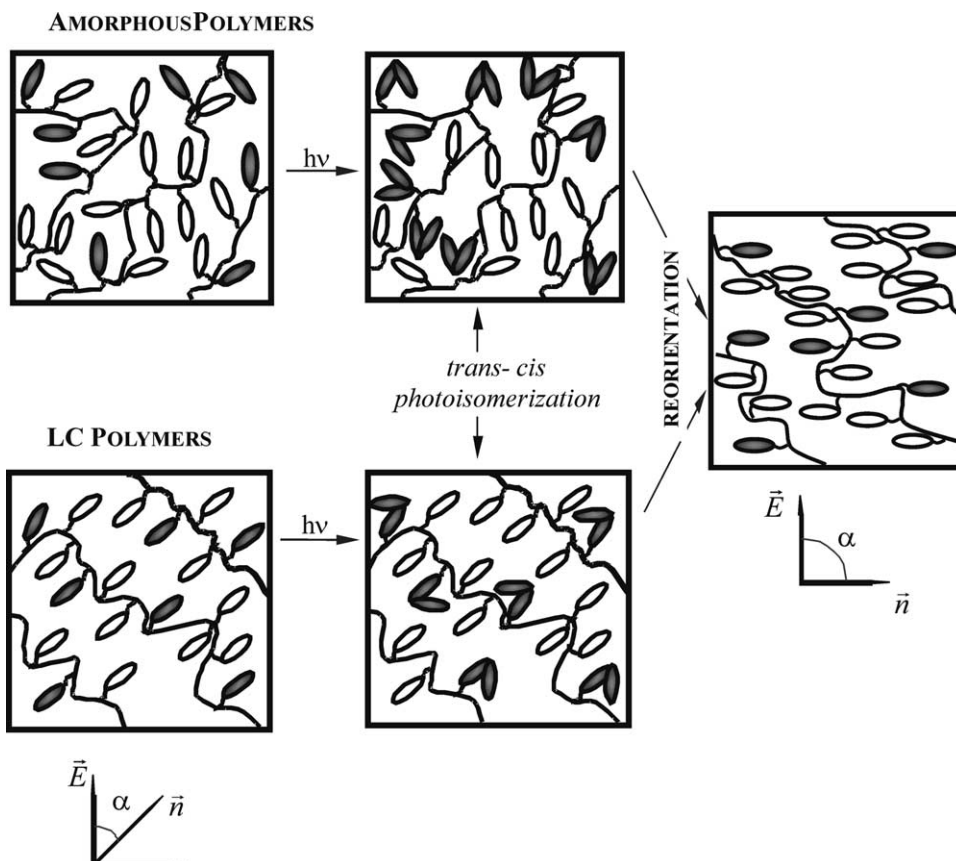


Fig. 14. Schematic representation of mesogenic groups reorientation in the amorphous non-oriented and LC planarly oriented polymer films under a laser-irradiation (\vec{n} is the director of liquid crystal; \vec{E} is the electric vector of the light wave) [46].

process is not related to long-term preservation of the birefringence. After switching the irradiation off (curve 2), Δn_{ind}^f very rapidly reduces almost to zero (Fig. 16).

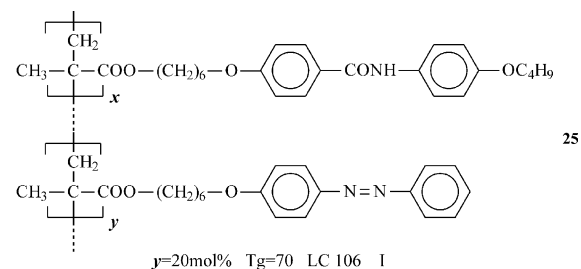
At the same time, the slow growth in Δn_{stab} , which corresponds to the long-term preservation of birefringence in the polymer sample even after the irradiation has been stopped, may cause significant changes in the structure of the sample. The slow process is accurately described by the monoexponential equation

$$\Delta n_{\text{ind}}^s(t) = (\Delta n_{\text{ind}}^s)_{\text{max}} [1 - \exp(-t\tau_s^{-1}(I))] \quad (9)$$

where $(\Delta n_{\text{ind}}^s)_{\text{max}}$ is the highest Δn_{ind}^s which is attained at $t \rightarrow \infty$; τ_s is the characteristic time during which the photoinduced birefringence reaches the value $(1 - e^{-1})(\Delta n_{\text{ind}}^s)_{\text{max}}$; I is the intensity of the recording beam. Maximum Δn_{ind}^s values were found

to be almost independent of the intensity of recording light at $t \rightarrow \infty$ that is, $(\Delta n_{\text{ind}}^s)_{\text{max}} = \text{const}$.

Fig. 17 shows the kinetic curves of the photoinduced birefringence for some aryllic copolymers **22a–22c** containing different concentrations of azo dye fragments as well as for methacrylic copolymer **25**



At least three short conclusions follow from this data. First, the higher the concentration of azo dye fragments, the greater the level of Δn_{stab} , as seen by

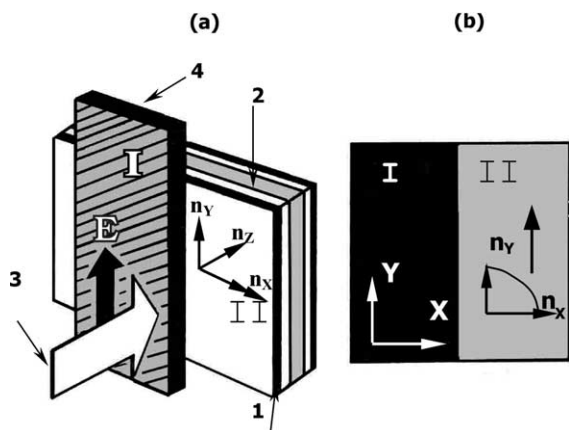


Fig. 15. (a) Schematic depiction of the electrooptical cell (1) for recording information on homeotropically oriented film of LC polymer (2). (b) Microphoto of the film in crossed polarizers (I) before and (II) after the irradiation. The left-hand part of the cell (I) was not irradiated; the right-hand part of the cell (II) was irradiated with a laser beam. \vec{E} is the electric vector of the laser beam (3); n_x , n_y and n_z are the refractive indices of the film in different directions; (4) metal screen [44].

comparing curves 1 and 2. Second, the comparison of Δn_{stab} for the same polymers in glassy and LC states (Fig. 17(a) and (b)) clearly shows that the Δn_{stab} values in the LC phase are one order of magnitude higher than those of Δn_{stab} in the glassy state. This means that the photoinduced process is much more efficient in the viscoelastic (LC state) than in the solid glassy polymer matrix. Third, as the laser beam is switched off Δn_{stab} slightly decreases, and the stable values of Δn_{stab} are preserved in the glassy state.

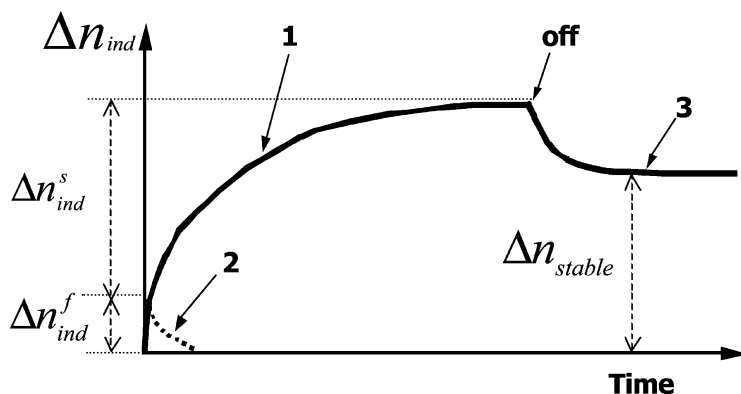


Fig. 16. A typical kinetic curve describing the growth of birefringence Δn_{ind} during the irradiation of polymer film with a laser beam; (1) growth of photoinduced birefringence; (2 and 3)—reversible relaxation of Δn_{ind} after switching off the light for the fast (Δn_{ind}^f) and the slow (Δn_{ind}^s) processes, respectively [44,118].

Δn_{stab} is achieved faster for more rigid polymers [poly(methacrylates)] which have higher T_g (see, for example, curves 1 and 4 in Fig. 17(a)).

The two stage growth in birefringence and relaxation was also observed and described in many publications [131,135,139]. For example, Natansohn et al. [136] found that the total growth and decay in birefringence for some amorphous azobenzene containing copolymers can be fitted with the following biexponential equation

$$\Delta n_{\text{ind}}^t = A\{1 - \exp(-k_a t)\} + B\{1 - \exp(-k_b t)\} \quad (10)$$

where Δn_{ind}^t represents the birefringence achieved at time t ; k_a and k_b are the time constants for the writing process and A and B are constants. The sum of A and B represents the maximum induced birefringence, according to the authors opinion, and the normalized A and B values should represent the contribution of each of the two terms to the induced birefringence. The experimental points for some of the azobenzene-containing polymers [131] and the fitted curve were in good agreement. The two terms in Eq. (10) mean that the whole writing process can be approximated by two modes of motion: the faster mode is associated with side groups, whereas the slower mode is associated with the main chain. The relaxation of Δn_{ind} can also be described with the biexponential equation.

Upon irradiation, photoinduced birefringence Δn_{ind} increases with increased time of exposure until a certain saturation level is attained; once laser irradiation ceases the birefringence decreases, and a

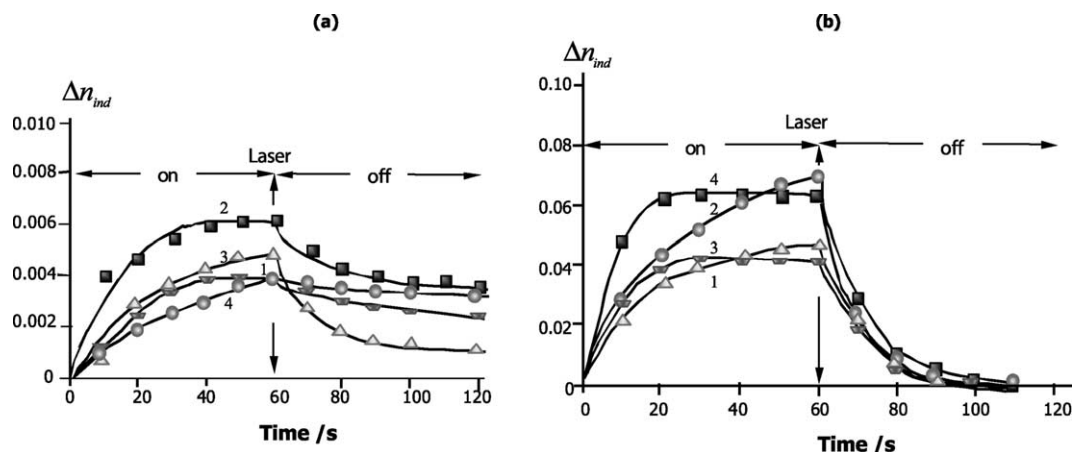


Fig. 17. Time dependence of laser-induced birefringence Δn_{ind} in homeotropic films of copolymers (1) **22a**, (2) **22b**, (3) **22c** and (4) **25** on irradiation ($P = 40 \text{ W/cm}^2$) followed by relaxation (a) at room temperature and (b) at temperature above T_g (copolymers **22a–22c**: $T = 70 \text{ }^\circ\text{C}$; copolymer **25**: $T = 90 \text{ }^\circ\text{C}$) [125].

stable stationary level Δn_{stab} is attained. The influence that the molecular structure of amorphous and LC azo polymers exerts on the stable and maximum values of birefringence has been studied in many experimental works (Section 3.3.1.2).

As was mentioned above, the Δn_{stab} values essentially depend on the irradiation temperature (compare curves in Fig. 17(a) and (b)). At elevated temperatures (above T_g) all light-induced structural transformations proceed at a higher rate due to the higher mobility of photochromic and mesogenic groups covalently linked to the backbone. In this case, a growing number of the neighbouring non-photochromic mesogenic groups is involved in the orientation. As a result, the photoinduced birefringence usually increases.

Fig. 18 shows the effect of temperature on the photoinduced birefringence [125]. As is seen in the glassy state, Δn_{stab} is almost independent of temperature. At the same time, above T_g , photoinduced birefringence shows a steep growth. Maximum Δn_{stab} values are observed at temperatures 30–40 $^\circ\text{C}$ above T_g ; these values are one order of magnitude higher than the initial Δn_{stab} values. Then, Δn_{stab} dramatically decreases, and at about 100 $^\circ\text{C}$ (i.e. at temperatures close to the clearing temperature T_{cl} of LC polymers), this value approaches zero. The plot with the maximum is related to the two opposite trends. On one hand, with increasing temperature, the mobility of mesogenic groups increases, and more efficient structural

rearrangements and a faster diffusion of photochromic fragments are promoted. On the other hand, with increasing temperature, the opposite *cis–trans* isomerization is enhanced. In addition, further growth in the mobility of mesogenic groups is accompanied by the attainment of orientational order because of a marked growth of microBrownian motion. The closer the temperature of the photooptical experiment is to T_{cl} , the greater the deterioration of the orientational order of mesogenic groups; this orientational order is

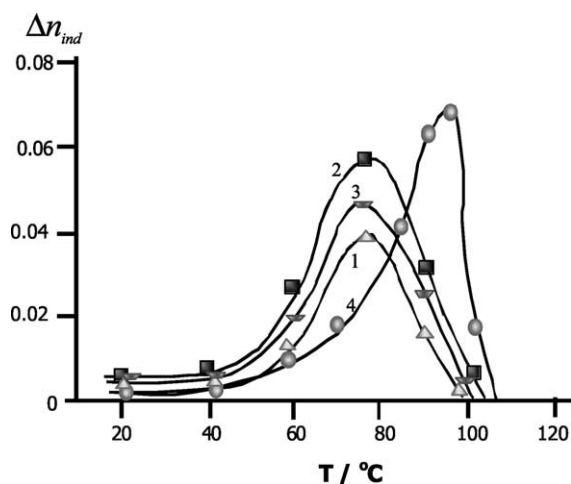


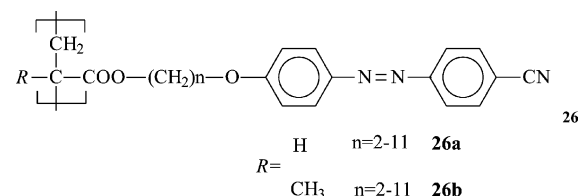
Fig. 18. Temperature dependence of photoinduced birefringence for photochromic copolymers (1) **22a**, (2) **22b**, (3) **22c** and (4) copolymer **25**. (Irradiation time 60 s) [125].

completely faded at temperatures by several degrees below T_{cl} (Fig. 18).

One of the interesting features of amorphizable LC polymers is related to an amplification of photoinduced birefringence. As was shown in Refs. [44,144,145], Δn_{stab} can be significantly increased by heating the quenched samples of LC polymers.

3.3.1.2. The influence of aggregation on photoorientation and a gain effect. As follows from Section 3.3.1.1, the principal features of the photochemical and photoinduced orientational processes were studied for copolymers containing a certain amount of photochromic azobenzene monomer units. At the same time, azo-containing homopolymers also present evident interest as systems with a much higher content of photochromic groups.

Synthesis and structure of acrylic and methacrylic homopolymers containing mesogenic groups and spacers with different lengths were described in Refs. [146–148].



The above homopolymers are characterized by rather low degrees of polymerization ($DP \sim 10-60$), which provide their low viscosity in the LC phase and easy rearrangements under the action of the electric field.

Photooptical behaviour of polyacrylates **26a** with different lengths of spacers was studied both by Russian and German scientists, and interesting results were obtained. According to the structural data, the polymers with short spacers ($n = 2$) form the nematic phase; at $n \geq 3$, the smectic mesophase (SmA) is developed. Analysis of UV/Vis spectra of the spin-coated films of polymers **26a** indicated the aggregation of the azobenzene groups caused by $\pi\pi$ stacking. While the polymer **26a** with $n = 2$ is non-aggregated, polymer **26a** with $n = 3$ forms H-aggregates (anti-parallel, head-to-tail dipole arrangement). It appears that, in addition to the smectic phase, the specific ordering effects are caused by H-aggregation of photochromic groups.

Upon irradiation of the isotropic films with linearly polarized light (488 nm, 0.5 mW/cm^2), a dichroism is induced by photoorientation of the azobenzene moieties of polymers with a short spacer ($n = 2$ and 4) and high T_g values. However, the process is strongly restricted by the aggregation (and probably by smectic phase formation) in polymers with longer spacers. Table 3 shows the photoinduced dichroism of homopolymers **26a** depending on spacer length. It is clearly seen that dichroism of polymers with $n = 8$ and 10 is very low. However, this restriction can be prevented by irradiating with increased power density (Table 3). In this way, higher values of dichroism are induced, even in the case of the polymers with longer spacers as compared to the polymer with $n = 2$.

An alternative efficient method to overcome the restriction caused by initial order is the photochemical distortion of the aggregation and any orientational LC order by preliminary UV photoirradiation (365 nm) of polymer films. While the photoinduced anisotropy is constant for the polymer with $n = 2$ (no aggregation under any conditions), the photoinduced anisotropy significantly increases for other polymers after such photochemical pretreatment. Starting with such isotropic, non-aggregated films, the order parameter increases with increasing spacer length from 0.14 at $n = 2-0.53$ at $n = 8$ (Table 3). This means that photopretreatment strongly increases the efficiency of the photoorientation process. Upon annealing the photooriented film of the nematic polymer **26a** with $n = 2$ at temperatures above T_g , a significant amplification of the optical anisotropy was observed, and the order parameter increased from 0.14 to 0.34.

Table 3

Photoinduced dichroism of homopolymers **26a** with different spacer length (n) in dependence of power density (P) of argon laser ($\lambda = 488 \text{ nm}$) without and with preliminary UV-irradiation ($\lambda = 365 \text{ nm}$, 1 mW/cm^2) [149]

Polymer	$T_g, ^\circ\text{C}$	Photoorientation without photo-pretreatment			Photo-orientation after photo-pretreatment	
		0.5	10	50	0.5	10
$n = 2$	85	0.13	–	–	0.14	0.14
$n = 4$	53	0.31	0.43	–	0.33	0.40
$n = 8$	25	0.01	0.20	0.22	0.51	0.53
$n = 10$	29	0.08	0.16	0.32	0.52	–

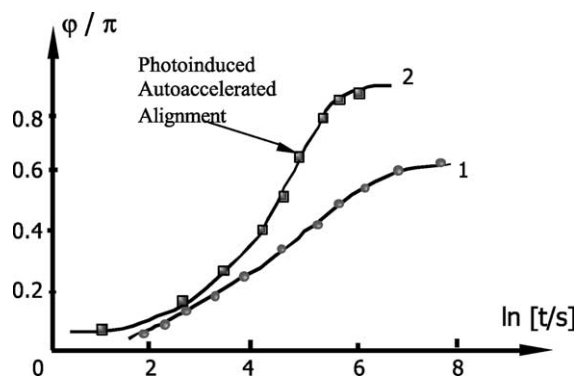
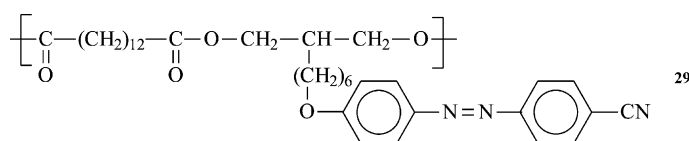


Fig. 19. Time dependence of the phase shift φ/π for (1) amorphous and (2) amorphizable copolymers.

Fig. 19 shows the phase shift φ/π (which is proportional to the photoinduced birefringence) as a function of time in the semilogarithmic coordinates for amorphous and amorphizable copolymers. The initial part of the curve shows a much lower slope and, after the inflection point, the phase shift values sharply increase. In other words, this curve appears similarly to that of an autoaccelerated process. This autoacceleration can be considered as a certain cooperative effect caused and activated by the LC phase formation of an initially amorphizable sample. In the amorphous polymer, the phase shift values monotonically increase but, in the case of amorphizable sample, the LC phase formation stimulates the further alignment of mesogenic groups. This effect was referred to as photoinduced autoaccelerated alignment [44].

The cooperative effect in LC polymers leads to another phenomenon referred to as 'a gain effect' [144,149]. Haarer et al. showed that if a grating was written into a LC polymer at ambient temperature in the glassy state, after heating the sample's diffraction efficiency was amplified by one order of magnitude.

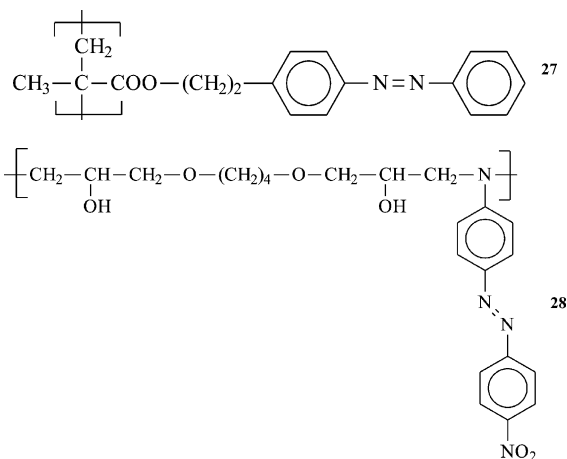


This means that the photoinduced orientation of mesogenic groups and Δn_{stab} essentially increase. As was shown in Ref. [44], Δn_{stab} increases from 0.22 to

0.30 upon laser irradiation of amorphizable samples of LC photochromic polymers and subsequent heating at temperatures above T_g .

3.3.1.3. Surface relief gratings and command surfaces. As was shown recently, irradiation of azobenzene-containing amorphous and LC polymers with an interference pattern of coherent light can induce not only an alignment of chromophores throughout the whole volume of the sample, but also a controlled modification of the film surface, coincident with the light interference pattern. The formation of such holographic surface relief gratings (SRG) has been observed for different azobenzene polymers, including azo dye doped materials, and side-chain and main chain azo containing polymers [150–154].

This phenomenon was discovered in the study of LC and amorphous azobenzene side chain polymers using atomic force and scanning near-field optical microscopic investigations [153]. Structural formulae of the azobenzene polymers, which have been used by Canadian [150], Danish [153], and American [151] researchers, are shown below:



A typical AFM profile of the SRG on one of the azobenzene containing polymers is shown in Fig. 20. Similar SRG were observed in LC azobenzene

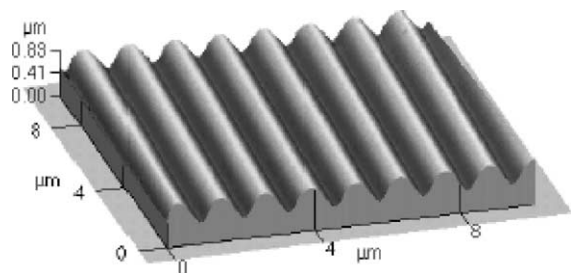


Fig. 20. Atomic force microscopic scan of a grating recorded on azobenzene-containing polymer. Courtesy of Prof. J. Kumar [151].

polymer films in Refs. [154,155]. As was found immediately after laser irradiation a surface grating structure appears. The surface is sinusoidal in shape, with depths from peak to trough greater than $1\ \mu\text{m}$. These modifications can be achieved in initially flat films of a similar thickness. This is not a destructive process, since heating the films to their glass transition temperature, returns them to their original thickness, allowing another grating to be inscribed.

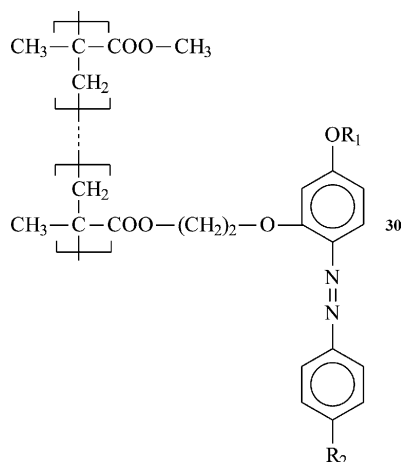
It has been established that azobenzene groups (which can undergo *trans*–*cis* photoisomerization) are necessary for this process. Films incorporating absorbing but non-isomerizing dyes produces no surface gratings. This process has been demonstrated to be reversible as well, with many gratings inscribed coincidentally in the film, a full recovery for the featureless film occurring upon heating to the glass transition temperature.

Although there is little agreement on the exact nature of the SRG mechanism, this process is clearly one of large-scale and reversible mass transport of polymer chains by low power laser irradiation below the glass transition temperature. Such large-scale polymer chain migration leads to dramatic changes in the surface of thin films of azo-functionalized polymer. Recent reviews [150,156,157] described the effect of different factors such as molecular structure, molar mass, and viscosity of azo polymers, as well as irradiation conditions, polarization and light intensity, and film thickness on the grating formation. Several hypotheses were advanced. Unfortunately, the role of liquid crystallinity in these processes was not directly touched in all publications; nevertheless, new approaches to novel materials design for various applications were reviewed. Photofabrication of SRG

and other patterns [151,157] in combination with the well-established photoanisotropic properties of azo polymers will certainly be utilized in other novel devices.

Various substrate surfaces (polymers, glass plates, ceramics, etc.) modified with photochromic molecules, particularly azobenzene derivatives, can be used as the so-called ‘command surfaces’ or ‘command layers,’ which create photoswitching low-molar-mass liquid crystals on such surface. This elegant photocontrolled alignment of liquid crystals was first reported and investigated by Ichimura et al. [158–160]. The command layers are azobenzene moieties, which are chemically attached to the glass surface of an electrooptical cell. The alignment of liquid crystals in these cells can be reversibly switched between homeotropic and planar orientation by an alternating exposure to UV and visible light. Japanese authors [158] showed that two isomerizing azobenzene units can control the orientation of about 15 000 of liquid crystal molecules, which, due to their high birefringency, can produce marked changes in the optical transmission.

The command surface concept was extended for photochromic azobenzene polymers as LC alignment layers. In principle, all azo polymers are suitable for command surfaces, but a perfect switching between different directions in the planar state should be performed for copolymers with laterally attached azobenzenes such as:



Copolymers with laterally attached azobenzene moieties functioning as a ‘molecular rotor’ were synthesized in Ref. [161]. Photochromic moieties

capable of performing the in-plane photoalignment (apart from azobenzene) include stilbene, cinnamate, and spiropyran derivatives. The review by Ichimura [160] gives an excellent overview of recent activities on photoalignment of liquid crystal systems and covers the synthesis of photochromic LC polymers, preparation of command surfaces, surface-mediated photoalignment control of nematic liquid crystals, and photocontrol of tilt angle. It should only be emphasized that a correct and reliable photocontrol of molecular orientation is based on the combination of reversible photochromic reactions and a long-range order of LC molecules. Command effects may be used as low-cost, large-area, optically addressed spatial light modulators.

Based on the same switching mechanism of command layers, a novel type of surfaces were used for light-driven motion of liquids on surface-modified glass tubes. These results were recently obtained by Japanese authors [162] headed by Ichimura. When a liquid droplet of olive oil (or some other organic compound) several millimeters in diameter is placed on a substrate surface modified with a calyx resorcinarene derivative with photochromic azobenzene units, asymmetrical photoirradiation leads to a gradient in surface free energy due to photoisomerization of surface azobenzene fragments, thus providing the directional motion of the droplet. The motion of liquids can be reversibly manipulated by light irradiation. The direction and rate of the motion were tunable by varying the direction and steepness of the gradient in light intensity. The described light-driven motion of the fluid substances on a surface—a modified glass tube—suggests a potential applicability in microscale chemical process systems.

3.3.1.4. Application and optical storage. However, despite abundant information on photooptical and photochemical studies of azo dye polymers, no well-defined correlations between their molecular structure and photooptical characteristics are available. This is due to the fact that too many parameters, such as, polarity of mesogenic groups, spacer length, free volume of sample, type of mesophase, etc. must be taken into account. Analysis of photooptical data shows that the maximum values of $\Delta n_{\text{stab}} = 0.25\text{--}0.30$ are inherent in the most disordered amorphous and amorphizable LC polymers;

somewhat lower values of $\Delta n_{\text{stab}} = 0.15\text{--}0.20$ are typical of LC polymers with planar orientation; even smaller birefringence $\Delta n_{\text{stab}} < 0.10$ is observed in homeotropic oriented films. This situation is explained by a decrease in the mobility of mesogenic groups with increasing polymer order (from amorphous to nematic and smectic) and by the less 'favourable' (from the standpoint of light absorption and the *E–Z* isomerization) character of the homeotropic orientation as compared with the planar one. Nevertheless, the photoinduced birefringence is high enough and comparable with those observed for LC polymers oriented in the electric field. Furthermore, the Δn_{stab} values remain unchanged over a time period of several years; hence, these LC films may be used as data recording and storage media. When an arbitrary test lattice is placed onto the surface of a polymer film and irradiated with a polarized laser beam, one may obtain an image of the lattice and evaluate the contrast and resolution characteristics. It should be emphasized that the image is invisible to the naked eye and can only be revealed in the crossed polarizers. Fig. 21 gives an example of the test lattice imaging, and Fig. 22 shows a photograph of Moscow State University recorded on a photochromic LC copolymer film.

LC azo-containing polymers may be used as holographic recording media [35,111,112,114,127,163,164]. The first azo-containing LC polymers used for holographic recording were synthesized by Wendorff and co-workers, who obtained a copolymer of the acrylic series and aromatic polyesters

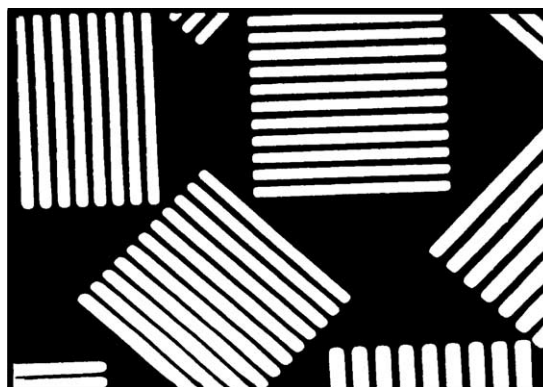
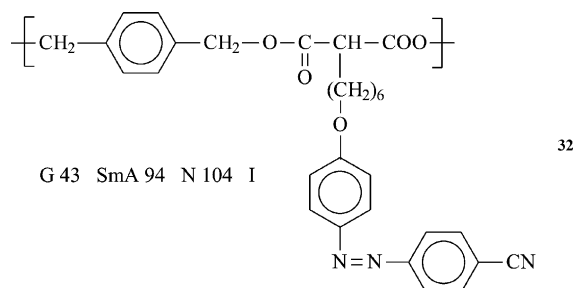
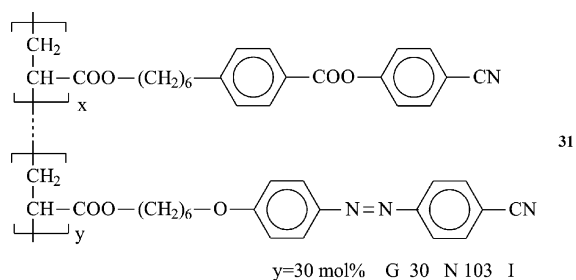


Fig. 21. Photomicrograph of a film of LC copolymer **22a** obtained with a test-pattern. The film thickness is 20 μm ; distance between the stripes, 3 μm [16].



Fig. 22. Photograph of black–white image of the Moscow State University recorded on a photochromic LC copolymer film.

containing azobenzene fragments with polar nitrile groups [127,163].



Using the holographic technique, variable interference patterns were recorded on the LC polymer **32** at the mutual intersection of different angles of planar and spherical ways. In this way, the diffraction pattern of ‘Frenel zones’, frozen in a solid polymeric matrix, have been obtained with different periodicities up to 1 μm . Experiments run along these lines indicate the high quality of the holograms, characterized by high spatial resolution (above 3000 lines/mm) with a very high diffraction efficiency reaching 50% for phase lattices of large thickness. The intensity required for recording the holograms was about 1 mW/cm^2 .

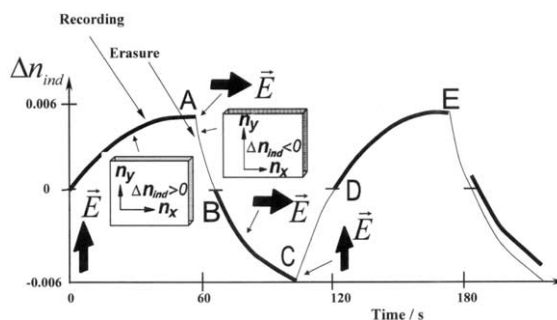


Fig. 23. Schematic diagram illustrating reversible optical data recording by means variable photoinduced birefringence in laser-irradiated homotropically oriented LC copolymer film. Black arrows indicate the electric field vector orientation in the recording laser beam. The insets show electrooptical cells and indicate relationships between the refractive index components n_x and n_y [116].

Later, researchers from Bayer Corporation demonstrated the reconstruction of an X-ray pattern of the image of a tooth, which had previously been recorded with high optical resolution into a LC azo-containing polymer film by exposure to an s-polarized argon ion beam [145].

An important advantage of photochromic LC polymer films is the possibility of data recording and erasing. The latter process may be controlled at room temperature by changing the polarization of the initial recording laser beam, which effectively changes the ratio of refractive indices n_x and n_y . This is clearly illustrated by the diagram in Fig. 23, which shows the initial increase in the photoinduced birefringence Δn_{stab} upon irradiation (recording), where n_x becomes higher than n_y ($\Delta n > 0$). At point A, the laser beam polarization is rotated by 90° relative to that of the initial recording beam (point O). The A B curve describes the disappearance of the recorded signal, where point B corresponds to $\Delta n = 0$; it implies that the signal is completely erased. Upon further irradiation with the same light polarization direction, a new signal is recorded for the opposite birefringence sign $\Delta n < 0$. Once the polarization of the recording beam is changed at point C, the process is restarted. This illustrates the reversible data recording, which not only allows the switching between maximum and minimum birefringence states (producing a black–white image), but ensures the intermediate Δn_{stab} values, thus providing the entire grey scale (as seen in Fig. 23).

Some optical characteristics of the comb-shaped LC polymers with cyanobiphenyl and azobenzene side groups are as follows:

Laser beam power density, W/cm²: 10⁻¹–10⁻²
 Resolution, line/mm: 800–900
 Data record density, byte/cm²: 10⁹
 Number of record/erase cycles: 4–5 × 10²

Unfortunately, high stability (fatigue resistance) and cyclic recording in these polymer films are accompanied by rather long times required for data recording, which are naturally much longer for the LC polymers than for their low-molar-mass analogs. However, this disadvantage is fully compensated for by the ability of these polymeric media to be used for long-time data storage. Long-term data storage is exceptionally important for various optical memory devices (laser disks, holograms, smart cards) and long-term data storage systems (micromapping, micrographic products).

The above characteristics can be markedly improved by selecting the appropriate mesogenic groups and comonomer chain units with various side-chain substituents (e.g. significantly increasing the anisotropy of dielectric polarizability of the mesogenic units). It is by no means an accident that well-known companies such as Bayer AG (Leverkusen, Germany) and IBM (San Jose, USA) planned joint research in developing photochromic azo-containing polymers (analogous to those considered above) with a view to obtaining new holographic materials for three-dimensional (3D) image recording. By estimates published in a Bayer scientific journal, the data capacity of a 3D holographic laser disk may be as high as 1000 GB, which is about 1500 times the average value for compact disks currently in use [165].

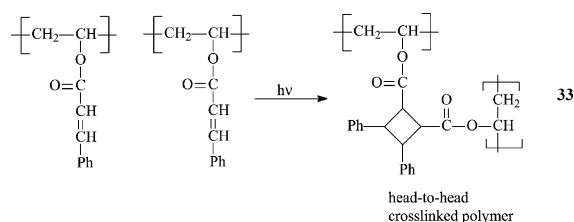
Therefore, 1 mm³ of a new material may accommodate up to 1024 × 1024 pixels, which corresponds to about 1000 standard A4 pages [165]. Although these figures present only rough estimates, some new photosensitive azo-containing LC materials have been already synthesized by a small International Optilink AB Company (Ronnely, Sweden) [166]. One of the main directions in this research is aimed at creating optical medical records, similar to credit cards, to replace conventional medical records and case history charts of patients in hospitals and clinics. The case

report together with all the necessary information for each patient can be readily recorded onto such a card and read into a computer. This may serve as a principal basis for a global medical network capable of following the dynamics of any disorder and offering timely aid to any patient. Such a case record may accommodate up to 3 000 standard A4 text pages at a data recording density of 27 MB/cm². In other words, eight cards may save about 1 ton of paper. In this case, the cost price per 1 B recording is \$0.016, which is much lower than the typical value for magneto-optical data recording (\$0.83/byte). Undoubtedly, the optimization of the optical properties of these recording media will make them competitive in the world market and applicable in various fields.

3.3.2. Cinnamate-containing polymers

In contrast to the azo dye-containing polymers which undergo *trans*–*cis* isomerization under irradiation, polymers with cinnamate side chains also undergo *E*–*Z* isomerization and may be cross-linked by light irradiation [53,56,61,98,99].

