Cholesteric Polymer Liquid Crystals and their Optical Properties

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Cholesteric Polymer Liquid Crystals and their Optical Properties

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Synthesis of a number of cholesteric polymer liquid crystals (PLCs) is reported. Phase behavior and structures of thermotropic cholesteric PLCs are discussed. Optical properties of such materials are reported also, including their textures, effects of composition variation on the helix twisting power and temperature dependence of the helix pitch. Effects of molecular mass variation on the optical properties of PLCs are determined. Prospects of applications of these materials are pointed out.

Keywords: Polymer liquid crystals; PLCs; synthesis of cholesteric PLCs; phase behavior of thermotropic cholesteric PLCs; optical properties of PLCs; helix twisting power; temperature dependence of the helix pitch; molecular mass effects in PLCs; applications of PLCs

1. INTRODUCTION

Long time ago, polymers liquid crystals (PLCs) with helical super-molecular structure have attracted the attention of many scientists involved in studying chemistry and physics of macromolecular compounds. One family of PLCs is provided by cholesteric PLCs-with their ability to produce supermolecular structures characterized by a helical organization with a certain identity period. This spatial organization is responsible for unique optical properties of cholesteric PLCs such as selective reflection of light at different wavelengths, very high optical activity, high sensitivity of selective reflection of light to

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temperature variations and to the action of external electrical and magnetic fields [1, 2].

Historically, the name *cholesterics* arose from the fact that cholesteric structures were first identified for the derivatives of cholesterol [3]. As was shown in later publications, cholesteric helical mesophase is induced in the nematic phase *via* the introduction of small amounts of chiral additives (so-called dopants). Traditionally, cholesterol-containing compounds are referred to as *cholesterics*, whereas *other chiral systems with the nematic ordering are referred to as chiral nematics* (even though, in some cases, the latter compounds are also called *cholesterics*). In this paper, the preference is given to the term *cholesterics*, but with a clear understanding that cholesterics and chiral nematics are characterized by quite similar structures. However, discussing the results of some particular publications, we will adopt the original terminology used by the authors.

Let us note that, more than one hundred years ago, just cholesteric type of mesophase was first identified for low-molecular-mass crystals (cholesteryl benzoate) [3], and much later this type was described for high-molecular-mass lyotropic systems (solutions of poly-γ-benzyl-L-glutamate) [4, 5]. Even first attempts to prepare thermotropic LC polymers were closely related to studying the development of just cholesteric polymers [6–8] by introduction of optically active molecules of cholesterol as side groups into the polymers of acrylic and methacrylic series.

The recent advances concerning the development of chiral systems based on PLCs with helical structure allowed preparation of a new class of polymeric cholesterics and ferroelectrics, which may be considered as the promising materials for microelectronics, optics, holography, data storage systems as well as for the preparation of the promising thermochromic and electrochromic materials, piezoelectrics and pyroelectrics. At the present time, and abundant information concerning synthetic aspects of the preparation of the chiral PLCs, structure and specific features of their thermal and optical properties, behavior of cholesterics and ferroelectrics under the action of electrical fields is available [9–17].

In this article, we are not going to provide a comprehensive description of all milestones and history of scientific activities in this particular direction, and our principal attention is focused on most recent

studies and advances. We restrict our consideration to *cholesteric polymers* (to be more precise, to *chiral nematics*), whereas lyotropic LC cholesterics and LC ferroelectrics prepared from chiral smectics are beyond the scope of this review. Let us note that, at the present time, a correct and unequivocal interpretation of some evidence discussed in this review is not available but we believe that this approach to the description of the state-of-the-art will stimulate further interest to this intriguing and challenging area of polymer science.

2. GENERAL DESCRIPTION OF THE SPECIFIC FEATURES OF THE STRUCTURE AND OPTICAL PROPERTIES OF CHOLESTERICS

First of all, let us mention, that the principal condition providing the development of cholesteric phase is associated with the presence of an asymmetric (chiral) center in molecules, which is able to produce a helical supermolecular structure. It is worth emphasizing that, as a rule, optically active compounds with the traditional type of chirality, that is asymmetric carbon atom, which is able to provide the appearance of two different spatial forms of a molecule, two optical antipodes, are used as the chiral fragments of LC cholesterics.

However, as will be shown below, another type of spatial isomerism, which is referred to as *atropoisomerism* may be applied. This phenomenon is associated with a hindered free rotation of certain chemical fragments about a conventional carbon – carbon bond. Chirality of such compounds is associated with the possible existence of conformational isomers produced by the hindered rotation of bulky groups. As a result, two optically isomers appear, and each of these isomers may be used as an individual chiral compound. The only high-molecular-mass representative of this class of compounds is provided by binaphthyl-containing cholesteric PLCs, which were first described by our team together with our Danish colleagues [18].

For monomer LCs (MLCs), the structure of cholesterics is modeled as a set of quasinematic layers (Fig. 1a). According to this model, in the neighboring layers, the axis of principal orientation of molecules (director **n**) is turned by angle φ on moving along the axis of cholesteric helix Z (Fig. 1b). The as-formed helical structure is

(a)   (b)
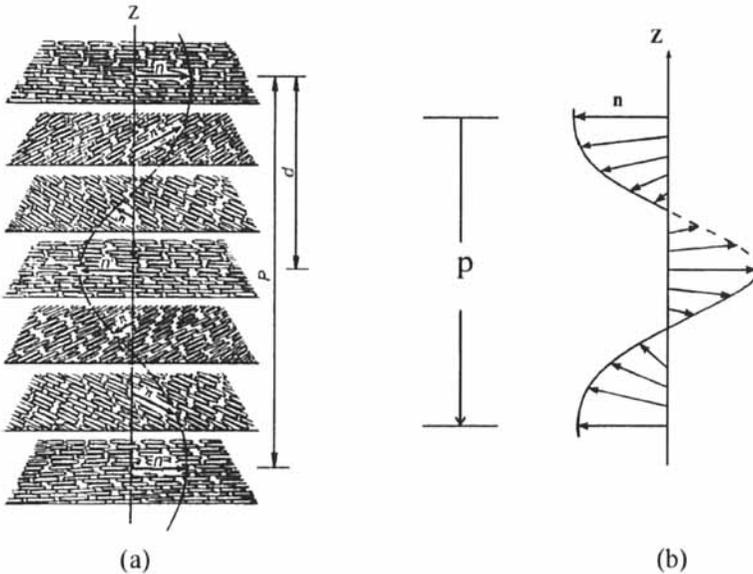
FIGURE 1   Schematic representation of (a) helical twisting of molecules and (b) precessing of the local director n around an axis Z in cholesteric phase.

characterized by periodicity along the axis of cholesteric helix. The helix pitch P is controlled by the chemical nature of molecules (as well as by a number of some other factors) and is associated with the rotation of the director by angle 2π. Hence,

$$P = 2\pi r/\varphi \tag{1}$$

where φ is the angle of twisting of the helix, and r is the distance between quasinematic layers, which corresponds to the mean distance between the neighboring molecules along the axis of the helix [1, 2].

Therefore, such helical supermolecular structure of cholesteric mesophase is responsible for the reflection of light with wavelengths, which obey the Wulff-Bragg condition:

$$m\lambda = \bar{n}2d \sin \vartheta \tag{2}$$

where m stands for the number of order; ϑ is the angle between the incident beam and cholesteric plane; $\bar{n}$ is the average refractive index; d

is the period of change in the optical properties, which is equal to $P/2$ due to the nonpolarity of the structure (n and, $\bar{n}$ are equivalent).

Helical structure of cholesterics is responsible for their unique optical properties. Some of them are reviewed below:

1. Since periodic cholesteric structure reflects the incident light similar to a conventional diffraction grating, the selective reflection wavelength λ is controlled by the angle of incidence. For normal incidence of light ($\vartheta = 90°$), the first order of diffraction is observed, and expression (2) may be written as:

$$2\bar{n}d = \lambda_{max} \quad \text{or} \quad \bar{n}P = \lambda_{max} \tag{3}$$

In other words, at a given angle of incidence, selective reflection wavelength is controlled by the pitch of the helix. This situation is realized only when all molecules (or mesogenic fragments) involved in the helix lie in the plane of the supporting surfaces (usually, glasses), whereas the axis of helix is perpendicular to them. This texture is referred to as planar texture (see Section 5.1). Considering optical aspects, this planar texture operates as a plate of the negative single crystal, which is cut parallel to the optical axis;

2. Cholesteric structure is characterized by circular dichroism: the light selective reflected by cholesteric liquid crystal is circularly polarized. The direction of circular polarization of the reflected beam coincides with the direction of the twisting of cholesteric helix. Let us note that, in this case, 50% of the light of the same wavelength but with opposite circular polarization passes through liquid crystal without any changes (Fig. 2);

3. One of the principal features of cholesteric structure is associated with a strong rotation of polarization plane, which may be as high as $10^4 \deg \cdot mm^{-1}$. Note that, in conventional organic liquids, this parameter is provided only by chirality of molecules and does not exceed $10^2 \deg \cdot mm^{-1}$. In this case, rotation of polarization plane is controlled by the wavelength of incident light: anomalous dispersion of rotational ability is observed;

4. In many cases, the pitch of cholesteric helix is primarily controlled by temperature. Theoretical description of the temperature dependences of helix pitch P was performed in terms of the different theoretical models based on molecular-statistical theories. However, so far, there

λ

↑ 50% L

P   L-helix

↓ 50% R
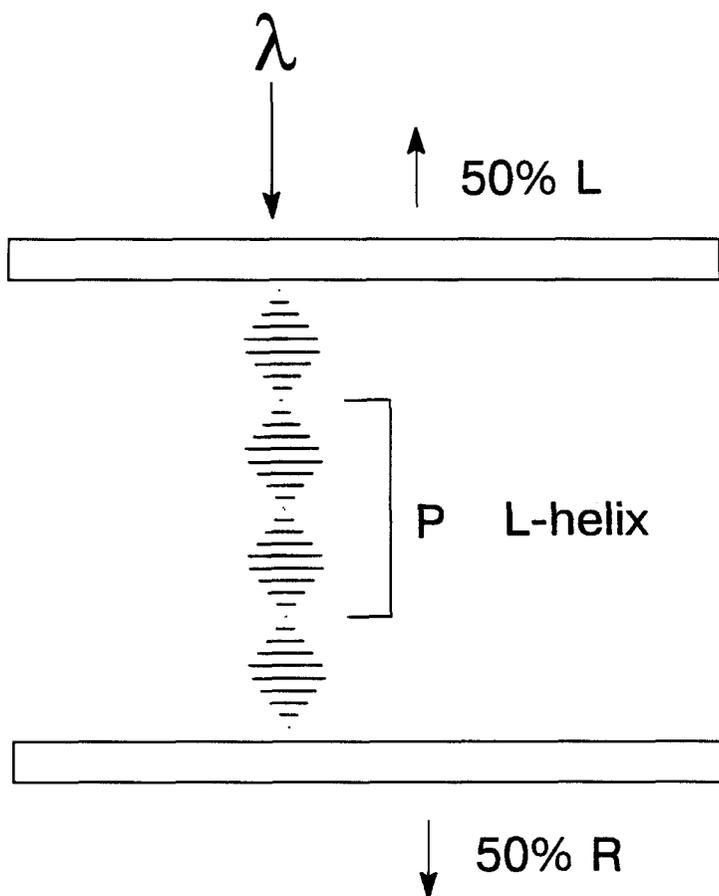
FIGURE 2 Schematic representation of the selective reflection of left-handed, circularly polarized light (L) by the cholesteric mesophase with L-helix. The right-handed circularly polarized light (R) passes through the sample.

is still no universal theory providing a correct description of temperature dependences of P in the wide temperature range as a function of molecular structure of both low-molecular-mass and high-molecular-mass compounds.

At the same time, high sensitivity of the pitch of the helix to temperature changes as well as to the action of electrical and magnetic fields offers substantial advantages for practical application of such

LC polymers as thermometers and thermoindicators for techniques and medicine [2, 9, 13, 16].

3. PRINCIPLES OF THE SYNTHESIS OF CHOLESTERIC POLYMERS WITH MESOGENIC GROUPS

At the present time, various molecular structures of thermotropic LC polymers providing cholesteric mesophase are available. However, chiral LC polymers containing mesogenic groups either in the main chain or in side chain (comb PLCs) are better characterized. Figures 1a and 1b show the schematic representation of these polymers.

As follows from Figure 3a, principal structural elements are rigid mesogenic groups, which are arranged into a linear chain by means of the flexible (usually, aliphatic or oxyaliphatic) fragments of macro-molecules (spacers). In the case of the comb-shaped polymers, meso-genic groups in side groups of the branched macromolecules are attached to the main chain *via* the above flexible fragments, *i.e.*, *via* spacers (Fig. 3b).

Usually, main-chain cholesteric PLCs are prepared by polyconden-sation (copolycondensation) of bifunctional derivatives containing both rigid mesogenic fragments and flexible spacers. Typically, chiral centers are involved in flexible spacers [19], even though their location in aromatic rings of mesogenic groups is also allowed [20].

In the comb PLCs usually, side chiral mesogenic groups (such as derivatives of cholesterol or phenylethylamine) are used [21, 22]. In some cases, chiral groups are involved in spacers when aliphatic opti-cally active bifunctional alcohols and acids are used. In rare cases, optically active sites are introduced into the main chains of the comb-shaped macromolecules [23].