One type of cross-linking reaction of poly(vinylcinnamate) leading to head-to-tail photoproduct **6** was shown above (Section 2.1.1). The second cross-linking reaction of the photoreactive cinnamate polymer leading to the head-to-head cross-linked product under polarized UV-light is shown below:



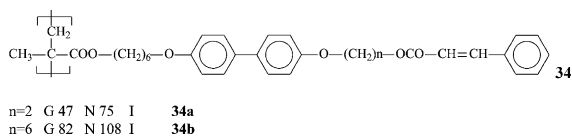
Photoinduced anisotropic cross-linking of side-chain cinnamate polymers aims at two goals. These reactions are used for the synthesis of photoresists in commercial applications and preparation integral microschemes in electronics. Depending on the compositions of such poly(vinylcinnamates), their photosensitivity varies from 2 to 20 cm²/J, and the resolution ranges from 100 to 1000 mm⁻¹ [56].

Photoinduced cross-linking presents the most promising approach as compared with non-contact alignment technologies. In this case poly(vinylcinnamate) films are exposed to linearly polarized UV-light

and anisotropic layers are developed, which are used for orientation of low-molar-mass liquid crystals in an electrooptical cell. The alignment of liquid crystals is associated with an anisotropic consumption of cinnamate side chains due to $\{2 + 2\}$ cycloaddition reactions, even though some authors suggest that *trans*–*cis* isomerization is also involved. In both cases, the samples of poly(vinylcinnamate) do not form a LC phase, although under irradiation a stable anisotropic network is formed.

Several research groups synthesized LC polymers with mesogenic cinnamic acid esters. Noyle et al. synthesized the LC methacrylate containing 4'-pentyloxyphenyl-4-alkyloxy cinnamate mesogen and studied the aggregation of chromophores and its photochemical behaviour [167]. Photo-cross-linkable polysiloxane LC polymers with cinnamate and optically active side chains were synthesized by Chien and Cada [168]. Mitchel et al. also synthesized several sets of LC polymers with cinnamate ester side groups and investigated their photochemical behaviour [169]. These authors and others research groups emphasized that, in the case of aryl esters of cinnamate acid, a photo-Fries rearrangement reaction takes place [168,169].

Systematic studies on the synthesis and photo-optical characterization of cinnamate-containing LC polymers have been carried out in several works by Kawatsuki et al. [170–173]. They described the anisotropic photoreactions of photoreactive LC methacrylic polymers containing biphenyl mesogen and a photoreactive cinnamoyl group by irradiation with a linearly polarized UV-light:



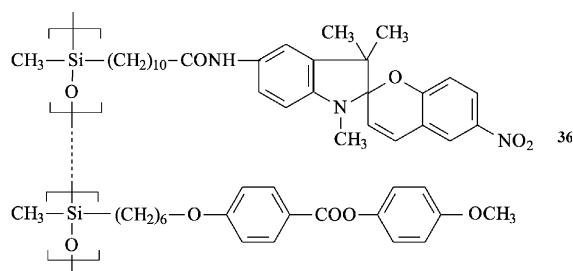
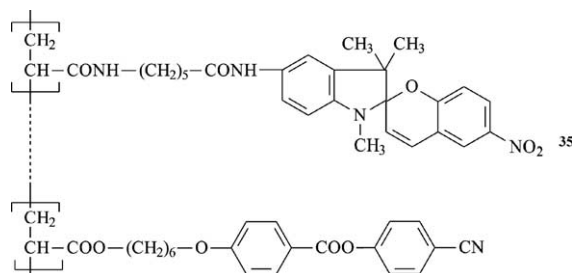
During photoirradiation, both polymers **34a** and **34b** undergo a $\{2 + 2\}$ cycloaddition reaction of the cinnamoyl group, forming cross-linked polymers, which essentially influence the alignment of low-molar-mass liquid crystals deposited on the polymer film surface. The photo-cross-linked LC thin film at room temperature after the photoreaction (below T_g) showed a low negative dichroism, whereas in a temperature range above T_g , exhibited LC polymers

show a positive dichroism. In this way, the photo-reacted cinnamoyl-containing LC films can align the director of low-molar-mass liquid crystals both parallel and perpendicular to the incident electric field vector \vec{E} of the linearly polarized UV-light.

Recently, American authors reported the synthesis of a new family of silane-based molecules, which contain the photosensitive cinnamoyl groups chemically linked to the substrate surface [174]. The irradiation of such systems with a linearly polarized light leads to cross-linked cinnamoyl groups and to the formation of a monolayered morphology with a smooth surface, which may be used for liquid crystal alignment similar to the above command surface (Section 3.3.1.3).

3.3.3. Spiropyran-containing LC polymers

Spiropyran-containing LC polymers were the first photochromic LC polymers obtained and studied by Krongauz et al. [175–177]. They synthesized and described polyacrylic and polysiloxane photochromic LC polymers containing mesogenic groups and spiropyran (and spirooxazine) moieties as side chains. Recent data on spiro LC polymers was published in two comprehensive reviews by Krongauz [178,179]. Therefore, we shall confine our consideration to the two examples:

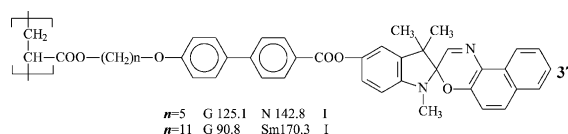


Incorporation of the bulky photochromic spiro groups into the macromolecules of nematogenic polymers leads to a sharp decrease of the clearing point and transition enthalpy. Nevertheless, even copolymers with 30% spiro dye units show mesomorphic properties. Phase transitions and colour changes of spiropyran side groups of LC polymers are controlled by the thermochromic spiropyran–merocyanine transitions (Section 2.2.3). Spectacular colour transformations occur in spiropiran-containing polysiloxane copolymers **36**. As a result of the characteristic high flexibility of the polymer chain, polysiloxanes polymers show glass transition temperatures below room temperature; that in turn affects the photochromic transformations in these polymers.

Copolymers containing 11 mol% of spiropyran units cast from solution form yellow films with the mesophase. Upon UV-irradiation ($\lambda = 365$ nm) and at temperatures below the glass ($T_g \approx 10$ °C), these films experience a photochromic spiropyran \rightarrow merocyanine transition; the polymer becomes blue due to the presence of isolated merocyanine groups (Fig. 24). As the temperature is increased above T_g , the polymer is transformed by aggregation of the merocyanine groups (only in the mesophase), and the yellow film becomes a deep red. Colour variations of polymeric LC films occurring on exposure to light irradiation and temperature changes [178] offer new, interesting advantages in the development of colour displays for information technology.

In addition to spiropyranes containing LC copolymers, Krongauz et al. and later Japanese authors [180] synthesized LC copolymers and homopolymers containing spirooxazine groups. Hattori and Uryu [180] obtained and studied photochromic LC spirooxazine

containing poly(acrylates) with different spacer lengths for nematic ($n = 5$) or smectic ($n = 11$) phase formation:



As is well known, photochemical behaviour of spirooxazines is very similar to that of spiropyran derivatives and the formation of merocyanine form takes place. Under UV-irradiation ($\lambda = 365$ nm, $P = 0.95$ mW/cm²) all films come to the photostationary state in about 25 min. However, a marked difference in the photoinduced colouring and thermal decay between the two different LC phases was not observed. Photochromic properties of polymers such as colour density, photocoloration rate, and thermal decay rate depend only on photoreaction temperature and the glass transition temperature of the photochromic polymers.

American authors [181] reported the synthesis of an LC cyclic siloxane composed of photochromic, spiropyran, biphenyl, and cholesterol units. This siloxane formed a cholesteric film with selective light reflection. Similar systems will be considered in detail in Section 3.4.4, which is devoted to cholesteric polymers. Here we would like to note that such films might be used to write, erase, and rewrite holograms. Writing was achieved by UV laser light, which led to the closed spiropyran form opening to the blue merocyanine form. As the temperature is increased to 60 °C, blue colour faded due to the formation of the closed form. In our opinion, further refinement in the synthesis of spiro-LC polymers is required, and more

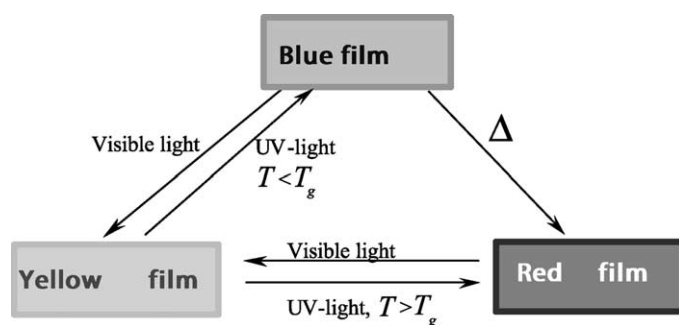


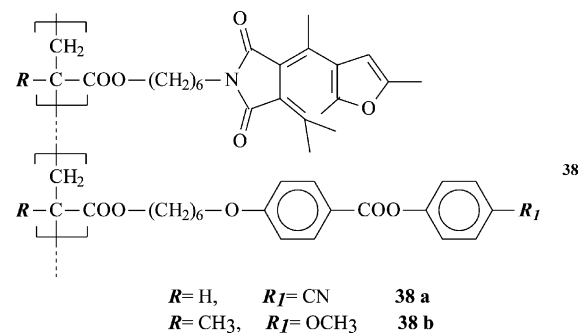
Fig. 24. Scheme of photo- and thermo-induced colour transformations in the film of photochromic spiropyran-containing LC polymer [178].

extensive studies on the processing and stability of these materials are very important.

3.3.4. Other photochromic LC polymers

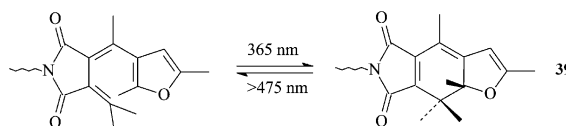
In the previous sections, we have extensively considered the most-used LC polymers containing photosensitive azobenzene, cinnamoyl, and spiro-pyran fragments in the side chain of macromolecules. The number of other photochromic groups introduced to the polymer chain is limited. Since there is very little in the literature on these polymer systems, we briefly consider a few examples.

The first fulgimide containing copolymers were obtained by Ringsdorf et al. [182]:



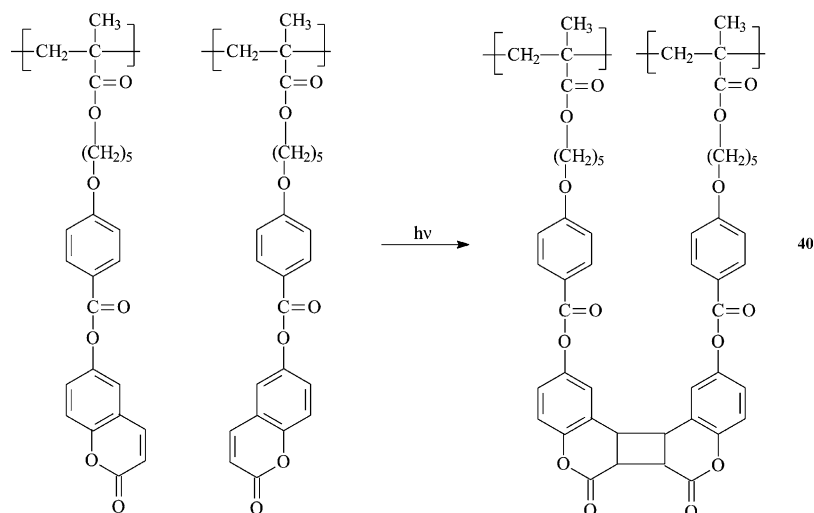
Polyacrylate **38a** and polymethacrylate **38b** show a nematic phase up to ~15 mol% of fulgimide units.

Under UV-irradiation, the open-ring form of fulgimide units is transformed into the close-ring form according to the scheme:



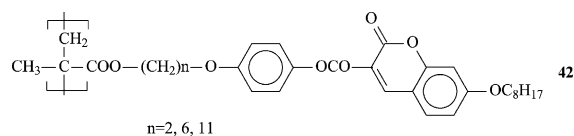
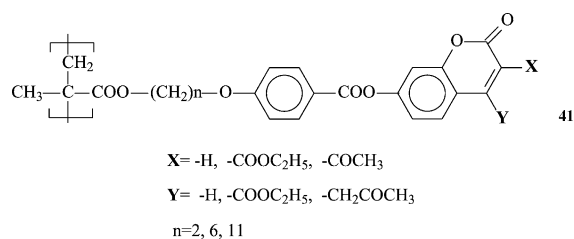
Whereas the photoreaction is induced at 365 nm, the back reaction requires visible light. The written information was shown to be stable at room temperature; no change in absorption is observed when the polymer films of copolymers **38b** containing 2.5 mol% of fulgimide units are kept in the dark for 300 h.

Another example is related to coumarin-containing polymers, which are of significant interest for many fields, such as fluorescence materials and laser dyes, etc. [183,184]. Several research groups have extensively studied non-liquid crystalline photoreactive coumarin polymers; a detailed discussion of this subject may be found in Refs. [185–188]. The main principle of their use is based on the photoinduced anisotropic cross-linking of coumarin moieties for homogenous liquid crystal alignment perpendicular to the polarization direction of the light as is shown below [185,186]:



This scheme shows the anisotropic cross-linking of photoreactive coumarin polymer under polarized UV-light irradiation; a stable anisotropic network **40** as a non-contact alignment layer is obtained. According to the above process and photoproduct, subpixelated multidomain devices with improved viewing-angle dependence of the contrast were produced [186–188].

For the first time, LC polymers containing coumarin moieties were described in Ref. [189]. The synthesis of two series of novel LC polymethacrylates **41** and **42** containing different coumarin derivatives in side groups with spacers of different lengths ($n = 2, 6,$ and 11) were described.



Depending on the type of spacer, tail groups, and the direction of the connection of the mesogens with coumarin units, the polymers exist in amorphous, crystalline, or LC phases (in particular, nematic and smectic A). Each polymer in series **41** tends to the glassy state, whereas each polymer in series **42** exhibits a crystalline phase. The preliminary UV/Vis absorption and fluorescence spectral data show an evident effect of the types of mesophase and annealing on the aggregation of chromophore groups. Further investigations of these interesting systems will allow an understanding of the role of liquid crystallinity in the photochemical and photooptical behaviour taking place in the coumarin-containing polymers.

In conclusion, we would like to pay attention to the photoresponsive polymers composed of polypeptide main chains and photochromic side groups. Photosensitive polypeptides represent interesting

systems because of definite ordered structures such as α -helix and β -structures. As is known, α -helical polypeptide can form a LC phase in specific solvents, characterized by the cholesteric (chiral nematic) structure. Furthermore, their structures are similar to the protein nature of biological photoreceptors. The azobenzene group is the most common photochromic component used to induce light phenomena in polypeptides, but stilbene and spiropyran units are also used [54,67,70,115]. Light excitation of the chromophoric group can lead to dramatic conformational changes, such as changes from a left-handed to right-handed helix or from random coil to α -helix. Presently, the very interesting photosensitive polypeptides were mainly studied in the dilute solutions, but their study in concentrated solutions forming LC mesophases and in bulk are of a great interest from both academic and practical points of view. The photocontrolled chirality in helical polymers offers intriguing possibilities for the development of multifunctional photoswitchable materials, taking into account an important role of helical organization in biopolymers and the attractive properties of such photochromic polymers.

3.4. Photosensitive polymer systems with cholesteric (chiral nematic) structure

As was shown in Section 1.3, the development of the cholesteric mesophase is typical of LC compounds containing chiral fragments that provide the twisting of the nematic phase. In the case of polymers, a chiral nematic phase may be obtained by the introduction of small amounts of chiral low-molar-mass dopants to nematic polymers. However, due to a poor compatibility between polymers and chiral low-molar-mass compounds, in some cases this approach fails to ensure the positive results. Therefore, the most convenient means for the preparation of cholesteric polymers (chiral nematics) is provided by the copolymerization of nematogenic and chiral monomers. This method makes possible the preparation of stable cholesteric copolymers when the ratio between the components is easily controlled by the initial feed concentration of monomers. In this case, both mesogenic and non-mesogenic compounds may be used as chiral

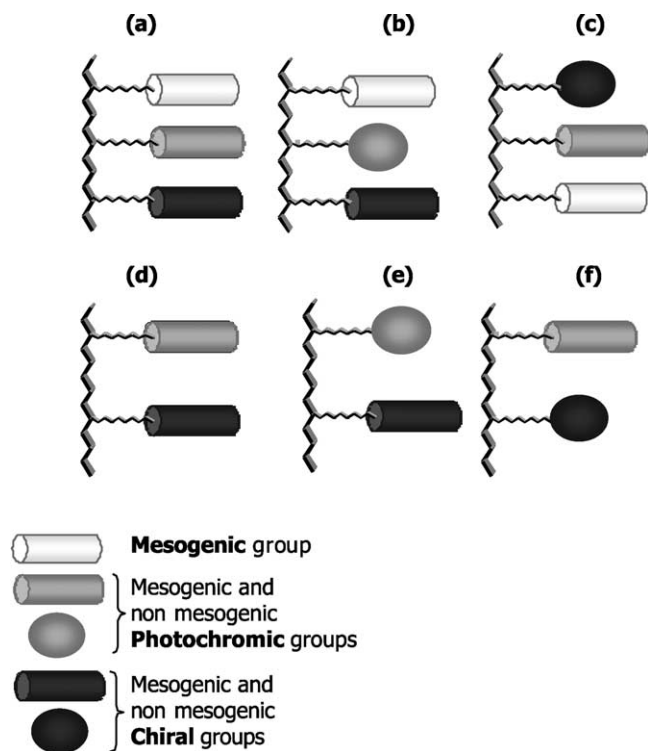


Fig. 25. Schematic representation of the structure of binary and ternary chiral photochromic copolymers displaying cholesteric mesophase.

monomers; the concentration of non-mesogenic chiral components may be as high as 15–20%, yet the as-obtained polymer still preserves its ability to form the cholesteric mesophase.

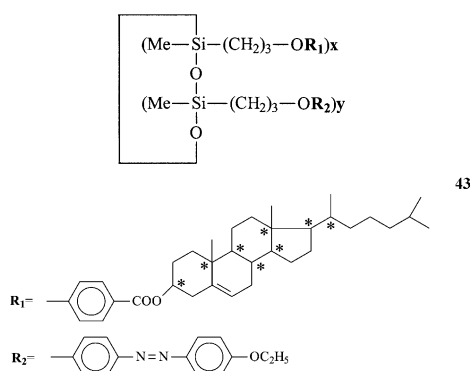
A simple method for the preparation of photosensitive cholesteric polymers involves the synthesis of binary or ternary copolymers; the schematic representation of the related macromolecules is shown in Fig. 25. In our opinion, the macromolecular structures as shown in Fig. 25 vividly demonstrate the strategy of the molecular design of the most common photosensitive cholesteric polymers. Let us note that not all structural versions of copolymers as shown above have found their practical embodiment as real polymer systems, though the feasibility of their synthesis is beyond any doubts. Nevertheless, it seems expedient to resort to the above scheme, not only for the demonstration of the feasibility of the synthesis of such polymers, but also for a comparative analysis of their structural and physical properties to select the optimal structure and composition of

polymer systems with photocontrolled optical properties.

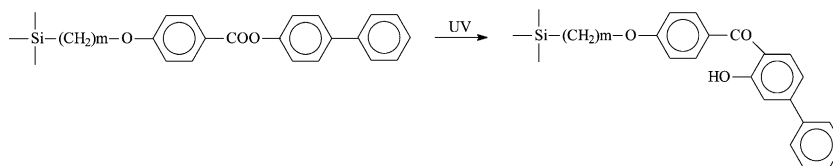
3.4.1. Cholesteric copolymers with photosensitive achiral fragments

According to Fig. 25, let us start our consideration with simple copolymers composed of the two mesogenic fragments. In addition to LC character (LC nature), each component possesses its own individual functionality when one component is photosensitive and another is chiral.

Unfortunately, the number of well-characterized and well-studied copolymers is rather limited; because of this, it seems expedient to consider the cyclsiloxane cholesterics which, to a certain extent, may be considered as certain analogs of cooligomers containing different side groups. These compounds were first synthesized by Kreuzer et al. [190,191] and contain cycles of 4–10 siloxane units with chiral and photochromic azobenzene moieties:

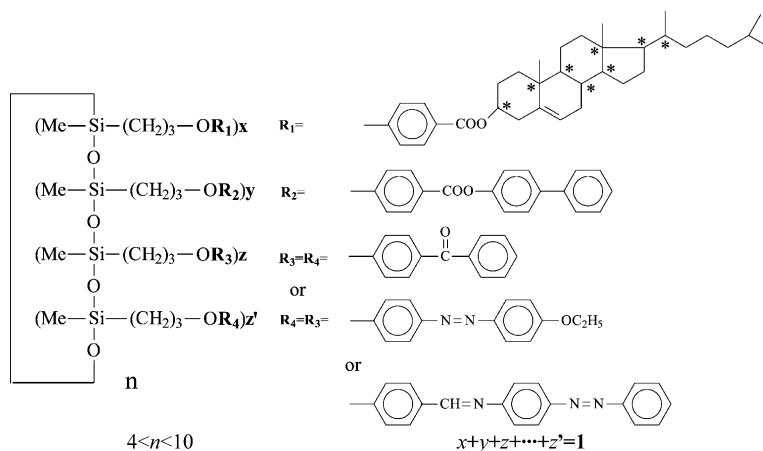


materials with photosensitive groups based on benzophenone may be used for a single-run recording of optical information. UV-irradiation (350.7 nm) leads to an irreversible disruption of the cholesteric structure and ‘degeneration’ of helical supramolecular structure and disappearance of the selective light reflection maximum due to the photochemical decomposition of the above compound. Another possible photoinduced process is provided by the photo-Fries rearrangement, which takes place in nematogenic biphenylbenzoate groups.



Somewhat later [190–192], the same authors described the synthesis of ternary copolymers containing photochromic, chiral, and mesogenic groups in one cycle.

In the course of this process, one may observe a dramatic decrease in the anisotropy of the above groups and breakdown of the LC order. To create materials sensitive to light irradiation with longer



Possible applications of such compounds as photo-sensitive materials were demonstrated. Cholesteric

wavelengths (including the near IR region), mixtures of the above co-polysiloxanes with carbon black were

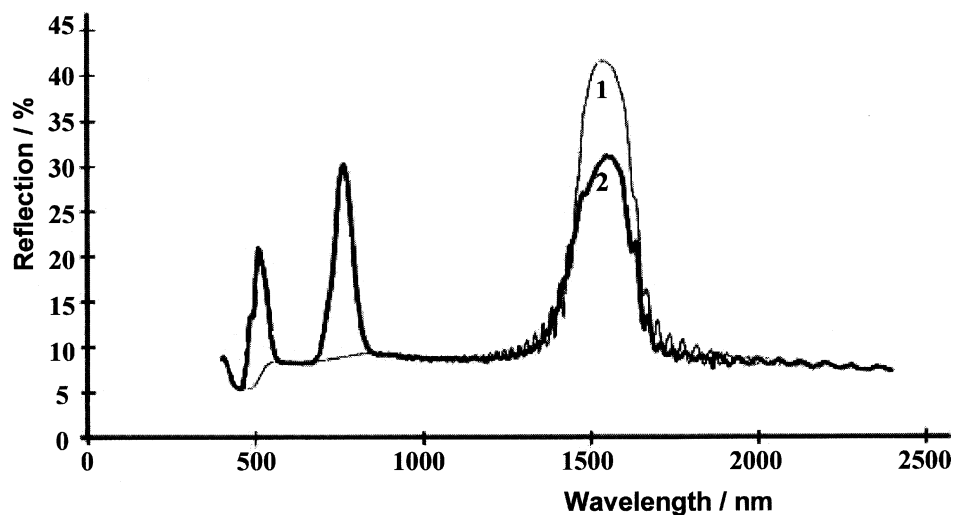


Fig. 26. Higher order Bragg reflection bands generated by irradiation of a cholesteric LC siloxane layer with linearly polarized light (Hg-lamp, intensity 200 mW/cm^2 , irradiation time: 5 min); (1) before and (2) after irradiation. Reprinted with permission of Springer-Verlag GmbH [190].

used. The carbon black additive reduced the time of optical information recording down to 10 ns.

In the case of copolysiloxanes with azobenzene photosensitive groups, the corresponding photochemical transformations are reversible and show unconventional variations in the optical characteristics of cholesterics. Upon the polarized UV-irradiation of glassy planarly oriented films of such polymers, an interesting phenomenon was observed: the generation of higher orders (second and third orders) of selective light reflection (Fig. 26). This behaviour may be explained by Fig. 27. Taking into account the fact that the probability of the absorption of the linearly polarized light is minimum, the electric field vector \vec{E} coincides with the moment of the chromophore transfer. The interaction of the linearly polarized light leads to the reorientation of azobenzene groups perpendicular to the electric field vector \vec{E} [193]. When cholesteric cyclosiloxane is irradiated with the linearly polarized light, the layers containing azobenzene groups oriented along the polarized light vector \vec{E} alternate with a period equal to half of the helix pitch $P/2$. As a result, the photoorientation of azobenzene groups commences in the regions where vector \vec{E} almost coincides with the director of liquid crystal, that is, in the regions with the period $d = P/2$. Hence, the periodicity of cholesteric is doubled and the generation of higher orders of selective light reflection is seen.

Such distortion of the cholesteric helix may take place under the action of both electric and magnetic fields [194,195] but, at temperatures below the glass transition temperature, this phenomenon is absent and no recording of optical information is possible.

Photoorientation of mesogenic groups is possible under irradiation with non-polarized or circularly polarized light [196,197]. In this case, azobenzene chromophores tend to be oriented along the light direction and as a result, homeotropic orientation of LC material is attained. Irradiating the planarly oriented film with non-polarized light leads to a complete degeneration of the selective light reflection and, in the crossed polarizers, the irradiated regions become pseudoisotropic.

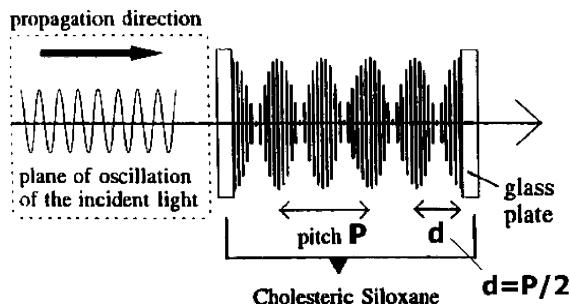
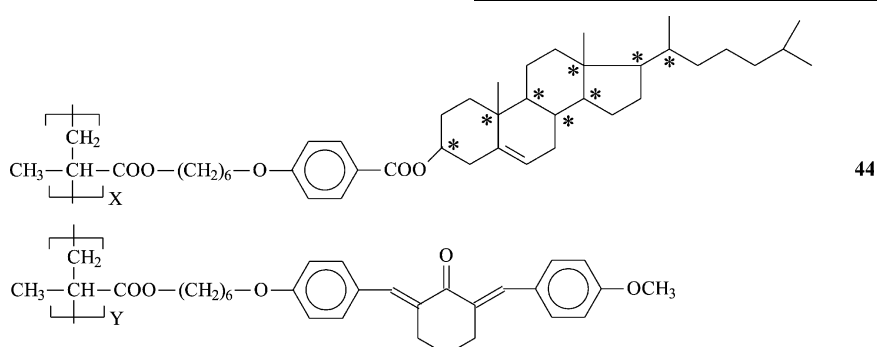


Fig. 27. The interaction of linearly polarized light with azo dyes in cholesteric LC siloxanes. Reprinted with permission of Springer-Verlag GmbH [190].

More complex polymer systems as judged from the viewpoint of photochemistry are described in Ref. [198]. These systems are copolymers of cholesterol-containing monomers with photosensitive nematogenic derivatives of EE-bis(benzylidene)cyclohexanone:



The content of photosensitive groups varied from 0 to 100%. In this case, nematogenic units are able not only to experience the light-induced *trans-cis* isomerization but yield the products of {2 + 2} cycloaddition. As a result, formation of the cross-linked polymer takes place. Non-mesomorphic character of bis(benzylidene)cyclohexanone fragments produced by UV-irradiation may explain the degeneration of selective light reflection peak. The above publications studied copolymers in which the photochemical transformation leads either to the distortion of the helical supramolecular structure or to its complete breakdown and degeneration of the selective light reflection maximum.

Recently [199], the possibility of controlled light-induced changes in helix pitch was demonstrated for the first time for certain polymer systems.⁶ The chemical structure and phase transitions of copolymers and related blends are presented in Table 4. In this case, the copolymer structure corresponds as shown in Fig. 25(c). As follows from Table 4, all the above systems contain photosensitive achiral azobenzene groups that

⁶ In Refs. [200,201], the possibilities of the light-induced changes in the helix pitch were demonstrated for the low-molar-mass cholesteric mixtures with achiral photochromic azobenzene dopants; however, the specific features of the kinetics of photoprocesses were ignored.

are capable of *E-Z* isomerization. The composition of the copolymers **45** and related mixtures **46**, **47** was selected so that the selective light reflection wavelength lay in the visible or near IR spectral regions and did not markedly overlap with the absorption bands of the azobenzene groups.

Irradiation with visible or UV-light leads a dramatic untwisting of the cholesteric helix (for blend **46**, the shift in the selective light reflection peak is equal to more than 300 nm). Fig. 28 presents the transmission spectra of mixture **47** before and after the light irradiation and also after annealing. As is seen, the process of helix untwisting is thermally reversible because, upon annealing, a backward shift in the selective light reflection maximum takes place. The above spectral variations are related to the light-induced *E-Z* photoisomerization of azobenzene fragments. This process is accompanied by a decrease in the degree of ordering due to a low anisometry of the bent-shaped *Z*-isomers. In turn, this trend leads to the untwisting of the cholesteric helix in the copolymer and related mixtures. Probably, a reduced ordering of the nematic polymer matrix is accompanied by a decrease in its ability to twist into the helical supramolecular structure.

Due to the reversible character of *E-Z* photoisomerization for the copolymers and related blends as described in Ref. [199], one may arrive at repeated photoinduced helix untwisting—annealing—helix twisting cycles. As was shown, the fatigue resistance of the above systems to the repeated cycles is rather high.

Recently [202], cholesteric mixtures of copolymers containing spirooxazine photochromic groups with cholesteroloyl carbonate were studied. Upon the

Table 4

Structure and phase transitions of photochromic azobenzene-containing polymers and their mixtures with chiral isosorbide dopant [199]

Chemical structure of components	Phase transitions, °C	
	SmA90-94 N*104-105 I	45
	SmA94-95 N*119 I	46
	N*97-98 I	47

UV-irradiation of the films, a reversible shift in the selective light reflection maximum to the short-wavelength spectral region was observed. Such spectral changes were associated with the heating of the film caused by the irradiation.

3.4.2. Cholesteric copolymers with combined chiral-photochromic groups and mixtures of LC polymers with chiral-photochromic dopants

In our work and in the work by Phillips research group, pioneering approaches for the development of polymer cholesteric liquid crystals with photocon-

trolled helix pitch and selective light reflection maximum were advanced [203–214]. The main principle in the development of such light-controlled LC polymers is based on the synthesis of photochromic copolymers whose macromolecules consist of mesogenic (as a rule, nematogenic) and combined chiral-photochromic groups which are chemically linked in the common monomer unit (Fig. 29(a)). In this case, mesogenic fragments are responsible for the formation of the nematic phase and chiral groups provide the twisting of the nematic phase with formation of helical supramolecular structure. Finally, photochromic frag-

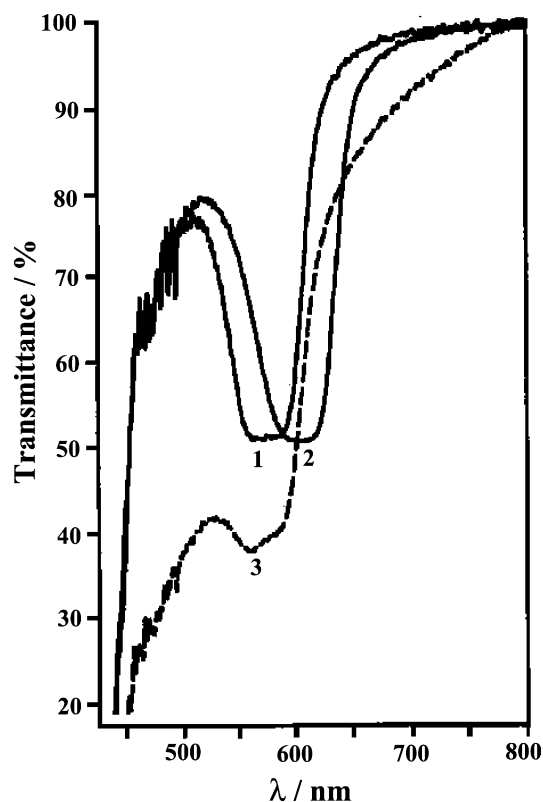


Fig. 28. Transmittance spectra of planarly oriented film of mixture 47: (1) before irradiation; (2) after 10 min of UV-irradiation (365 nm); temperature of the samples 90 °C; (3) after annealing during 20 min at the same temperature [204].

ments can easily change their molecular structure under light irradiation.

Light irradiation with a certain wavelength leads to photoinduced transformations of the photochromic groups which (being directly bound to chiral fragments) affect both the configuration and shape of the side-chain group. This leads to a decreased helical twisting power β of the given chiral group (Eq. (3)), which is related to a decrease in the anisotropy of molecules (Fig. 29(b)). A decrease in β leads to the untwisting of the cholesteric helix, which is accompanied by a shift in the selective

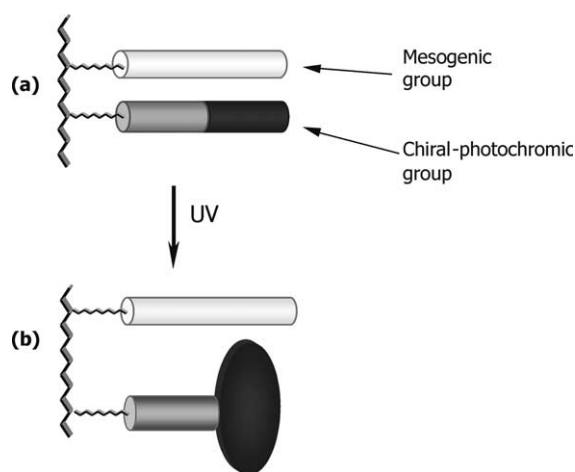


Fig. 29. Scheme illustrating the structure of a LC copolymer with combined chiral-photochromic side group (a) before and (b) after UV-irradiation.

light reflection maximum to longer wavelengths. Thus, using light irradiation as the external control factor, one may effectively modify the optical properties of polymer films by changing the local supramolecular helical structure.

The chemical formulae of the selected LC copolymers containing chiral and photochromic groups in the same monomer units are shown in Table 5. As is shown, copolymers 48–54 contain the same nematogenic group, while the molecular structures of photochromic groups varied widely. The number of photochromic copolymers containing photosensitive fragments (such as double C=C and N=N bonds) and chiral menthone and menthyl groups were synthesized.

3.4.2.1. Copolymers with irreversible photoregulation of optical properties. First, let us consider the photochromic copolymers with menthone-containing chiral-photochromic groups (Table 5, 48–51, 55). Spectral data [83,205,212] indicate the occurrence of a single photoprocess for all menthone-containing copolymers, that is, *E*–*Z* isomerization (see also data for low-molar-mass compound 17):

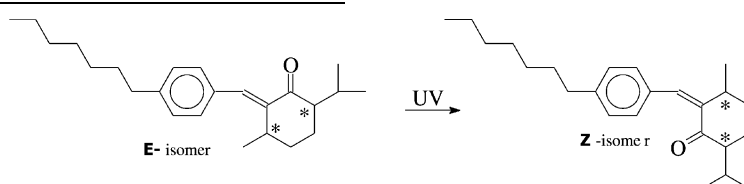


Table 5
Molecular structure of chiral-photochromic copolymers

Polymer, m, n and R	Reference
<p> $\left[\begin{array}{c} \text{CH}_2 \\ \\ \text{CH}-\text{COO}-(\text{CH}_2)_5-\text{COO}-\text{C}_6\text{H}_4-\text{OOC}-\text{C}_6\text{H}_4-\text{OCH}_3 \\ \\ \text{---} \end{array} \right]_y$ $\left[\begin{array}{c} \text{CH}_2 \\ \\ \text{CH}-\text{COO}-\text{R}^* \\ \\ \text{---} \end{array} \right]_x$ </p>	
<p>$\text{R}^* =$</p>	48 ^a [209–211]
	49
	50
	51
	52
	53 [216]
	54 [217,218]
<p> $\left[\begin{array}{c} \text{CH}_2 \\ \\ \text{CH}-\text{COO}-(\text{CH}_2)_6-\text{O}-\text{C}_6\text{H}_4-\text{COO}-\text{C}_6\text{H}_4-\text{CN} \\ \\ \text{---} \end{array} \right]_y$ $\left[\begin{array}{c} \text{CH}_2 \\ \\ \text{CH}-\text{COO}-(\text{CH}_2)_6-\text{O}-\text{C}_6\text{H}_4-\text{COO}-\text{C}_6\text{H}_4-\text{CH}=\text{CH}-\text{COO}-\text{spiro} \\ \\ \text{---} \end{array} \right]_x$ </p>	55 [208,212]

^a The numbers (48–54) correspond to the appropriate copolymer.