To prepare comb PLCs, different polymerization methods are applied: (a) homopolymerization of chiral mesogenic monomers; (b) copolymerization of nematogenic monomers (monomers, the homo-polymers of which are able to produce nematic phase) with chiral meso-genic and nonmesogenic monomers; (c) copolymerization of chiral mesogenic monomers with nonmesogenic monomers (Figs. 3a–c).

Furthermore, these polymers may be prepared by interaction of reactive polymers with chiral MLCs or with their mixtures; such

reactions are usually referred to as polymer analogous reactions (Figs. 4d). The particular case of this reaction may be provided by the reaction of initial nonchiral LC polymer with chiral reagent, which allows transformation of a certain fraction of the side groups into chiral fragments. The typical example of this chemoselective reaction is the

(a)

(b)

(c)
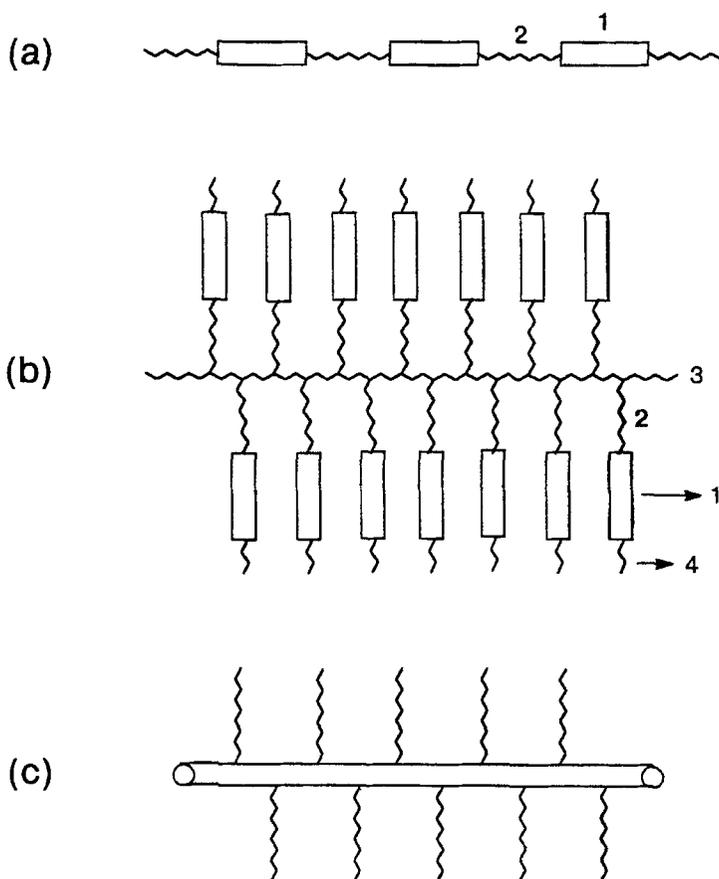
FIGURE 3   Schematic representation of the major types of macromolecules forming the cholesteric mesophase. (a) main chain LC polymers; (b) side chain LC polymers (in both the cases the chiral centre (or chiral fragment) can be disposed in any part of the macromolecule; (1) mesogenic groups; (2) spacer; (3) backbone and (4) terminal group; (c) rigid or semirigid chain LC polymers with flexible branches (chiral groups are located in the backbone).

Polymerization

(a)

Chiral
mesogenic
monomer

(b)

Mesogenic
monomer

(c)

Chiral
nonmesogenic
monomer
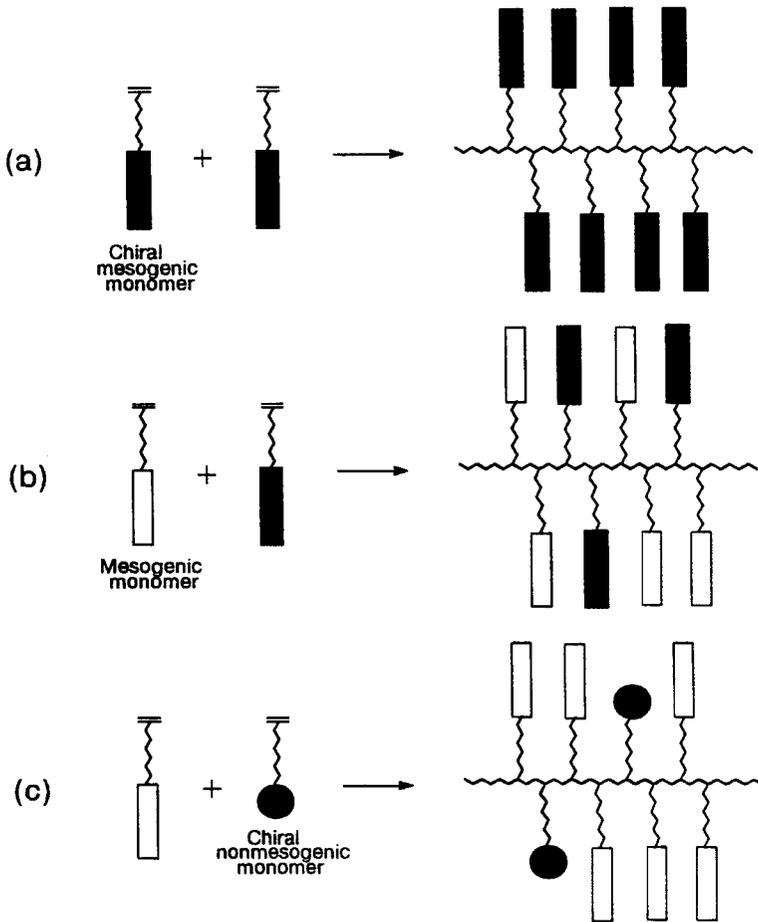
FIGURE 4   Synthesis of cholesteric LC polymers with mesogenic side groups: (a) homopolymerisation of chiral mesogenic monomer; (b) copolymerisation of chiral meso-genic and nematogenic monomers; (c) copolymerisation of chiral nonmesogenic and mesogenic monomers; (d) polymeranalogous reaction (covalent bonding); (e) ion-ex-change reaction and (f) hydrogen bonding; (chiral groups can be located in any part of the macromolecules – mesogenic group, spacer or terminal group).

oxidation of sulfide groups of polyacrylic side-chain polymer with chiral sulfoxide groups to yield chiral polymer with the following structure [24]:

Polymeranalogous Reaction

(d)

A, B -functional groups

Ion- and Hydrogen Bonding

(e)   (f)
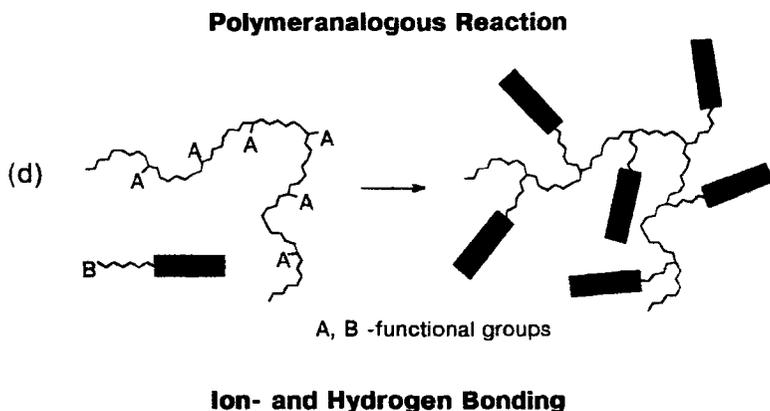
FIGURE 4   (Continued).
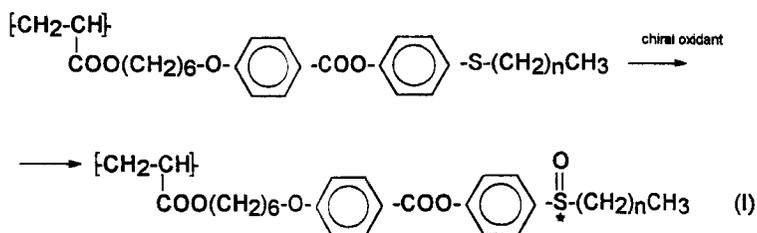
Let us emphasize that, in the case of the comb PLCs the development of cholesteric mesophase is controlled by the ordering of mesogenic fragments rather than main chains as was observed for main-chain polymers. Usually, as in the case of MLCs, rodlike mesogenic groups are used.

In addition to thermotropic PLCs, cholesteric type of mesophase is also provided by a great number of lyotropic systems primarily based on natural rigid-chain polymers (cellulose ethers and esters), biopolymers (DNA, RNA, some viruses) as well as synthetic polypeptides.

In certain solvents (often called helical solvents), macromolecules of the above compounds exists as the α-helices (rigid rods), which are

stabilized by intramolecular hydrogen bonds. According to Flory [25], at a certain critical concentration of polymer, in these solvents, separation of the solution to isotropic and anisotropic LC phases takes place. However, even though the consideration of liotropic systems is beyond the scope of this review, we would like to emphasize the follow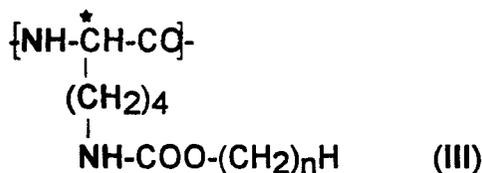ing observation. In many cases, removal of the solvent from cholesteric lyotropic systems is not accompanied by any destruction of cholesteric structure, which provides a clear example of the "frozen" thermotropic cholesteric mesophase with rather high stability in the wide temperature range [15, 16].

Furthermore, in recent years, a number of rigid-chain or semirigid-chain polymers (for example, n-alkyl derivatives of poly-L-glutamic acid, N^{α}-acyl derivatives of poly (N^{ε}-methacryloyl-L-lysine as well as n-acyl derivatives of hydroxypropyl cellulose, $etc.$) were synthesized. The main chains of these polymers are characterized by helical conformation and contain chiral sites providing the development of cholesteric mesophase [26–28]. As an example, molecular structures of poly-α-glutamates (II) [26] and derivatives of poly (N^{ε}-methacryloyl-L-lysine) (III) [27] with different lengths of side groups are presented below:

$$\{NH\text{-}\overset{*}{C}H\text{-}CO\}\text{-}$$
$$(CH_2)_2\text{-}COO\text{-}(CH_2)_nH \qquad \text{(II)}$$
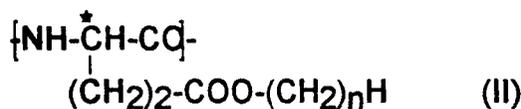
where n = 5, 6, 8, 10, 12, 14, 16, 18
and

$$\{NH\text{-}\overset{*}{C}H\text{-}CO\}\text{-}$$
$$(CH_2)_4$$
$$NH\text{-}COO\text{-}(CH_2)_nH \qquad \text{(III)}$$

where n = 5, 9, 17.

Figure 3c shows the schematic representation of macromolecules of such polymers. Even though, in this case, LC phase is provided by rodlike macromolecules, usually, they do not contain any typical

mesogenic groups and may be classified as an independent third group of chiral LC systems. In this case, flexible side n-aliphatic side groups function as a specific plasticizing solvent, which is able, on one hand, to lower high (often hypothetical) melting temperatures of such rigid-chain polymers and, on the other hand, to provide favorable thermo-dynamic and kinetic conditions for the development of cholesteric mesophase. In essence, such systems are similar to lyotropic systems, in which rigid α-helical macromolecules are dissolved in the hydrocarbon matrix of side chains. However, in contrast to the comb-shaped poly-mers with mesogenic groups in side chains, in this case, the development of cholesteric helix is associated with the packing of the rigid main chains.

The development of cholesteric phase is also allowed when chiral center is involved in the side chain. This situation was observed for chiral homopolymers and copolymers of (R)- and (S)-2,6-dimethyl-heptyl isocyanates (IV) [29]:

$$\{N-C\}_{}^{O} $$

$$CH_2-\overset{*}{C}H-(CH_2)_3-CH(CH_3)_2 \qquad (IV)$$

$$CH_3$$
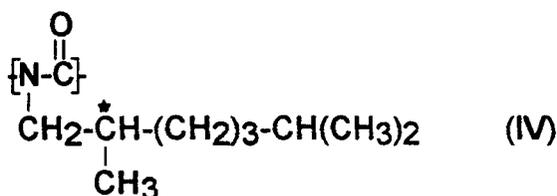
Obviously, molecular structure of polymer cholesterics is not restricted by three types of structures shown in Figure 3. In this case, we only considered a general description of the architecture of the syn-thesized and well-studied thermotropic polymers and copolymers with cholesteric mesophase. At the same time, one may advance the follow-ing *a priori* conclusion that the potential polymer cholesterics will show a variety of new molecular structures.

Introduction of mesogenic groups into main chains and side groups of macromolecules, combination of rigid rodlike and disklike meso-gens in one macromolecule containing chiral centers or antropoisomers in any of the chain fragments as well as the combination of these frag-ments within one and the same macromolecule offer fascinating

advantages for designing new chiral systems. Let us note that, in addition to "covalent binding" between chiral fragments and polymer chain, chiral fragments may be also attached to polymer main chains *via* hydrogen and ionic bonds (Figs. 4e and 4f). As far as we know, such polymers are not available yet, but their appearance in the near future is beyond any doubts.

Finally, let us consider another group of chiral thermotropic systems based on the cross-linked LC polymers. In such chiral networks, optically active fragments may be involved both in main chains and side groups [30, 31]. Further studies of chiral elastomers are of great scientific and practical interest because they will allow preparation of rubbery elastic polymer materials with unique optical properties.

Preparation of chiral macromolecules containing enantiomers with different signs of optical rotation will increase the number of optically active compounds, which allow one to control not only the intensity but also the direction of optical rotation providing thus "stereoselection" of optically active polymer materials.

## 4. PHASE BEHAVIOR AND STRUCTURE OF THERMOTROPIC CHOLESTERIC PLCs

In most publications concerning the structural studied of thermotropic polymer LC cholesterics, principal attention was focused on polarization microscopic observations and identification of a specific colouring (*i.e.*, selective reflection of light) in a certain spectral range, which proved the realization of cholesteric mesophase.

A correct quantitative structural description (for example, by using the data of X-ray analysis) is not available, and this is likely to be related to "uninteresting" X-ray diffraction patterns, which show only diffuse scattering at high angles, which is also characteristic of nematic polymers.

Nevertheless, a thorough examination of the published evidence concerning the structure of main-chain and comb-shaped cholesteric polymers unequivocally shows that, in the latter case, some unique types of structural organization (they will be discussed later) are allowed. We believe that the discovery and identification of so-called layered cholesterics are primarily provided by numerous investigations focused

on the characterization of comb-shaped polymers rather than by the fact that comb-shaped polymers constitute a peculiar class of cholesteric systems (even though one may hardly ignore this possibility).

The point is that chiral main-chain polymers readily crystallize and produce cholesteric mesophase at high temperatures approaching the temperatures of chemical degradation, and this makes their studying rather difficult. In connection with this, let us discuss only two cases. For example, chiral homopolyesters containing azoxy groups (V) [33] and copolyesters containing bulky mesogenic groups based on *L*-camphoric acid (VI) [32] are able to produce cholesteric mesophase at temperatures above 220°C:
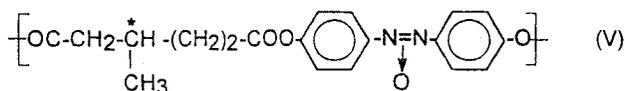
T_m 221 Ch 295 I
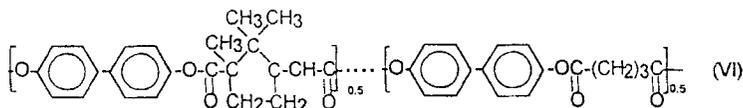
T_m 225 Ch 290 I

In order to provide the existence of cholesteric mesophase at lower temperatures, usually, flexible fragments (spacers) with higher length or aliphatic branched spacers are used [34]. However, let us note that, only in rare cases, crystallization may be prevented. In other cases, after cooling polymer from its cholesteric phase, even when the development of planar texture with the selective reflection of light of a given wavelength is realized, polymer either assumes smectic phase and then experiences crystallization or the structure with a strong light scattering is produced. In other words, in the case of crystallizable main-chain polymers, on cooling the samples, the development of planar texture of cholesteric with its unique optical properties is not allowed.

Quite different situation is observed for the comb-shaped cholesteric polymers. To say nothing about an abundant experimental evidence

obtained in this direction, two important features of these polymers should be mentioned.

First of all, as compared with the main-chain polymers, crystallization is not typical for all comb-PLCs. Usually, on cooling from LC phase, most of the PLCs preserve their structural type of mesophase, which is characteristic of this particular compound. When more than one type of mesophase is observed, on cooling, lower-temperature modification will be preserved. For example, when a PLC is able to produce both cholesteric and smectic types of mesophase, on cooling, smectic mesophase is fixed. From the view point of optical properties of this polymer, this situation seems to be rather unfavorable: as in the case of the crystallization of mainchain polymers, the textures with a strong light scattering are produced.
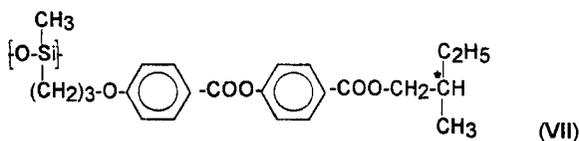
The second peculiar feature is associated with the comb-shaped structure of macromolecules, when the main chain functions as a certain structuring factor, which controls the layered ordering of side groups, *i.e.*, assists the development of the smectic type of mesophase [35, 36].

Taking into account both specific features, let us consider the development of helical supermolecular structure in the comb-shaped cholesteric polymers and let us answer the question how to preserve the unique optical properties of cholesterics in the solid phase under normal conditions when cholesteric mesophase is produced at higher temperatures.
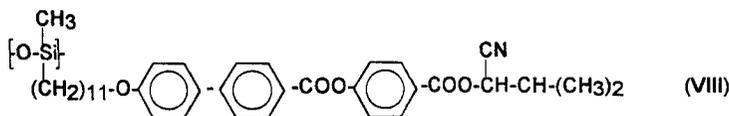
To approach the first problem, let us remind that the first attempts to prepare cholesteric comb-shaped polymers by the addition of chiral optically active fragments (cholesterol, cholestanen, *etc.*) to the main chain have failed. The as-formed polymers were either amorphous or only smectic mesophase was produced [12, 37].

Later, an alternative approach based on the application of spacers was advanced. In the presence of spacers, steric hindrances from the main chain preventing the packing of mesogenic groups were lifted, and thermotropic cholesteric side-chain polymers were obtained [8, 38].

However, even in this case, the development of cholesteric mesophase in chiral polymers should be considered as an exception rather that a rule, and the number of chiral homopolymers, which produce only cholesteric mesophase, is rather limited. Below, as an example, the structures of two polymers are presented [39, 40].

$$\underset{CH_3}{[O\text{-}Si]}\ (CH_2)_3\text{-}O\text{-}\langle\bigcirc\rangle\text{-}COO\text{-}\langle\bigcirc\rangle\text{-}COO\text{-}CH_2\text{-}\overset{C_2H_5}{\underset{CH_3}{\overset{*}{C}H}}$$

(VII)

T$_g$ 2 Ch 13 I

$$\underset{CH_3}{[O\text{-}Si]}\ (CH_2)_{11}\text{-}O\text{-}\langle\bigcirc\rangle\text{-}\langle\bigcirc\rangle\text{-}COO\text{-}\langle\bigcirc\rangle\text{-}COO\text{-}\overset{CN}{\underset{}{C}H\text{-}CH\text{-}(CH_3)_2}$$

(VIII)

T$_g$ 39 N* 272 I

Usually, in chiral homopolymers, in addition to cholesteric mesophase, smectic phase is produced [21]. As was mentioned earlier, optical properties of this system are rather poor, and polymer films show a strong light scattering.

In connection with this, the most advantageous procedure for the development of cholesteric mesophase is provided by copolymerization of mesogenic (usually, nematogenic) and chiral monomers (Fig. 4). This approach offers a convenient means for the preparation of cholesteric copolymers and allows one to control phase and optical properties of polymer cholesterics by varying their composition.

Just this method of copolymerization allows us to answer the second question how to preserve the unique optical properties of cholesterics in polymer material. Let us mention that only chiral copolymers offer this fascinating opportunity.

Let us consider some features of the structural behavior of copolymers in more detail. Table I shows the information concerning various copolymers and demonstrates the effect of chiral units on their thermal and optical properties.

As follows from Table I, when copolymer is composed of nematogenic units and optically active comonomer, whose homopolymer is amorphous, usually the development of only cholesteric phase induced by chiral units is produced (copolymers 3, 7, 10, 11, 13 and 14). For these copolymers, the corresponding X-ray diffraction patterns show only amorphous halo at high scattering angles, which suggests that the

TABLE I Cholesteric copolymers

Series	Chemical structure of copolymer	Chiral units, mol fraction	T_g, °C	Phase transitions, °C	λ_{max} at $T^* = 0.99\ Tcl$, nm	Ref.
A	B	C	D	E	F	G
1.	CH3-C-COO-(CH2)14-COO-Chol / CH2 CH3-C-COO-(CH2)2-O-COO-⬡-O-⬡-OCH3 / CH2	0.12 0.16 0.24	132 125 120	Ch 260 I Ch 245 I Ch 238 I	1500 1200 1100	[41]
2.	$n = 3$: CH3-Si-(CH2)3-COO-Chol / O $n = 6$: CH3-Si-(CH2)n-O-COO-⬡-COO-⬡-OCH3 / O	0.03 0.07 0.15 0.05 0.10 0.15		Ch Ch Ch Ch Ch Ch	1700 800 380 1500 800 380	[42]
3.	CH-COO-Chol / CH2 CH-COO-(CH2)5-COO-⬡-COO-⬡-OCH3 / CH2	0.15 0.33 0.40 0.52	20 60 80 100	N* 120 I N* 95 I N* 90 I amorphous	780 500 440	[43, 44]

TABLE I (Continued)

Series	Chemical structure of copolymer	Chiral units, mol fraction	T_g, °C	Phase transitions, °C	λ_{max} at $T^* = 0.99\ Tcl$, nm	Ref.
A	B	C	D	E	F	G
	CH-COO-(CH2)10-COO-Chol	0.17	20	N^* 120 I	750	[45]
4.	CH-COO-(CH2)5-COO-◯-COO-◯-OCH3	0.22	25	N^* 114 I	650	
		0.24	25	N^* 116 I	590	
		0.28	25	N^* 116 I	560	
		0.36	26	N^* 109 I	500	
5.	CH-COO-(CH2)10-COO-Chol / CH-COO-(CH2)5-COO-◯-OOC-◯-OCH3	0.21	10	N_B^* 40 N_A^* 120 I	760	[45]
		0.34		N^* 113 I	560	
		0.41		S_A^* 90 N^* 121 I	510	
6.	CH-COO-(CH2)10-COO-Chol / CH-COO-(CH2)5-COO-◯-COO-◯-OC3H7	0.28	25	S_A 100 S_A^* 110 N^* 118 I	710	[45]
		0.31	26	S_A 98 S_A^* 104 N^* 110 I	660	
		0.40	26	S_A 94 S_A^* 100 N^* 106 I	550	
		0.55	30	S_A 95 S_A^* 100 N^* 104 I	440	

No.	Structure				Ref.
7.	CH₃ backbone: CH₃-C-COO-(CH₂)₆-O-⟨⟩-COO-⟨⟩-OCH₃ / CH₃-C-COO-(CH₂)₂-O-⟨⟩-COO-⟨⟩-CH=N-CH-⟨⟩ CH₃	0.09 / 0.16 / 0.20 / 0.25	70 / 73 / 77 / 80	N* 247 I / N* 229 I / N* 216 I / N* 203 I	1260 / 712 / 562 / 467	[46]
8.	CH₂: CH-COO-(CH₂)₅-COO-⟨⟩-OOC-⟨⟩-C₄H₉ / CH₃-C-COO-(CH₂)₂-O-⟨⟩-COO-⟨⟩-COO-CH- CH₃	0.07 / 0.11 / 0.17	20 / 17 / 16	S 56 Ch 81 I / S 48 Ch 70 I / Ch 59 I	1517 / 769 / 519	[47]
9.	CH₃-C-COO-(CH₂)₅-COO-Chol / CH₃-C-COO-(CH₂)₅-COO-⟨⟩-OOC-⟨⟩-C₄H₉	0.10 / 0.16 / 0.22		S 55 Ch 89 I / S 49 Ch 92 I / S 48 Ch 98 I	1030 / 700 / 586	[47]
10.	CH₂: CH₃-C-COO-(CH₂)₆-O-⟨⟩-COO-⟨⟩-OCH₃ / CH₃-C-COO-[CH₂]₂-O-⟨⟩-COO-⟨⟩-COO-CH₂-CH-⟨⟩ OCH₃	0.2 / 0.24 / 0.28	44 / 65 / 64	Ch 216 I / Ch 213 I / Ch 208 I	937 / 714 / 626	[48]

TABLE I (Continued)

Series	Chemical structure of copolymer	Chiral units, mol fraction	T_g, °C	Phase transitions, °C	λ_{max} at $T^* = 0.99\ Tcl$, nm	Ref.
A	B	C	D	E	F	G
11.		0.12 0.14 0.17 0.22	30 31 33 40	Ch 97 I Ch 93 I Ch 84 I Ch 87 I	983 873 650 538	[49]
12.		0.16 0.19 0.26	69 72 81	Ch 218 I Ch 203 I Ch 186 I	1088 785 575	[50]
13.		0.05 0.10 0.30	36 35 27	N* 130 I N* 109 I N* 98 I	$18 \cdot 10^3$ $13 \cdot 10^3$ $7 \cdot 10^3$	[51]

14.

0.10	30	N^* 102 I	1508
0.15	26	N^* 92 I	1120
0.20	24	N^* 71 I	850

[51]

15.

|			
0.05	28	N^*_B 56 N^*_A 117 I	2480
0.1	24	N^*_B 55 N^*_A 92 I	1280
0.15	23	N^*_B 54 N^*_A 77 I	870
0.2	23	N^*_B 53 N^*_A 63 I	650

[51]

Ch and N^* - Cholestric and chiral nematic phases, respectively; (see page 1 of this chapter 11); S - Smectic phase;   Chol - Cholestryl.

arrangement of mesogenic groups is characterized by a certain orientational order as was observed for conventional nematic phase of low-molecular-mass liquid crystals.