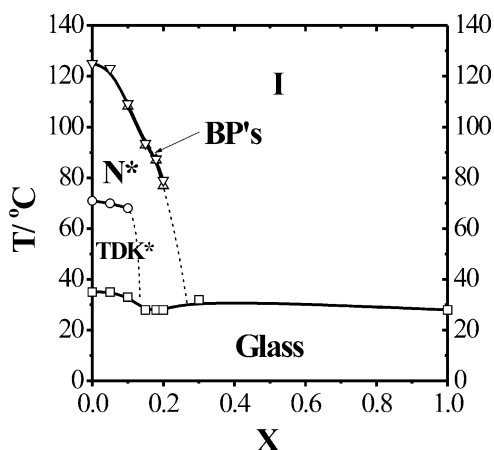


Fig. 30. Phase diagram of copolymers 48. X is the mole fraction of chiral-photochromic groups [46]. Bps—blue phases.

It should be noted that all menthyl- and menthone-containing homopolymers in Table 5 are amorphous (except for 51). This fact may be explained by the presence of bulky terminal chiral fragments [204]. For this reason, copolymers with one- and two-ring chiral side chain groups show cholesteric (chiral-nematic N^*) and ordered chiral (two-dimensional, TDK^*) phases, and the clearing temperature decreases with increasing the content of the chiral-photochromic groups (Fig. 30).

The formation of the cholesteric phase over a wide temperature-concentration range accounts for the selective reflection of a circularly polarized light from the planar-oriented copolymer films. The wavelength corresponding to the maximum selective light reflection depends on the content of the optically active side groups and temperature. Fig. 31 shows the typical plots of the selective light reflection peak wavelength versus temperature for one series of copolymers. Analysis of the photochemical properties of the copolymer films shows that the helix pitch remains unchanged if irradiation proceeds at room temperature. Annealing of the samples above T_g leads to a shift in the selective light reflection wavelength to the long-wavelength spectral region.

As follows from Fig. 32, as the duration of irradiation increases, the selective light reflection wavelength shifts to a longer wavelength region; that is, untwisting of the helix occurs. Obviously, the $E-Z$ isomerization is responsible for an increase in the helix pitch, and the twisting power of the Z -isomer is likely

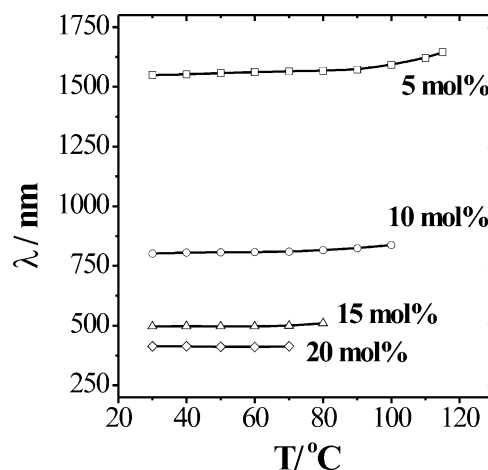


Fig. 31. Temperature dependencies of the maximum of selective light reflection for copolymers 49 with different content of chiral units [46].

to be much lower. An intrinsic helical twisting power β/n of the E -isomer of the menthone-containing group is equal to $13-17 \mu\text{m}^{-1}$ depending on the molecular structure of chiral side groups. After irradiation, this value is lowered by a factor of 10 [83].

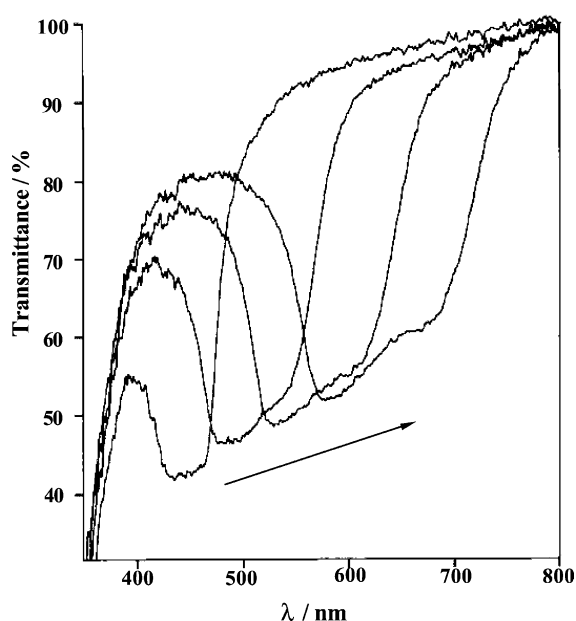


Fig. 32. Change of the transmittance spectrum of the copolymer 51 with 20 mol% of chiral units during UV-irradiation (365 nm). Spectra were recorded each 2 min of irradiation; temperature of the sample 110°C [46].

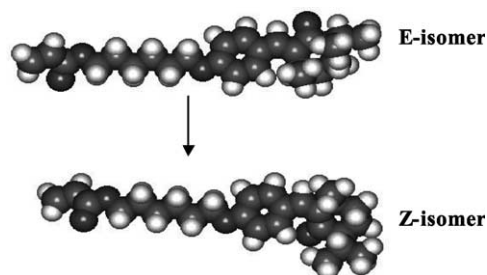


Fig. 33. Changes of benzilidenemethanone group anisometry of copolymer **46** during *E*–*Z* photoisomerization.

Irradiation-induced variations in the helical twisting power of copolymers are associated with a strong change in anisometry of chiral fragments (Fig. 33). The decrease in anisometry of chiral molecules has a certain effect on the thermal stability of the meso-phase. As a rule, clearing temperature decreases (on average, by 10 °C) after 2 h irradiation [205]. The untwisting rate is strongly temperature dependent: the higher the temperature at which the sample was irradiated, the higher the process intensity (Fig. 34). Note that the shift in the maximum of the peak of selective light reflection is accompanied by its pronounced broadening. Finally, this leads to its complete degeneration.

As was demonstrated [204,205], the observed broadening of the selective light reflection peak can be explained by assuming that the diffusion of macromolecules enriched with chiral groups in the

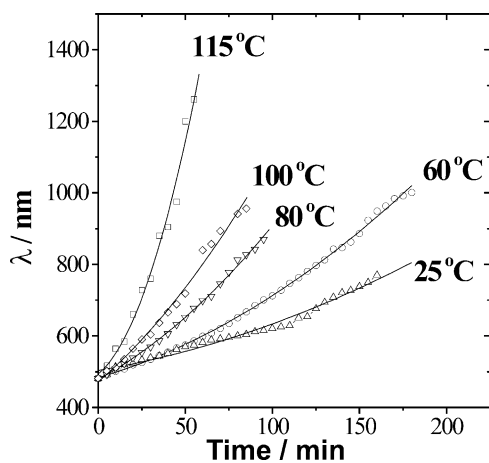


Fig. 34. Selective light reflection wavelength as a function of the irradiation time (313 nm, $P = 0.7 \text{ mW/cm}^2$) for copolymer **46** with 15 mol% of chiral units at various temperatures [205].

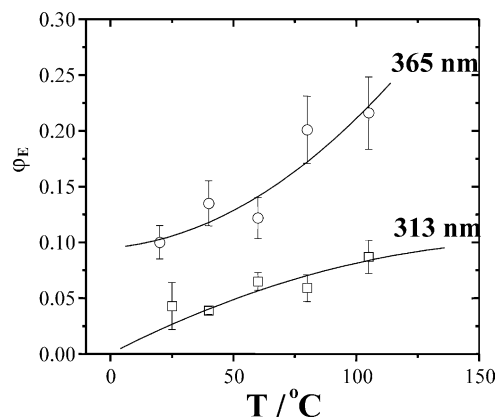


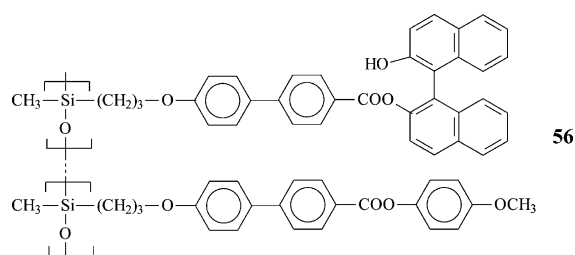
Fig. 35. Dependence of apparent quantum yield on temperature for copolymer **48** with 15 mol% chiral-photochromic units UV-irradiated at 365 and 313 nm [209].

Z-isomer conformation, throughout the copolymer film thickness, is a limiting stage in the photoinduced untwisting of the helix. This diffusion leads to a considerable inhomogeneity of the sample composition upon UV-irradiation.

To evaluate the efficiency of the photochemical process in copolymer samples in various phase states, the effective quantum yields of the process were calculated [204]. Fig. 35 shows typical plots of the quantum efficiency versus temperature for one of the menthone-containing copolymers irradiated at two different wavelengths. Analysis of this data allows the following conclusions:

- (i) Increase in the temperature leads to a significant increase in the rate of helix untwisting. Maximum values of the apparent quantum yields are observed for the isotropic melt. A significant increase in the helix untwisting rate is probably related to a strong decrease in polymer viscosity and increase in the self-diffusion constants with the temperature. The temperature growth facilitates ‘stirring’ in the system, thus increasing the efficiency of the helix untwisting process.
- (ii) UV-irradiation of the copolymer film samples with a higher wavelength (365 versus 313 nm, Fig. 35) increases the process efficiency. This is related to a higher width of the ‘reaction zone’ (at 365 nm the optical density is 0.15; hence the photoinduced reaction takes place over the entire film thickness of 20 μm).

It should be noted that similar features in photochemical behaviour were observed for copolymers with menthyl-containing chiral side-chain cinnamic acid fragments (samples **52**, **53**, Table 5) [209] as well as for the binaphthyl-containing cholesteric copolymers studied by Chien et al. [215]:



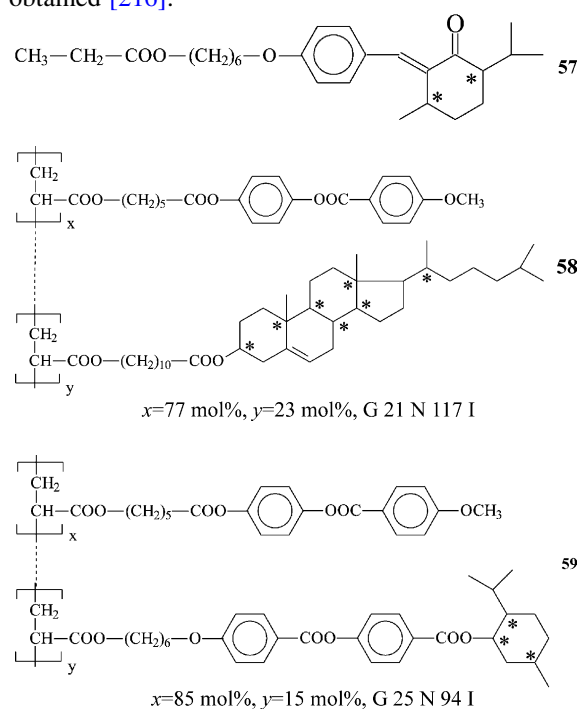
However, in Ref. [215], the mechanism of the photoinduced processes was not studied in detail; only the irreversible helix untwisting was observed and explained by the photodegradation of chiral binaphthyl groups.

As was shown, all the menthone-containing copolymers, as well as the copolymers with chiral-photochromic side-chain fragments of cinnamic acid, do not exhibit reversible thermoinduced *E*–*Z* isomerization, at least at temperatures below 150 °C. This is an evident disadvantage of such systems which may limit their possible application. Another important disadvantage is the aforementioned broadening of the selective light reflection peak in the course of the photoinduced helix untwisting. Naturally, the question arises regarding whether or not these drawbacks may be eliminated.

3.4.2.2. Cholesteric mixtures with irreversible photoregulation of optical properties. The above approach, based on the synthesis of combined chiral-photochromic monomers and copolymers, was also successfully used for obtaining low-molar-mass chiral-photochromic dopants which could be introduced in LC polymers and copolymers [216]. The preparation of such mixtures offers new possibilities for variations in optical and photooptical properties of LC polymer systems, and in the preparation of cholesteric mixtures with irreversible photoregulation of the helix pitch. In addition, the introduction of chiral-photochromic low-molar-mass dopants to LC polymers follows three principal objectives:

1. To increase the diffusion rate of the chiral photochromic component and, as a consequence, to increase the helix untwisting rate and attainment of photostationary equilibrium.
2. To provide a homogeneous distribution of chiral component in the mixture and to prevent the UV-radiation-induced broadening of the selective light reflection maximum.
3. To investigate the possibility of the development of photosensitive materials in which the helix pitch may be either increased or decreased under the action of light.

Towards these objectives, mixtures of the low-molar-mass left-handed dopant **57** with chiral nematic copolymers forming left-handed (cholesterol-containing units) **58** and right-handed (*d*-menthyl-containing units), **59**, supramolecular helical structure have been obtained [216]:



Upon the introduction of the left-rotating chiral dopant **57** to the left-twisted cholesterol-containing copolymer **58**, an additional twisting of the cholesteric helix takes place (Fig. 36(a) and (c)), because the concentration of chiral groups with the same sign of rotation increases. In the case of the right-twisted menthyl containing copolymer, the cholesteric helix

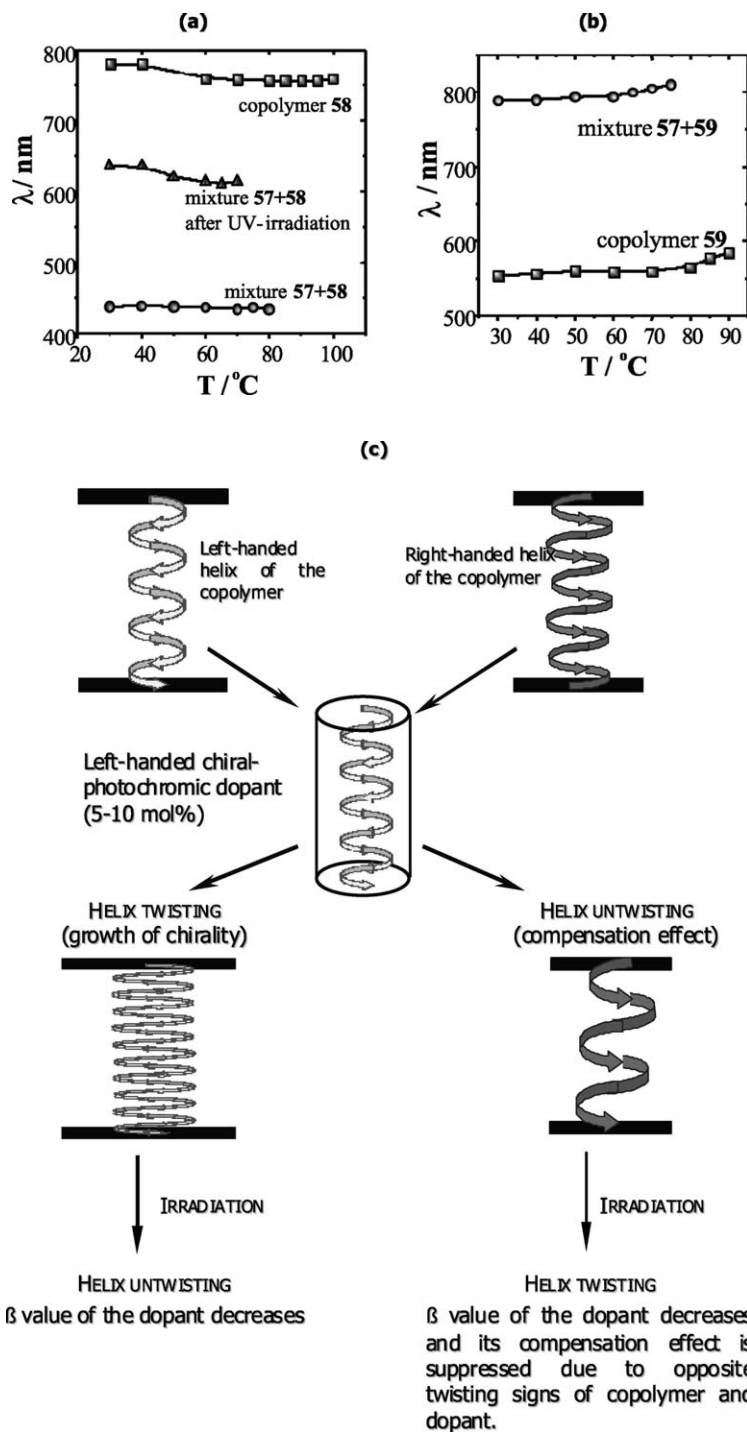


Fig. 36. Temperature dependencies of selective light reflection wavelength for (a) cholesterol-containing copolymer **58** and (b) menthyl-containing copolymers **59** and their mixtures with **57** (in the case (a) content of **57**, 10 mol%, in the case (b) 5 mol%); (c) schematic representation of helix pitch changes for the mixtures of cholesteric copolymers of different handedness with left-handed chiral dopant before and after UV-irradiation [216].

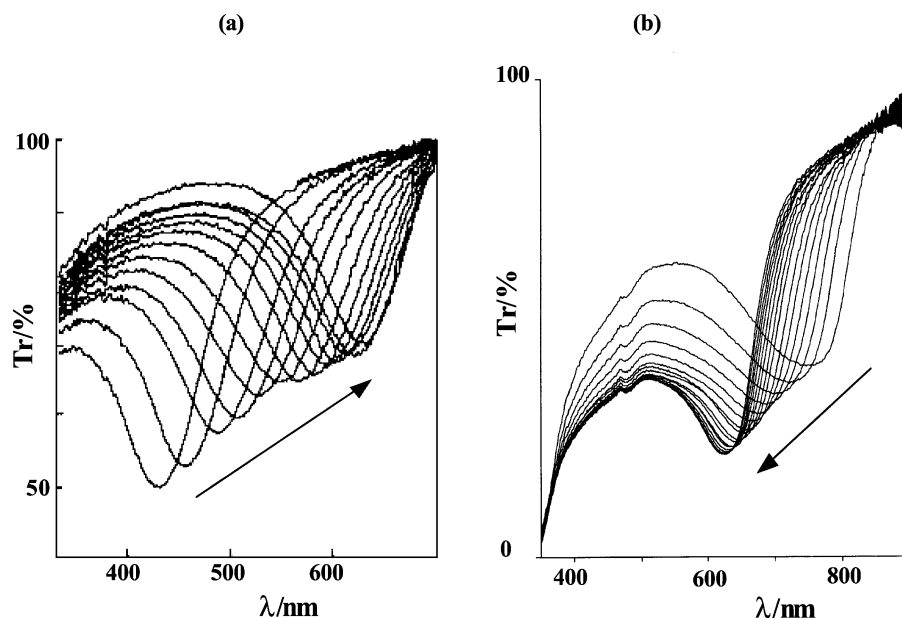


Fig. 37. Time variation of the transmittance spectrum of (a) blend **57** + **58** and (b) **57** + **59** during the UV-irradiation (313 nm). The spectra were sequentially recorded at a 2-min interval at 60 °C [216].

experiences untwisting due to a partial compensation of chiral units with different signs (Fig. 36(b) and (c)).

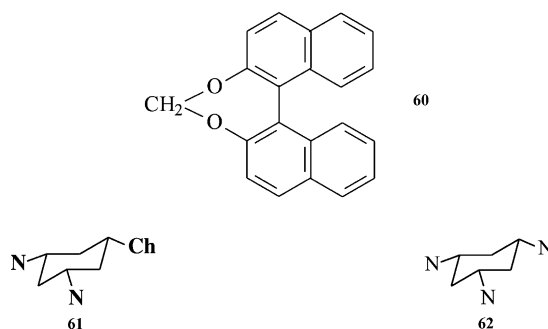
As was shown above, UV-irradiation leads to a decrease in the twisting power of the dopant; in the case of blend **57** + **58**, the cholesteric helix experiences untwisting and λ_{\max} increases. In the case of blend **57** + **59**, λ_{\max} decreases (Fig. 37). In both cases, no widening in the selective light reflection maximum was seen.

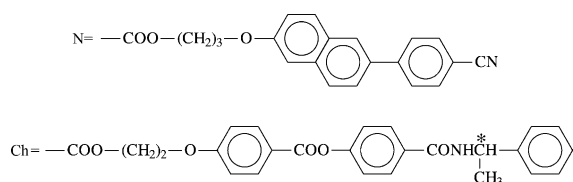
Therefore, cholesteric compositions containing a photosensitive chiral dopant allow the preparation of polymer films with cholesteric structure. In this case, UV-irradiation may provide either twisting or untwisting of the cholesteric helix; that is, selective light reflection may be shifted to different spectral regions. One should mention that the local irradiation of such systems allows a coloured recording on a coloured background, and this finding creates possibilities for their application as active photooptical media. A scheme for optical recording using planarly oriented cholesteric film is shown in Fig. 38. It is clearly seen how the helix is untwisted in the irradiated zones and the selective reflection maximum is shifted to the long wavelength of the spectral range, i.e. $P_2 > P_1$.

Studies on materials containing menthone derivatives and other similar compounds were also per-

formed at the Philips Research Laboratory [203,207, 208,217,218]. Authors of the cited publications demonstrated some advantages of the polymer mixtures with low-molar-mass dopants. In particular, they pointed out that the mixtures of copolymer **55** (Table 5) with commercial nematic host *E-7* show a higher rate of helix untwisting but no significant broadening of the selective light reflection peak [203, 217,218].

Chen et al., studied the blends of binaphthyl-containing chiral dopant **60** (characterized by the specific type of enantiomerism related to a hindered rotation of naphthalene rings) with glassy low-molar-mass cholesteric liquid crystals **61**, **62** [219,220]:





Although these compounds are mixtures of low-molar-mass substances, they are able to produce glassy films that can be used as promising materials for optical data storage. In this case, UV-irradiation (334 nm) leads to an irreversible photoracemization

of chiral dopant, and untwisting of the cholesteric helix (Fig. 39).

In this study, however, the authors were trying to prepare the cholesteric materials which, under light irradiation, showed a marked broadening in the selective light reflection peak (by 2.4 times).

3.4.2.3. Reversible photoregulation of optical properties. The above-mentioned papers were devoted to cholesteric materials with photoinduced irreversible helix pitch. However, quite recently [210,211], we

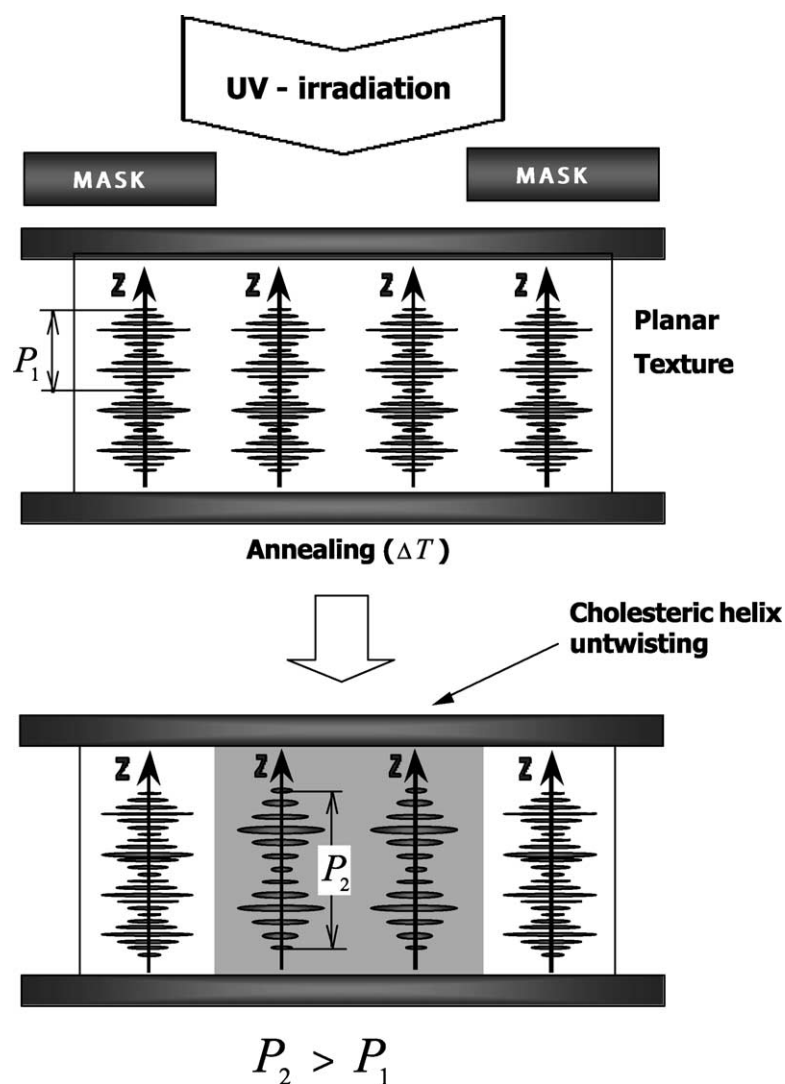


Fig. 38. Schematic representation of optical recording using planarly oriented films of copolymers or mixtures with photoregulated helical pitch.

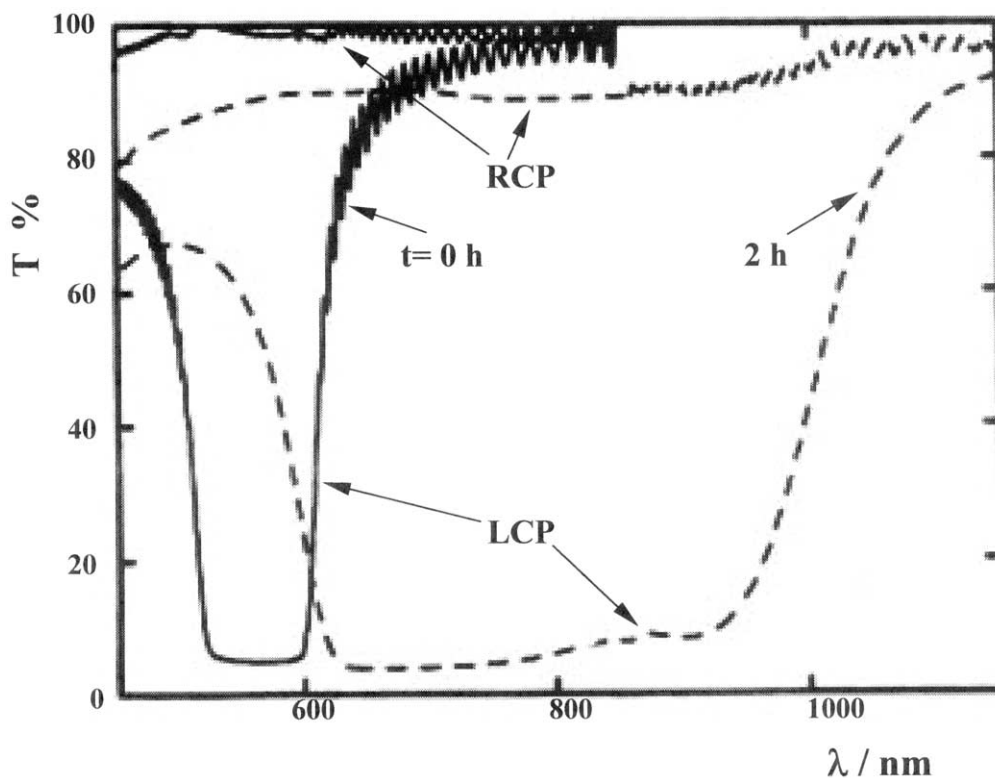
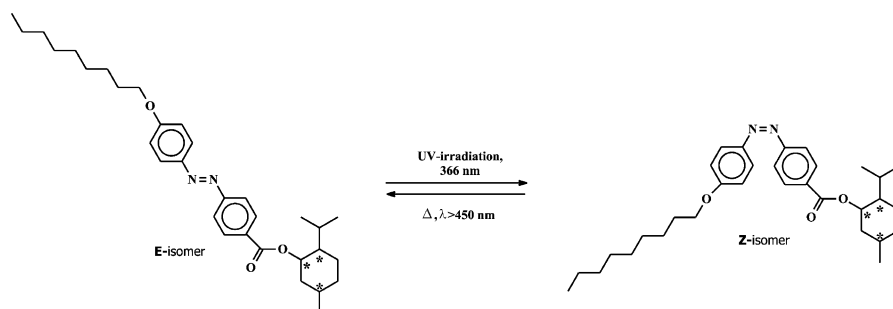


Fig. 39. Circular polarization spectra measured with right- and left-handed circularly polarized (i.e. RCP and LCP) incident light at normal incidence at a molar ratio **61/62/60** = 1.00/4.36/0.55; solid curves: pristine film; dashed curves: photoracemized at $140 \mu\text{W}/\text{cm}^2$ (at 334 nm) and 100°C for 2 h [220].

demonstrated a possible synthesis of cholesteric polymers with reversible photoregulation of optical properties (helix pitch and selective light reflection peak). These results were obtained for mixtures of cholesteric copolymers with low-molar-mass dopants containing azobenzene fragment, as well as copolymers with chiral-photochromic groups (copolymer **54** in Table 5).

Light irradiation of the planarly oriented films of copolymers **54** leads to helix untwisting, and the

selective light reflection wavelength is shifted to the long-wavelength spectral region. Prior to irradiation, films of copolymer **54** with 15 mol% of chiral groups show selective light reflection in the green spectral region. After UV-irradiation, their selective light reflection is shifted to the red spectral region. These changes are related to a decrease in the anisotropy of chiral photochromic fragments, and consequently a concomitant decrease in its twisting power during the *E*–*Z* isomerization:



An evident advantage of the samples concerns the reversible character of isomerization. For example, as a result of annealing the irradiated films at $T \geq 45$ °C, a reverse shift of the selective light reflection wavelength to the short-wavelength spectral region is observed. This fact implies that this process is completely thermally reversible. It is important to note that at room temperature the films of copolymers exist in the glassy state ($T_g > 25$ °C); as a result, optical information may be preserved for a long time (at least several months).

An important property of the synthesized chiral photochromic materials concerns their high fatigue resistance, which allows a possible repeated (cyclic) recording and erasing of optical information. As follows from Fig. 40, one may achieve reversible changes in the recorded image without any marked loss in the coloured characteristics over repeated ‘recording-erasing’ cycles. In each cycle, the film was UV-irradiated for 30 min at 90 °C and then annealed for 20 min at the same temperature.

Thus, the menthyl-containing chiral photochromic copolymers with azobenzene photosensitive fragments may be used for the preparation of cholesteric materials with a reversibly controlled helix pitch. High fatigue resistance of the materials to ‘recording-erasing’ cycles allows one to consider these materials as promising candidates for coloured recording and storage of optical information with possible repeated ‘re-recording’. Fig. 41 shows an example of a coloured image on a coloured background.

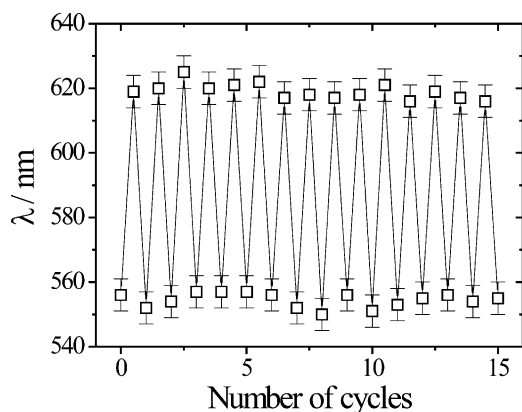


Fig. 40. Fatigue resistance properties of the film of copolymer 54 with 15 mol% of chiral units under the recording-erasing conditions [210,211]. Reprinted with permission from Adv Mater 2000;12:1180. © 2000 Wiley-VCH [210].



Fig. 41. Microphoto of the film prepared from the copolymer 50 with 15 mol% of chiral-photochromic units exposed to UV-irradiation (365 nm, 15 min). In the figure the red characters which mean Russian abbreviation of Moscow State University corresponding to the irradiated zones are clearly seen on the blue background of the initial sample [46].

3.4.3. Cholesteric copolymers and mixtures combining photochromism with optical properties of cholesteric phase

A possible approach in the synthesis and study of cholesteric copolymers concerns the preparation of LC copolymers and their mixtures with low-molar-mass dopants that combine photochromism with the unique optical properties of the cholesteric phase. This approach is based on the introduction of photosensitive monomer units or dopants to the matrix of cholesteric copolymers. The ratio between different monomer units in the

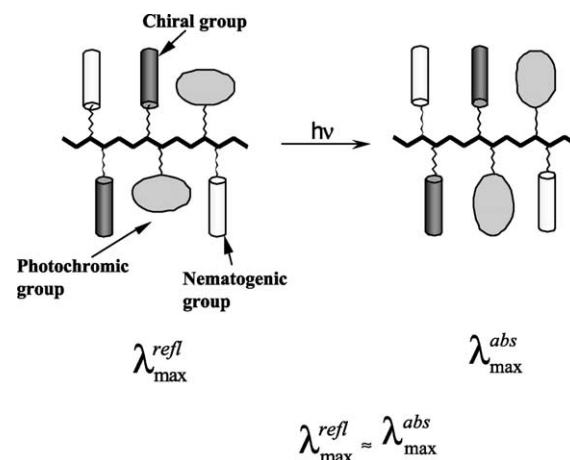


Fig. 42. Schematic representation of cholesteric copolymer combining photochromism with optical properties of cholesteric phase. The maximum selective reflection of light ($\lambda_{\max}^{\text{refl}}$) of cholesteric film (before irradiation) should coincide with the maximum light absorption of photoinduced isomer ($\lambda_{\max}^{\text{abs}}$) after irradiation.

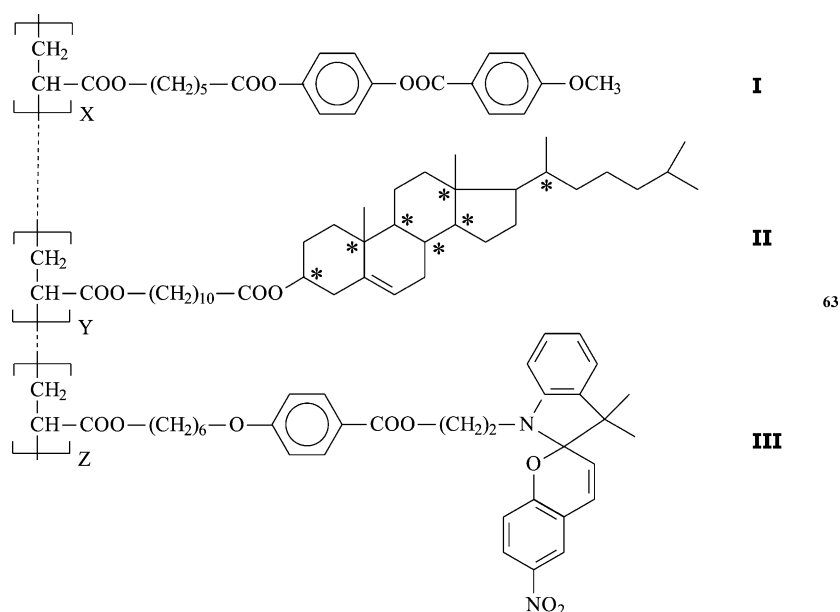
copolymer should be selected so that the maximum selective light reflection of cholesteric film coincides with the maximum light absorption of the photoinduced new isomer formed during irradiation [221–225] (Fig. 42).

This principle was first applied for cholesteric terpolymers containing spiropyran-based photochromic side groups [222–225], and later was extended to copolymers and dopants containing photochromic diarylethene groups [221]. Both systems will be considered in the two subsections that follow.

3.4.3.1. Cholesteric terpolymers with spiropyran-based photochromic side groups. New ternary copolymers containing photochromic spiropyran units that experience photoisomerization under UV-irradiation were synthesized as the desired photochromic LC copolymers.

the development of the chiral nematic mesophase with a selective light reflection at a certain wavelength, while the spiropyran groups are responsible for photochromic properties.

Examination of the phase behaviour of the as-synthesized copolymers shows that the samples with relatively low content of dye units (below 20 mol%) are able to produce the chiral nematic phase over a wide temperature range. Planar texture of these copolymers is characterized by selective reflection of circularly polarized light in a visible spectral region (Fig. 43), which is associated with the presence of the left-handed helical supramolecular structure. Note that λ_{\max} and, correspondingly, helix pitch slightly depend on temperature. On cooling below T_g , helical supramolecular structure of copolymers are fixed in glassy state. The effect of



As was shown above (Section 3.3.3), spiropyran fragments were transformed to the merocyanine form under UV-irradiation and an intensive absorption peak in the region of 550–630 nm appears. Copolymers **63** contain three different types of side groups: nematogenic phenylbenzoate groups (I), chiral cholesterol-containing groups (II), and photochromic spiropyran groups (III) [222–225]. The presence of phenylbenzoate and cholesterol groups should enable

UV-irradiation on the planarly oriented polymer film leads to dramatic changes in the corresponding transmission spectra. In the region of selective reflection, one may observe a well-pronounced absorption peak of the merocyanine form ($\lambda_{\max} = 575$ nm) which is produced during the photoprocess (Fig. 44). Once the photostationary state is achieved, transmission of the test samples in this spectral region becomes almost zero.

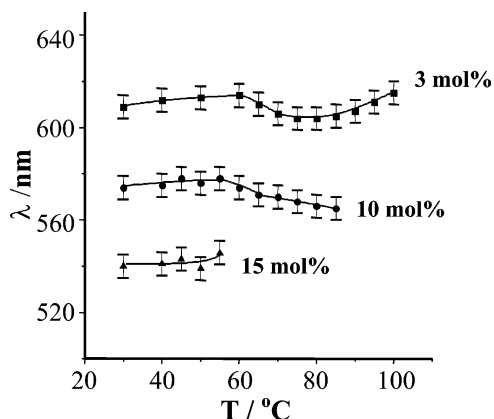


Fig. 43. Temperature dependence of selective light reflection maximum (λ_{\max}) for copolymers **63** with different concentration of the dye units [222,223]. Reprinted with permission from Adv Mater 1999;11:1025. © 1999 Wiley–VCH [222].