Quite different situation is realized for copolymers, where cholesteric helix is developed in the matrix of smectogenic polymers (see Tab. I, copolymers 6). Such copolymers are able to produce the induced cholesteric mesophase, which on cooling is transformed into the smectic A phase.

For these copolymers in cholesteric phase, the corresponding X-ray patterns are characterized by the existence of amorphous halo at high scattering angles, whereas in the vicinity of the transition to S_A phase, the X-ray pattern shows small-angle reflections, the intensity of which increases. In this temperature region, selective reflection of light is preserved.

For the first time, we identified this structure for cholesterol-containing polymer:

$$
\begin{array}{l}
\overline{} \\
CH_2 \\
| \\
CH\text{-}COO\text{-}(CH_2)_{10}\text{-}COO\ Chol \qquad\qquad (IX) \\
\underline{}
\end{array}
$$
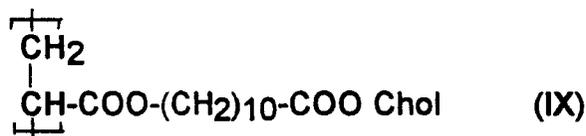
where **Chol** is the cholesteryl fragment.

This structure was first described in [52, 53] and then in [9, 45]. This polymer provides an interesting example of cholesteric mesophase with some elements of layered order, where side groups are perpendicular to the plane of layers, which in turn are twisted along the direction perpendicular to the long axes of the side mesogenic groups. Schematic representation of the arrangement of mesogenic groups in S_A and chiral S_A^* phases is shown in Figure 5. The development of this structure is provided by the interplay between the tendency of mesogenic groups to form a layered structure similar to the normal smectic phase and their tendency to pack up together and form a helical structure similar to chiral nematic phase [45].

Quite similar structural ordering was advanced by Samulski *et al.* [54] for cyclic copolysiloxane (X), which is characterized by the
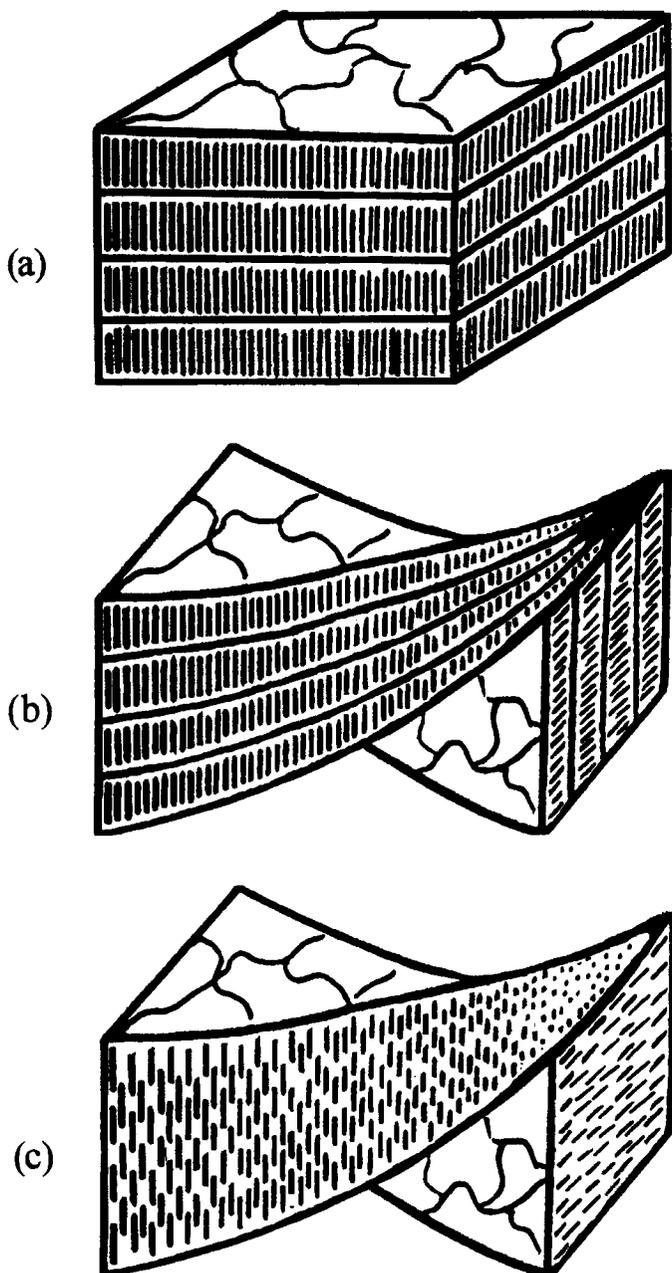
FIGURE 5 Schemes of the packing of mesogenic groups in (a) the S_A, (b) the twisted S_A^* and (c) the cholesteric phases of side-chain liquid crystal polymer (IX) according to the works [52, 53]; (d) the twisted S_A phase of LC oligomer (X) according to [54].
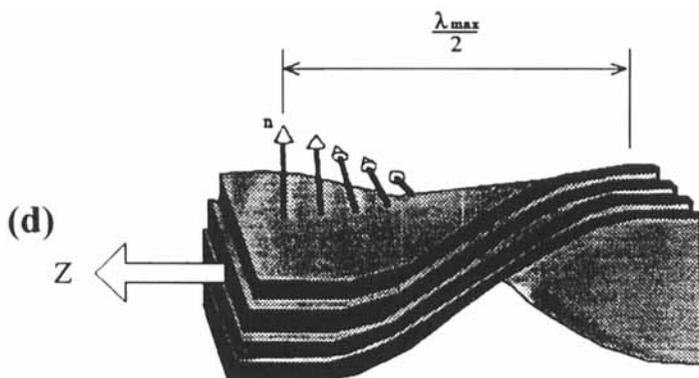
FIGURE 5   (Continued).

existence the helical twisted layers. To a certain extent, this polymer is a model oligomer of cholesteric copolymer:

$$CH_3\text{-}Si\text{-}(CH_2)_3\text{-}O\text{-}\langle\bigcirc\rangle\text{-}COO\text{-}\langle\bigcirc\rangle\text{-}\langle\bigcirc\rangle$$

$$CH_3\text{-}Si\text{-}(CH_2)_3\text{-}O\text{-}\langle\bigcirc\rangle\text{-}COO\text{-}Chol \qquad\qquad (X)$$
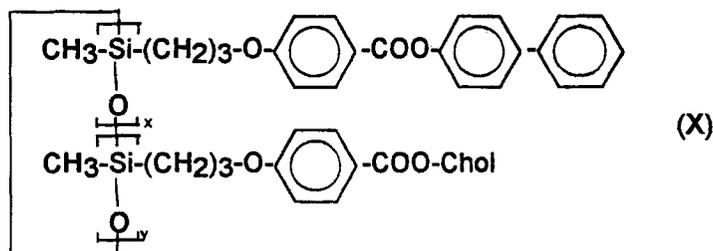
where $x + y = 5$.

As follows from Figure 5d, in this case, side groups are arranged into lamellae (ribbons), so that the long axes of mesogens are perpendicular to their surfaces, whereas the directions of local directors **n** are also normal to the ribbon surface. The stack of lamellae is twisted so that the set of local directors traces out a helicoidal path. The axis of cholesteric helix Z is normal to the surface of the macroscopic film samples; Figure 5d shows one quarter of the pitch of the helix ($\lambda_{max/2}$).

Let us note that, recently, a special attention was focused on studying the chiral ordered phases. This interest was primarily associated with an unorthodox structure of such systems, which is of great importance for fundamental science, as well as with the promising application of such chiral compounds (especially, chiral

smectics C^*) as optically nonlinear materials, pyroelectrics, ferro-electrics and antiferroelectrics [55, 56].

Without approaching a detailed description of the structure of chiral ordered phases, let us mention that immediately after the experimental discovery of chiral smectic A^* for polymer IX [52, 53], Renn and Lubensky [57] published their theoretical work, in which the development of cholesteric phase with the fragments of layered ordering was predicted. Within one year after this publication, this type of mesophase was experimentally identified and described in detail by Goodby *et al.*, for a number of MLCs [58].

According to this data, in the layered smectic A^* phases, the molecules actually prefer to form a helical macrostructure perpendicular to the long axes of the molecules; ho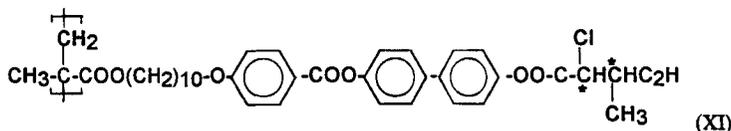wever, this "desire" is suppressed by the fact that the molecules are organized in layers like to cholesteric polymer mentioned above. When the "molecular chirality" as Goodby writes, is strong and/or the layers are weak enough, the inclination to produce a twisted structure overcomes the layers ordering, and a helical structuring is produced perpendicular to the long axes and parallel to the layers. The helical ordering is a result of the *frustration* between molecular chirality and layer ordering and is unusual in the fact that the twist is manifested by a regular array of screw dislocations. Sheets or blocks of the smectic A^* phase are rotated through a small angle, relative to one another, by rows of screw dislocation-hence the name of this phase-twist grain boundary one (TGB). The schematic representation of this phase showing the screw dislocation and melting process of TGB*. A phase is presented in Figure 6. It was suggested that this phase is analogous to the so called Abrikosov phase found in Type II superconductors [59].

Similar type of TGB* A phase was observed in polymethacrylate containing chiral terminal group with two chiral centres

$$CH_3-\underset{|}{\overset{|}{\underset{}{C}}}-COO(CH_2)_{10}-O-\langle\bigcirc\rangle-COO-\langle\bigcirc\rangle-\langle\bigcirc\rangle-OO-C-\overset{Cl}{\underset{CH_3}{\overset{|}{C}H}}CHC_2H$$

with CH_2 group.

(XI)

I 160 N* 149 TGB$_A$·140 S$_A$·73 S$_C$·

(DP=15)

TGBA* Phase

Screw Dislocations

Lattice melting

Liquid-like Regions
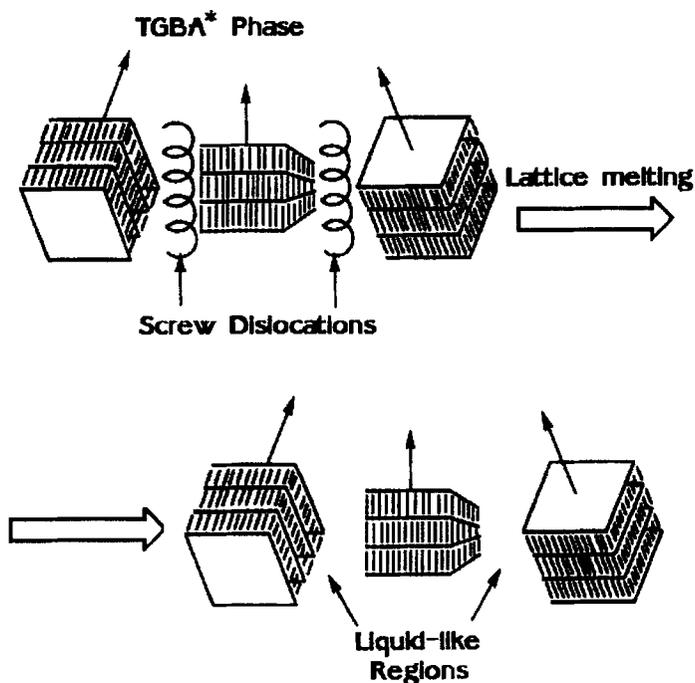
FIGURE 6   Structure of the Abricosov TGB_A^* phase and its melting to the amorphius liquid [56].

It is interesting to note that the directly analogous polyacrylate does not exhibit a TGB phase [60]. One can suggest that the role of the main chain in TGB phase formation in the PLCs essential.

The development of chiral smectic A^* phase, which exists in the wide temperature range, was also described by Chiellini and Galli for the following chiral biphenyl-containing polymers [19]:

$$\begin{array}{c} CH_3 \\ | \\ \left[Si\text{-}O\right] \\ | \\ (CH_2)_n\text{-}O\text{-}\langle\bigcirc\rangle\text{-}\langle\bigcirc\rangle\text{-}OR^* \end{array} \qquad (XII)$$

$$+CH_2-CH+ \quad COO(CH_2)_n -O-\langle\bigcirc\rangle-\langle\bigcirc\rangle-OR^* \qquad (XIII)$$

$$+CH_2-CH+ \quad O(CH_2)_n -O-\langle\bigcirc\rangle-\langle\bigcirc\rangle-OR^* \qquad (XIV)$$

where

$$R^* = -CH_2\overset{*}{C}H-C_2H_5 ; \overset{*}{C}H-C_6H_{13} ; -\underset{O}{\overset{||}{C}}-\underset{Cl}{\overset{|}{C}}H-\underset{CH_3}{\overset{|}{C}}H-C_2H_5 ; -\underset{O}{\overset{||}{C}}-\underset{Cl}{\overset{|}{C}}H-CH\overset{CH_3}{\underset{CH_3}{<}}$$

with CH_3 substituents as shown.
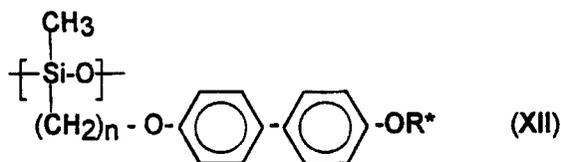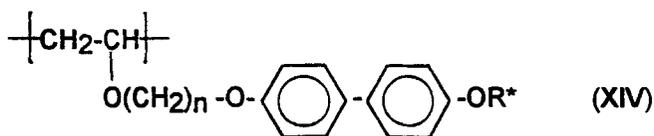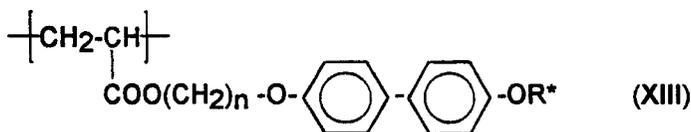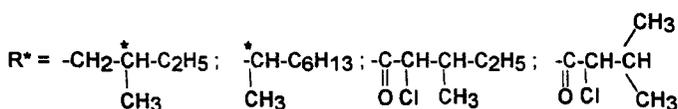
and n was varied from $n = 5$ to $n = 11$.