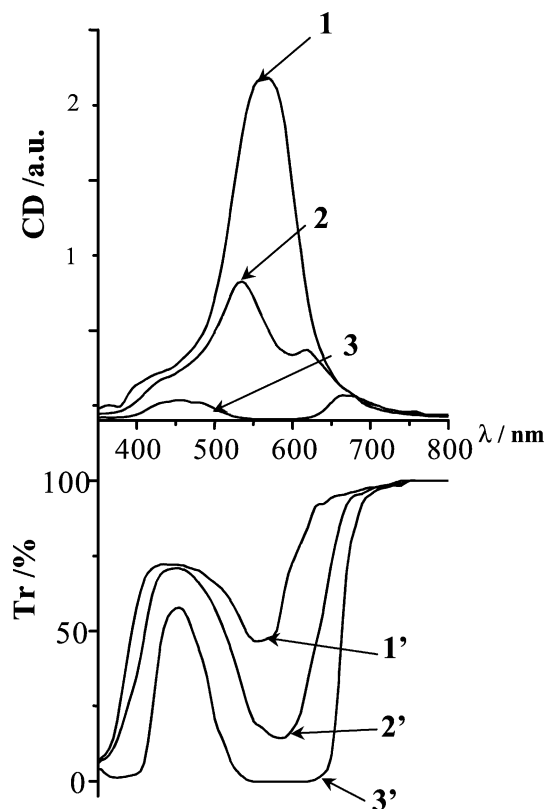


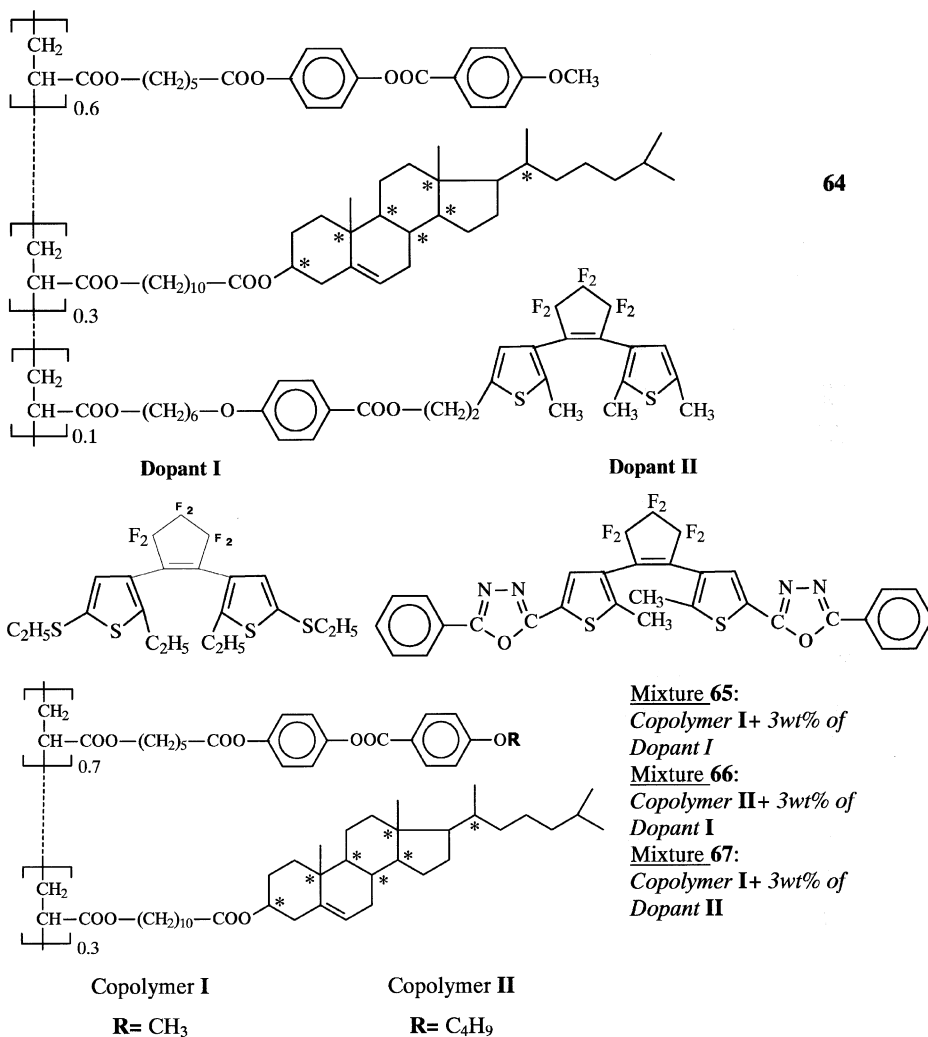
Fig. 44. (1–3) Circular dichroism and (1'–3') transmittance spectra of spiropyran-containing copolymer **63** with 10 mol% of dye units during the UV-irradiation: (1) before irradiation; (2) after 30 s of UV-irradiation; (3) after achieving the photostationary state (500 s) [222,223]. Reprinted with permission from Adv Mater 1999;11:1025. © 1999 Wiley–VCH [222].

As was mentioned above, planarly oriented films of copolymers are characterized by selective light reflection of the left-handed circularly polarized light, and this fact is well seen in the spectrum of circular dichroism (Fig. 44, curve 1). This spectrum shows an intensive peak whose maximum coincides with the maximum of selective light reflection. The UV-irradiation also leads to dramatic changes in the CD spectrum (Fig. 44, curves 2 and 3). Before irradiation, the CD peak is well pronounced. After irradiation, it completely degenerates. The appearance of two poorly pronounced maxima in the CD spectrum, instead of one intensive peak, is likely to be associated with the fact that the width of the absorption band of the formed merocyanine form is somewhat smaller than the width of the band corresponding to the initial CD peak. This phenomenon suggests that the irradiated regions of copolymer film lost their ability for selective light reflection in the spectral region of the absorption of the merocyanine form.

These drastic light-induced changes in optical properties make it possible to use such materials for data recording. The possible procedure for data recording and read-out is presented in Fig. 45. After masked irradiation, read-out is performed by scanning the sample with a wavelength corresponding to the selective light reflection maximum. When non-irradiated regions are scanned, selective light reflection of the left-handed circularly polarized light is observed; when irradiated regions are scanned, almost complete light absorption takes place. Fig. 46 shows the micrograph of a copolymer film after masked irradiation. The transparent green regions are non-irradiated ones; the dark regions correspond to the irradiated regions and contain a merocyanine form capable of a strong light absorption. Such regions appear as dark bands on the colour background.

3.4.3.2. Cholesteric copolymers and mixtures based on diarylethene photochromes. Spiropyran fragments used as photosensitive groups show some drawbacks, such as low fatigue resistance [226] and thermal instability of the photoinduced form. Even at room temperature, one may observe the back transition to the initial spiropyran form [227,228].

In this connection, alternative systems based on copolymer **64** and mixtures **65–67** composed of binary cholesteric copolymer and low-molar-mass photochromic diarylethene dopant were advanced and studied [221,229,230].



As was shown above, diarylethene fragments show a well-pronounced photochromism: UV-irradiation accompanied by photocyclization which led to the formation of the coloured closed form of diarylethene fragments (see Section 2.2.2, Table 2) [231–235].

Copolymer **64** and mixtures **65**, **67** are capable of forming only the cholesteric mesophase, whereas mixture **66** may also produce a more ordered Sm \tilde{C} phase.⁷ For

such systems, their planar structure is characterized by the selective light reflection in the visible and IR spectral regions. Upon UV-irradiation with a wavelength of 313 nm, the absorption spectra of the planarly oriented films show an intensive peak with its maximum ranging from 522 to 615 nm, depending on the structure of the photochromic compound (Fig. 47). Such spectral changes suggest the occurrence of photoinduced cyclization. The photoinduced ring-opening back reaction takes place upon visible light irradiation.

In Refs. [229,230], the kinetics of forward and back reactions of photocyclization as well as ring opening were studied. As was shown for all systems, the rate of

⁷ For the corresponding butoxy-substituted phenylbenzoate homopolymer, a local order in the arrangement of mesogenic groups in this phase was studied in detail in Ref. [236].

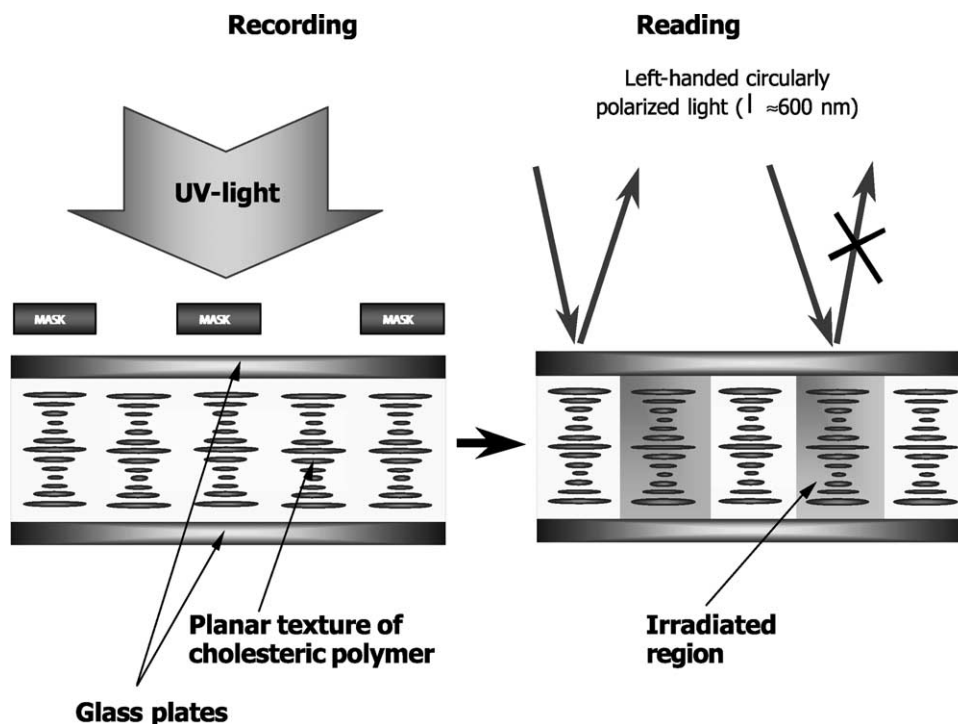


Fig. 45. Principal scheme of the optical data recording on planarly oriented film of photochromic cholesteric copolymer (left part) and reading of information from the same film (right part) [222,223]. Reprinted with permission from Adv Mater 1999;11:1025. © 1999; Wiley–VCH [222].

the forward photoinduced process is weakly controlled by temperature and the phase state of the system. This implies that the local surrounding of photochromic groups in the polymer matrix has no effect on the kinetics of the photoinduced process. That is, the system possesses a certain free volume, which allows the photoinduced reaction to occur.⁸

As mentioned above, the important advantages of photochromic diarylethylene derivatives are related to the high thermal stability of their photoinduced closed form. To this end, the films of the copolymer **64** and blends were irradiated with UV-light at different temperatures. Then, the changes in the optical density at the wavelength corresponding to the selective light reflection maximum of the closed form were assessed. For copolymer **64** and mixtures **65** and **66**, the photoinduced form is stable,

⁸ This experimental fact reveals the important advantages of the photochromic diarylethylene systems as compared with, for example, azobenzene or stilbene photochromes where the photoinduced processes may be markedly inhibited by the polymer matrix [237–240]. In the latter case, a relatively high free volume is needed for photoisomerization.

whereas for the mixture **67** at temperatures above 50 °C, the closed form of dopant **II** is transformed into an open form at a high rate of transfer. To prove that the decolouration process is related to the ring opening reaction rather than thermal decomposition of dopant **II**, the annealed films were subjected to additional

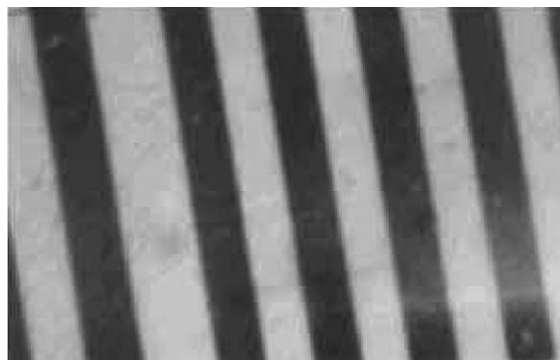


Fig. 46. Optical microphoto showing cholesteric planar oriented film of spiropyran-containing copolymer **63** with 10 mol% of dye units after UV-irradiation through a mask. Dark bands correspond to the irradiated regions (width of dark line: 25 μm) [222,223]. Reprinted with permission from Adv Mater 1999;11:1025. © 1999; Wiley–VCH [222].

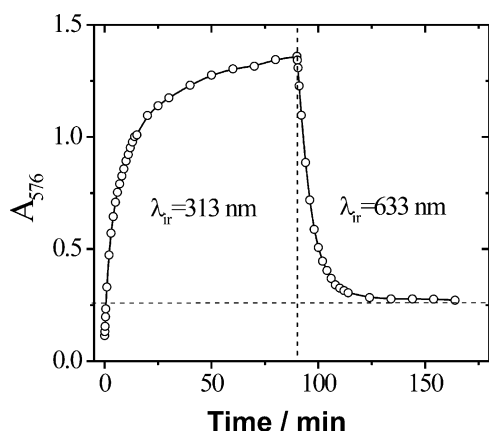


Fig. 47. Absorbance growth for mixture **65** during UV-irradiation (313 nm) and subsequent decrease during irradiation by visible light (HeNe laser, 633 nm). Film thickness: 20 μm , temperature 20 $^{\circ}\text{C}$ (Arrow shows the UV-irradiation switching off and the visible light switching on.). Reprinted with permission from J Mater Chem 2001;11:2004. © 2001 Royal Society of Chemistry [229].

UV-irradiation. In this case, one may observe again the appearance of the absorption peak of the closed form, and the maximum optical density coincides with the values as obtained prior to annealing. Recently in Refs. [241,242], diarylethylene compound was studied; upon annealing, the closed form of this compound is also transformed to an open form. In this case, the compound contains isopropyl substituents in the vicinity of the bond produced upon the photoinduced cyclization. As a result, destabilization of the closed form is seen. In the case studied in Ref. [230], the nature of the thermal instability for the closed form of dopant **II** is still unclear. The presence of substituents in the thiophene rings changes the electron structure of the closed form and reduces the energy barrier of the back transition. However, it seems important to emphasize that at room temperature, the closed forms of all diarylethylene derivatives in the ternary copolymer and blends are stable.

As was mentioned above, for all systems the back process of ring opening is provided by irradiation with visible light (Fig. 47). In this case, a decolouration process takes place even at room temperature. For copolymer **64** and mixture **66**, the rate of this process slightly depends on temperature, whereas for mixture **67**, the rate of the process increases with increasing temperature.⁹ This

⁹ As was shown in Ref. [229], for mixture **65**, the rate of the back photoprocess also increases with increasing the temperature but, in this case, this trend is related to an increase in the free volume of the polymer matrix.

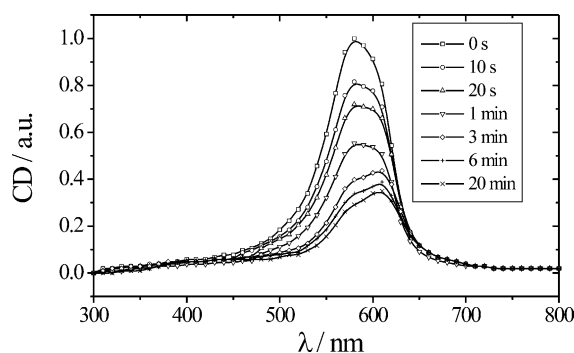


Fig. 48. Changes of circular dichroism spectra during UV-irradiation of the planarly oriented film of the mixture **65** ($T = 20\text{ }^{\circ}\text{C}$). Irradiation time is shown in figure. Reprinted with permission from J Mater Chem 2001;11:2004. © 2001 Royal Society of Chemistry [229].

result may be explained by the fact that, in the latter case, both thermoinduced and photoinduced processes of ring opening occur, and the higher the irradiation temperature, the higher the total rate of the back reaction.

For the ternary copolymer **64** and mixtures **65** and **67**, the selective light reflection maximum almost coincides with the absorption peak of the closed form of the photochromic component. Upon UV-irradiation of the films, one may observe a gradual degeneration of the selective light reflection maximum due to a marked absorption of the photochromic molecules in this spectral region. This phenomenon manifests itself in the variations of the circular dichroism spectra (Fig. 48). Upon irradiation of films, photoisomerization is accompanied by a noticeable decrease in the circular dichroism in the region of the selective light reflection due to a marked absorption of the closed form of diarylethylene groups.

For blend **66**, where the selective light reflection maximum is located in the IR spectral region and does not coincide with the absorption peak of the closed form, the circular dichroism spectra show no marked changes. In addition, no induced circular dichroism was detected in the region of the absorption of the photoinduced form of the dye, which is an important feature of the chiroptical behaviour of the system. This phenomenon was repeatedly observed in Refs. [243–246] for cholesterics doped with various dichroic dyes. However, in the case studied in Ref. [230], the degree of orientation of the dopant molecules in the cholesteric phase is likely to be so small that the above behaviour may hardly be detected.

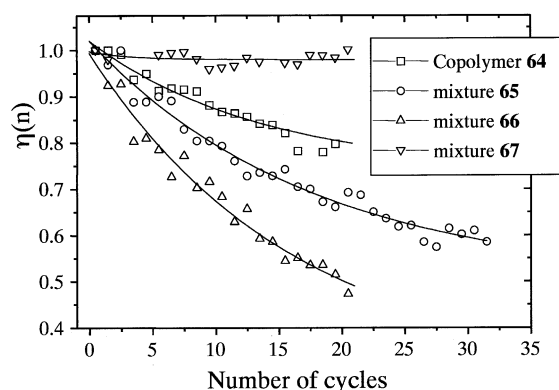


Fig. 49. Fatigue resistance of the copolymer **64** and mixtures **65–67** under the recording–erasing conditions. In each cycle film of mixture was irradiated by UV-light (313 nm), then was irradiated by visible light. ‘Recording’ was performed using UV-light ($\lambda_{ir} = 313$ nm, $t = 10$ min); ‘erasing’ was performed using visible light: $\lambda_{ir} = 550$ nm (copolymer) and $\lambda_{ir} = 633$ nm (mixtures); time: 25–30 min [229,230]. Reprinted with permission from J Mater Chem 2001;11:2004. © 2001 Royal Society of Chemistry [229].

An important parameter characterizing the fatigue resistance of the photochromic material in recording–erasing cycles is given as

$$\eta(n) = \frac{A_{ir}(n) - A_0(n)}{A_{ir}(1) - A_0(1)} \quad (11)$$

where n is the number of cycles, and A_{ir} and A_0 stand for the absorbance of the closed form before and after irradiation, respectively.

Fig. 49 presents $\eta(n)$ plotted against the number of cycles. In each cycle, the recording is performed by UV-irradiation whereas the erasing is provided by irradiation with visible light. The fatigue resistance of the ternary copolymer **64** and mixtures **65** and **66** appears to be rather low (Fig. 49). This trend is related to irreversible secondary photoinduced reactions. On the other hand, mixture **67** shows a good resistance to repeated recording–erasing cycles. This behaviour occurs because of the absence of any secondary processes in dopant **II**.

Comparing the photochromic properties of mixtures **65** and **66**, one may conclude that the difference in the phase behaviour of both systems has no marked effect on the kinetics of photoinduced processes and fatigue resistance. The specific features of the photochromic behaviour of the blends are primarily related

to the difference in the structure of photosensitive groups. In this respect, the behaviour of mixture **67** containing dopant **II** appears to be maximally different.

The results obtained in this work allow one to conclude that such systems may be used as materials for the reversible recording of optical information. From the viewpoint of fatigue resistance in repeated recording–erasing cycles, the best characteristics are presented by mixture **67**.

3.4.4. Multifunctional cholesteric systems

Combined LC copolymers containing different photosensitive groups in one macromolecule could be of significant interest. Versions of the molecular design of such polymers are presented in Fig. 50. One may conclude that the ‘simplest’ copolymer (from a synthetic viewpoint) should contain four types of monomer units including one mesogenic, one chiral, and two photochromic groups (Fig. 50(a)). Such a copolymer may be obtained, for instance, by radical polymerization of four monomers with the appropriate functionalities. However, as far as we know, such copolymers are not described in literature. Light irradiation of a hypothetical copolymer might induce photochemical reactions only in the photochromic groups, leaving the chiral fragments and the helical twisting power β unchanged. Therefore, it is difficult to expect that the optical properties of such a copolymer will be essentially changed, because the helical twisting power of the chiral fragments might remain the same during irradiation. It seems likely that the same situation will occur for the molecular structure shown in Fig. 50(b).

In this case, copolymers with the molecular structure shown in Fig. 50(c) and (d) appear to be better candidates for photoregulation. Hence, one (Fig. 50(c)) or two (Fig. 50(d)) chiral centres are covalently linked with photochromic groups. Using light of the appropriate wavelength, one can separately stimulate the photochemical reactions in each photochrome. As the latter ones are chemically connected with chiral groups, the helical twisting power of each group is changed. All side photochromic and chiral groups shown in Fig. 50 look like rigid rods, i.e. they have a mesogenic shape. However, this requirement is not necessary. An important point is that a liquid crystalline phase should be retained.

As a result, the unique possibility arises that each photochrome will respond to a certain

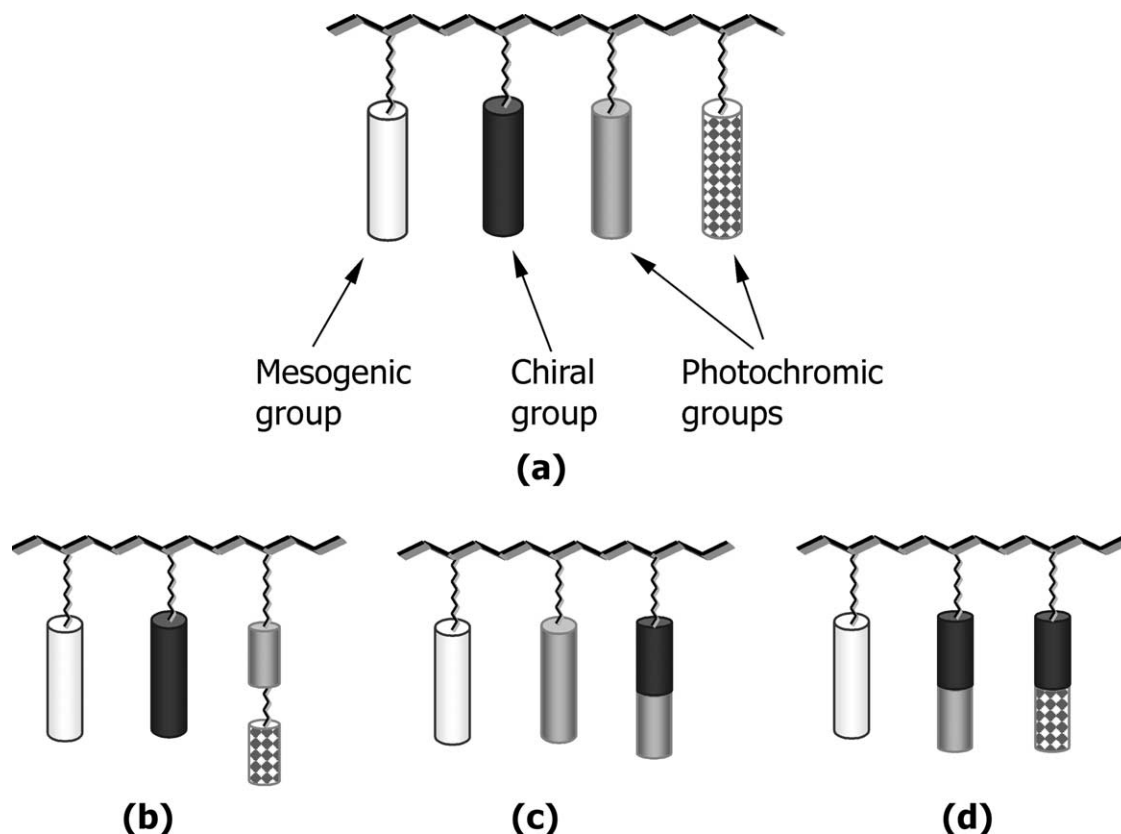
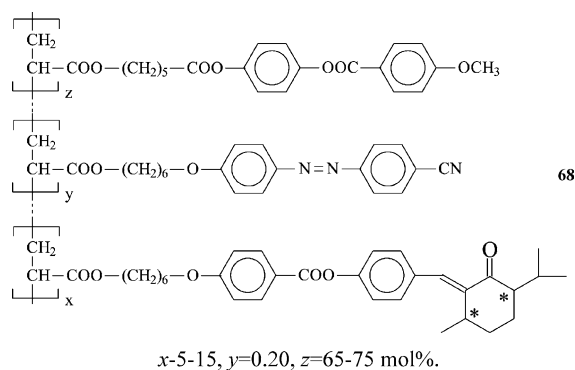


Fig. 50. Some variants of molecular structure of multifunctional chiral photochromic LC copolymers containing two photochromic groups.

wavelength of light irradiation. The photoinduced chemical transformations will lead to changes in the helical twisting power of both chiral groups, and the helical supramolecular structure will be modified. The development and design of such complicated multifunctional polymer systems allows the preparation of novel materials with fascinating optical properties. Let us consider few examples of multifunctional LC copolymers as described in the literature.

3.4.4.1. Copolymers containing combined chiral-photochromic and photosensitive azobenzene groups. For the first time, the synthesis of terpolymers containing various monomer units with their own functionality and types as shown in Fig. 50(c) was described in our work [247]. The structural formula of the terpolymer is shown below:



The mesogenic methoxyphenylbenzoate groups of the copolymer are responsible for the formation of the nematic mesophase. Photochromic azo-containing fragments are also mesogenic and do not interfere with the mesophase [146,248]. They usually undergo *E-Z* isomerization under irradiation and produce photoinduced birefringence, which can be controlled

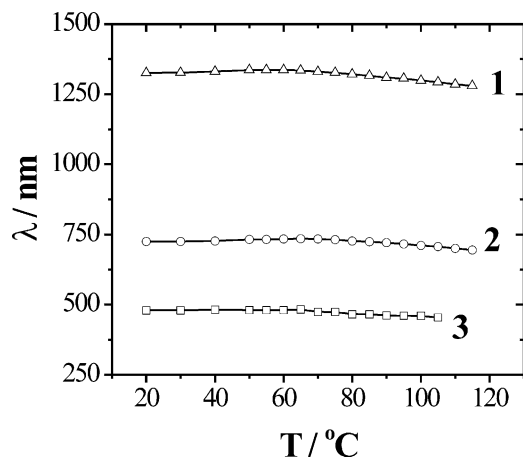


Fig. 51. Temperature dependence of selective light reflection wavelength for copolymers **68** with different concentration of the chiral-photochromic groups: (1) 5; (2) 10 and (3) 15 mol%. Reprinted with permission from *J Mater Chem* 2000;10:1075. © 2000 Royal Society of Chemistry [247].

by temperature or light irradiation with another wavelength or polarization direction. Finally, the terpolymer macromolecule contains combined chiral-photochromic fragments in the common monomer units. Using light irradiation of the other wavelength one can irreversibly change the configuration of these fragments and their helical twisting power, leading to changes in other parameters of the polymer such as helix pitch, light transmission, viscosity, etc.

It should be emphasized that the optical absorption bands of the azobenzene groups are seen in the visible and near-UV spectral regions, while the absorption band of the benzylidenemethanone fragments falls entirely within the UV range [205,206]. Therefore, by selecting the copolymer composition and the irradiation wavelength, we may control and modify the optical properties of the polymer films, inducing birefringence or cholesteric helix untwisting.

Despite obvious difficulties related to the combination of two photochemical and photooptical processes, this approach is of considerable interest from an academic and technological viewpoint for the development of unique multifunctional polymeric materials.

As seen from Fig. 51, the planarly oriented films of the copolymers exhibit selective light reflection in the visible range; the position of the selective reflection peak depends on the temperature and the content of chiral units in the terpolymer.

To determine the important features in the optical properties of these terpolymers, let us first consider the photochemistry of their dilute solutions. As follows from Fig. 52, the spectrum of copolymer **68**

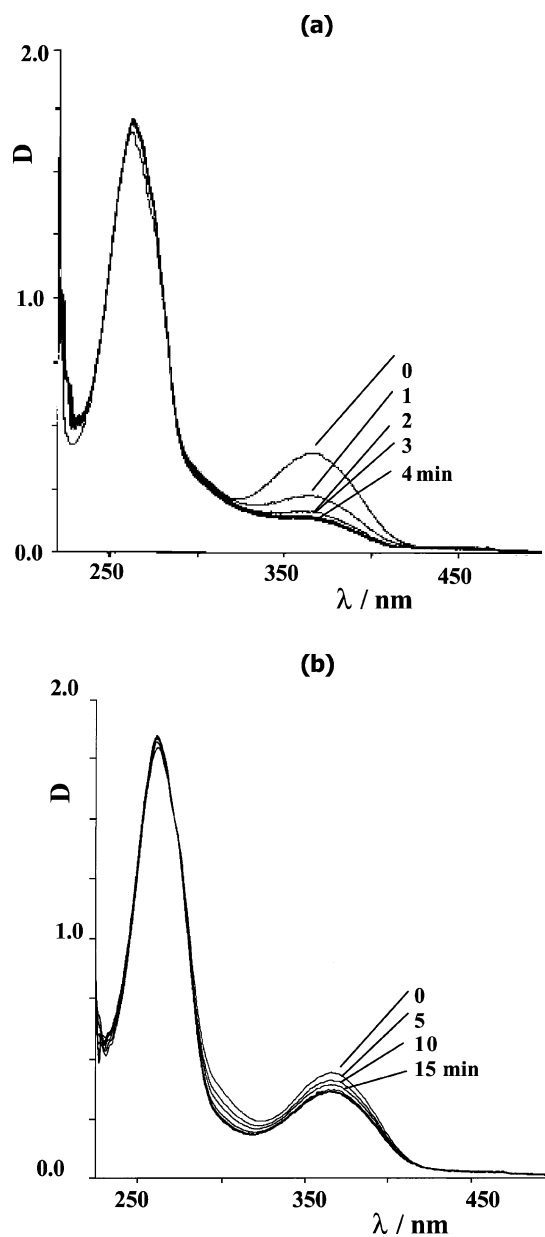


Fig. 52. Changes of the absorbance spectra for dichloroethane solution of copolymer **68** containing 15 mol% of chiral groups during UV-irradiation with light of different wavelength: (a) 365 and (b) 313 nm. Irradiation time is shown in figure. Reprinted with permission from *J Mater Chem* 2000;10:1075. © 2000 Royal Society of Chemistry [247].

shows two principal peaks: the long-wavelength peak ($\lambda_{\max} = 365$ nm) corresponds to the $\pi-\pi^*$ electron transition of cyanoazobenzene groups, whereas the short-wavelength peak at $\lambda_{\max} = 262$ nm corresponds to the $\pi-\pi^*$ electron transition of mesogenic phenylbenzoate units. The peak associated with the absorption of benzylidene-*p*-menthanone fragments appears only as a shoulder at 290–325 nm.

UV-irradiation leads to significant changes in the absorption spectra of the copolymers (Fig. 52(a) and (b)). Depending on the wavelength, the character of these changes appears to be somewhat different. At $\lambda_{\text{ir}} = 365$ nm, one observes a marked decrease in the absorption peak associated with the $\pi-\pi^*$ electron transition of the cyanoazobenzene groups, whereas at $\lambda_{\text{ir}} = 313$ nm, changes in the shoulder at 290–325 nm are observed.

In other words, when dilute solutions of copolymers are irradiated with a wavelength of 365 nm, benzylidene-*p*-menthanone groups experience almost no *E-Z* isomerization; isomerization is observed only for azobenzene groups. At $\lambda_{\text{ir}} = 313$ nm, both groups undergo isomerization; this conclusion is supported not only by changes in the absorption spectra but also by the corresponding kinetic dependency of the absorption at different wavelengths. Similar dependencies are observed for thin films of copolymers prepared by evaporation from dichloroethane solutions.

The *E-Z* isomerization of azobenzene groups is thermally and photochemically reversible. Under the irradiation of the solution with a visible light, a reversible increase in the absorption peak at $\lambda_{\max} = 365$ nm is

observed. One may conclude that by varying the wavelength of the incident light beam isomerization of various photochromic groups may be controlled; in the case of azobenzene groups, one may also change the direction of the whole process. Let us note that chiral photochromic groups are irreversibly transformed to the *Z*-form. However, in the case of cyanoazobenzene chromophores, the *E-Z* isomerization is fully reversible.

Irradiation and subsequent annealing of planarly oriented films of copolymers shifts the selective light reflection peak from 750 nm to the long-wavelength region. As was shown above [205,206], this effect is associated with the *E-Z* isomerization of menthone-containing chiral photochromic groups, which is accompanied by a dramatic decrease in their twisting power. It is interesting to note that helix untwisting is likely to be induced by UV-irradiation with both wavelengths (313 and 365 nm). In a relatively ‘thick’ copolymer film, benzylidene-*p*-menthanone groups are capable of a marked absorption even at a wavelength of 365 nm. Hence, the effect of UV-light on the planarly oriented films of copolymers may locally change the helix pitch, and correspondingly, the selective light reflection maximum.

On the other hand, isomerization of the azobenzene groups of copolymer **68** leads to photoinduced birefringence. The preliminary data [247] shows that copolymer **68** can be used for holographic image recording on copolymer films (Fig. 53).

The variation of the ratio between the *E*- and *Z*-isomers created by UV-irradiation allows one to

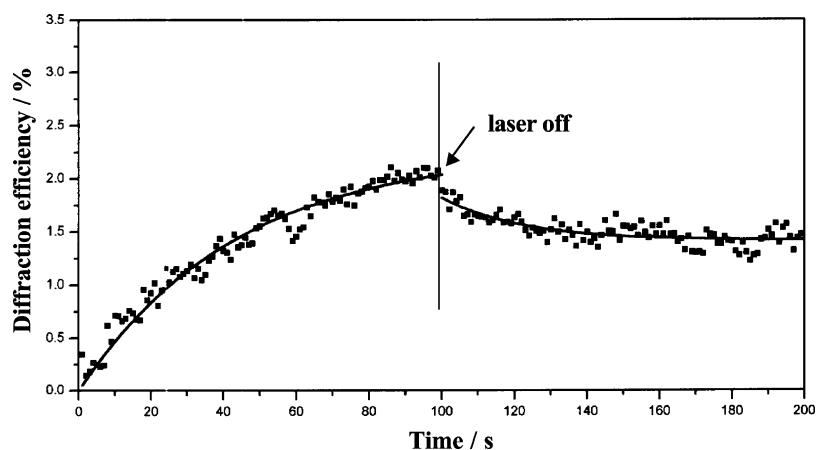


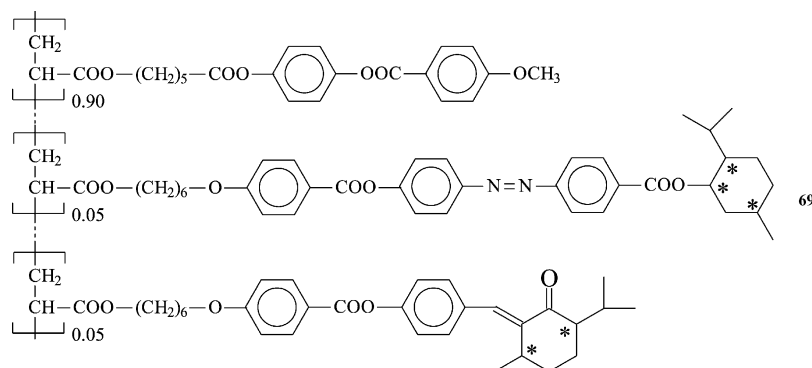
Fig. 53. First order diffraction efficiency growth during holographic recording on a film of the copolymer **68**. (Ar laser, $\lambda = 514$ nm, $P = 143$ mW cm⁻²). Reprinted with permission from J Mater Chem 2000;10:1075. © 2000 Royal Society of Chemistry [247].

smoothly change the optical properties (wavelength at selective light reflection maximum). This effect should also allow one to change the rheological properties of the system as well, since a disordering effect of *Z*-isomeric form should decrease the viscosity of copolymer.

The dual photochromism of ternary copolymers of this class allows one to record optical information of two types on the same sample: first, by varying the helix pitch (λ_{\max}) due to the short-wavelength light irradiation, and second, by changing the photoinduced birefringence due to polarized light irradiation (with $\lambda \geq 400$ nm).

The synthesized copolymers' high optical density creates possibilities for the preparation of planarly oriented films with a high gradient of helix pitch along the sample. Examination of such multifunctional chiral photochromic cholesteric copolymers is interesting not only from the viewpoint of optical data recording; investigation of at least two competing photochemical processes taking place in such systems presents an independent interest.

3.4.4.2. Copolymer containing two different chiral photoactive groups. The terpolymers containing nematogenic fragments and two monomer units with different combined chiral-photochromic groups (Fig. 50(d)) are of significant interest due to their complex dual nature. Synthesis and photooptical behaviour of one such copolymer (**69**) with a dual photochromism is described in Ref. [248]:



Such a structure was selected for the following reasons: first, benzylidene-*p*-menthane-3-one and azobenzene groups absorb light in somewhat different spectral regions, and absorption of benzylidene-*p*-

menthane-3-one chromophore is located in a shorter wavelength region; second, even though both groups are able to experience the *E*-*Z* photoisomerization, the character of this process is different. As was mentioned earlier, isomerization of benzylidene-*p*-menthane-3-one fragments is irreversible. However, for azobenzene groups, this process is thermally and photochemically reversible. This difference allows one to initiate photoisomerization of either the benzylidene-*p*-menthane-3-one or azobenzene groups by selecting the wavelength of incident light (λ_{ir}). In other words, irradiation with short-wavelength UV-light should lead to a preferential *E*-*Z* isomerization of benzylidene-*p*-menthane-3-one groups and to an irreversible untwisting of the cholesteric helix, whereas irradiation with visible light should initiate a reversible isomerization of the azobenzene groups only and lead to a reversible shift in the selective light reflection wavelength.

Planarly oriented copolymer films are characterized by selective light reflection in the near IR spectral region ($\lambda_{\max} \sim 940$ nm). Upon irradiation with UV ($\lambda_{\text{ir}} = 365$ nm) and visible light ($\lambda_{\text{ir}} > 450$ nm and $\lambda_{\text{ir}} \sim 550$ nm), such films experience untwisting of the cholesteric helix and a shift in the selective light reflection wavelength to long-wavelength region (Fig. 54). Let us emphasize that, upon light irradiation with $\lambda_{\text{ir}} = 365$ nm, a shift in the selective light reflection peak is irreversible; at the same time, irradiation with visible light leads to reversible

changes in λ_{\max} . In this case, annealing the sample at temperatures above ~ 50 °C provides for the recovery of the selective light reflection wavelength to its initial position. This behaviour suggests the occurrence of the

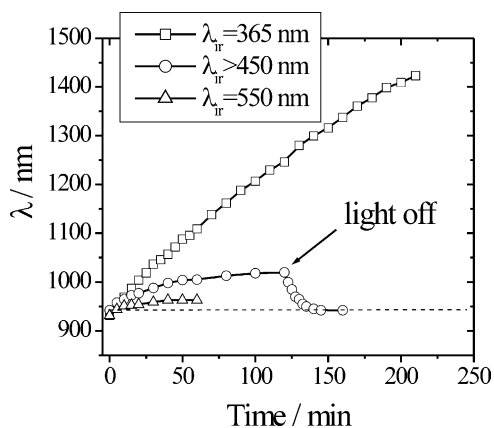


Fig. 54. Selective light reflection wavelength growth during irradiation of copolymer **69** with light of different wavelength ($T = 80\text{ }^{\circ}\text{C}$) [248].

E–*Z* isomerization of benzylidene-*p*-menthane-3-one groups under the action of UV-light and the photoisomerization of azobenzene groups only under irradiation with visible light. In both cases, *E*–*Z* isomerization decreases the helical twisting power of chiral groups due to the lower anisometry of their *Z*-isomer.¹⁰ Under UV-irradiation, one may hardly exclude the possible photoisomerization of azobenzene fragments, but the films annealed after light irradiation with $\lambda_{ir} = 365\text{ nm}$ show no back process of helix twisting even at short irradiation times. This behaviour is likely related to the fact that isomerization of benzylidene-*p*-menthane-3-one groups leads to a more pronounced decrease in helix twisting power as compared with that of azobenzene fragments. Under given experimental conditions and light irradiation with $\lambda_{ir} = 365\text{ nm}$, only irreversible changes in helix pitch related to the isomerization of only benzylidene-*p*-menthane-3-one groups were observed.

By providing photoinduced changes in the selective light reflection wavelength, irradiation with visible light allows one to perform repeated data recording–erasing cycles. As follows from Fig. 55, fatigue resistance of the copolymer is rather high, although one may observe a minor systematic shift in the selective light reflection wavelength to a long-wavelength region.

¹⁰ The values of helical twisting power of benzylidene-*p*-menthane-3-one and azobenzene groups before irradiation calculated for phenylbenzoate matrix were equal to 16.9 ± 1.1 and $18.5 \pm 2.1\text{ }\mu\text{m}^{-1}$, respectively [206,211].

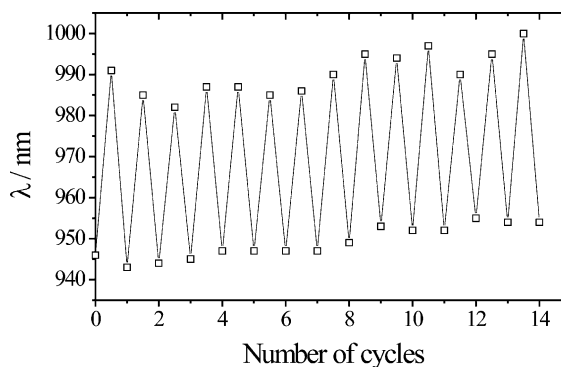


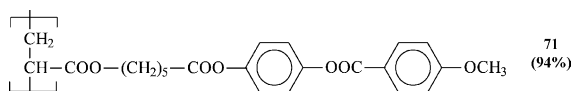
Fig. 55. Fatigue resistance properties of the copolymer **69** under the recording–erasing conditions. In each cycle film of copolymer was irradiated during 30 min by light $\lambda_{ir} > 450\text{ nm}$ at $80\text{ }^{\circ}\text{C}$, then was annealed during 30 min at $100\text{ }^{\circ}\text{C}$ [248].

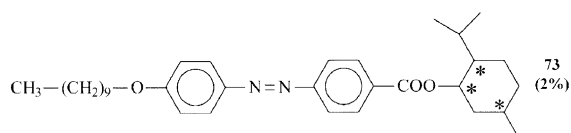
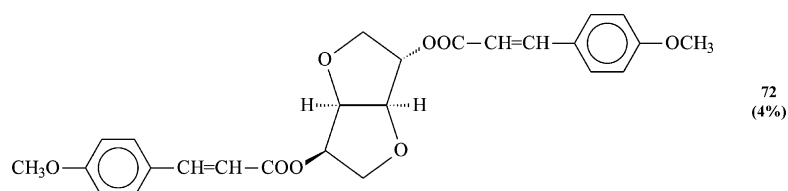
One may conclude that copolymerization of a nematogenic monomer with the two different, combined, photosensitive chiral monomers makes it possible to obtain a new class of multifunctional polymers with different responses to light irradiation at different wavelengths. These copolymers may be used both for reversible and irreversible recording of optical information.

3.4.4.3. Photosensitive LC polymer mixtures with variable direction of photoinduced change in helix pitch. Blends of nematogenic polymers with chiral photochromic dopants having a different (left- or right-) twisting sign offer an interesting opportunity for controlling the supramolecular structure of copolymers. Such mixtures allow one to obtain materials with variable directions of change in the photoinduced helix pitch. Two types of these blends will be considered below.

The first mixture **70** is composed of phenyl benzoate homopolymer **71**, responsible for the development of the nematic phase, and two chiral photochromic dopants containing both chiral fragments and double C=C (**72**) and N=N bonds (**73**), which are capable of irreversible and reversible photoisomerization, respectively:

Mixture **70**:

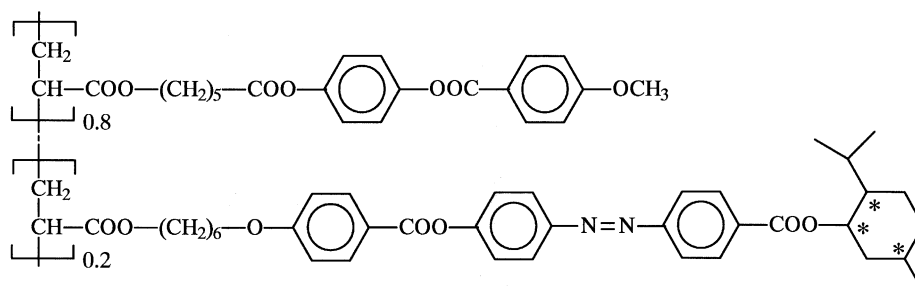




Mixture **70** shows a chiral nematic phase (cholesteric mesophase) with a clearing temperature of 93–95 °C. Note that dopant **72** is a right-handed conformer, able to develop a cholesteric helix with right twisting direction [250], while the second dopant **73** is a left-handed conformer [211]. The composition of the mixture is selected so that the twisting direction of this ternary mixture is controlled by enantiometric excess of **72**, that is, the mixture is right-handed.

The second mixture **74** is composed of the left-handed cholesteric copolymer **54** (Table 5) containing nematogenic phenylbenzoate groups, chiral menthol and photochromic azobenzene groups, and dopant **72**:

Mixture **74**:



UV absorption bands for the azobenzene chromophores of dopant **73** and the azobenzene groups of copolymer **54** are located in the higher wavelength region ($\lambda_{\text{max}} = 367$ nm for **73** and $\lambda_{\text{max}} = 339$ nm for **54** in dichloroethane solution) as compared with that of dopant **72** ($\lambda_{\text{max}} = 312$ nm in dichloroethane solution) [250]. Furthermore, azobenzene chromophores are characterized by the existence of a high-wavelength $n-\pi^*$ electron transition at about 450 nm (Section 2.1.2); upon irradiation with a wavelength coinciding with this absorption band, *E-Z* photoisomerization takes place. Another important feature of cinnamoyl and azobenzene groups is that, in the case of dopant **72**, isomerization of azobenzene fragments is thermally and photochemically reversible, while all light-induced changes are irreversible [250]. Therefore, upon light irradiation with a wavelength coinciding with the UV absorption band of the dopant in enantiometric excess, one should observe a decrease in chirality of the system and helix

Mixture **74** is also able to produce a chiral nematic phase (cholesteric mesophase) with a clearing temperature of 102–103 °C. The composition of this mixture is selected so that the twisting direction is left; that is, azobenzene-containing chiral photochromic groups dominate. For both mixtures, the glass transition temperature is equal to about 25 °C.

untwisting. Upon light irradiation with a wavelength overlapping with the UV absorption band of another dopant, integral chirality of the system, in contrast, should increase due to a decrease in helical twisting power. The above reasoning allows one to assume that, for mixture **70**, UV-irradiation should lead to the untwisting of the cholesteric helix, whereas

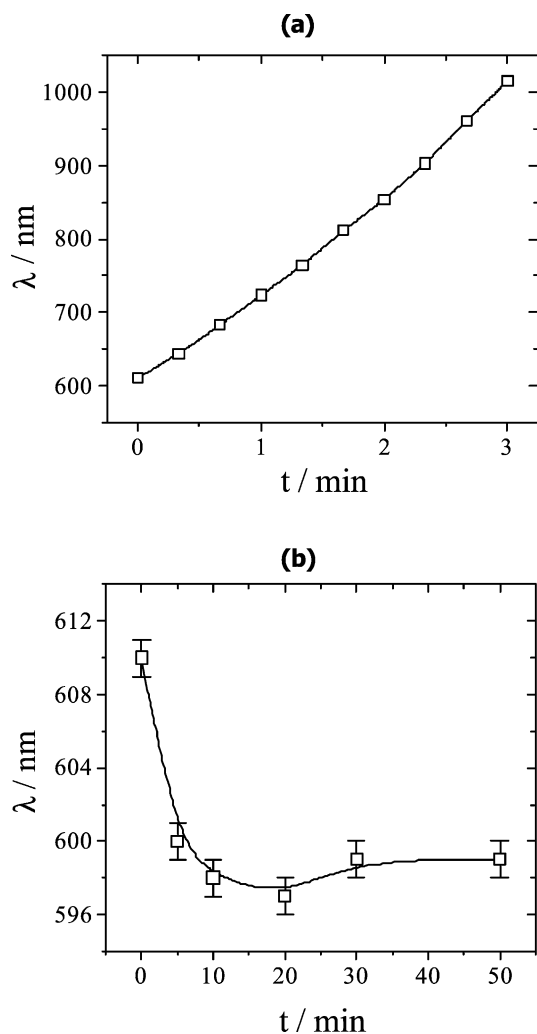


Fig. 56. Change of selective light reflection wavelength during (a) UV-irradiation (365 nm) and (b) visible light irradiation (>450 nm) for mixture **70**. Temperature of irradiated sample is 70 °C [249].

irradiation with visible light results in helix twisting. In the case of mixture **74**, the whole behaviour is reversed.

The specific features of the photooptical properties for mixture **70** are discussed below. UV-irradiation (365 nm) leads to untwisting of the cholesteric helix and a shift in the selective light reflection maximum to the high-wavelength spectral region, whereas upon irradiation with visible light (>450 nm), the selective light reflection maximum is shifted to the short-wavelength spectral region (Fig. 56(a) and (b)).

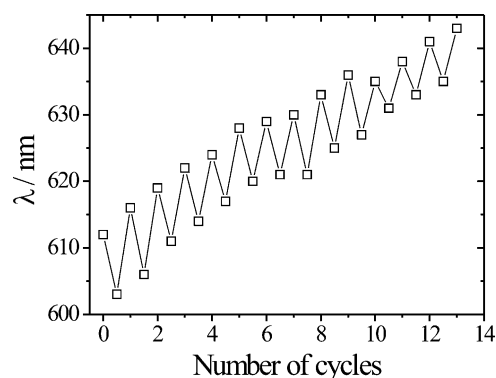


Fig. 57. Fatigue resistance properties of the mixture **70** film under the 'recording-erasing' processes. In each cycle the film was irradiated during 20 min by light (>450 nm) at 70 °C, then the film was annealed during 20 min at the same temperature [249].

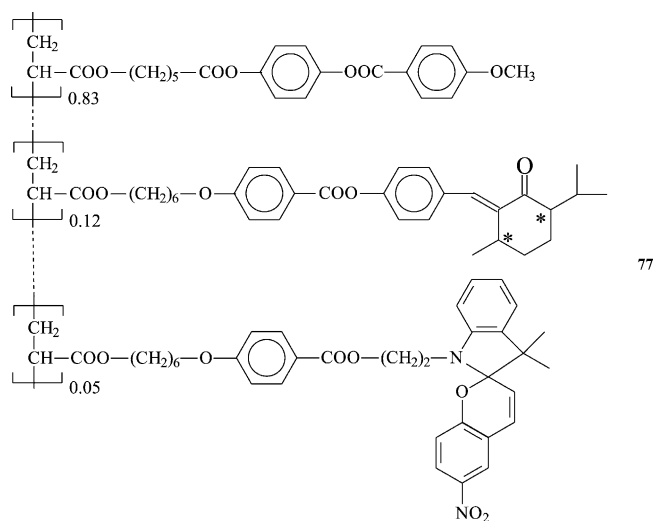
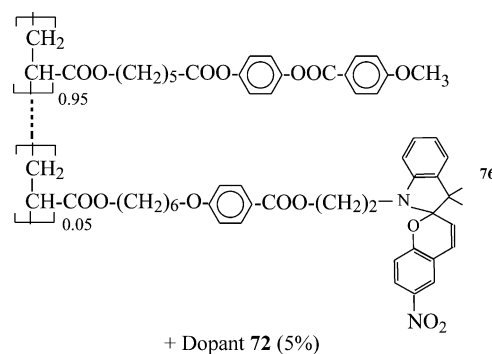
Furthermore, upon irradiation with visible light, this shift in the selective light reflection maximum is much lower and is observed once the photostationary state is attained.

Under irradiation with visible light, the shift in the selective light reflection maximum is thermally reversible; upon annealing, this peak is shifted in the reverse direction (Fig. 57). It is interesting to note that even though, upon repeated recording-erasing cycles (Fig. 57), the amplitude of the changes of selective light reflection maximum remains almost unchanged. However, upon several recording-erasing cycles, a systematic shift in the position of selective light reflection maximum to long-wavelength region takes place (610–640 nm). This trend suggests that, upon light irradiation with a wavelength >450 nm, one may observe photoisomerization of not only dopant **73** but also irreversible *E-Z* photoisomerization of cinnamoyl dopant **72**.

In the case of mixture **74**, photooptical behaviour appears to be quite different. Upon UV-irradiation and annealing, the selective light reflection maximum is shifted to the short-wavelength region, whereas in the case of irradiation with visible light, this maximum is shifted to the long-wavelength region (Fig. 58). As with mixture **70**, irradiation with visible light leads to a preferential photoisomerization of azobenzene groups; upon UV-irradiation, photoisomerization of cinnamoyl groups of dopant **72** and azobenzene groups of copolymer **54** takes place. However, in the latter case,

annealing leads to a reverse transformation of azobenzene groups from *Z*-isomers to *E*-form. The resultant shift in the selective light reflection maximum is controlled by the ratio between *E*- and *Z*-isomers of dopant **72**. Upon irradiation with visible light, the amplitude of the changes to the selective light reflection maximum is much higher than that in the case of mixture **70**; this trend is related to the much higher content of azobenzene chiral photochromic groups in mixture **74**.

Let us emphasize the unique character of the above cholesteric polymer mixtures, where the direction of the changes in helix pitch may be easily



G~30 N* 102-103 I

controlled by varying the wavelength of light irradiation. This approach allows one to widen substantially the possibilities for photooptical control of the optical properties of polymer materials.

3.4.4.4. Cholesteric copolymer and mixture combining photochromism with helix pitch photo-regulation. Another complex photochromic system was obtained from the mixture **75** consisting of photochromic copolymer **76** with 5 mol% chiral-photochromic dopant **72** and cholesteric terpolymer **77** [251].

Mixture **75**: G ~ 25N* 93–94I

UV-irradiation on the films of copolymer **77** and mixture **75** should lead to two parallel photoinduced processes. (1) The transition of the spirocyclic form to the merocyanin modification, and (2) the *E*–*Z* isomerization of the chiral photochromic fragments of dopant **72** and the benzylidenemethanone groups of copolymer **77**. Fig. 59(a) presents the absorption spectra of mixture **75**'s film as recorded upon UV-irradiation at 20 °C. As is shown, even short-term UV-irradiation leads to an increase in the intensive absorption peak of the photochromic groups' merocyanine form. This phenomenon is also observed for copolymer **77**. The transition of

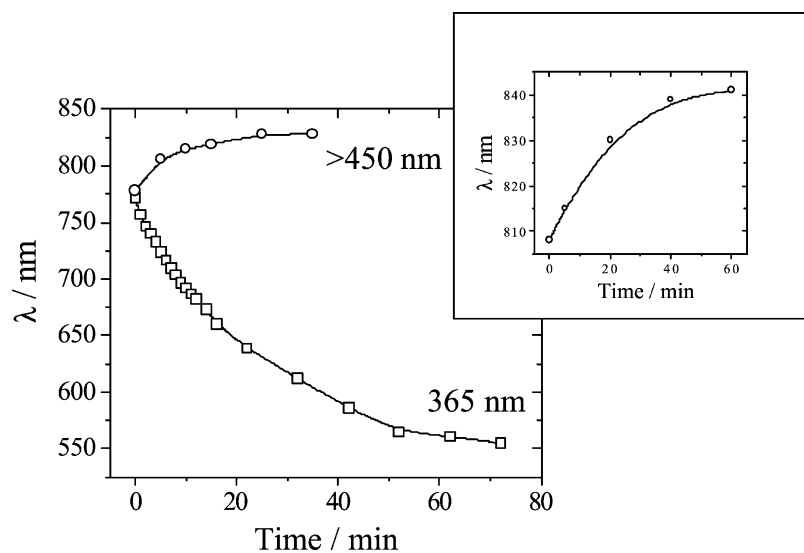


Fig. 58. Changing of selective light reflection wavelength during irradiation with light of different wavelengths for mixture **74** ($T = 90\text{ }^{\circ}\text{C}$). Inset: the change of selective light reflection wavelength during irradiation with light of 550 nm at 80 °C. In the case of irradiation with light of 365 nm the sample was annealed after each cycle of light action during 20 min at 90 °C [249].

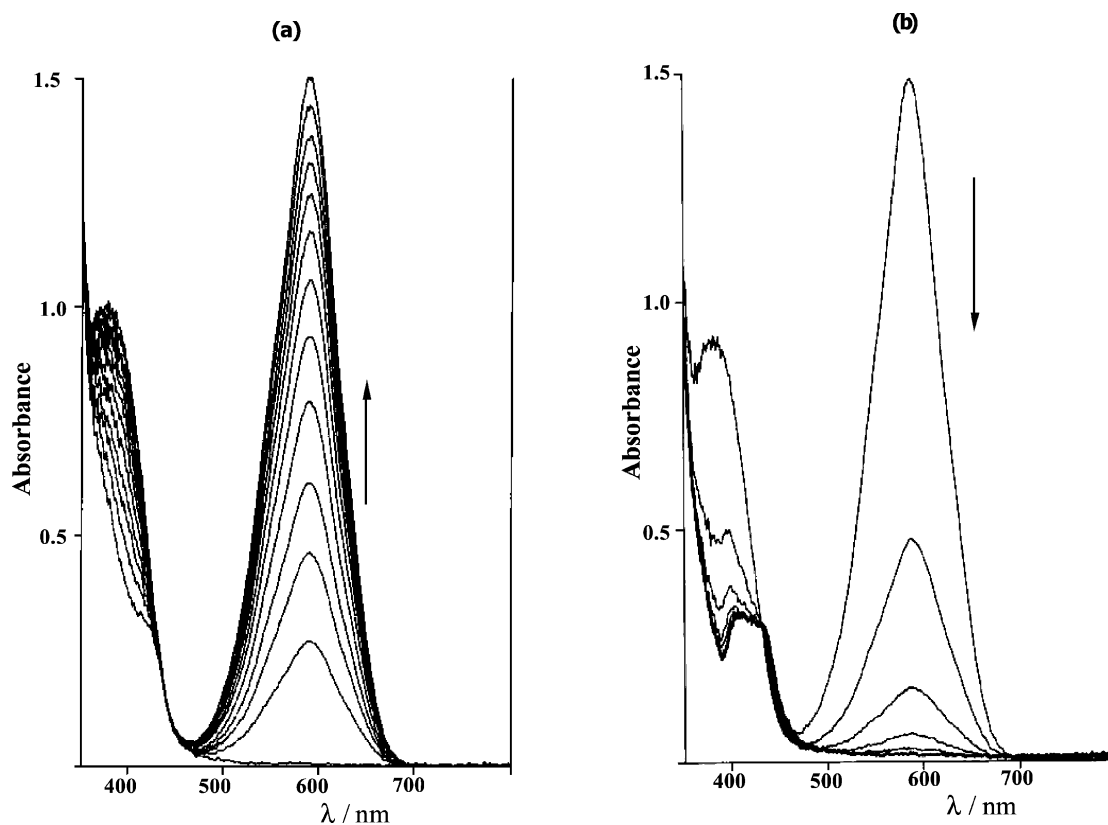


Fig. 59. Changes of the absorbance spectra for mixture **75** during (a) UV-irradiation at 20 °C and (b) annealing (50 °C) of the same sample previously irradiated by UV-light during 1 min; (a) spectra were recorded each 5 s of irradiation; (b) spectra were recorded each 200 s [251].

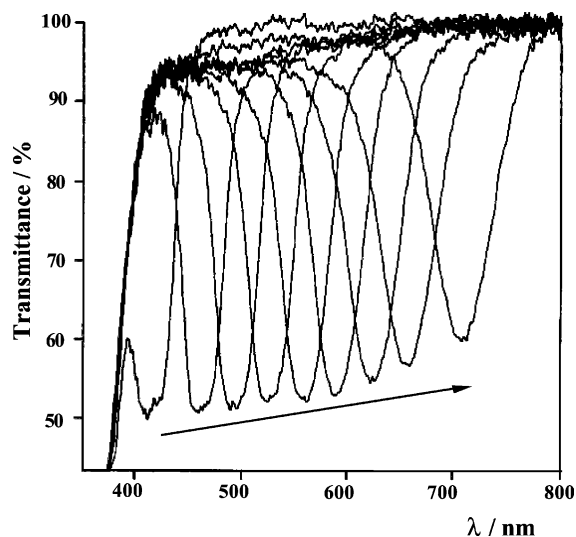


Fig. 60. Spectral changes in mixture **75** during UV-irradiation. Spectra were recorded each 30 s of irradiation, after each cycle of irradiation film was annealed at 80 °C during 20 min [251].

spiropyran units to the merocyanine form is thermally reversible: upon annealing, the back reaction occurs and the absorption peak disappears (Fig. 59(b)).

Let us now discuss the *E–Z* isomerization of the chiral photochromic groups of dopant **72** in its blend and the benzylidenemethanone groups in copolymer **77**. Fig. 60 presents the transmission spectra of the blend's planarly oriented film as recorded in the course of the UV-irradiation with a wavelength of 365 nm. Upon irradiation and annealing, the selective light reflection maximum is shifted to the long-wavelength spectral region. This trend is related to the *E–Z* photoinduced isomerization of chiral photochromic groups and to a decrease in their helix twisting power. Note that the rate of helix untwisting for the blend is much higher. Upon cooling the samples to room temperature (below T_g), one may easily fix the helix pitch after UV-irradiation.

Therefore, by selecting the temperature range, one may either control the helix pitch and selective light reflection maximum of the blend and copolymer, or induce an intensive blue colouring due to the photochromic groups' formation of the merocyanine form. Although upon UV-irradiation both photochemical

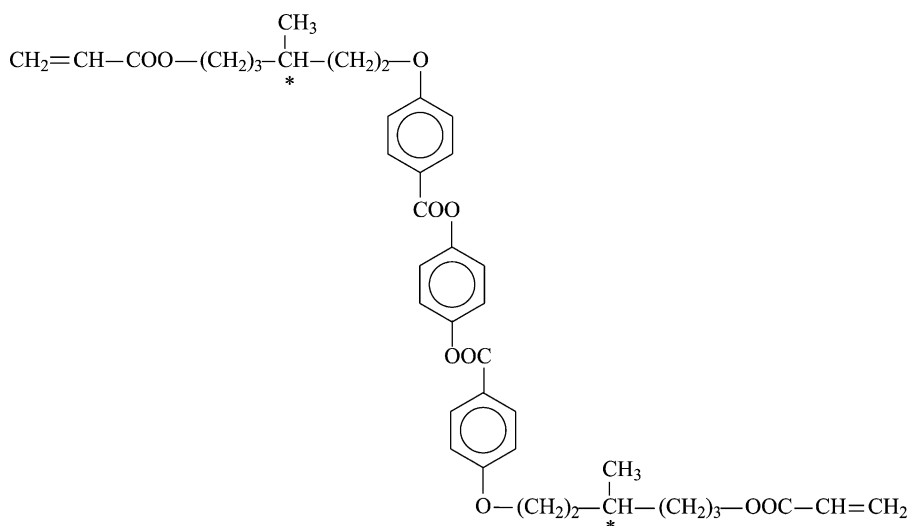
processes are induced, such factors as the different photosensitivity of the spiropyran and benzylidenemethanone groups, quite different thermal stability of the photoreaction products, and an important stage of annealing providing the untwisting of cholesteric helix allow one to identify the two processes in the systems studied.

Furthermore, using the above materials, one may record two images at once: the lower image is recorded due to the changes in the helix pitch while the upper image is provided by the photochromism of spiropyran groups. Using the principle advanced in Ref. [251], one may extend the range of the materials with a dual photochromism; a special interest is placed on the substitution of spiropyran with diarylethylene groups in which the photoinduced process is thermally irreversible. In this case, the back recovery to the uncoloured form may be easily accomplished by visible light irradiation.

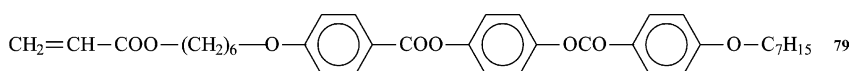
3.4.5. Cholesteric polymer networks

From practical application viewpoint, cholesteric networks offer interesting and important advantages. Usually, the above networks are obtained by the photopolymerization of the mixtures of monomers (usually, acrylates) containing bifunctional polymerizing compounds [252–256]. Photopolymerization of the blends of cholesteric acrylates and diacrylates in the presence of a photoinitiating agent fixes the helical supramolecular structure due to the development of a three-dimensional network. Even though the consideration of such cross-linked polymer cholesterics is beyond the scope of the present review, let us discuss the most vivid examples of such systems. The principal attention will be focused on polymer networks with photocontrolled optical properties, controlled either during or after their processing.

In Ref. [252], a well-pronounced broadening of the selective light reflection maximum upon the photopolymerization of the mixtures of diacrylates **78** and monoacrylates **79** was described. A thin coating of the monomer mixture of **78** and **79** was applied to a birefringence-free substrate and cured by light irradiation. The supramolecular structure within the polyacrylate film separates light on its state of circular polarization.



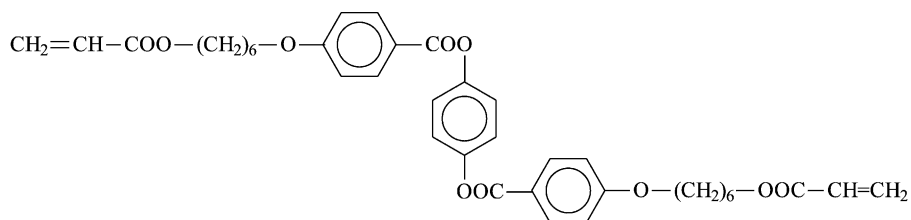
78



79

To get sufficient bandwidth the molecular helix pitch is subjected to a gradient over the film thickness (Fig. 61). The helix pitch gradients are controlled by photoinduced diffusion of the chiral nematic diacrylate **78** and the nematic monoacrylate **79**.

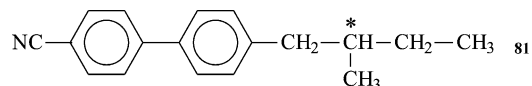
pioneering work on the utilizing of the cholesteric networks for the above purposes has appeared only in 1993 [253]. In this work, blends of diacrylate **80** with 28 wt% of chiral low-molar-mass dopant **81** were prepared:



80

This behaviour may be explained by the combination of different reactivities of mono- and bifunctional monomers, and the existence of the light intensity gradient along the thickness of the irradiated film. The above phenomena support the development of a high gradient in helix pitch values and, as a consequence, a well-pronounced broadening of the selective light reflection maximum.

Even though, in principle, all photopolymerizing cholesteric blends may be used for data recording and storage (due to a local fixation of the helix pitch),



81

Optical properties were studied, and the order parameter of the network was estimated as a function of the photopolymerization conditions. Under Nd/YAG irradiation (300 nm), the optical information may be recorded at the micron scale only due to a local irradiation-induced evaporation of the dopant (Fig. 62). However, one should mention that this kind of laser

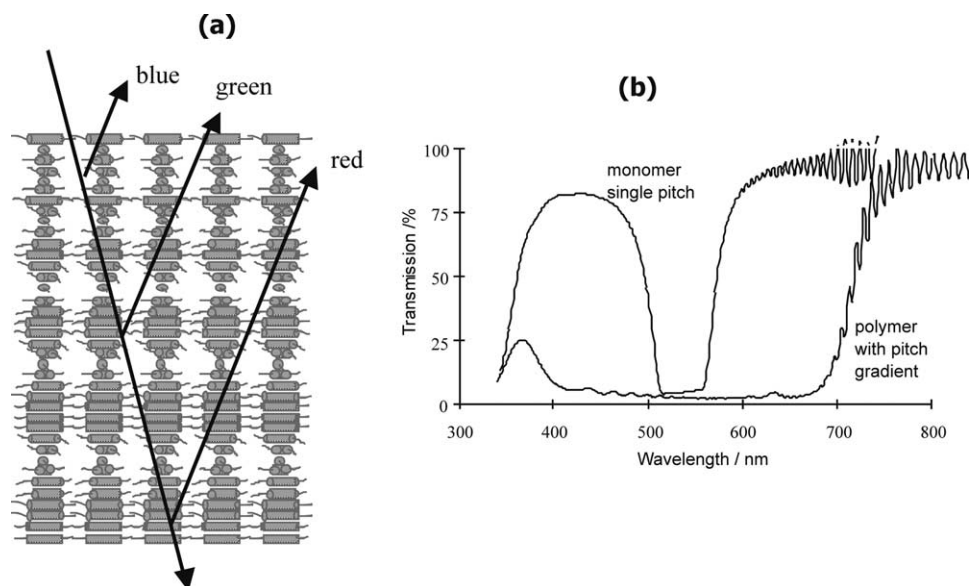
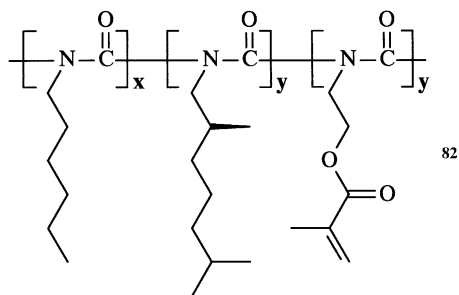


Fig. 61. (a) Scheme of helix gradient provided polarized reflection over entire visible wavelength region. The pitch gradient is established by photoinduced diffusion of the chiral-nematic diacrylate **78** and the nematic monoacrylate **79** [252]. (b) Transmission spectra of monomer mixture and polymer films after polymerization of monomers. Reprinted with permission from *Macromol Symp* 2000;154:1. © 2000 Wiley–VCH [252].

addressing requires the fulfilment of several conditions, such as the absence of a covering glass, a high laser power, long irradiation times, etc. Unfortunately, the effects of the last two factors were not studied.

An interesting example of the use of a lyotropic cholesteric mesophase for obtaining the cross-linked polymer films under UV-irradiation at different temperatures was demonstrated by Zentel et al. [254]. In this case, the styrene solutions of chiral poly(isocyanate) **82** were prepared; this chiral compound contains chiral and reactive fragments as side groups.



The above solutions form a lyotropic cholesteric phase with a selective light reflection maximum in the visible spectral region; in this case, the selective light reflection wavelength depends on the temperature.

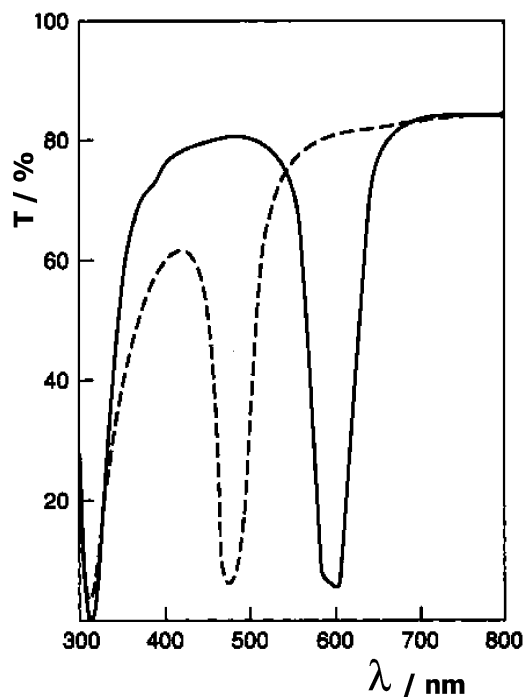
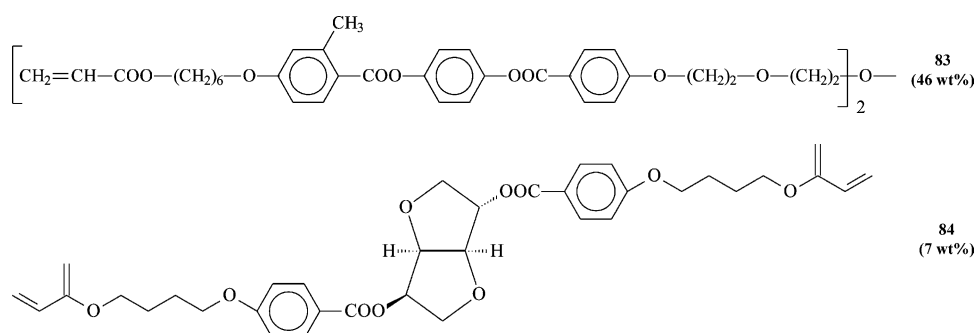


Fig. 62. Transmittance measured as a function of wavelength for a blend containing diacrylate **78** with 28 wt% of **81** polymerized at 60 °C before (solid line) and after (dashed line) evaporation of **81** molecules. Reprinted with permission from *Liq Cryst* 1993;13:561. © 1993 Taylor & Francis [253].

This finding allows a coloured data recording via photopolymerization at different temperatures. This approach was applied to cellulose derivatives. By varying the temperature of photoinduced cross-linking, they obtained cholesteric networks with different selective light reflection wavelengths.

Quite recently [255,256], an unorthodox approach to the preparation of materials for holographic data recording has been advanced. As a starting material, a blend composed of 46 wt% of diacrylate **80** with 46 wt% of dimesogenic diacrylate **83** and 7 wt% of chiral **84** diacrylate was used:



This chiral dopant is a left-rotating isomer, inducing the right-twisted cholesteric helix. As an initiating agent, 1% Irgacure 784 was used; this compound is sensitive to light irradiation with a wavelength of 532 nm (Nd/YAG laser). The ratio between the components of the blend was selected so that the selective light reflection maximum and laser wavelength coincide.