Depending on the length of spacers, these polymers were shown to produce a number of polymorphic modifications such as a monolayer A_1^* and a bilayer A_2^* modifications as well as partially interdigitated A_d^* mesophase with circular dichroism [61].

Comb-shaped structure of LC polymes contributes to the development of new phases, which are unknown for low-molecular-mass liquid crystals.

Previously [62] in the acrylic polymer (XV)

$$+CH_2-CH+ \quad COO(CH_2)_5-COO-\langle\bigcirc\rangle-OOC-\langle\bigcirc\rangle-OCH_3 \qquad (XV)$$
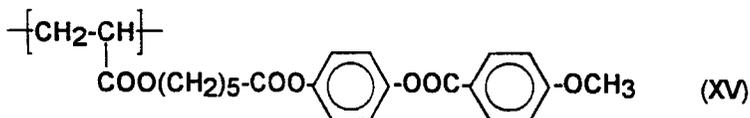
a new type of nematic mesophase with the ordered arrangement of mesogenic groups in the direction normal to their long axes was discovered. This, most likely, hexagonally ordered phase was denoted as the N_B phase, whereas a convential nematic phase, followed the N_B was denoted as the N_A phase.

Copolymerization of the monomer of polymer (XV) and chiral menthyl-containing monomer gave rise to the obtaining a series of chiral copolymers characterized by the same ordered (probably

hexagonal) arrangement of mesogenic groups in the plane perpendi-
cular to long axes of the side chains (Tab. II, copolymer series 15). All
these copolymers selectively reflect the light in the temperature interval
of mesophase existence. Their X-ray diffraction patterns are char-
acterized by a single sharp reflection at wide scattering angles
corresponding to the interplanar distance of 0.44 nm; the small-angle
reflexes are completely lacking (Fig. 7). Coexistence of the selective
reflection of light and the ordered structure of copolymers synthesized
gives grounds to tell about unusual cholesteric structure with the ordered
arrangement of the mesogenic groups in the absence of periodicity in
their long axes direction. At heating of these samples the sharp reflex in
these X-ray diffraction patterns is transformed into the diffuse one (see
Fig. 3) that corresponds to the usual N^* phase formation. DCS curve

TABLE II Molecular masses and transition temperatures of cholesteric copolymers
(XIX)

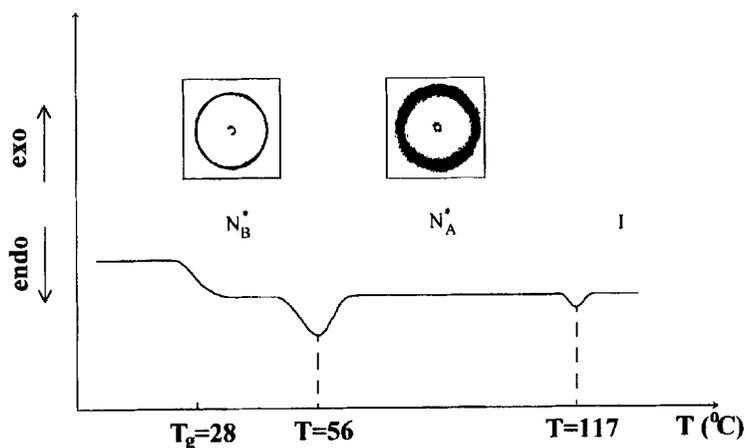| Copolymer	Concentration of cholesterol units, mol %	$\overline{M}_W$	$T_g, °C$	$T_{Ch-I}, °C$
A_1	22	$5.6 \cdot 10^4$	28	116
A_2	22	$4.1 \cdot 10^3$	25	114
B_1	36	$4.3 \cdot 10^4$	26	109
B_2	36	$8.5 \cdot 10^3$	26	108

FIGURE 7 DSC curve and X-ray diffraction patterns of menthol-containing copoly-
mer containing 5 mol% of chiral monomer units (copolymer 15, Tab. I).

also has endothermic peak corresponding to $N_B^* \rightarrow N^*$ transition (Fig. 3). The same type of N_B^* phase was also observed for cholesteryl-containing copolymer with 21 mol% of cholesteryl monomer units (see Tab. I, copolymer series 5) [45].

At consideration of cholesteric N_B^* phase the question arises how the ordered arrangement of mesogenic group is combined with the helical structure of copolymers? In order to answer this question was carried out very simple calculations on the basis of the value of the order parameter ($S = 0.83$) characteristic for the N_B phase of homopolymer (XV) in which the cholesteric phase was induced. We started with the simple model of cholesteric helix presented in Figure 1 in the belief that pitch of the helix (for copolymer 15.4 in Tab. I) corresponds to $P = 433$ nm (see Eq. (1) $\bar{n}$ is the average refractive index equaling 1.5). The angle by which the neighbouring molecules are twisted around the helix axis is $\approx 0.4°$. In this case the correlation length corresponding to the "hexagonal arrangement" in the direction perpendicular to their long axes will be equal around $35 - 40$ nm.

Thus, simple calculations show that the helical structure of copolymers does not prevent the ordered arrangement of mesogenic groups in cholesteric N_B^* mesophase.

5. OPTICAL PROPERTIES OF CHOLESTERIC PLCs

5.1. Textures of Cholesterics

Optical properties of polymer cholesteric liquid crystals and low-molecular-mass liquid crystals are controlled by their specific helical supermolecular organization. In turn, this structural organization is provided by the existence of chiral (optically active) fragments in molecules or macromolecules. In general case, when, in the different regions of cholesteric samples, a random distribution of the directions of helical axes is observed, a *focal-conic texture* is produced. This texture is characterized by polycrystalline structure (Fig. 8a) and is capable of light scattering. In the case of the reflection of visible light, this structure is pearly colored.

Another type of structure is associated with the *fingerprint texture*, when helical axis is parallel to the surface of the cell (Fig. 8c).
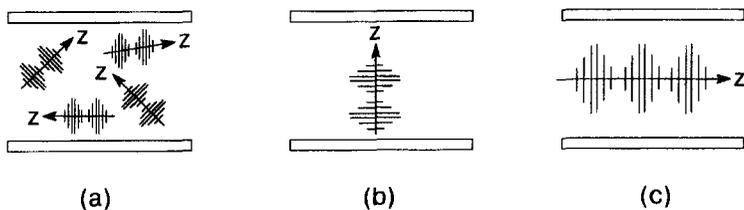
FIGURE 8   Three types of textures in cholesteric liquid crystals: (a) focal conic; (b) planar and (c) fingerprint. The arrows show the direction of helix axes.

Finally, the most interesting type of texture, that is, *planar texture*, is observed, when mesogenic fragments lie in the plane of glasses, whereas the axes of cholesteric helices are perpendicular (Fig. 8b). Just this planar structure of polymer cholesterics provides the selective reflection of light, which obeys the above Eqs. (1 – 3) and offers interesting advantages for their practical application. The point is that even when cholesteric planar texture is produced at elevated temperatures, on fast cooling to the temperatures below glass transition temperature, this planar structure is preserved, and selective reflection of light is provided. This is the principal difference between cholesteric polymers and their low-molecular-mass analogs. Hence, films based on PLCs are selective circular polarizers. For cholesteric films, the choice of spectral region of selective scattering and prediction of its magnitude are based on the studied of so-called helix twisting power of the chiral additive [2, 21, 22]. In the case of PLCs chiral additive is the number of monomer chiral units involved in cholesteric copolymer.

5.2. The Effect of the Composition of Cholesteric Copolymers on the Selective Reflection of Light. Helix twisting Power of Chiral Units

When studying optical properties of the induced cholesteric mesophase both in low-molecular-mass nemato-cholesteric mixtures and in cholesteric copolymers, the terms of **helix twisting power** or **helix-induction force** are widely used. The later factor is defined by the following relationship:

$$\beta = dP^{-1}/dx_{ch} \text{ at } x_{ch} \ll 1 \qquad (4)$$

where x_{ch} is the molar fraction of the chiral additive (dopant) in the low-molecular-mass nemato-cholesteric mixtures or the molar fraction of chiral monomer units in copolymers.

Taking into account the fact that at normal of light $\lambda_{max} = \bar{n}P$ the following relationship is valid:

$$\beta = \bar{n}(d\lambda_{max}^{-1}/dx_{ch}) \tag{5}$$

i.e., the helix twisting power of chiral units is controlled by the slope of linear region of the dependence of λ^{-1} on x_{ch}.

Helix-induction force characterizes both the ability of nematic matrix to twist into the helix under the action of chiral additives and helix twisting power of chiral additive, which is controlled by geometrical shape and the magnitude of molecular optical rotation [63].

Let us note that, for all available cholesteric copolymers with mesogenic groups in main chains as well as for the comb-shaped copolymers, with increasing the content of chiral units, the pitch of the helix decreases, and this tendency is well demonstrated by the dependence of λ_{max} on the composition of copolymers (see Tab. I).

Figure 2 shows the dependence of λ^{-1} on the molar fraction of chiral additive x_{ch} for various cholesterol-containing copolymers. As follows from Figure 9, copolymers based on one and the same nematic monomer and different cholesterol-containing monomers (Tab. I, copolymers 3 and 4) are characterized by similar dependence of λ_{max}^{-1} on x_{ch}. At $x_{ch} = 0$ ($\lambda_{max}^{-1} = 0$), the phase is nematic. For such copolymers, the helix-induction force β is as high as $15\,\mu m^{-1} \cdot mol^{-1}$ (see upper curve in Fig. 2). This evidence shows that, on the introduction of cholesterol-containing units, the ability of nematic matrix to twist into the helix is similar for all cholesterol-containing monomers, independently of their chemical composition. Geometrical shape of cholesterol groups and its molar optical rotation, which is similar for all mono-mers, i.e., is associated with the chirality of cholesterol groups, is the governing factor for both LC polymers and low-molecular-mass liquid crystals.

For the above LC copolymers, the magnitude of helix-induction force agrees well with the corresponding values for the mixtures of low-molecular-mass LC based on n-butoxybenzylidene-n-butyl aniline and cholesteryl propionate, where no specific interactions take place in the nematic phase, and chirality is provided only by cholesterol fragment.
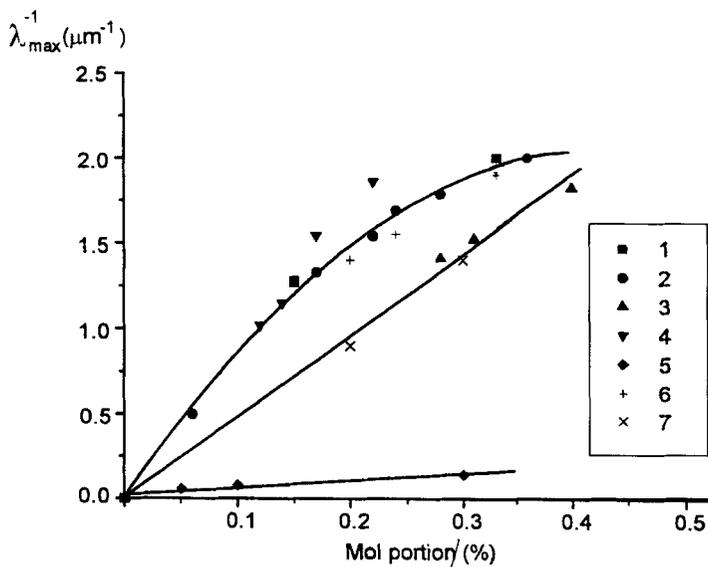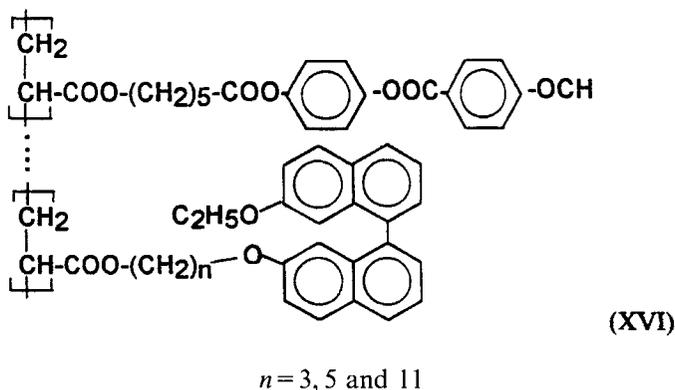
FIGURE 9 Dependence of λ_{max}^{-1} on the molar fraction of the chiral component for the copolymers of series (1) 3, (2) 4, (3) 6, (4) 11, (5) 13 (see Tab. I) and for (6) the mixtures cholesteryl propionate-p-butylhydroxy-benzilidene-p'-butylaniline and (7) cholesteryl propionate-p-butoxybenzilidene-p-aminobenzonitrile.