Holographic phase grating was generated by one s- and one p-polarized writing beams. In the regions where light circularity matches the helicity of the cholesteric mixture, the light is able to penetrate the whole depth of the sample. These regions of the irradiated film may be referred to as light regions (Fig. 63(a)). The regions with selective light reflection from the cholesteric film may be conditionally referred to as dark regions. Photopolymerization commences at the light regions and, in the course of this process, monomers diffuse from dark to light regions because their concentration in the active polymerization zone is low. As a result, the film develops density and refractive index gradients. Fig. 63(b) presents the typical dependencies,

describing an increase in the diffraction efficiency during photopolymerization of the blend. The typical feature of such dependencies concerns the existence of the induction period. This fact is related to the reaction of the radicals of the photoinitiating agent with foreign mixtures, including the oxygen present in air. Then, one may observe an increase in diffraction efficiency. It seems interesting that its maximum value (of about 4%) is achieved at minimum laser power (Fig. 63(b)). In the case of *ss* writing geometry, similar time dependencies for diffraction efficiency were obtained, but the values appear to be lower.

3.5. Hydrogen-bonded photochromic LC polymer systems

The use of non-covalent interactions (hydrogen bonding, ionic interactions, etc.) between different molecular species recently spurred interest in the preparation of new LC compounds. To prepare non-covalently bonded side and main chain LC polymers and networks [17,257–264] various approaches have been developed. Some examples of the complexes between macromolecules and low-molar-mass compounds leading to mesophase formation are shown in Fig. 3 (see Chapter 1). Hydrogen bonding is one of the most important non-covalent interactions in the field of chemistry and biology, providing molecular aggregation and formation of supramolecular structures. It is this type of non-covalent bonding that will be discussed in this chapter.

It should be noted out that the number of publications related to such non-covalent LC polymers is limited by so-called functionalized LC polymers. Functionalized LC polymers are

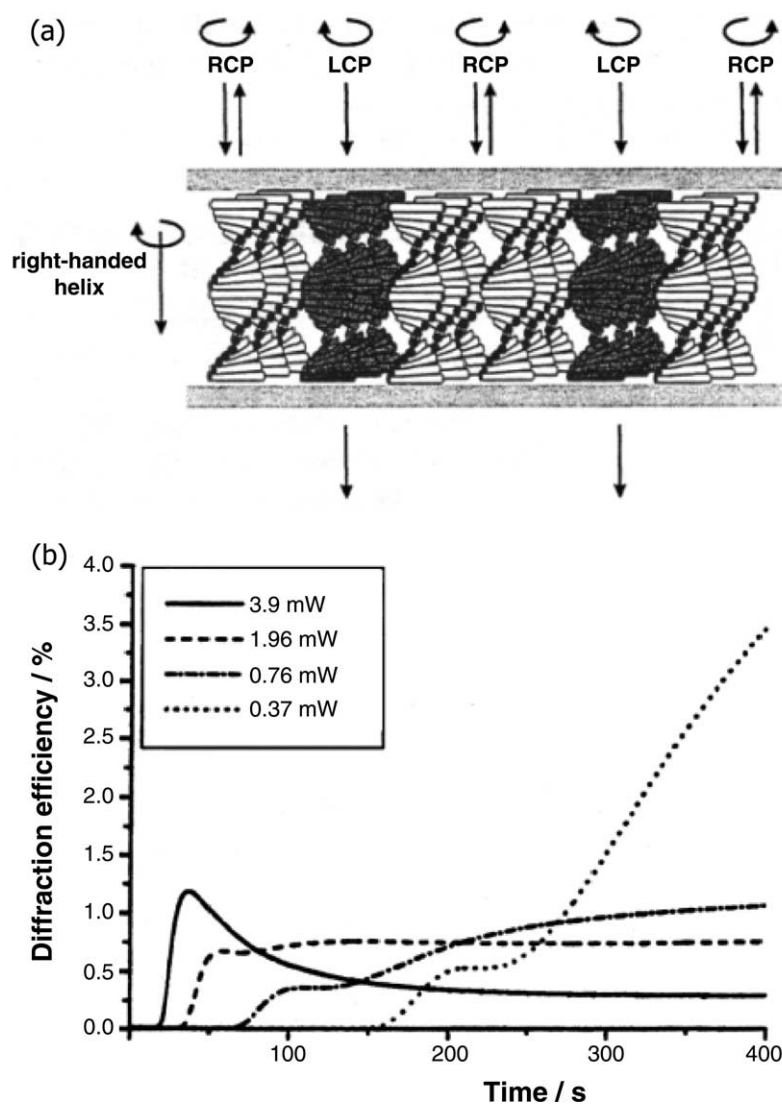
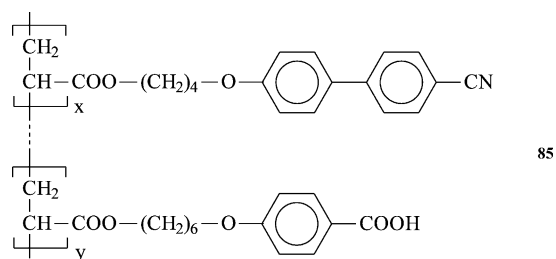


Fig. 63. (a) The phase grating inscription on a cholesteric liquid crystal of the mixture of **80**, **83** and **84** (see text). RCP and LCP denote the right- and left-handed circular polarized regions of the grating. The RCP light is reflected by the right-handed cholesteric helix, whereas the LCP light is transmitted. (b) Diffraction efficiency at different writing intensities of the laser in *sp*-geometry for the same mixture after irradiation [255,256]. Reprinted with permission from *Macromol Chem Phys* 1998;199:755. © 1998 Wiley–VCH [255].

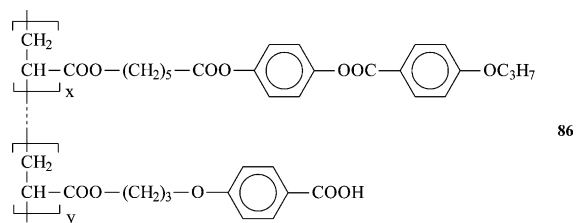
the polymer matrices used in the preparation of new polymers with desired properties through their modification by low-molar-mass dopants—for example, chiral or photochrome molecules [6].

The method for the preparation of functionalized LC polymers containing mesogenic side groups responsible for the formation of a LC phase and carboxylic side groups capable of hydrogen bonding was reported in Refs. [17,107,

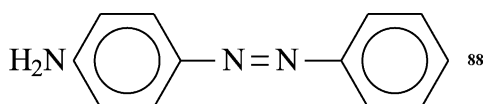
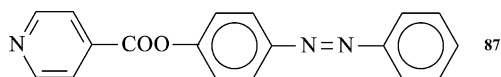
262–264]. The schematic representation of the functionalized LC copolymer is shown in Fig. 64. Similar nematic and smectic acrylic copolymers were used for the synthesis of hydrogen-bonded blends with photosensitive azobenzene-containing low-molar-mass dopants [265]. Two series of the functionalized copolymers containing different concentrations of acidic groups are shown below:



$y = 30\text{--}80 \text{ mol}\%$



$y = 60 \text{ mol}\%$



The presence of a pyridine ring or primary amino group in the structure of azobenzene-containing dopants **87** and **88** ensures the formation of donor–acceptor hydrogen bonds. The pyridine (or amino group) acts as a proton acceptor, while the carboxylic group acts as a proton donor.

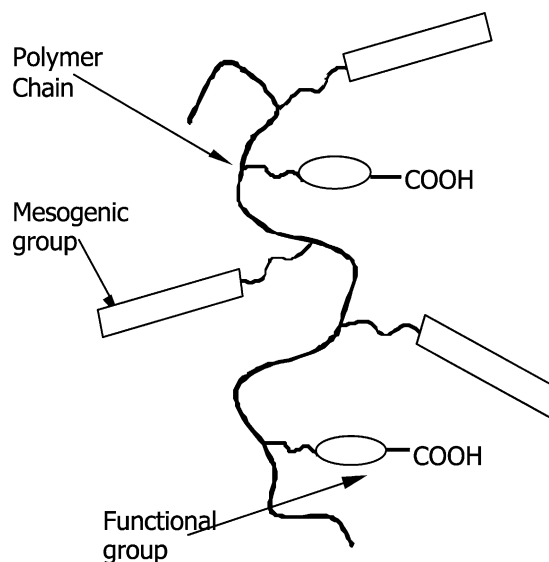


Fig. 64. Scheme of a functionalized LC copolymer containing carboxylic groups.

Analysis of the phase diagrams of the hydrogen-bonded blends of copolymers **85** and **86** with photochromic dopant **87** and **88** reveals the nematic or smectic phase formation depending on the ratio of the components.

Let us consider the photooptical behaviour of the H-bonded complexes of copolymer **85** with two photochromic dopants **87** and **88** undergoing laser irradiation. As was considered above (Section 2.1.2), the molecules with azobenzene moieties undergo reversible *trans*–*cis* isomerization, followed by orientation in the planarly polarized laser irradiation. Fig. 65 demonstrates the kinetic curves of photoinduced birefringence expressed as the time dependence of the phase shift φ/π between the components of the reading beam polarized in parallel and perpendicular directions to the electric vector of the writing beam. The phase shift appears and increases under the laser irradiation. Once illumination is switched off, the value of birefringence decreases somewhat ($\sim 10\text{--}20\%$) over a period of ~ 5 min, and then remains unchanged for a long time (months). Comparison of the amorphizable sample and the homeotropically oriented LC sample shows that

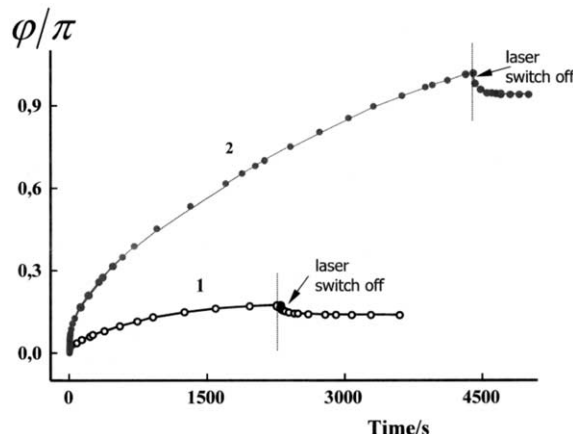
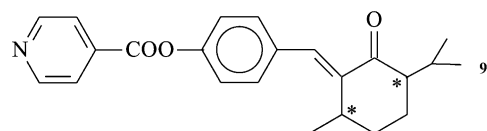
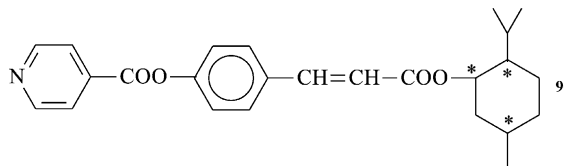
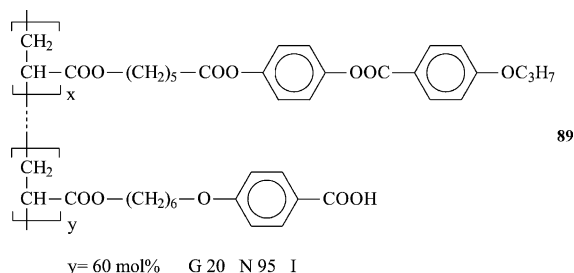


Fig. 65. Kinetic curves for the growth of phase shift φ/π versus the duration of irradiation ($\lambda = 488$ nm) of the films: (1) copolymer **85** ($y = 40$ mol%) with 15 mol% of dopant **87** and (2) copolymer **85** ($y = 40$ mol%) with 20 mol% of dopant **88** at room temperature [265].

the maximum birefringence for amorphizable samples (1.55×10^{-2}) is higher by an order of magnitude (Δn_{stab} for homeotropic orientation is equal to 1×10^{-3}). The analysis of kinetic curves for photochromic LC blends shows that the behaviour of such systems and photochromic LC copolymers are essentially similar.

Other hydrogen-bonded polymer blends were obtained from functionalized copolymers with low-molar-mass chiral photochromic dopants inducing the chiral phase formation. One approach to creating stable photochromic systems was based on LC copolymers **89** containing carboxylic groups. Two chiral photochromic dopants containing a pyridine group capable of forming hydrogen bonds, photoisomerizable C=C double bond and optically active groups based on menthol (dopant **90**) and menthone (dopant **91**) have been synthesized [266]



The introduction of chiral photochromic dopants **90** and **91** into the nematic matrix of copolymer **89** leads to the development of the chiral nematic phase over a wide temperature and concentration interval. Because the chiral dopants introduced in the systems exhibit a non-mesogenic character, the clearing temperature decreases while the concentration of these dopants increases. The glass transition of the blend is virtually independent of the nature of dopants.

It should be emphasized that both blends show stability over time; no phase separation is observed. This is evidence that hydrogen bonding of dopants with functionalized polymers is favourable.

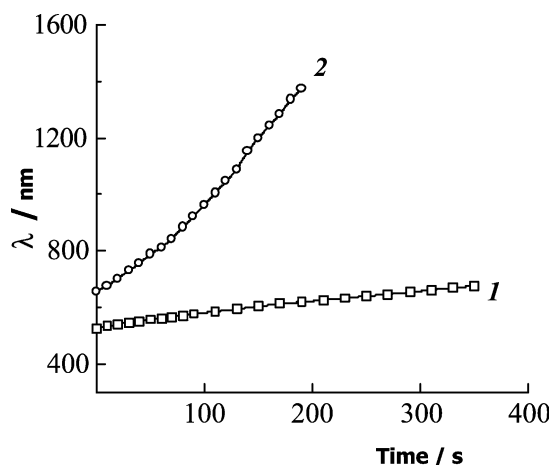


Fig. 66. Kinetic curves of helix untwisting in the UV-irradiated planarly oriented films of LC copolymers **89** containing (1) 10 mol% photochromic dopant **90** and (2) 20 mol% of dopant **91**. The temperature of the irradiated samples: (1) 70 and (2) 60 °C [266].

Upon UV-irradiation of the planarly oriented polymer blends consisting of LC copolymer and dopants, *E–Z* isomerization of the dopants (with respect to the C=C double bond) is induced, and the anisotropy of their molecules significantly decreases [266]. This leads to a decrease in their helical twisting power, which appears as helix untwisting. Fig. 66 shows the kinetic curves for an increase in the wavelength of the selective light reflection during UV-irradiation of the planarly oriented films of LC copolymers **89** with two chiral photochromic dopants **90** and **91**.

Analogous photooptical behaviour was described for the menthone-containing copolymers, the photosensitive menthyl-containing copolymers, and the derivatives of cinnamic acid (Section 3). For all the blends, light-induced changes in the selective reflection wavelength are irreversible. The blend films, cooled below the glass transition temperature, can store the recorded image in the frozen state for a long time.

Nevertheless, the problem concerning long-term stability of similar blends consisting of LC polymer and low-molar-mass photochromic dopants is still unsolved. The potential phase separation of such blends may cause erasure of the recorded data. It is obvious that further investigation in this direction is necessary. At the same time, the results clearly demonstrate that the compatibility of polymer LC

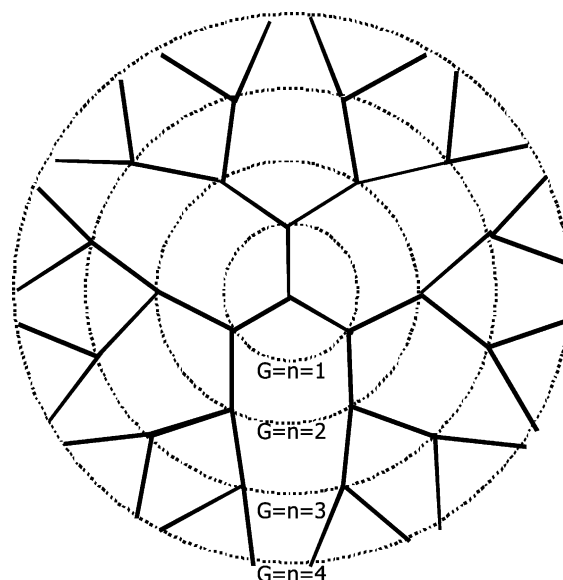


Fig. 67. Schematic representation of a dendrimer of the fourth generation. The generation number (G) corresponds to the number of the circles drawing through the branching points in dendritic molecule. Branching centre corresponds to three arms.

blends with low-molar-mass dopants may be improved by the formation of hydrogen bonds, which can be used for the preparation of photosensitive hydrogen-bonded LC polymer systems.

4. Photoresponsive dendrimers

4.1. Dendritic architecture of molecules

Dendrimers are macromolecules with a regular tree-like array of branching units. Depending on the number of branching spherically located 1, 2, 3, ..., n generations, (G)¹¹ may be distinguished as shown in Fig. 67.

In such a way, a generation number can be defined as the number of branching layers in a spherically symmetric dendrimer molecule [18].

Dendrimers' unusual molecular architecture specifies various features of their physico-chemical properties, such as high solubility [267], low viscosity in solution [268,269] and melt, absence of entangle-

¹¹ In our further consideration, symbol G as used for description of sample's generation, and figure n corresponds to the generation number.

ments, low glass transition values [270], and a capacity to act as dendritic boxes, i.e. to encapsulate certain molecules [271].

Numerous dendritic structures have been synthesized and studied, including polyamidoamines [18], polyamides [19], polyphenylethers [267], carbosilanes [272], etc. In recent years, dendrimers with different functionalities became objects of academic and practical interest due to their unique superbranched architecture, high density of peripheral functionalities, symmetrical shape, and monodispersity. Such compounds have units capable of performing specific functions, such as electron-transfer processes (transition-metal units [273,274]), antenna effects (different chromophoric groups [275–284]), photoinduced processes (photoisomerizable groups [285–290]), etc. Recent achievements in this promising field concerning the synthesis and relationship between the molecular structure and properties of dendrimers have been published in numerous publications, reviews [33,291–293], and in the monograph [19].

Dendrimers containing mesogenic groups can also display LC phases [24,25,28,294–302]. LC dendrimers have attracted considerable attention from researchers working both in the areas of polymers and low-molar-mass liquid crystals. As a result, many publications have appeared during the last 5–6 years. A comprehensive review on LC dendrimers was published in Ref. [33]. However, in the literature, there is almost no information on photochromic dendrimers forming LC phases, although, as was shown above, various photochromic LC polymers have been intensively investigated.

Meanwhile, photochromic LC dendrimers could potentially be a new type of photooptical media for optical recording, as LC dendrimers have physical properties falling between macromolecular compounds and low-molar-mass liquid crystals. They usually combine the low viscosity inherent to all dendrimers and a rapid response to the action of external fields (for instance mechanical, electric and magnetic fields) similar to low-molar-mass liquid crystals. The combination of these two factors is very important in the synthesis of new promising photochromic LC materials.

Such materials were first synthesized and described in our recent studies [303,304]. However,

let us first consider some results obtained for photochromic dendrimers which display no LC properties. We will discuss the photochemical behaviour of some photochromic dendrimers in dilute solutions, and then discuss the photochemical and photooptical properties of photoresponsive Langmuir and LB monolayer films. Finally, we will proceed to the analysis of data on the synthesis and characterization of photochromic LC dendrimers. This presentation order seems to be quite reasonable because, when passing from molecularly disperse systems to more ordered forms of structural organization, one may assess the contribution of the supramolecular structure to the photochemical behaviour of the above systems.

Depending on the molecular structure, all the synthesized photochromic dendrimers may be conditionally divided into two groups: dendrimers in which all photosensitive fragments are localized within one molecule, and dendrimers containing the end photochromic groups as grafted on their surfaces.

4.2. Photochemical and photooptical behaviour of dendrimers in dilute solutions

4.2.1. Dendrimers with photochromic groups in the exterior

On passing to the consideration of photochromic dendrimers with the terminal photosensitive groups, let us first mention that the end groups are usually provided by azobenzene and cinnamoyl derivatives; photoisomerization of the above compounds has been well studied (Section 2.1). In this connection, the principal problem is related to the specific features of the molecular structure of dendrimers containing many photosensitive fragments. Therefore, in several publications devoted to photochromic dendrimers, certain relationships between the generation number in dendrimers (in other words, the content of photosensitive groups) and their photochemical properties were established.

One such publication is devoted to the consideration of poly(propylene imine) dendrimers with a generation number from 1 to 4 [290] functionalized with *para*- and *meta*-carboxamide-substituted azobenzene groups (Fig. 68). As was shown, $\pi\pi^*$ and $n\pi^*$ absorption bands do not change within each family of these

dendrimers. This indicates the presence of strong interchromophoric interactions (the experiments were carried out in CH_2Cl_2 at room temperature) even for higher generations of dendrimers. All the compounds studied were to undergo $E-Z$ and $Z-E$ photoisomerization and $Z-E$ thermal isomerization. The photochemical isomerization experiments revealed that azobenzene dendrimers can be reversibly switched like the corresponding monomeric azobenzene derivatives, and the quantum yields of photoisomerization of a single azobenzene unit were the same for all representatives of each family. The absence of any dependence between the quantum yield of a photoactive unit and the number of such units in the species

shows that there is no effective steric constraint for photoisomerization as the generation number of the dendrimer increases. It was noted that while the qualitative features of the photoisomerization reactions were the same in all cases, quantum yields from the $E-Z$ and $Z-E$ photoreactions were found to depend on the nature of the examined compound and to be related to the different positions of the carboxamide substituent. The quantum yields of *para*-carboxamide-substituted azobenzene were lower for the *meta*-carboxamide-substituted azobenzene.

Thin films of a good optical quality were prepared from these dendrimers. As was shown, holographic gratings with a diffraction efficiency up to $\sim 20\%$ can

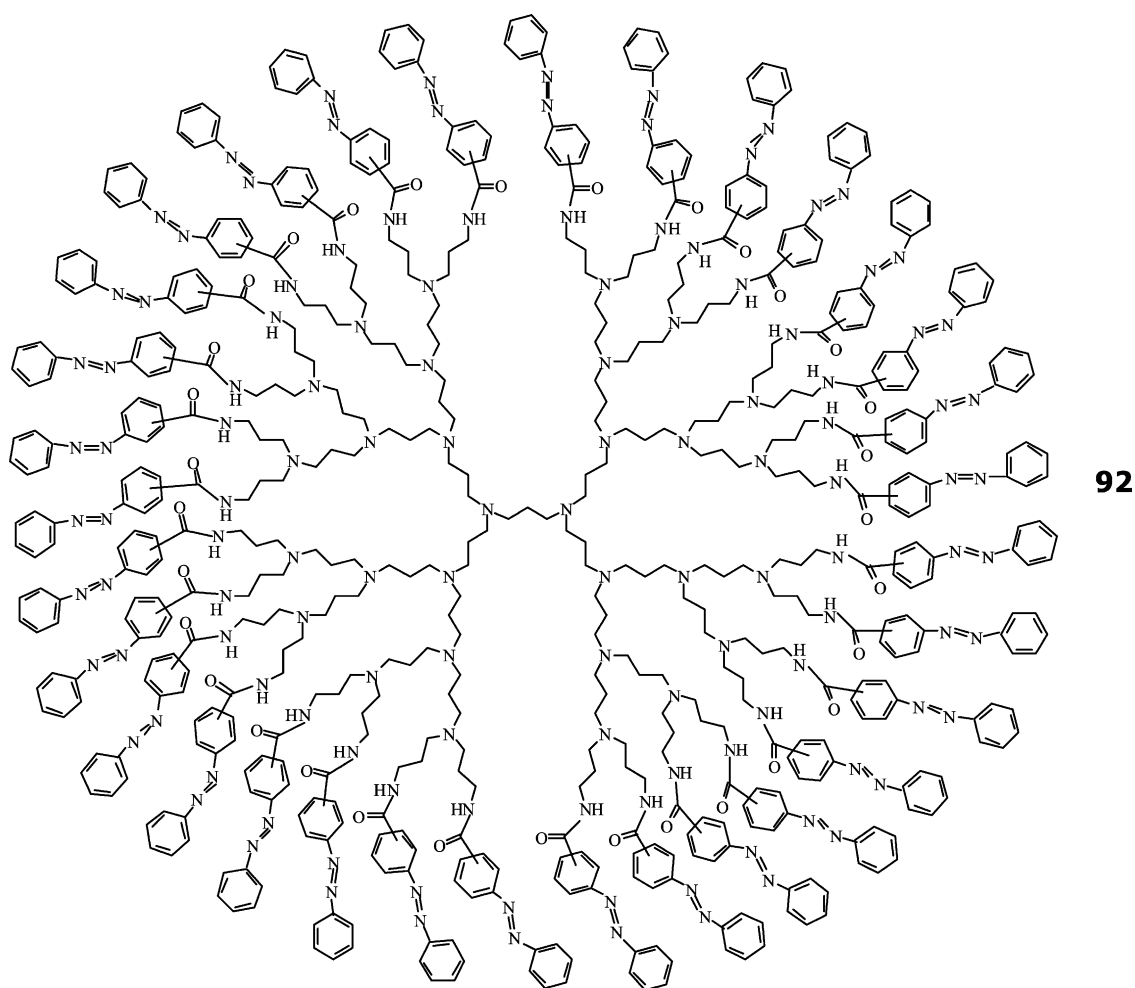


Fig. 68. Carboxamide-substituted azobenzene dendrimers of the fourth generation **92**. Reprinted with permission from Chem Eur J 1998;4:699. © 1998 Wiley–VCH [290].

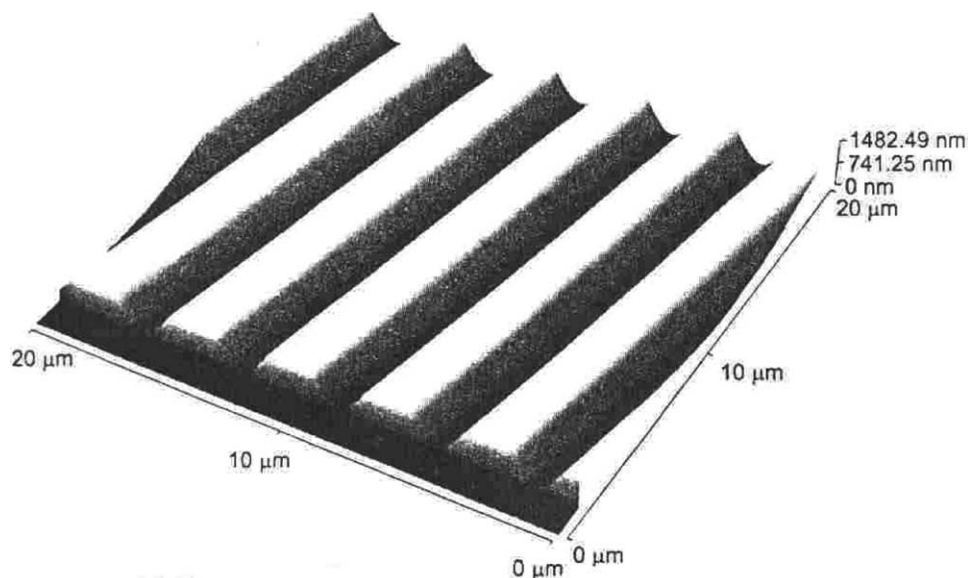
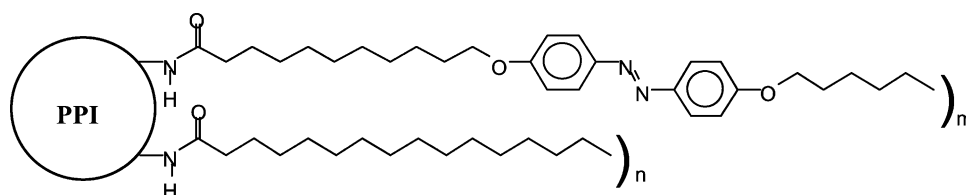


Fig. 69. Atomic force microscopic scans of the polarization gratings recorded in the film of *meta*-carboxamide-substituted dendrimer of the second generation. Film was exposed to a total of 1400 mW/cm² for 55 s. Reprinted with permission from Chem Eur J 1998; 4:699. © 1998 Wiley–VCH [290].

be optically recorded in thin films of second generation *meta*-carboxamide-substituted azobenzene dendrimer **92** (Fig. 69).

The photochromic behaviour of poly(propylene imine) dendrimers (Fig. 70), substituted with different ratios of palmitoyl- and azobenzene-containing alkyl chains in organic solvents were described by Meijer and Weener [285]. Upon irradiation at 365 nm most of the azobenzene moieties were transformed from the

trans to the *cis* configuration. By plotting $\lambda_n(A_\infty - A_t)$ vs. time for thermal *cis* to *trans* back-isomerization, straight lines were obtained for all dendrimers **93–97** and **99** showing the first-order kinetics in each case (Fig. 71). Authors noted that the first-order rate constants were found to be independent of dendrimer generation or composition and to be the same order as those of monomeric azobenzene units ($k \approx 10^{-5} \text{ s}^{-1}$). However, as follows from Fig. 71, their values can be



- 93** m=64, n=0
94 m=32, n=0
95 m=16, n=0
96 m=8, n=0
97 m=4, n=0
98 m=0, n=64
99 m=32, n=32

Fig. 70. Poly(propylene imine) dendrimers (PPI) randomly substituted with palmitoyl- and azobenzene-containing alkyl chains. Reprinted with permission from Adv Mater 2000;12:741. © 2000 Wiley–VCH [285].

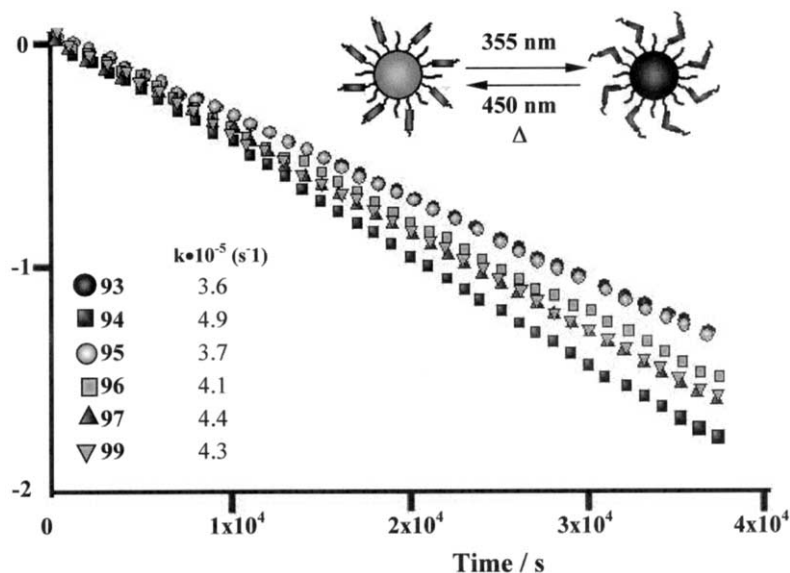


Fig. 71. Plot of $\ln(A_\infty - A_t)$ vs. time at $\lambda = 355 \text{ nm}$, illustrating the first order kinetics of the *cis*–*trans* isomerization for dendrimer **93**–**97** and **99**. Reprinted with permission from Adv Mater 2000;12:741. © 2000 Wiley–VCH [285].

distinguished in 1.4 times for different generations, while a clear correlation between these two parameters is absent.

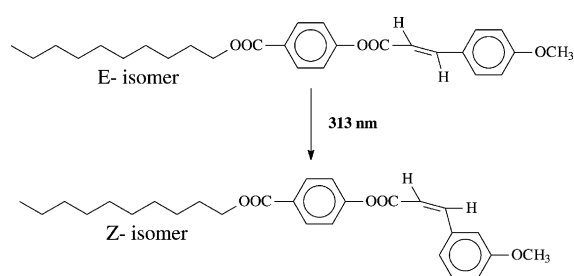
The photooptical properties of the first (**100**) third (**101**), and fifth (**102**) generations of carbosilane dendrimers with 8, 32, and 128 terminal azobenzene groups, respectively (Fig. 72) were studied in our work [305].

Fig. 73 shows the dramatic spectral changes corresponding to the *E*–*Z* photoisomerization process during UV-irradiation at 365 nm of the solution of dendrimer **100** in dichloroethane. A marked decrease in absorption in the region representing the π – π^* electron transition ($\lambda_{\text{max}} = 359 \text{ nm}$) and a small increase in the region representing the n – π^* transition of azobenzene chromophores occurs. Based on the spectral changes, the isomerization process is thermally reversible; even at ambient temperature, one can see a complete recovery of the initial shape of the spectra of the dendrimers.

Another type of photochromic dendrimer was described in Ref. [286]. Chinese researchers have synthesized and investigated the photochemical properties of a third generation poly(amidoamine) dendrimer **103** with cinnamoyl end groups (Fig. 74). They explored the possibility of cyclization of the cinnamoyl dendrimer shell within the molecules; as

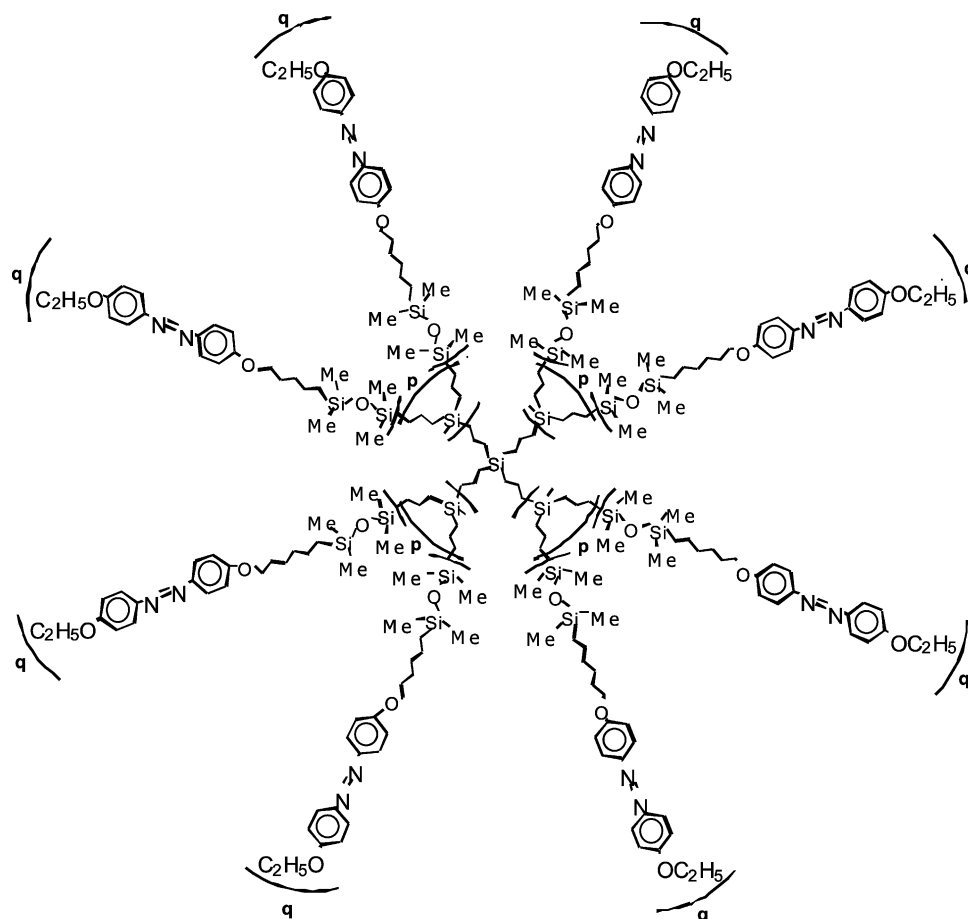
was found, intramolecular bonding (cycloaddition reaction) takes place within the dendrimer molecules (see Fig. 74, compound **104**) in dilute solution under UV-irradiation. These results were confirmed by FTIR and ^1H NMR studies. The relationship between the spectral violet shift and irradiation time of the cinnamoyl-containing dendrimer is shown in Fig. 75. As is seen, the spectral violet shift was 13 nm in 3 h. After this period equilibrium was reached; 80–85% double bonds disappeared after irradiation.

In our recent study [303], the synthesis and photochemical properties of first generation carbosilane dendrimers bearing eight peripheral metoxycinnamic groups was described (Fig. 76). Fig. 77 shows the spectra corresponding to dilute solutions of dendrimer **105** in dichloroethane ($C = 1.36 \times 10^{-2} \text{ mg/ml}$) during UV-irradiation ($\lambda_{\text{ir}} = 313 \text{ nm}$). As follows from Fig. 77, the optical density of the peaks corresponding to the π – π^* and n – π^* electronic transitions of the cinnamoyl chromophore decreases as a result of light irradiation (shown by the arrow); in addition, an isosbestic point at 280 nm is observed at the initial step of irradiation. According to Ref. [306], the above-mentioned changes in the electron spectra of such photochromic compounds are associated with the *E*–*Z* isomerization of cinnamoyl groups as shown below:



Only one process, the *E*–*Z* photoisomerization of the carbon–carbon double bond of the first generation cinnamoyl-containing carbosilane dendrimer, is observed; the cyclization reaction is absent (Sections 2.1.1 and 3.3.2).

The different photooptical behaviour of cinnamoyl-containing dendrimers as observed in two above-mentioned works [286,303] can be explained by various factors, including generation number, spacer length difference, and different experimental



$$n = 1, 3, 5$$

$$p = 1, 7, 31 = 2^{n-1}$$

$$q = 1, 4, 16 = 2^{(n-1)}$$

$$m = 8, 32, 128 = 8q = 2^{(n+2)}$$

$$n = G$$

$$G-1 \quad \mathbf{100}$$

$$G-3 \quad \mathbf{101}$$

$$G-5 \quad \mathbf{102}$$

Fig. 72. Chemical structure of azo-containing carbosilane dendrimers of the first **100**, third **101** and fifth **102** generations. n is the generation number; m is the number of terminal groups [305].