On substitution of nematic matrix, helix-induction force, i.e., helix twisting power, also changes. In the smectogenic matrices (Tab. I, copolymers 6), helix induction power is lower ($\beta = 11\,\mu m^{-1} \cdot mol^{-1}$). This evidence suggests that strong "side interactions" between mesogenic groups, which are responsible for the appearance of smectic phase, hinder the helix twisting in such systems. As follows from the dependences of λ^{-1} on x_{ch} for the mixtures of n-butoxybenzylidene-n'-aminobenzonitrile (Fig. 9, curve 7), this system and copolymers 6 (Tab. I) (curve 3) are characterized by similar values of helix-induction force. Hence, to a certain extent, polymer matrix may suppress the twisting potency of chiral additives.

Let us compare the values of β for copolymers containing similar nematogenic matrix but different chiral "guests". The effect of geometrical shape of chiral fragment on helix twisting power is well demonstrated by copolymers 11 and 13 (see Tab. I). These copolymers are characterized by similar nematogenic matrix, in which cholesteric structure is induced by nonmesogenic optically active units based on hexylethylamine. As follows from Figure 9, for copolymers 13, the

values of β are minimal ($\beta = 2\,\mu m^{-1} \cdot mol^{-1}$), because chiral unit does not contain any flat fragment. In copolymers 11 (curve 4), increasing anisotropy of side chain *via* the introduction of benzene rings results in an improved compatibility with nematogenic units of polymer matrix. As a result, a dramatic increase in helix twisting power is observed ($\beta = 15\,\mu m^{-1} \cdot mol^{-1}$). Hence, high helix twisting power of chiral comonomer is well pronounced when, on one hand, its geometrical shape fits the molecular structure of the second nematogenic monomer and, on the other hand, chiral monomer units lead to a strong twist of "quasinematic" monolayers.

When copolymer units of binaphthyl atropoisomers (see copolymers XVI), in which chirality is provided not by asymmetric atoms in side chains but by hindered rotation about the $1-1'$ bond joining two pairs of naphthalene rings, are used as chiral units, cholesteric mesophase is also produced when, as the second copolymer, nematogenic monomer with the following structure is used:

$$CH_2$$
$$CH\text{-}COO\text{-}(CH_2)_5\text{-}COO\text{-}\langle\bigcirc\rangle\text{-}OOC\text{-}\langle\bigcirc\rangle\text{-}OCH$$

$$\vdots$$

$$CH_2 \qquad C_2H_5O$$
$$CH\text{-}COO\text{-}(CH_2)_n$$

(XVI)

$n = 3, 5$ and 11

However, in this case, as a result of large dimensions of bulky binaphthyl group, marked distortions in the mesophase structure take place, and the shorter the spacer, the more dramatic the consequences. As a result, at much lower concentrations of nonmesogenic chiral component (10–15%), disruption of helicoidal structure is observed, whereas, in the case of the chiral units such as cholesterol or menthol derivatives, mesophase is preserved even at concentrations of 40–50%. At the same time, even at small concentrations, twisting power of the above atropoisomers ($\beta = 12-13\,\mu m^{-1}\cdot mol^{-1}$) appears to approach the values of β typical of cholesterol-containing copolymers, the optical

activity of which is provided by the presence of asymmetric carbon atoms.

The problems concerning the effect of the length of spacer both in chiral and nematogenic fragment on β in copolymers are still open because no information concerning the optical properties of such co-polymers with the controlled length of spacer in each of copolymer units is available. As was shown only in [42] for cholesterol-containing copolymers containing phenylbenzoate mesogenic groups (Tab. I, co-polymers 2) with different length of spacers, with decreasing the length of spacers from six to three methylene units, higher twisting of meso-genic groups of copolymer is observed so that β $(n = 3) > \beta(n = 4) > \beta(n = 6)$.

At the same time, as was shown in [18] for binaphthol copolymers, binaphthal units attached to the main chain by short spacer are char-acterized by lower twisting power as compared with those attached to the main chain by longer spacers. As was mentioned earlier, in cholesterol-containing copolymers, with increasing the length of spacers, no dramatic changes in optical properties of the system are observed (see Tab. I). At the present time, this evidence does not allow one to make any correct predictions; and studying homological series of LC polymers with the controlled length of spacer and estimation of orientational and rotational parameters of order invite further studies.

5.3. Temperature Dependence of Helix Pitch

As was mentioned earlier, one of the principal characteristics of cholesteric liquid crystals is associated with the temperature depen-dence of helix pitch. For polymers, the related problems are of even greater importance taking into account the possible ways for preser-ving cholesteric helix (or structure) on cooling polymer films to the temperatures below glass transition temperature. However, despite an obvious importance of this evidence, the number of experimental works in this direction is rather moderate.

The profiles of temperature dependences of helix pitch are primarily controlled by the type of structural organization of matrix (nematic or smectic), in which helical structure is induced.

This effect is well demonstrated by Figure 10, where temperature dependence of the selective reflection wavelength λ_{max} for a series of
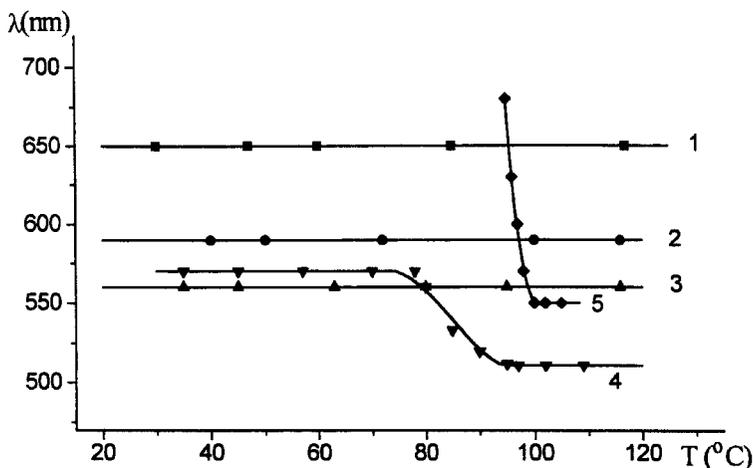
FIGURE 10 Temperature dependences of λ_{max} for the copolymers of series 4 (Tab. I) containing (1) 22, (2) 24, (3) 28 and (4) 36 mole% cholesteryl units and (5) the copolymer of series 6 containing 40 mol% cholesteryl monomeric units.

cholesterol-containing polymers is presented (Tab. I, copolymers 4). This evidence suggests that, when cholesteric mesophase is induced in the nematic mesophase by small concentration of cholesterol units (to 30 mol%), λ_{max} (and helix pitch) is almost independent of temperature in the entire temperature range of the existence of the mesophase (Fig. 10, curves 1–3). However, with increasing the content of cholesterol units to 36 mol% (curve 5), a well-pronounced dependence of λ_{max} on temperature is observed $(dP/dT < 0)$. This behavior is related to the fact that, with decreasing the temperature, the development of the layered order in copolymers is observed (the corresponding X-ray patterns show small-angle reflections).

By thermographic method, no transition to smectic phase is identified, and this evidence allows one to consider the dependence $\lambda_{max}(T)$ as a very sensitive "instrument" for detection any changes in the packing of mesogenic groups.

At the same time, in the case of copolymers, in which cholesteric mesophase is preceded by smectic, in the temperature interval of S_A phase appearance untwisting of cholesteric helix takes place. As a result, the selective reflection wavelength increases (Fig. 10, curve 4). At temperatures far from the transition to smectic phase, helix pitch is

almost independent of temperature and is controlled only by the composition of copolymer. Similar temperature dependences of λ_{max} were obtained for siloxane copolymers containing phenyl benzoate and cholesterol mesogenic groups (Tab. I, copolymers 2) [42].

Let us compare the temperature dependences of the selective reflection wavelength (or helix pitch) for copolymers with different types of chirality. To this end, two types of the synthesized copolymers were used. The copolymers were synthesized from one and the same nematogenic acrylic monomer XVII:

$$\text{CH}_2\text{=CH-COO(CH}_2\text{)}_5\text{COO-}\langle\bigcirc\rangle\text{-OOC-}\langle\bigcirc\rangle\text{-OCH}_3 \qquad \text{(XVII)}$$
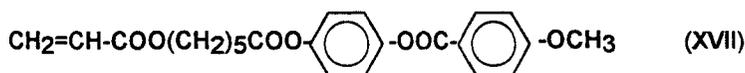
and two different monomers containing optically active groups of menthol (Tab. I, copolymers 15) and atropoisomers of binaphthol (see compounds XVI).

Figures 11a and b show the temperature dependences of λ_{max} for the two above series of copolymers with the different nature of chirality. Let us emphasize the two following factors.

First, in both cases, with increasing the concentration of chiral units, helix pitch (or λ_{max}) decreases, and this evidence suggests a "twisting" of helix with increasing the content of chiral component.

Second, at temperatures below glass transition temperature (for binaphthyl-containing copolymers) or the temperature of the phase $N_B^* - N^*$ transition (for menthol-containing copolymers) (Tab. I, copolymers 15), all curves are characterized by constant values of λ_{max}. On further increasing temperature, helix pitch increases, and for binaphthyl-containing copolymers, the values of $d\lambda_{max}/dT$ are 3–4 times higher than the corresponding values of menthyl-containing polymers.

The difference between the values of helix twisting power β for the two above series of copolymers is well demonstrated by Figure 12, where the temperature dependences of β are presented.

For menthyl-containing copolymers as well as for other cholesteric systems containing asymmetric carbon atoms as chiral centers, positive sign of dP/dT is well rationalized in terms of the theoretical models [63], according to which temperature dependence of helix pitch is controlled only the angle of twisting φ of molecules in the neighboring "quasinematic layers": the higher orientational order parameter, the higher the angle. Hence, in such copolymers, the temperature

(a)

(b)

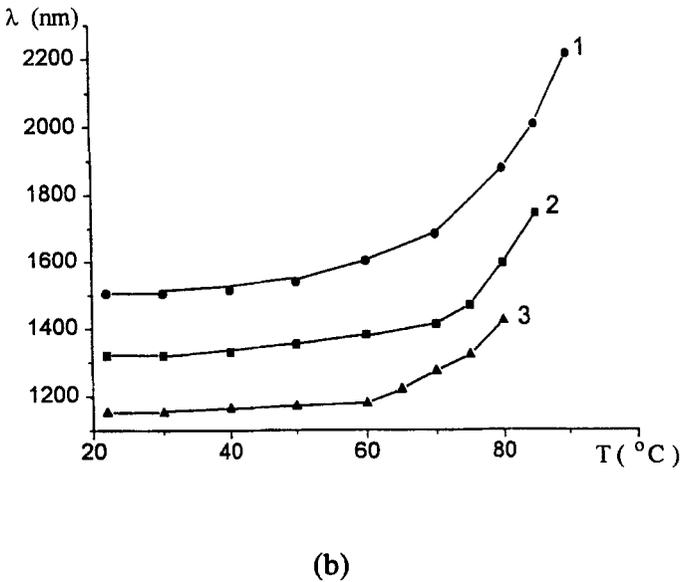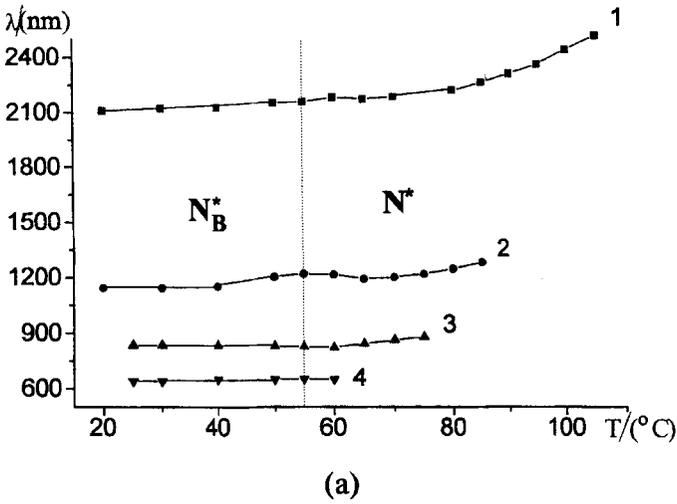FIGURE 11 Temperature dependence of λ_{max} for (a) the menthyl-containing copolymers of series 15 (Tab. I) with (1) 5, (2) 10, (3) 15 and (4) 20 mol% menthyl units and for (b) binaphthyl-containing copolymers XVI ($n = 5$) with (1) 6, (2) 8 and (3) 10 mol% binaphthyl units.

dependence of helix pitch should be controlled by the temperature dependence of the order parameter S, which decreases with increasing temperature.
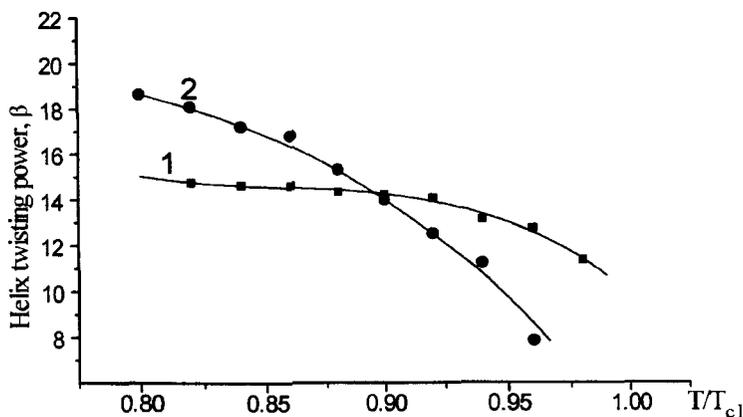
FIGURE 12 Temperature dependence of helix twisting power β for (1) the menthyl-containing copolymers (Tab. I, copolymers of series 15) and (2) binaphthyl-containing copolymers XVI ($n = 5$).