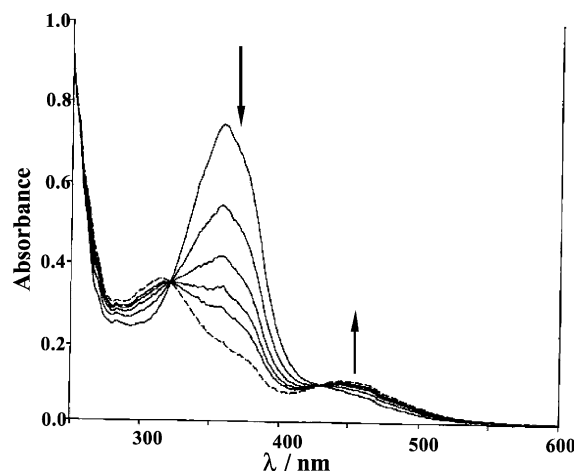


Fig. 73. Changes of absorbance spectra of the dendrimer **100** (dichloroethane solution, 8.13×10^{-3} mg/ml) during UV-irradiation (365 nm, intensity 1.9×10^{-8} einstein/(cm² s)). Spectra were recorded each 10 s of irradiation. Dashed line corresponds to the photostationary state (~10 min of irradiation) [305].

conditions. For instance, in our case the flexible spacer consisting of (CH₂)₁₀ groups located between the dendritic core and cinnamoyl groups may prevent {2 + 2} photocycloaddition, since this process is topochemically controlled.

4.2.2. Dendrimers with photochromic groups in the interior

One may predict a priori that, for dendrimers with definite photochromic groups (for instance, azobenzene) in the interior, rather than peripheral photochromic groups, small changes in configuration will

affect dramatic conformational changes through the dendrimer structure. This difference between the two dendrimer groups was first demonstrated in Refs. [287,307] where the effect of ‘macromolecular isomerism’ on the photomodulation of dendrimers’ physical properties was shown. Benzyl aryl ether dendrimers containing three photochromic azobenzenes constructed in two limiting isomeric forms **107**, **108** were compared (Fig. 78). All dendrimers exhibited photoresponsive behaviour characteristic of azobenzene-containing materials (reversible *E–Z* isomerization). Four diastereoisomers (*EEE*, *EEZ*, *EZZ*, and *ZZZ*) were easily detected by ¹H NMR in the solution after irradiation of all dendrimers with 350 nm light. More importantly, the relative appearance and disappearance of all four isomers during the thermal *E–Z* isomerization (shown by ¹H NMR) indicate more independent, rather than simultaneous, isomerization of the azobenzene units. It means that the behaviour of each dendrimer arm is unaffected by presence of the other two ones.

Meanwhile, the absorption chromatography shows that photomodulation of dendrimer polarity after irradiation (*Z*-azobenzene is more polar than *E*-isomer [308]) is insensitive to the relative location of the responsive groups within the structure. However, a marked decrease in hydrodynamic volume (29% for second generation dendrimers and 16% for fourth generation) was observed for dendrimers of type **107** after irradiation with 350 nm light to a photostationary state. A much smaller difference in hydrodynamic volume was observed for dendrimers **108** under the same

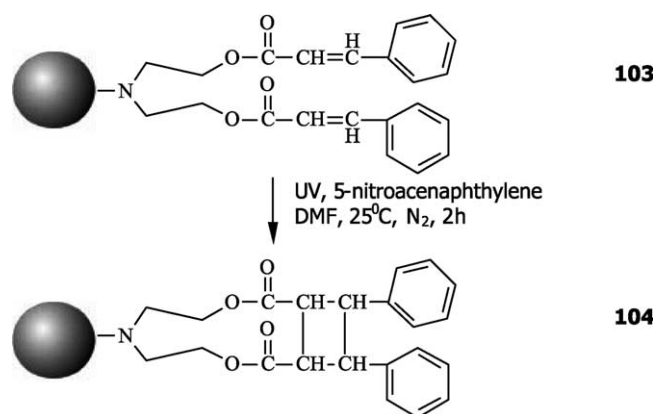


Fig. 74. Photocyclization of cinnamoyl shell-modified poly(amidoamine) dendrimer **103**. Reprinted with permission from J Polym Sci, Part A: Polym Chem 2000;38:4147. © 2000 American Chemical Society [286].

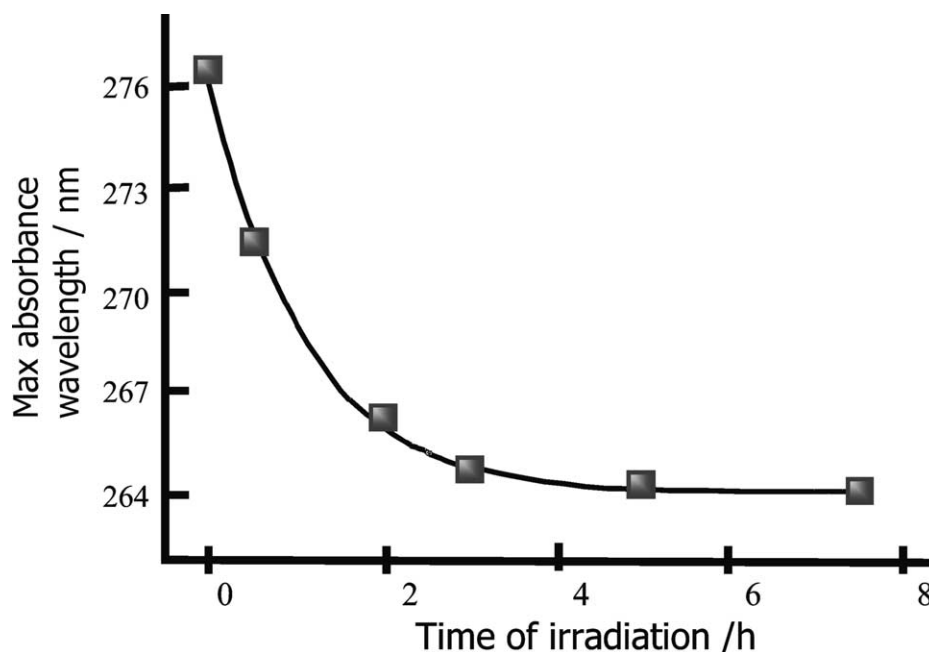


Fig. 75. The maximum UV absorbance wavelength of dendrimer **103** at different irradiation time; solvent: methanol; [chromophore] = 1.74×10^{-4} mol/l. Reprinted with permission from J Polym Sci, Part A: Polym Chem 2000;38:4147. © 2000 American Chemical Society [286].

conditions. The study of the influence of generation number on the kinetics of the thermal back-isomerization of dendrimers **107** (second and fourth generations) in methylene chloride allowed the following conclusion. The relative constancy of the first-order rate constants and activation energies of the dendrimers indicate no strong steric influence on the *cis*–*trans* thermal isomerization, that is, the isomerization process is independent of the dendrimer size.

The first-third generation dendrimers of **109** with a photochromic central linker of another chemical structure—diarylethene-moiety (Fig. 79) were synthesized in Ref. [309]. In spite of the aggregation processes of the dendrimers on a mica surface, the third-generation dendrimer (G-3) (colourless powder) turned blue upon irradiation with UV-light; the colour disappeared upon irradiation with visible light ($\lambda > 500$ nm) at room temperature. The colouration is due to the cyclization reaction [310] of the central hexatriene to a cyclohexadiene structure (Section 2.2.2). However, no appreciable changes in the three-dimensional molecular size of the dendrimer were observed after UV-irradiation, because of minor geometrical structural changes in the photochromic core group.

In Refs. [311,312] photoresponsive dendrimers **110** were prepared from azo-benzene derivative central linkers and benzyl-aryl ether monodendrons (wedges) as is shown in Fig. 80. All dendrimers exhibited photoresponsive behaviour (*E*–*Z* isomerization) upon irradiation with 350 nm light. Conversion from *Z*- to *E*-forms can be accelerated by irradiation with visible light, resulting in total control of the switching function for these dendrimers (Fig. 81). It should be noted that the first-order rate constant for the thermal reversion of dendrimer **110** ($n = 2$) is similar in magnitude ($k = 3 \times 10^{-4} \text{ s}^{-1}$; $t_{1/2} = 40$ min) to that of azobenzene, indicating a lack of steric influence on the isomerization process at the second generation level. As anticipated, such systems can be used in the fields of drug delivery, chemical sensing, and separation technology.

Photochemical behaviour of aryl ether azodendrimers of the first (**111**), the third (**112**), the fourth (**113**) and the fifth (**114**) generations (Fig. 82) in solution have been investigated via UV and IR irradiation [313]. As was shown, all dendrimers are isomerized from the *trans* to the *cis*-form under UV-irradiation. This isomerization can be reversed upon heating or exposure to visible light. In addition, the dendrimers of the fourth and fifth generations undergo *Z*–*E* isomerization upon

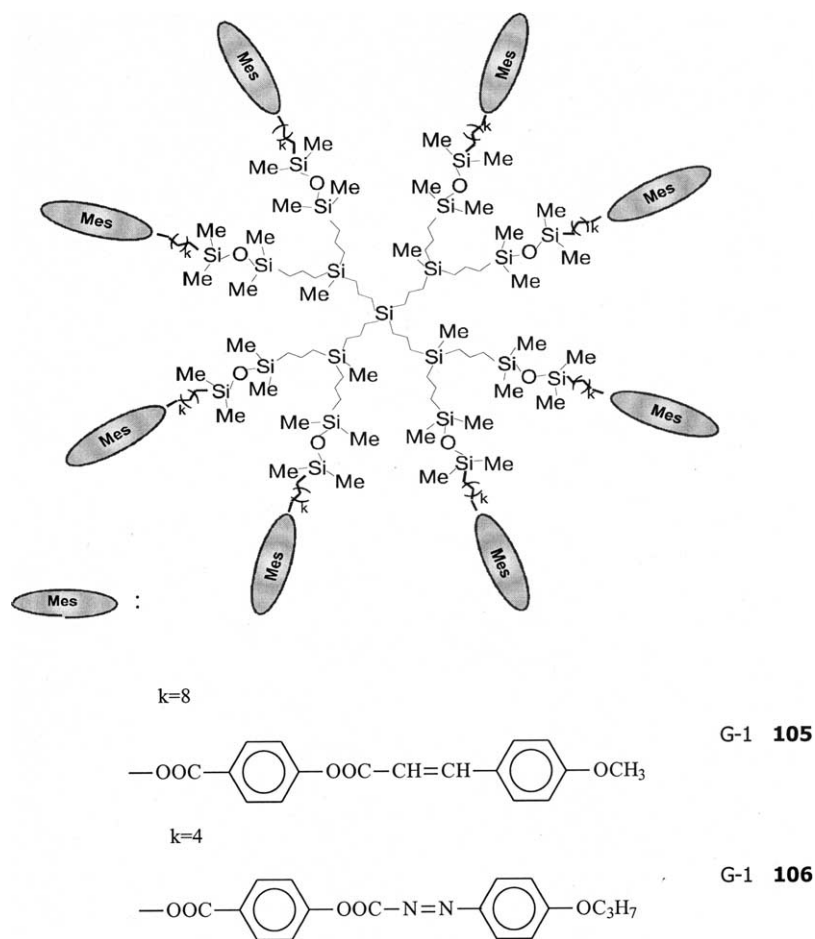


Fig. 76. Chemical structure of the first generation dendrimers with cinnamoyl-containing **105** and azobenzene containing **106** groups [303,304].

IR irradiation (1597 cm^{-1}), whereas the isomerization of the dendrimers of the lowest generations (G-1 and G-3) was not accelerated by IR radiation. Moreover, for dendrimer **114** (G-5), the isomerization rate constant is 260 times (250 times for the fourth generation) higher than that of the thermal isomerization at room temperature and even 23 times higher than that upon irradiation with visible light (Fig. 83).

Although the mechanism of the IR-induced *Z–E* isomerization of dendrimers **113** (G-4) and **114** (G-5) is still unclear, the role of the dendrimer matrix may be twofold, serving as an efficient light-harvesting antenna for IR photons, and maintaining vibrational excitations against collisional energy scattering.

Hence, a state-of-the-art analysis of the literature data does not allow one to reveal any evident

relationships between the number of generations and photochemical behaviour of photosensitive dendrimers in solutions.

4.3. Photochemical and photooptical behaviour of dendrimers in a solid

Let us now consider the photoinduced processes taking place in condensed state dendrimers. First, let us consider the case of monolayer films and then proceed to LC and amorphizable systems.

4.3.1. LB monolayer films of dendrimers

In recent years, research in the field of highly ordered, ultrathin coatings with molecularly controlled surface properties was generally focused on

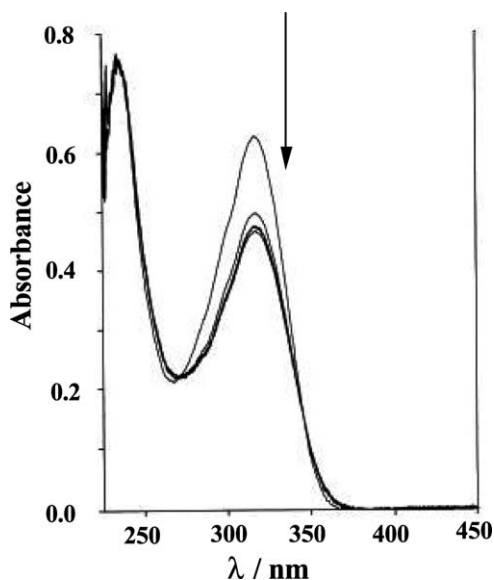


Fig. 77. Absorbance spectra changes of dendrimer **105** in dichloroethane solution during UV-irradiation. Spectra were recorded each 5 min of irradiation [303].

functional polymeric materials with non-linear, photochromic, and other physical properties, and with their ability to form organized suprastructure at interfaces [314–316]. This interest is explained by the potential use of ultrathin films for holographic SRG, command layer effects, optical storage media, etc. An alternative approach for the development of ultrathin ordered films is a Langmuir–Blodgett technique, which allows one to obtain mono- and multilayers. In this connection, dendritic photosensitive macromolecules can also be considered uniform building blocks in the construction of functionalized interfaces [317].

Langmuir and LB monolayer films of dendrimers were recently studied in Ref. [285]. Authors investigated the surface behaviour of azo-containing dendrimers with UV-irradiation that may initiate a photoisomerization reaction. As was found, the Langmuir films prepared from dendrimers **93–97** (Fig. 70) do not show any changes in the surface area upon UV-irradiation at a constant pressure (20 mN/m) due to the presence of H-aggregates. However, the

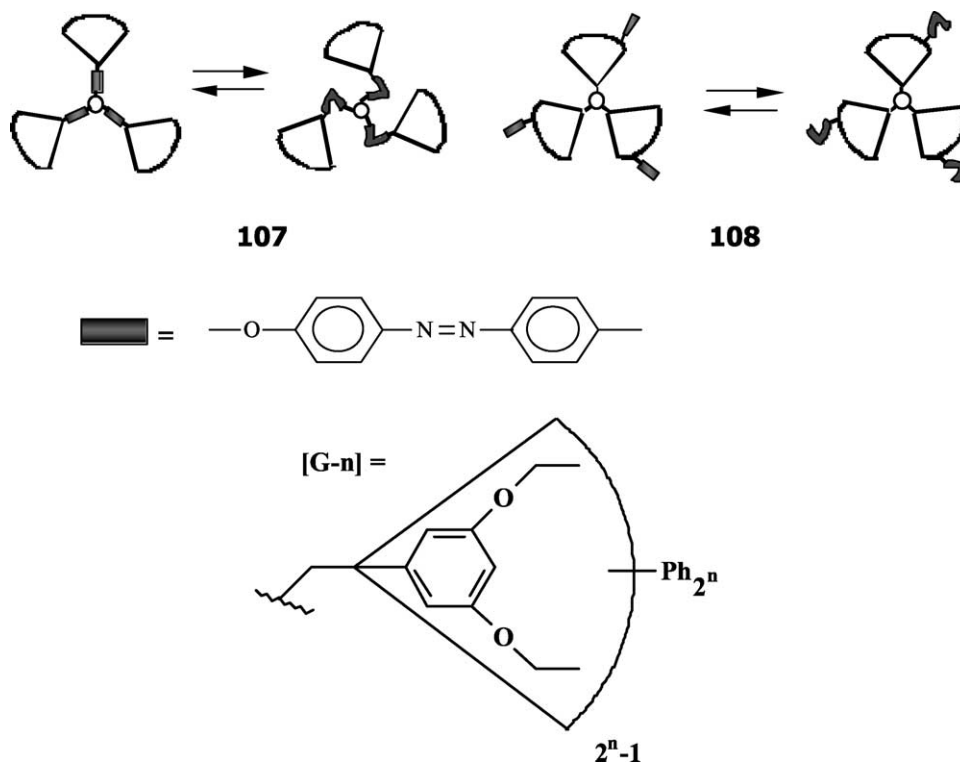


Fig. 78. Schematic representation of two types isomeric benzyl aryl ether dendrimers containing azobenzene core type **107** and photochromic group at the periphery type **108**. Reprinted with permission of J Am Chem Soc 1996;118:4345. © 1996 American Chemical Society [287].

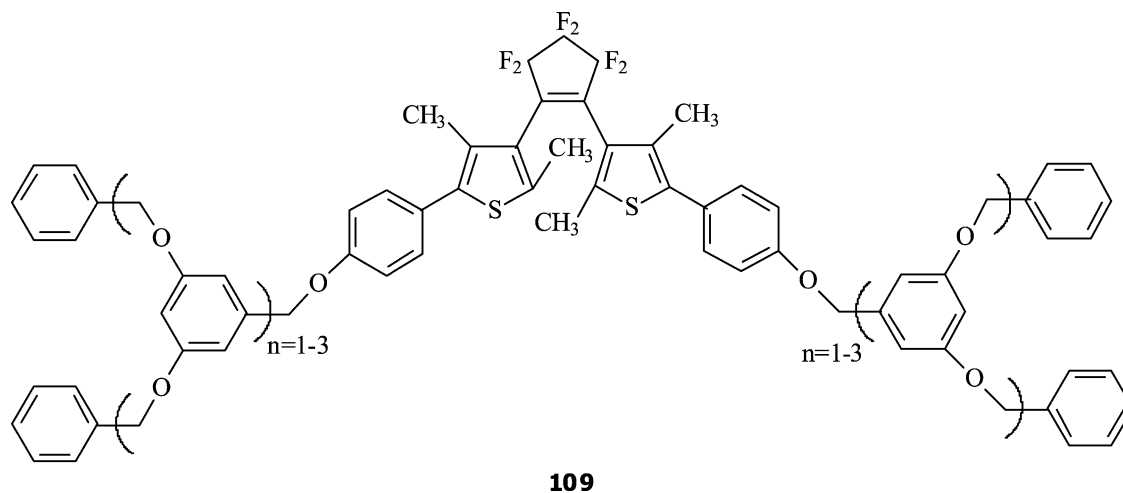


Fig. 79. Schematic representation of diarylethene containing dendrimers of the first–third generations [309].

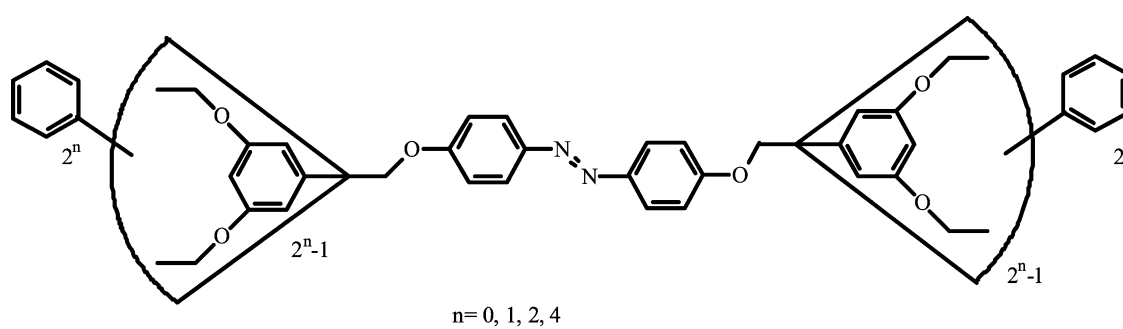
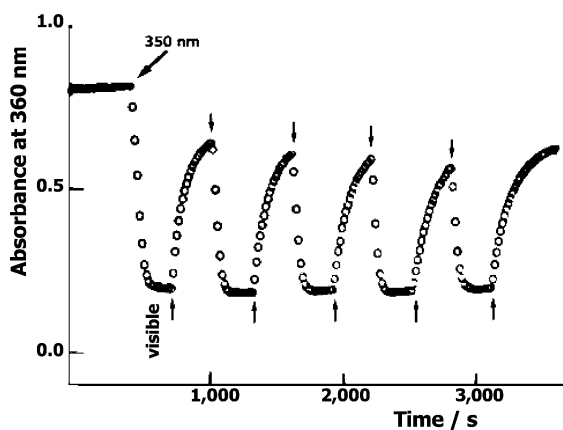


Fig. 80. Chemical structure of benzyl aryl ether dendrimers with azobenzene central linkers [311,312].

Fig. 81. Plot of absorbance at 360 nm of dendrimer **110** ($n = 2$) successively irradiated with 350 nm and visible light (5 min intervals). Reprinted with permission from Polym Mater: Sci Engng (Proc ACS, Div PMSE) 1999;77:79. © 1999 American Chemical Society [312].

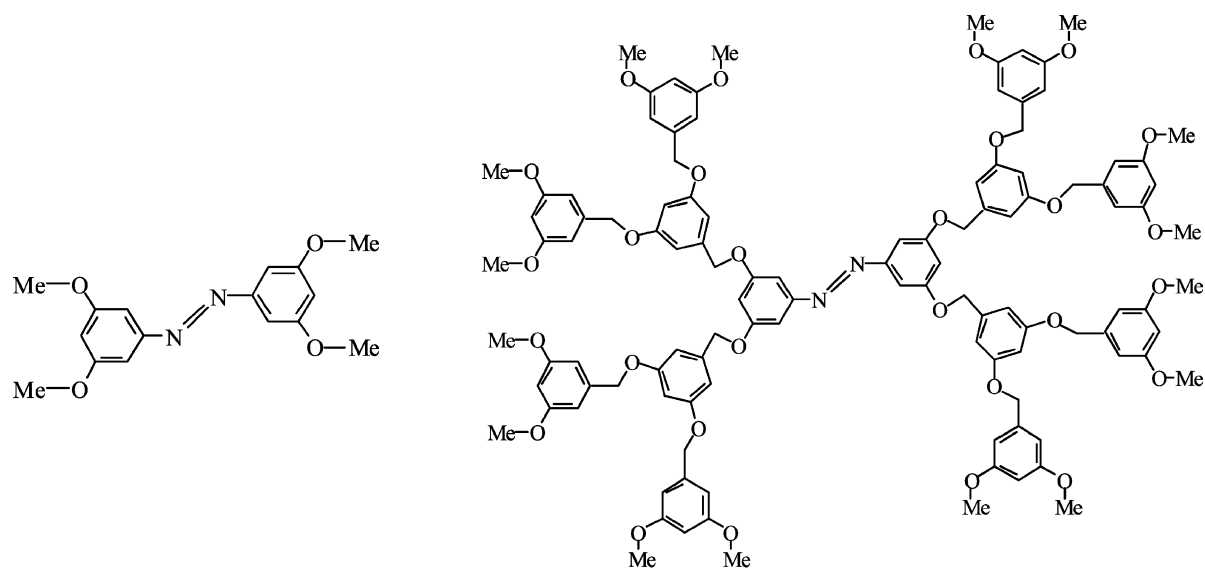
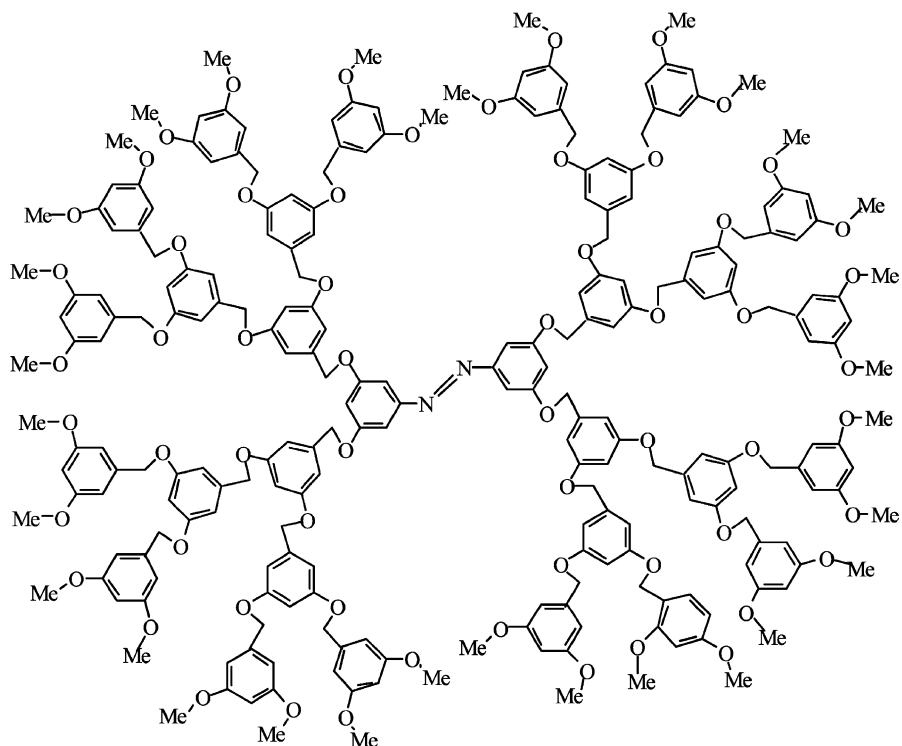
**(G-1) 111****(G-3) 112****(G-4) 113**

Fig. 82. Schematic structures of *trans*-aryl ether azodendrimers of the different generations. Reprinted with permission from Thin Solid Films 1998;331:254. © 1998 Elsevier Science [313].

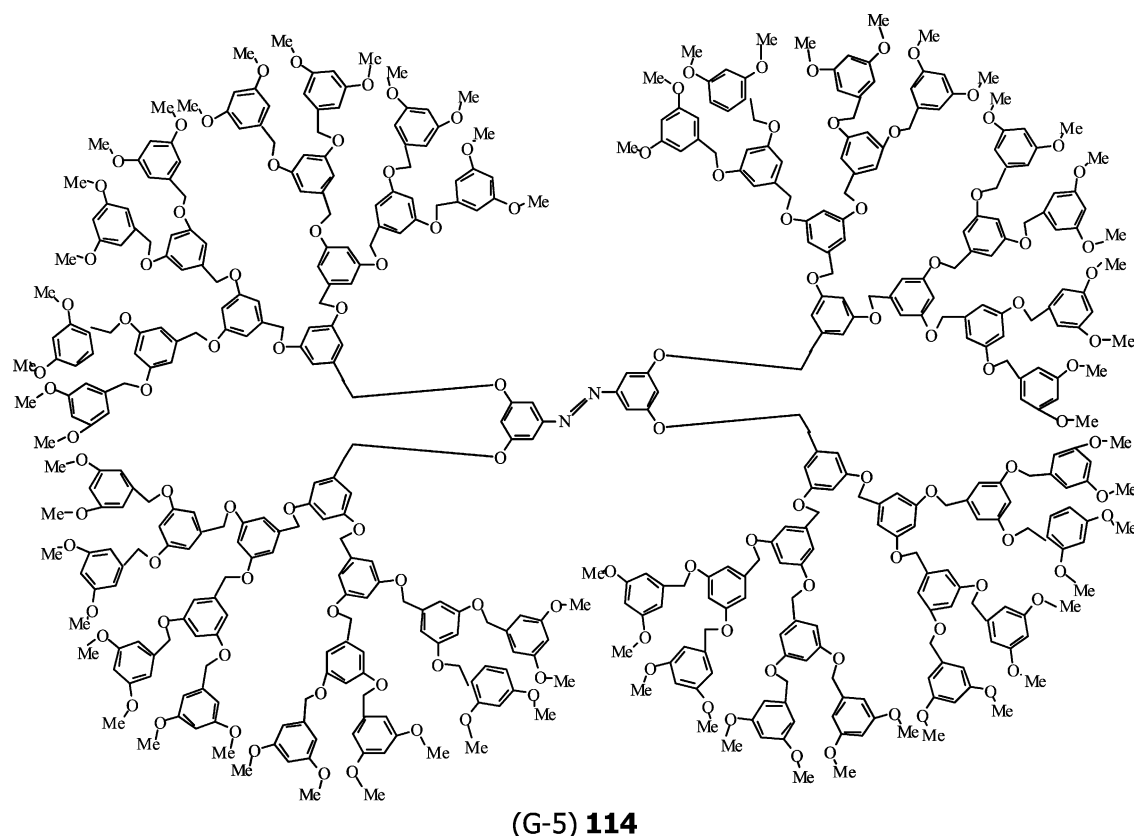


Fig. 82 (Continued)

monolayer and LB film prepared from **99** (Figs. 70 and 84) showed changes in surface area upon alternating UV- and IR-irradiation under the same conditions (Fig. 84(a)–(c)). As was noted, free volume induced by the incorporation of palmitoyl alkyl chains (Fig. 84(a)) is likely to be responsible for the photoisomerization of **99**. Since the volume occupied by the *cis* isomer is higher than that of the *trans* isomer, the isomerization is accompanied by an increase in the total surface area.

Photoresponsive Langmuir monolayers based on azobenzene-crown-containing monodendrons were investigated in Ref. [318]. However, in contrast to dendrimers where photochromic groups are localized on the exterior, these dendrimers contained photochromic azobenzene-crown groups at the focal point of monodendrons (Fig. 85). After UV-irradiation, an increase in the surface area values by 10–20% for **116** and **117** dendrons was observed, whereas higher (**118**), and lower (**115**) generations demonstrated

minor changes (5–10%) under the same conditions. The kinetics of surface area changes upon UV-irradiation at constant surface pressure were measured for all dendrons. Only monolayers of **116** and **117** showed significant reversible changes in surface area. This phenomena was explained by an optimal balance between cross-sectional areas of dendritic shells and bulky crown-ether polar groups, which led to a marked photomechanical response for intermediate generations (Fig. 86). The dependence of the rate constant of photoisomerization k on the surface pressure was found. Note that k increases by one order of magnitude for the first generation dendron when the monolayer becomes ‘solid’ at a pressure higher than 10 mN/m. As is assumed, the switching of a dendron from *trans* to *cis*-form initiates the isomerization of neighboring dendrons when they are densely stacked in the ‘solid’ monolayer.

For LB layers on a solid surface, a fast photoisomerization process occurs in 30–60 s and can be described

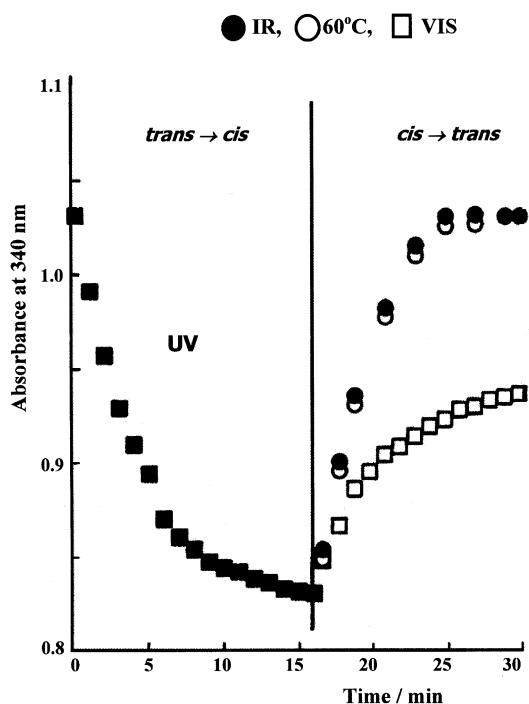


Fig. 83. Isomerization of dendrimer **114** (G-5) in chlorophorm solution under different conditions. Reprinted with permission from Thin Solid Films 1998;331:254. © 1998 Elsevier Science [313].

by first-order kinetics. The rate of photoisomerization decreases as the generation number increases.

In Ref. [319] the photoalignment of azo-functionalized dendrimer **119** (Fig. 87) films was described. Photoisomerization was initiated by the irradiation of the LB film with polarized UV (350 nm) light and visible light (>420 nm). A high dichroism (up to $A_{(90)}/A_{(0)} = 1.45$) was observed in the film upon irradiation with polarized UV-light. However, upon irradiation with polarized visible light, the photo-induced dichroism is rather low ($A_{(90)}/A_{(0)} = 1.094$). As was concluded, in the photostationary state, the *E*-isomer dominates in isomer mixture. Therefore, the induced dichroism is related to the *E*-isomeric chromophores located on the film surface.

4.3.2. Thin LC films of dendrimers

The first photosensitive LC dendrimer **105** with terminal cinnamoyl groups was synthesized in our group [303]. This dendrimer contains eight terminal mesogenic cinnamoyl groups (Fig. 76) and is able to form the SmA mesophase over a wide temperature

range ($T_{cl} = 58\text{ }^{\circ}\text{C}$, $T_g = -28\text{ }^{\circ}\text{C}$). Fig. 88 shows possible dendrimer packing in the SmA phase. Note that a spontaneous homeotropic orientation of mesogenic groups (perpendicular to the support) is observed in thin films obtained by either a slow evaporation of the dichloroethane-LC dendrimer solution, or the spin coating method. As is shown in Fig. 89, rapid growth in the optical density of the homeotropically oriented films is observed over the first minutes of UV-irradiation. This process is accompanied by a breakdown in the homeotropic orientation of the mesogenic groups. Upon further irradiation, the optical density of the films decreases (in this case, a decrease in the amplitude is much higher than that in the case of the dilute solution), the isosbestic point is lost, and the dendrimer films become insoluble. Hence, a strongly cross-linked structure is formed. The experimental data shows that at least two processes, *E*-*Z* photoisomerization and {2 + 2} photocycloaddition, take place in the dendrimer films.

In further studies on photoresponsive LC dendrimers, [304,320] attention was focused on first-generation of LC dendrimers with terminal azobenzene groups (see Fig. 76, dendrimer **106**), which is also capable of forming a SmA mesophase over a wide temperature range. A comparative analysis of the photooptical behaviour of the dendrimer in dilute solution and film was described in Refs. [304,320]. As follows from Fig. 90(a), irradiation of the dendrimers in solution (dichloroethane) leads to marked spectral changes associated with a single UV-light-induced *E*-*Z* isomerization of the azobenzene groups. Note that in the case of the film, absorption maximum corresponding to the π - π^* electron transition is somewhat shifted to the short-wavelength spectral region when compared to the spectrum of the solution (Fig. 90(a) and (b)). This behaviour is associated with the aggregation of azobenzene chromophores [321–324]. The phenomenon of aggregation is also promoted by the development of smectic order in the dendrimer.

The specific feature of the photochemical behaviour of the photochromic dendrimer is that, upon irradiation, the LC order deteriorates, and the dendrimer film transforms into an amorphous state. This process is related to the fact that *Z*-isomer of the azobenzene fragment is characterized by a low

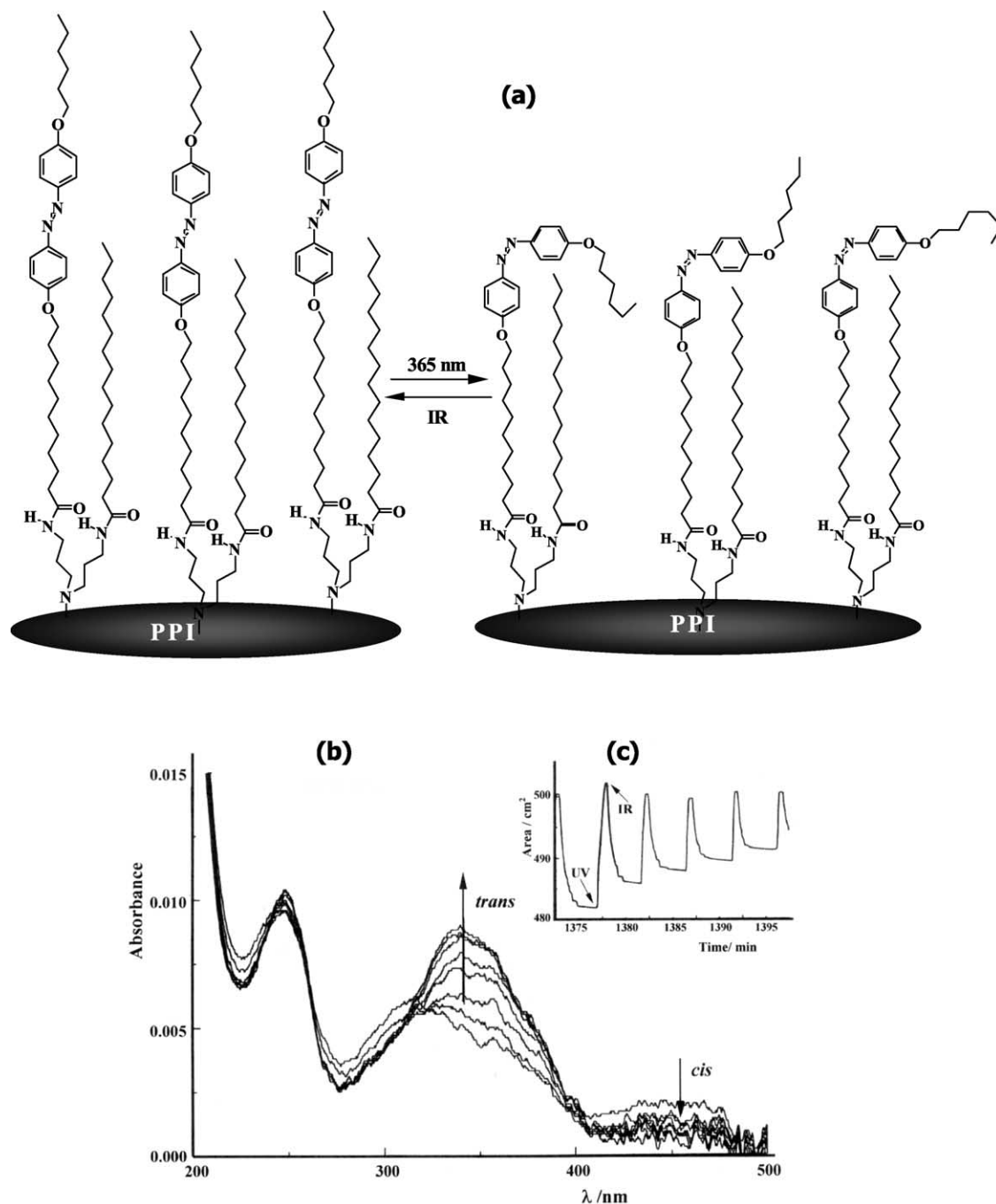


Fig. 84. (a) Reversible *trans*-*cis* photoisomerization in LB monolayer film of fifth generation of poly(propylene imine) (PPI) dendrimer **99**, deposited on quartz (365 nm, $P = 2 \text{ mW/cm}^2$). (b) Absorbance spectra of LB film of dendrimers **99** deposited on quartz and UV-irradiated (365 nm). (c) The insert shows the isomerization behaviour of the dendrimer at the water surface. Irradiation (60 s, 365 nm, $P = 2 \text{ mW/cm}^2$) results in *trans* to *cis* photoisomerization accompanied by an increase of the total surface area, while subsequent irradiation with IR reversed the event. Reprinted with permission from Adv Mater 2000;12:741. © 2000 Wiley-VCH [285].