For atropoisomeric binaphthyl-containing copolymers, with increasing temperature, a more dramatic decrease in β is observed. This behavior agrees well with the experimental evidence [64] concerning the temperature dependences of β for the mixtures of low-molecular-mass crystals with low-molecular-mass binaphthyl-containing compounds, which were used as chiral dopants. In both cases, well-pronounced temperature dependences of β are likely to be rationalized by conformational changes taking place in the binaphthyl fragments with increasing temperature: as the dihedral angle between naphthalene rings approaches 90°, twisting power decreases.

This evidence seems to be of a great scientific interest into account current theoretical and experimental calculations [64–66] of the helix twisting power for a series of low-molecular-mass binaphthyl-containing compounds, which may be used as dopants in their mixtures with low-molecular-mass liquid crystals. The next step in this direction involves the development of theoretical models for chiral polymers, which requires a thorough examination of the above evidence.

5.4. The Effect Molecular Mass on Optical Properties of PLCs

As was shown earlier, molecular mass of polymers has a strong effect on thermal stability of the comb PLCs. With increasing molecular

mass, clearing temperature increases, and, in the case of cholesteric polymers producing smectic phase, the temperatures of smectic A-cholesteric transition increase. Taking into account the fact that, with increasing molecular mass, transition temperatures tend to increase, the temperature interval of the existence of cholesteric mesophase is shifted toward higher temperatures. When the fractions of cholesteric polymers produce not only cholesteric phase but also low-temperature smectic phase A, in the temperature interval corresponding to the transition from cholesteric to smectic phase, helix experiences untwisting, i.e., $d\lambda_{max}/dT$ is negative. The latter observation is well demonstrated by Figure 13, which shows the effect of molecular mass of the fractions of cholesterol-containing acrylic polymer (IX) on transition temperatures and the regions of the selective reflection of light. The sample of nonfractionated polymers was characterized by the following transition temperatures: T_g 35 S_A 154 Ch 158 I.

Quite different situation is observed for cholesterol-containing copolymers, whose tendency to the development of smectic phase is fully suppressed, and copolymer is able to produce only cholesteric mesophase (Tab. I, copolymers 4). Studying the fraction of one representative of copolymers 4, which contains 24 mol% of cholesterol units, allows one to appreciate the effect of molecular mass on the optical properties and to consider temperature dependences of the helix pitch (Fig. 14)[1]. Let us emphasize that all copolymers are able to produce monochromic films; the absence of the low-temperature smectic mesophase allows one to preserve their optical properties in the wide temperature range, and $d\lambda/dT = 0$.

This evidence unequivocally shows that, varying molecular mass and composition of copolymers, one may control the optical proper-

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[1] Let us note that preparation of copolymers with similar composition but with different molecular mass is rather difficult because of the compositional inhomogeneity of copolymers. To this end, we used the method of fractioning and chromatographic separation of fractions. This examination allowed us to estimate compositional inhomogeneity of the samples: spread in the content of chiral units does not exceed 7 mol%. Therefore, selective reflection of light λ_{max} is the function of two variable parameters: molecular mass and composition of copolymer. Nevertheless, as follows from comparing curves 1–4 (Fig. 14), fractioning provides an efficient means for controlling selective reflection of light.
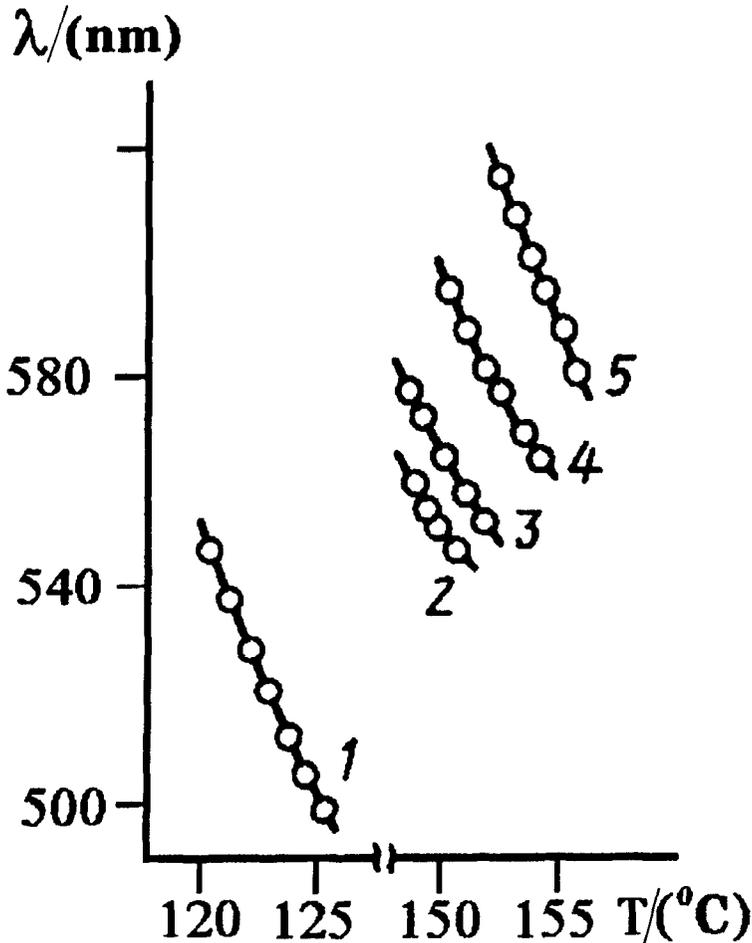
$\lambda/(nm)$

FIGURE 13 Temperature dependence of λ_{max} for the fractions of polymer (IX): (1) $\overline{M}_W = 1 \cdot 10^4$; (2) $\overline{M}_W = 6 \cdot 10^4$; (3) $\overline{M}_W = 1.2 \cdot 10^5$, (4) $\overline{M}_W = 14 \cdot 10^5$ and (5) $\overline{M}_W = 2.10 \cdot 10^5$.

ties of polymer cholesterics. On the other hand, temperature dependences of the selective reflection wavelength are controlled by the presence or absence of layered ordering in the temperature region preceding the development of cholesteric phase. This allows preparation of both enantiochromic $(d\lambda_{max}/dT \neq 0)$ and monochromic films $(d\lambda_{max}/dT = 0)$.
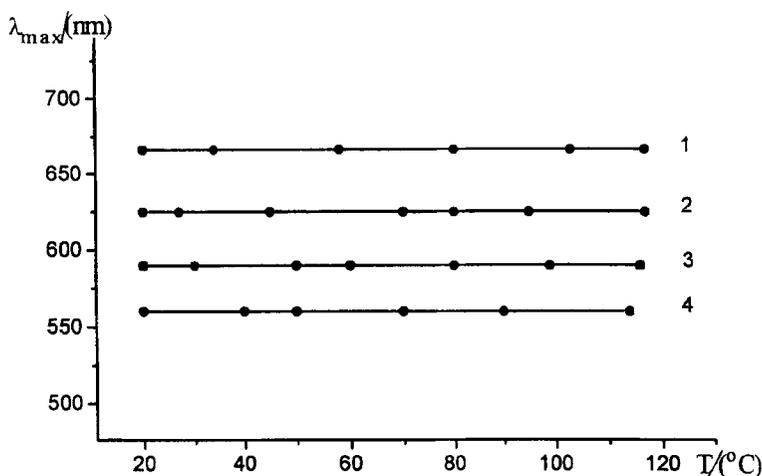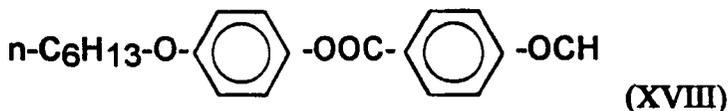
FIGURE 14   Temperature dependence of λ_{max} for the fractions of one of copolymers in series 4 (Tab. I) containing 24 mol% cholesteryl units: (1) $\overline{M}_W = 8.5 \cdot 10^4$; (2) $\overline{M}_W = 6.8 \cdot 10^4$; (3) $\overline{M}_W = 2.8 \cdot 10^4$ and (4) $\overline{M}_W = 5.3 \cdot 10^3$.

6. MIXTURES OF CHOLESTERIC PLCs WITH MLCs AND BLENDS OF CHOLESTERIC PLCs

One of the methods for regulating the temperature interval of the cholesteric mesophase existence and optical properties of cholesteric polymers is associated with the development of compositions of cholesteric polymers with low molar mass cholesteric or nematic liquid crystals. Addition of small amounts of cholesteric polymers to MLCs makes it possible to vary the properties of LCs [13, 67, 68].

Figure 15 shows the temperature dependences of the selective reflection wavelength for compositions of one of the cholesteric copolymers with different low molecular mass liquid crystals. For example, on addition of small amounts of low molecular mass nematic (XVIII)

$$\text{n-C}_6\text{H}_{13}\text{-O-}\langle\bigcirc\rangle\text{-OOC-}\langle\bigcirc\rangle\text{-OCH}$$

(XVIII)

to copolymer a relative content of cholesterol units decreases, shifting the selective light reflection towards the long wavelength region. As can
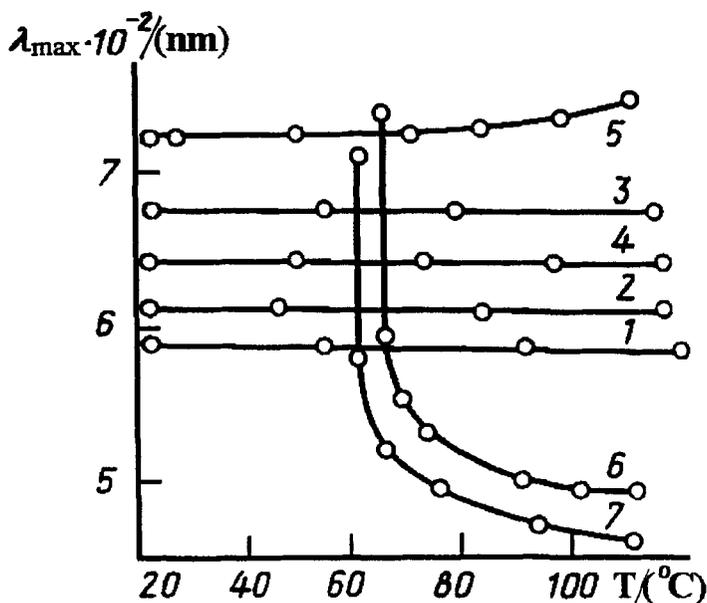
FIGURE 15   Temperature dependence of λ_{max} for (1) a copolymer in series 4 (Tab. I) containing 24 mol% cholesteryl units and mixtures with (2, 3) low-molecular-mass nematic XVIII, (4–5) cholesteryl chloride and (6, 7) cholesteryl pelargonate. Concentrations of low-molecular mass liquid crystals: nematic XVIII: (2) 10 and (3) 30 mol%; cholesteryl chloride: (4) 10 and (5) 20 mol%; cholesteryl pelargonate: (6) 20 and (7) 30 mol%.

be seen from Figure 15, introduction of 30 mol% of the nematic liquid crystal (XVIII) shifts the selective reflection of light by 100 nm (curve 3).

A stronger concentration dependence of the helix pitch is observed for the mixtures of a left-handed copolymer and right-handed cholesteryl chloride (Fig. 15, curves 4.5). Addition of 20 mol% cholesteryl chloride increases the selective reflection wavelength by almost 200 nm. Thus, addition of low molecular mass nematic liquid crystal and right-handed cholesteryl chloride, which untwists the cholesteric helix, shifts the λ_{max} to the long-wave region.

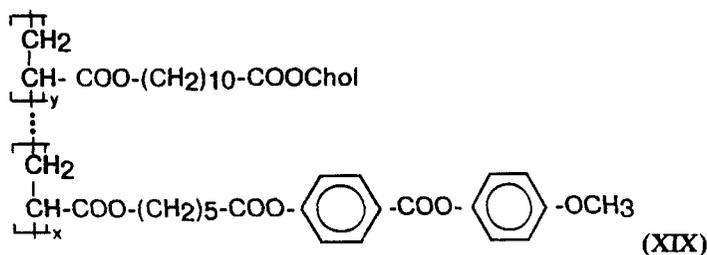It is necessary to increase the twist angle of the mesogenic groups for decreasing the selective reflection wavelength. This can be done if a left-handed liquid crystal, cholesteryl pelargonate, for example, is added to a cholesteric copolymer. Curve 7 in Figure 15 shows that the helix pitch of a composition containing 30 mol% cholesteryl pelargonate is significantly smaller than the pitch of the copolymer.