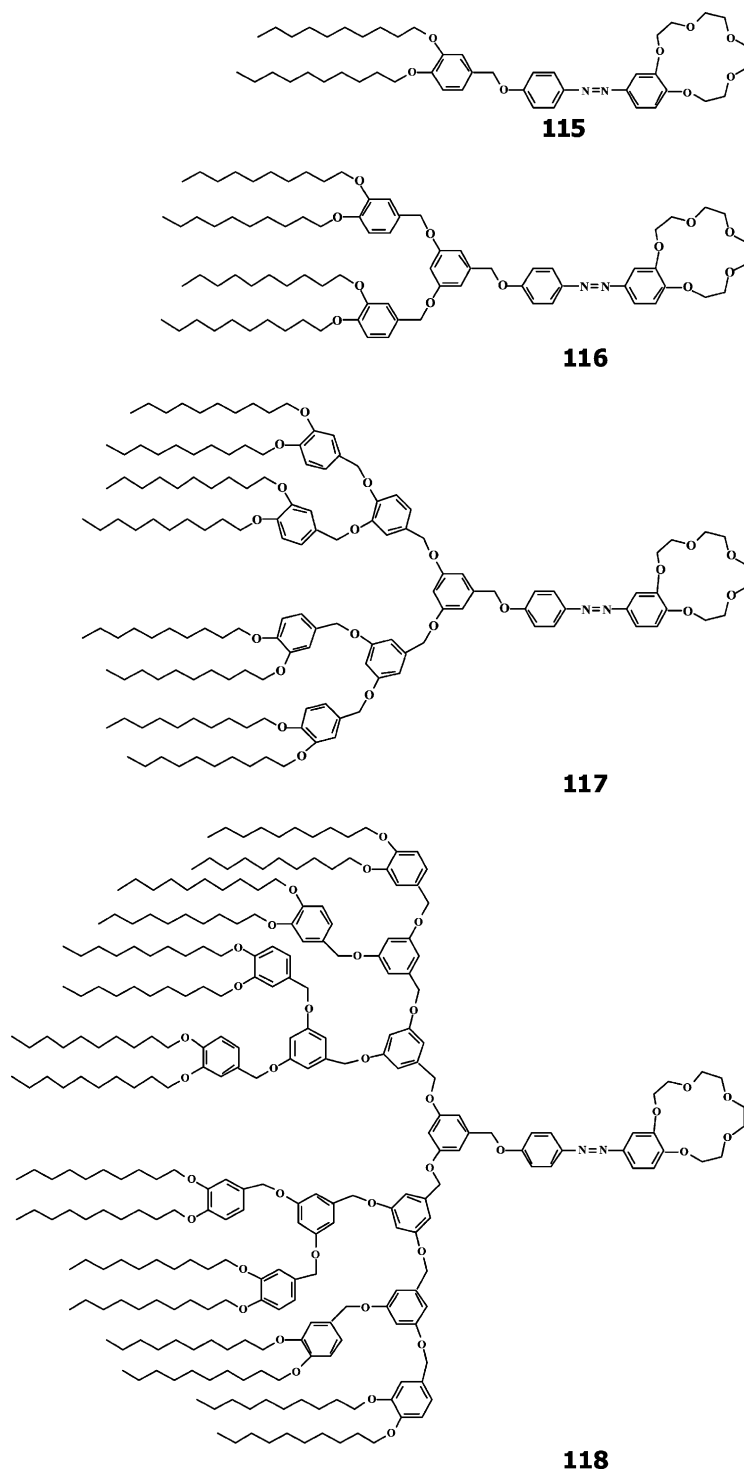


Fig. 85. Chemical structure of azobenzene-crown-containing dendrons of different generations. Reprinted with permission from Langmuir 2000;16:10569. © 2000 American Chemical Society [318].

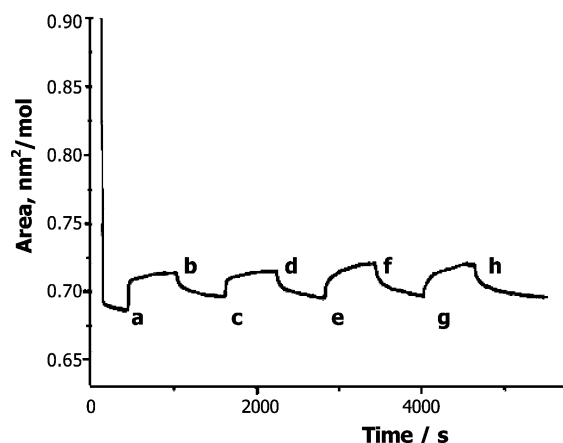


Fig. 86. Reversible photoinduced deformation of dendrimer **116** as a response to multiple switching the illumination lamp on (points a, c, e, and g) and off (points b, d, f, and h) at $\pi = 34$ mN/m. Reprinted with permission from Langmuir 2000;16:10569. © 2000 American Chemical Society [318].

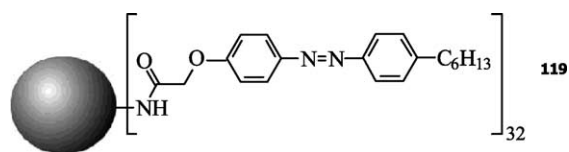


Fig. 87. Chemical structure a poly(amido amine) dendrimer **119** containing 32 azobenzene terminal groups. Reprinted with permission from Polym Mater Sci Engng 2001;84:236. © 2001 American Chemical Society [319].

anisometry. Deterioration of the LC order is likely to be accompanied by a breakdown of aggregates. As follows from Fig. 90(b), upon irradiation of the film, the wavelength maximum shifts to the long-wavelength spectral region.

The difference in spectra between the LC film and in isotropic melt (Fig. 91) proves the sensitivity of the azobenzene group aggregates to the phase state of the dendrimer. The maximum of the $\pi-\pi^*$ electron transition in the LC phase is somewhat shifted to the short-wavelength region and characterized by a lower intensity ($\lambda_{\max} = 328$ nm in SmA mesophase and $\lambda_{\max} = 350$ nm in isotropic melt).

Hence, upon irradiation of LC films of photosensitive dendrimer, one may observe the occurrence of several processes, such as *E-Z* photoisomerization, breakdown of aggregates, and phase SmA-I transition.

The kinetic study of the back thermal process (*Z-E* isomerization) of dendrimer **106** is the essential interest. To this end, the dendrimer film UV-irradiated for 20 min and annealed at different temperatures. In this case, an increase in optical density at the wavelength corresponding to the maximum of $n-\pi^*$ electron transition was fixed. As follows from Fig. 92, the isomerization rate depends dramatically on the temperature. Activation energy of the fast process has been calculated, and was found to be equal to about

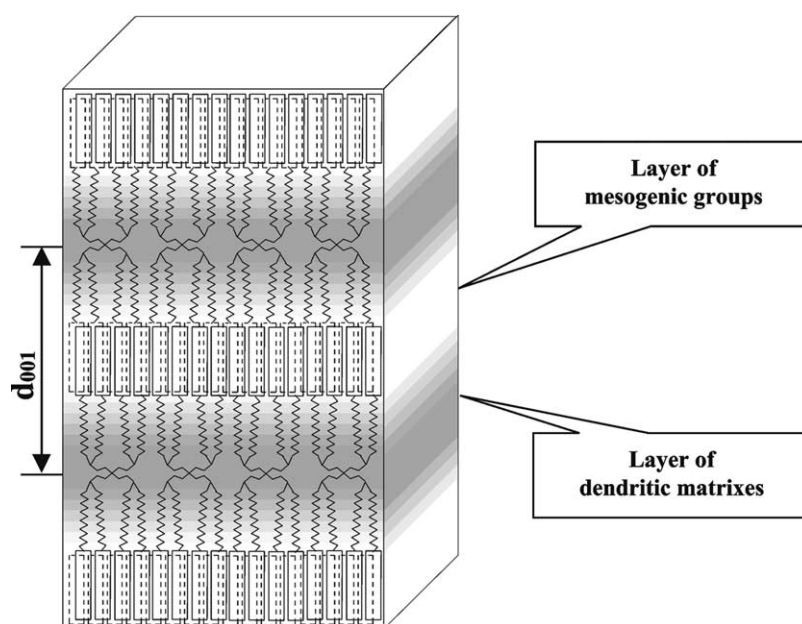


Fig. 88. Scheme of packing of LC dendrimer **105** (Fig. 76) in the SmA mesophase [303].

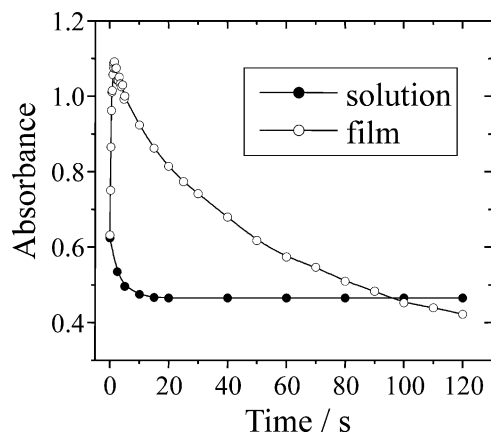


Fig. 89. Optical density changes of dendrimer **105** in dichloroethane ($c = 1.36 \times 10^{-2}$ mg/ml) solution and film at 25 °C during UV-irradiation [303].

19.5 kcal/mol. This activation energy value is typical of azobenzene derivatives [325].

In the case of dendrimer films in the SmA phase, irradiation with polarized light (488 or 365 nm) does not lead to an appearance of linear dichroism. This fact suggests that, in this case, smectic order completely prevents any possibility of photoinduced re-orientation of azobenzene groups. However, using the spin coating technique, thin ($< 1 \mu\text{m}$), amorphous (optically transparent) dendrimer films were prepared. Despite the low glass transition temperatures of such substances, the development of the smectic phase at room temperature takes several days, and therefore, the amorphizable films of dendrimer can be obtained. Fig. 93 presents the corresponding spectra for the amorphous dendrimer film **106** upon irradiation with UV and visible light. It should be emphasized that, in the case of the isotropic dendrimer film, UV-irradiation leads to better pronounced spectral changes as compared with those as seen for the LC sample (compare Figs. 90(b) and 93(a)). This evidence implies that, in the amorphous film, the conversion of $E-Z$ photoisomerization is much higher than that in the LC film. In this case, the LC order markedly prevents a possible photoisomerization. It should be noted that the absorption maxima wavelengths for smectic and amorphizable films almost coincide (326 nm). These facts suggest that, both in amorphous and LC films, the development of aggregates takes place. The absence of isosbestic points and the shift in the maximum of the $n-\pi^*$

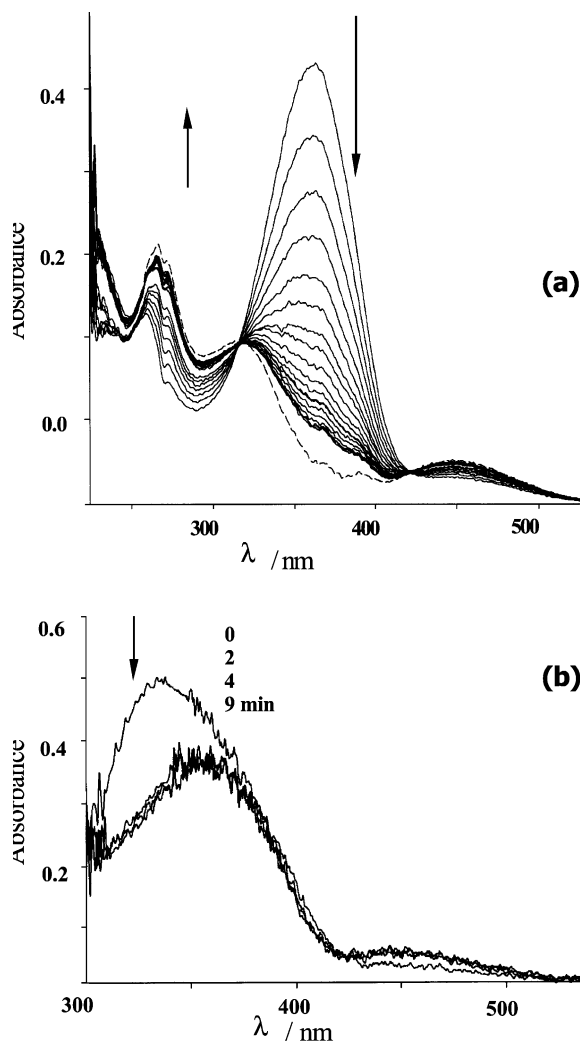


Fig. 90. Spectral changes for (a) solution and (b) LC film of dendrimer **106** during UV-irradiation (365 nm, mW/cm^2). In the case (a) spectra were recorded each 10 s of irradiation. The dashed line corresponds to a photostationary state ($T = 25 \text{ }^\circ\text{C}$) [320].

electron transition to the long-wavelength spectral region during the first seconds of UV-irradiation indicates the breakdown of these aggregates in the course of $E-Z$ isomerization.

As in LC films, the process of $E-Z$ isomerization in amorphizable films is thermally and photochemically reversible. Irradiation with visible light leads to an increase in the absorption in the spectral region of the $n-\pi^*$ electron transition but, compared with fresh film, its maximum is slightly shifted to a longer wavelength region (Fig. 93). This behaviour is related

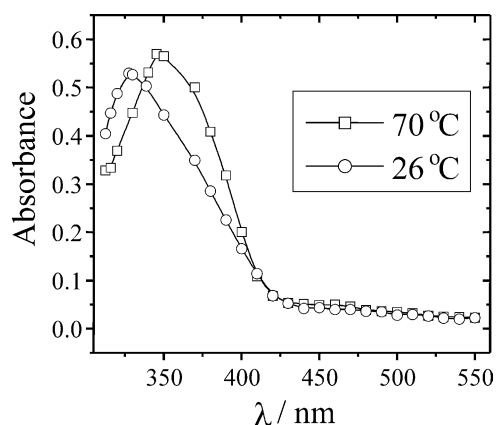


Fig. 91. Absorbance spectra of dendrimer **106** film in the SmA phase and in the isotropic melt ($T = 70\text{ }^{\circ}\text{C}$) [304].

to the fact that the development of aggregates requires a certain time; in the above-mentioned case, the initial profile of the corresponding spectra is restored within several minutes.

The photoorientation of azobenzene chromophores in amorphous films of dendrimer **106** upon irradiation with polarized light were studied in Ref. [320]. Upon irradiation with polarized UV-light (365 nm), only $E-Z$ photoisomerization takes place, and photoorientation is almost absent. Quite a different situation is observed when the dendrimer film is irradiated by an Ar laser (488 nm). A well-pronounced linear dichroism develops (Fig. 94). In this case, the maximum values for dichroism and order parameter are rather low ($D = 0.16$ and $S = 0.11$) when compared to the

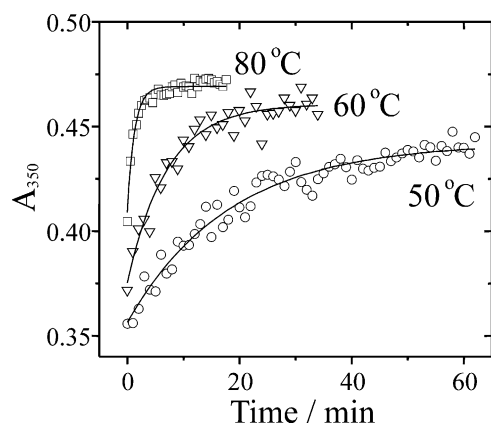


Fig. 92. Absorbance growth for the LC film of the dendrimer **106** at different temperatures during annealing [320].

comb-shaped polymers containing azobenzene side groups [324]. This evidence implies that the degree of photoorientation of azobenzene groups is low, and the photoinduced parameter of orientational order is much lower than order parameter of the SmA mesophase.

As compared with UV-irradiation (365 nm), light irradiation with a wavelength of 488 nm does not lead to Z -isomers of azobenzene groups since, in this spectral region, the extinction coefficient of a Z -isomer is much higher than that of an E -isomer [326]. In this case, photoorientation is provided by the photoselection of chromophores. This process is related to the transition of the groups into the excited state, with the transition moment parallel to the electric field vector \vec{E} of polarized light. Once irradiation ceases, the values of linear dichroism and order parameter tend to decrease (Fig. 95). This behaviour is associated with a relatively low dendrimer viscosity even at room temperature. Upon a prolonged annealing (several hours), dichroism decreases to zero.

The kinetics of photoorientation in the UV-irradiated film of dendrimer **106** with a high content of azobenzene groups in Z -form is presented in Fig. 96. The limiting values of the photoinduced order parameter almost coincide with those of the non-irradiated film. In this case, however, the rate of photoorientation is much higher. This trend is related to the fact that, as was mentioned earlier, $E-Z$ isomerization leads to the breakdown of aggregates, which in principle may hinder the processes of re-orientation.

In order to investigate the possible influence of dendritic matrix size on the photoorientation of azobenzene chromophores, the amorphous films of dendrimers **100–102** (Fig. 72) were prepared by spin coating and investigated in Ref. [327]. It should be emphasized that all such dendrimers form crystalline phases only. UV-irradiation leads to marked spectral changes in these films; these changes are primarily related to the $E-Z$ photoisomerization of azobenzene groups. The character of photochemical transformations was almost independent of the number of generations. Upon polarized UV-irradiation of the amorphizable films of dendrimers **100** and **102**, one may observe the photoinduced orientation of azobenzene groups in the direction perpendicular to

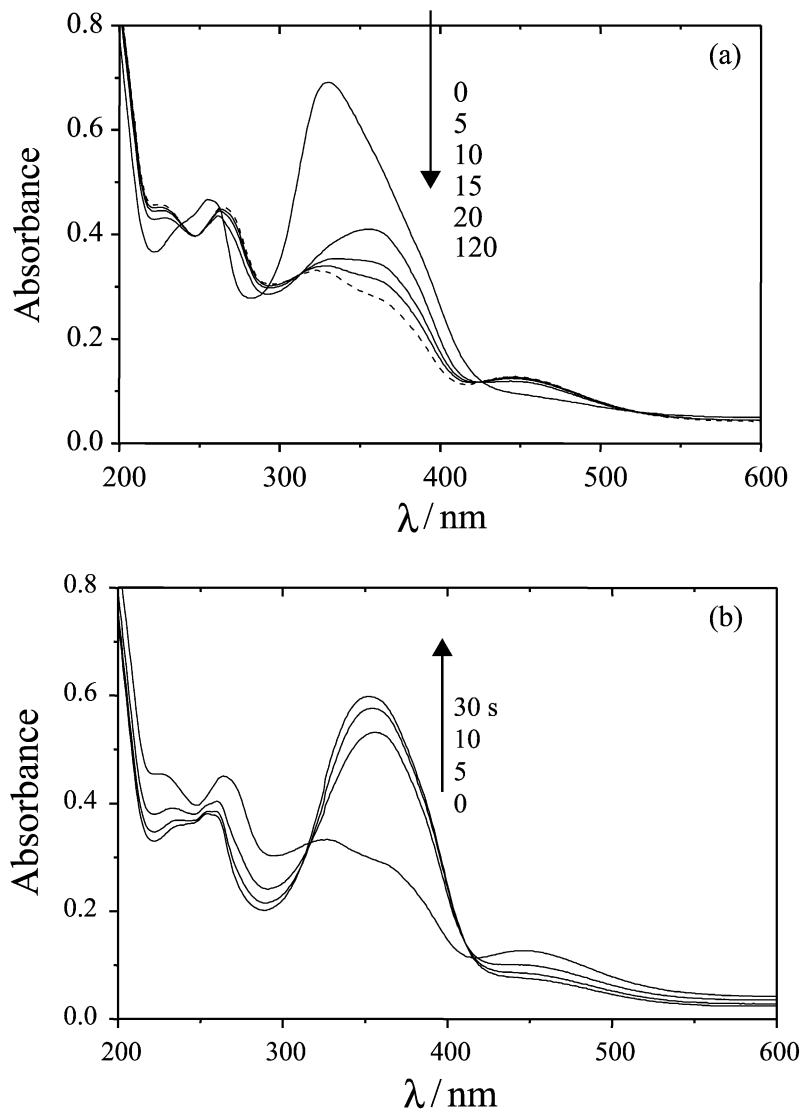


Fig. 93. Spectral changes for spin coated amorphous film of dendrimer **106** during (a) UV-irradiation (365 nm) and (b) visible light irradiation (436 nm) [320].

the direction of the incident light vector \vec{E} (Figs. 97 and 98). This trend manifests itself in a well-defined linear dichroism of the UV-irradiated films (Fig. 97).

Nevertheless, in our opinion, the following unorthodox features of photoorientation processes in such systems were observed. First, the kinetics of this process, the level of linear dichroism, and the induced order parameter are independent of the dendrimer's generation number. This finding suggests that, as compared with the solutions, in the amorphizable

films of dendrimers the local surrounding of azobenzene groups is almost the same and is independent of the generation number. The second feature is related to the absence of any photoorientation upon the polarized argon laser irradiation (488 nm). This finding appears to be rather unexpected, especially if one takes into account the fact that, for the first-generation dendrimer with propoxyazobenzoate end groups, quite the opposite behaviour was seen (Fig. 94). Upon polarized UV-irradiation, almost no

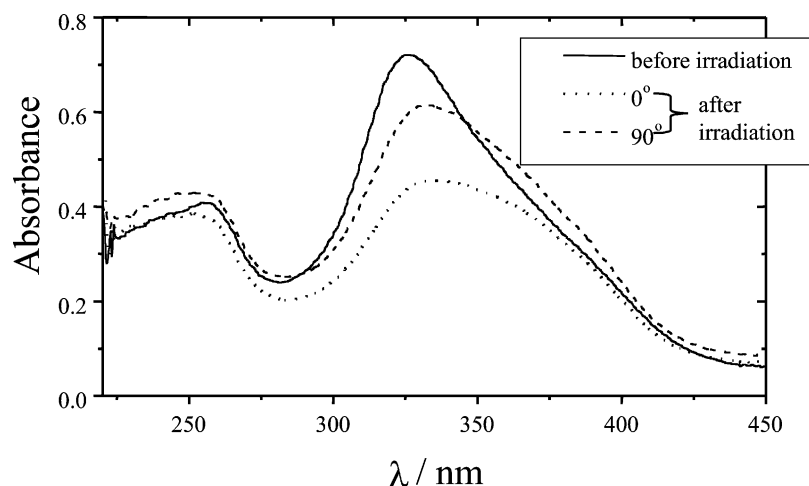


Fig. 94. Linear dichroic spectra measured for spin coated film of dendrimer **106** before irradiation and after irradiation by Ar laser (100 mW/cm^2) during 60 min; in the last case spectra were recorded along and perpendicular to electric vector ($T = 22 \text{ }^\circ\text{C}$) [320].

photoorientation takes place, whereas the argon laser irradiation is accompanied by the development of orientation. This difference is likely to be related to the presence of different substituents at the azobenzene fragments. For the dendrimers studied, the two alkoxy substituents are located in the para position, whereas for the dendrimer **106** (Fig. 76), one substituent is presented by the electron-accepting carboxylic group. In this case, the *E*-isomer shows a well-pronounced longitudinal dipole moment, and this factor is likely to provide such a marked

difference in the photoorientational behaviour of dendrimers. Similar tendencies were described in Ref. [328], where the photooptical studies of the comb-shaped polymers containing azobenzene fragments with end substituents of different polarities in benzene rings were studied.

One should also mention an unorthodox character of the kinetics of changes in the order parameter of azobenzene groups under the action of the polarized UV-light (Fig. 98). Initially, the order parameter

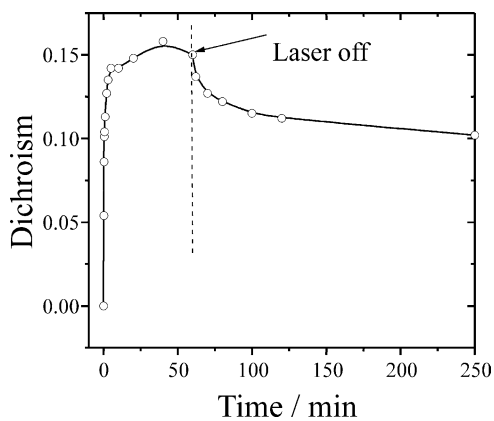


Fig. 95. Changes of linear dichroism of the amorphous film of dendrimer **106** (100 mW/cm^2) during Ar laser irradiation. Dichroic ratio was calculated at 332 nm [320].

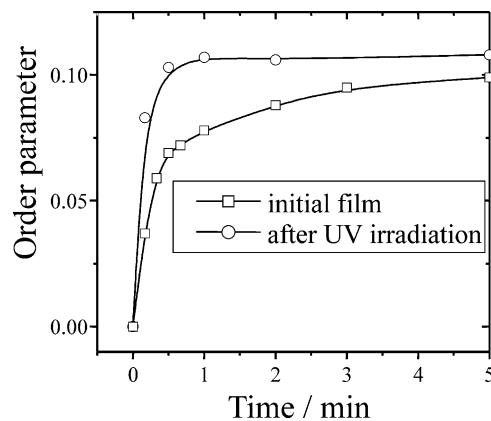


Fig. 96. Changes of the order parameter during Ar laser irradiation (100 mW/cm^2) for amorphous films of dendrimer **106** non-irradiated and irradiated previously by UV-light (365 nm, 2 min) calculated at 332 nm [320].

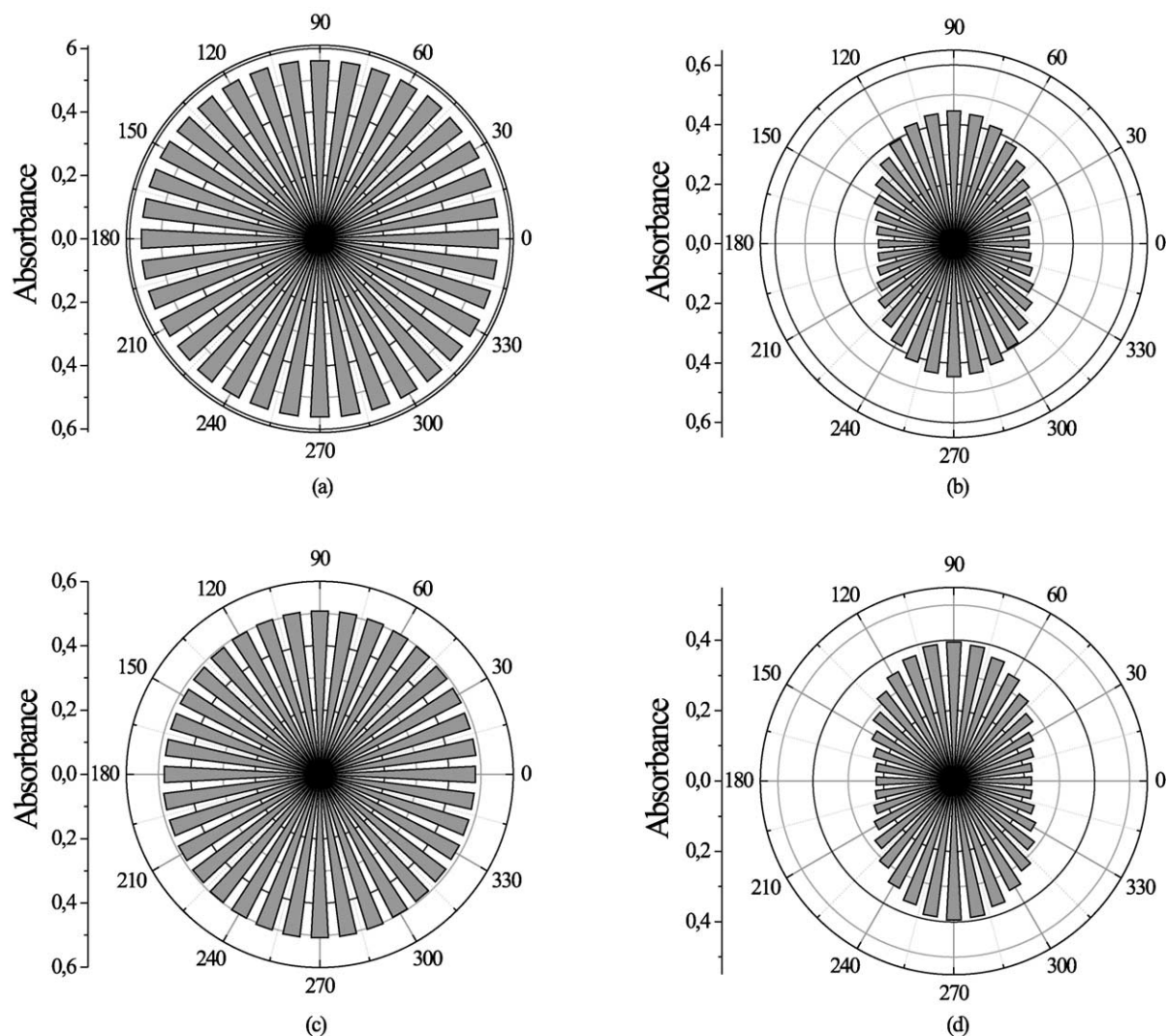


Fig. 97. Polar diagrams for ((a) and (b)) dendrimers **100** and ((c) and (d)) **102** obtained ((a) and (c)) before and after ((b) and (d)) irradiation with polarized UV-light during (b) 140 s and (d) 90 s; ($T = 22\text{ }^{\circ}\text{C}$). Polar diagrams were plotted for $\lambda = 328\text{ nm}$ [327].

increases, and its maximum level is attained (about 0.2); then, the behaviour becomes rather unexpected and decreases in value almost to zero. A similar trend was recently observed for polyacrylic homopolymers containing azobenzene groups [329]. This behaviour is likely to be related to an increase in the *Z*-isomer upon UV-irradiation. Taking into account the fact that the *Z*-isomer is characterized by an exceptionally low anisotropy, prolonged UV-irradiation leads to a complete degeneration of the orientational order, increasing the concentration of the *Z*-isomer in the system.

5. Conclusions and outlook

This review presents state-of-the-art information in the development of advanced, optically controlled polymer systems based on photochromic LC polymers and their blends, with low-molar-mass chiral compounds and photochromes acting as the specific switches. Furthermore, a novel family of photosensitive LC dendrimers containing mesogenic photochromic groups on the periphery of ‘ball-molecules’ and their photochemical behaviour are described.

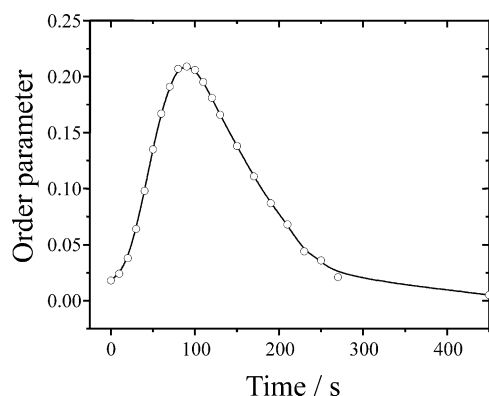


Fig. 98. Change of order parameter for dendrimer **102** during polarized UV-light irradiation calculated at 328 nm [327].

In a certain sense, light irradiation can be used as a very efficient ‘controlled external field’ for locally regulating the supramolecular structure and optical properties of polymer films. Taking into account the variety of laser sources covering a wide range of intensity and wavelengths, the development of polymeric materials with light-controlled optical properties offers considerable advantages in comparison with solving the same tasks using electric and magnetic fields. The use of polymers also advances the advantage of easy fabrication and the possibility to shape polymers into the desired structures by molecular engineering. The relative simplicity and greater convenience of recording and reading devices based on the use of photochromic thin polymer films, and the absence of stringent requirements for high-current electrodes (as in the case of LC electrooptical cells), is also worthy of notice.

The design and creation of highly sensitive optically controlled (photoaddressed) polymer-based materials with photochemical control of their molecular, supramolecular structure, and desired functions is now a very important task. Incorporation of photochromic molecules or their fragments into macromolecules leads to the development of photoresponsive systems, the properties of which can be easily manipulated by light. Interest in photochromic materials is related to by reversible (or irreversible) changes in the optical properties and colour; such materials appear to be very attractive and fascinating. At the same time, photochromism in polymer materials is responsible for various changes in their properties, such as optical and chemical, electrical,

and other bulk characteristics. (However, this review was primarily focused on the optical properties of polymeric materials.) Photochromic LC polymers are of special interest due to their complex molecular architecture, which is responsible for the formation of self-assembled supramolecular anisotropic structures, such as nematic, smectic, and cholesteric structures.

The above data vividly illustrate the effect of the structural organization of mesophases on the photo-optical behaviour of photochromic side chain LC polymers and their blends with low-molar-mass dopants. As for photoresponsive dendrimers, studies into their photooptical behaviour as a function of generation number and mesophase types is at its early stage.

All side chain LC polymers containing mesogenic and photochromic groups, or mesogenic and chiral-photochromic groups, are structurally and functionally integrated systems that show simultaneously liquid crystalline, chiral, and photochromic properties. In this case, light first switches the photochromic groups, which undergo photochemical transformations (isomerization, cyclization, cross-linking, etc.) leading to significant configurational and/or conformational changes of the fragments. Then the neighbouring structural fragments are rearranged, so that the changes in the molecular and supramolecular structure of initial sample take place. Reconstruction of the matrix is a complex, multistage process with a cooperative character that involves the motion of both side chain groups and backbone segments. This process leads to a serious modification of the supramolecular structure, including orientation of side groups (azobenzene-containing copolymers), cross-linking (cinnamate copolymers) of amorphous or nematic matrix, or changes in the helix pitch of the cholesteric phase. In more complex multifunctional polymer systems containing at least two different photochromes, light irradiation can lead to a dual photochromism which allows one to record the optical information of the two types on one sample: first, by varying the helix pitch due to short-wavelength light irradiation, and second, due to a photoinduced birefringence using polarized light of the visible range of the spectrum.

The feasibility to fix local changes in the molecular and supramolecular structure induced by light irradiation opens pathways for the development of

new types of polymeric materials with photomodulated supramolecular structure and controlled local optical properties: birefringence, refractive index, selective light reflection, colour characteristics, etc. The macromolecular nature of photochromic LC polymers offers fascinating advantages for the creation of solid glasses, thin films, and coatings with the desired and photoregulated optical properties, such as spectrum band filters, efficient polarizers, retarders, phase plates, and compensators. Optical storage can be provided by freezing the LC director into an aligned state due to the photopolymerization of the selected reactive photochromic monomers leading to the cross-linked samples. All these directions of research deal with the development of advanced polymer-based optical data storage systems in both black–white and colour versions for optics, optoelectronics, holography, etc.

At the same time, this class of photosensitive polymers, capable of reversible changes in their optical properties, offers new materials for optically controlled reverse operation systems, optical sensors, actuators, and transducers, which can be widely used together with the existing low-molar-mass ferromagnetic and magneto-optical materials.

Rapid progress in investigations related to the development of field-responsive polymers and other polymer-based ‘smart’ materials is evident. It should be noted that high expectations concerning the practical application of such materials are not always justified, because the polymer systems are characterized by a rather slow response to external factors, which is related to the slow rates of relaxation processes in polymers. On the other hand, the use of the blend compositions of polymers with low-molar-mass dopants, oligomers, lyotropic LC systems, and gels gives some benefits against excessive skepticism with respect to the operational speed of the systems based on these materials. The search for new practical applications not requiring ‘instantaneous’ response would favour further progress in the development of new polymeric smart materials.

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