Figure 15 also shows that although the helix pitch is independent of temperature for the copolymer and its compositions with nematic (XVIII) and cholesteric chloride, the pitch of the compositions containing smectogenic cholesteryl pelargonate increases sharply with decreasing temperature due to the formation of elements of smectic structure in the cholesteric mesophase. These data demonstrate that the formation of the helical structure in compositions of cholesteric polymers with low-molecular-mass nematics and cholesterics show similar behavior as cholesteric copolymers.

We have considered only few examples demonstrating the possibilities for obtaining homogeneous compositions consisting of polymer film and low-molecular-mass liquid crystals. Similar data was described in the works concerning the photopolymerisation of a mixture of monomers in the cholesteric phase leading to the formation of polymeric films, which preserve the optical characteristics of the initial monomers [69, 70].[2]

Another problem associated with LC compositions concerns the blends of cholesteric PLCs. Such blends are of a considerable interest both from academic (miscibility, structure formation) and practical standpoints (preparation of the materials combining the constructional convenience of the polymer films and the desirable optical properties controlled by external fields). This is a new direction in the area of LC polymers and we show only one example of an unusual optical behaviour of the blends of cholesteric polymers.

These blends are composed of two cholesteric copolymers with different compositions (XIX)

$$\begin{array}{l} \overbrace{\underset{\underset{y}{|}}{\underset{|}{CH_2}}}^{} \\ CH\text{- }COO\text{-}(CH_2)_{10}\text{-}COOChol \\ \vdots \\ \overbrace{\underset{\underset{x}{|}}{\underset{|}{CH_2}}}^{} \\ CH\text{-}COO\text{-}(CH_2)_5\text{-}COO\text{-}\hexagon\text{-}COO\text{-}\hexagon\text{-}OCH_3 \end{array} \qquad \text{(XIX)}$$

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[2]Some aspects of this problem are considered in the paper by R. Hikmet "Anisotropic Networks Obtained by Photopolymerization of MLCs in the Ferroelectric State" in this issue.

The molecular masses $(\overline{M}_W)$ and temperatures of two copolymers A (22 mol%) and B (36 mol%) with different $\overline{M}_W$ are presented in Table I. All copolymers, independently of $\overline{M}_W$, display the cholesteric mesophases which selectively reflect the visible light (λ_{max}). Using pairs of copolymers the blends of the cholesteric copolymers A_1 and B_1 with $\overline{M}_W > 10^4$ (Blends 1) and the cholesteric copolymers A_2 and B_2 with $\overline{M}_W < 10^4$ (Blends 2) were prepared and their phase behavior and optical properties were studied.

The phase diagram of Blends 2 of different compositions (Fig. 16a), consisting of cholesteric copolymers with $\overline{M}_W < 10^4$, shows a good solubility of two components in the entire concentration region. This type of thermal behavior is typical of low-molecular-mass liquid crystals.

Transmittance spectrum of Blends 2 is characterized by one peak of selective light reflection, which usually lies between two maxima associated with initial components and corresponds to the mean content of cholesteryl groups.
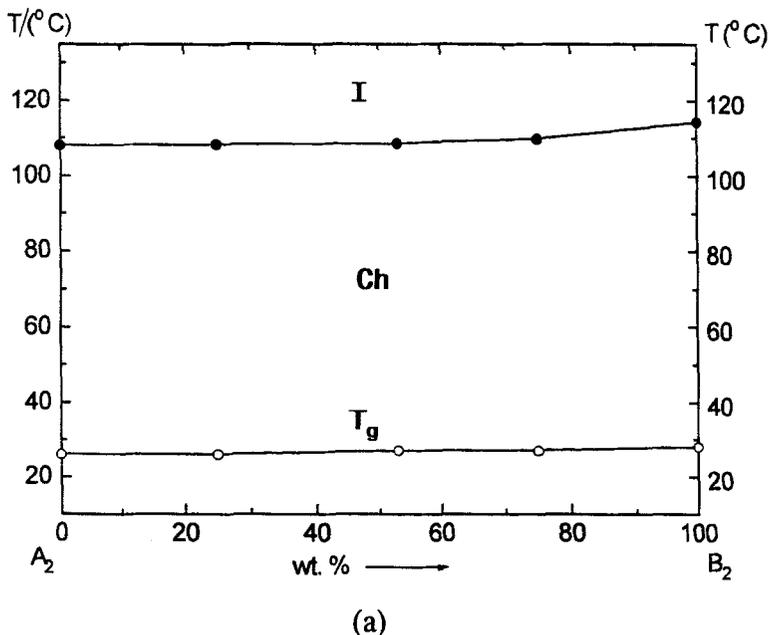

(a)

FIGURE 16   Phase diagrams of Blends of cholesteric copolymers: (a) Blends 2 consisting of copolymers A_2 and B_2; (b) Blends 1 consisting of copolymers A_1 and B_1.
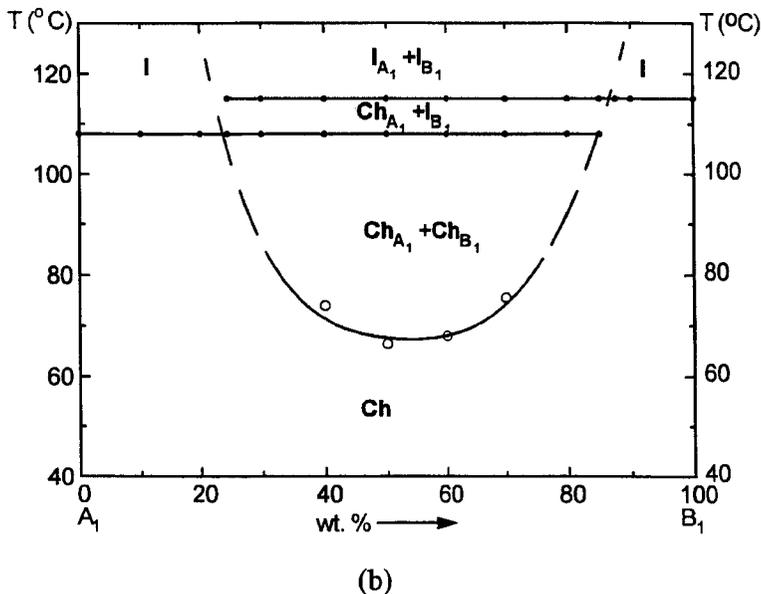
(b)

FIGURE 16 (Continued).

In contrast to Blends 2, Blends 1 consisting of cholesteric co-polymers A_1 and B_1 minimum critical point of the mixture (T_{crit}) (at concentration range 35 – 70 wt% of copolymer A_1), above which micro-phase separation into two cholesteric mesophases with different helix pitches, takes place (Fig. 16b).

Figures 17a and b show the transmittance spectrum of Blends 1 as a function of λ_{max} at different temperatures as well as the temperature dependence of λ_{max} for the same Blend 1, containing the equal molar contents of copolymers A_1 and B_1. As can be seen from Figures 17a and b, spectrum of Blend 1 has two minima at temperature above T_{crit}. It means that the values of wave length of selective light reflection λ_1 and λ_2 correspond to different helical supermolecular structures which are formed in Blend 1, as a result of "specific phase separation" at the supramolecular level. Below T_{crit} only one peak of selective light re-flection is observed. Thus, varying the temperature one may control reversible changes in the type of phase separation in cholesteric blends, obtaining bimodal or unimodal curves of selective reflection of light.
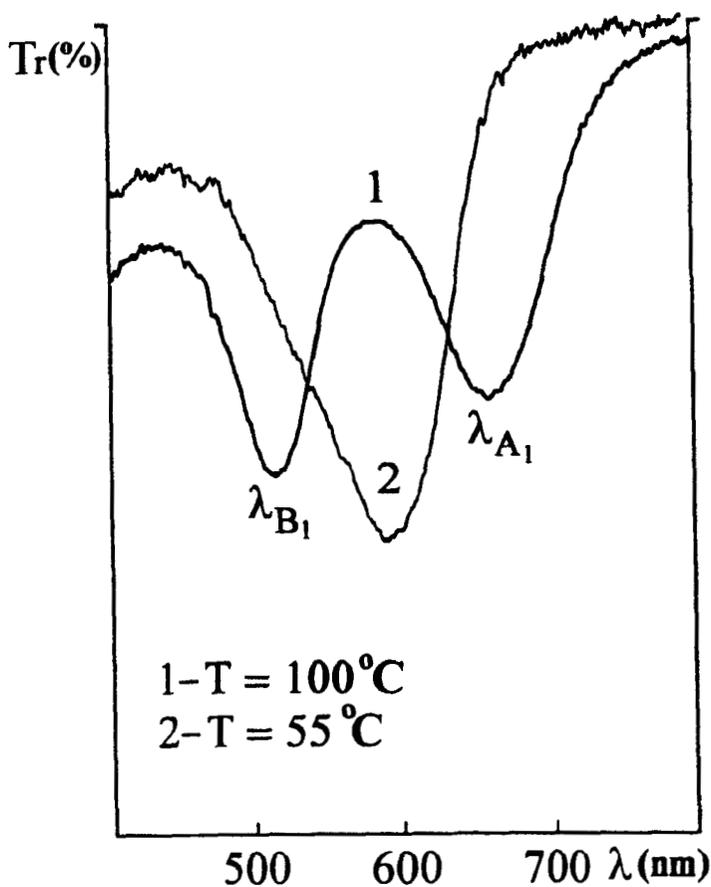
(a)

FIGURE 17   (a) Transmittance spectra of Blend 1 at different temperature and (b) temperature dependence of λ_{max} of the Blend 1 ($A_1 : B_1 = 1 : 1$).

Such unusual optical properties of cholesteric polymer blends, which were discovered by our team for the first time [71, 72] offer possibilities for development of optical materials with the temperature-controlled optical characteristics, displaying one or two regions of selective reflection of light.
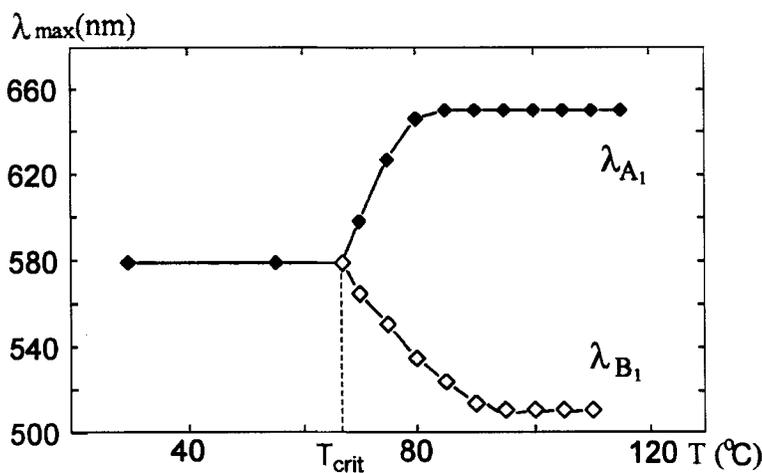
(b)

FIGURE 17   (Continued).

7. PROSPECTS FOR THE APPLICATIONS
OF CHOLESTERIC PLCs

Even though more than twenty years passed after the pioneering synthesis of polymer thermotropic cholesterics, their characterization is of a great academic, rather than practical, importance.

Nevertheless, scientists involved in both industrial and academic research of LC polymers are intrigued by the potential scope of new materials, which might combine the functionality of conventional liquid crystals with the properties of macromolecules.

From the practical viewpoint of the application of optical properties, planar texture of cholesterics, which provides the selective reflection of light in visible, IR and UV regions, is of utmost importance. Macromolecular nature of polymer cholesterics offers fascinating advantages for "freezing-in" this texture in solid glasses, films, and coverings.

This feature of cholesteric polymers opens up wide perspectives for obtaining spectrum filters, reflectors and circular dichroic optical elements [13, 17, 21].

By selecting the composition of the PLCs one may control the helix pitch and the selective reflection wave length λ_{max}, which are sensitive (or not sensitive) to temperature variations and to obtain "monochromic" and "enantiochromic" polymer films.

Cholesteric PLCs may be also used as the termooptical and photooptical active media [17]. Using the carbon dispersed black poly ethylene terephthalate film as a substrate for deposition of thin layer of cholesteric, Japanese scientists [10] observed so-called thermal head addressing. They used the planar texture of cholesterol-containing comb-shaped polysiloxanes which were locally heated by special thermal head, and polymer passed to the isotropic state. On subsequent cooling light scattering regions of confocal texture appeared; in other words symbols and letters were registered against the coloured background. The use of such cholesteric films combined with circular "right" and "left" polarizers makes it possible to change both the color of the symbols recorded and of the background [10].

Of no lesser interest is the use of cholesteric PLCs for reversible holographic recording as was demonstrated by German [73, 74] and Japanese [75] researchers.[3] Using the cyclic siloxane with side cholesteric and azobenzene groups the authors [73] recorded holograms using the principle of photo-induced *trans-cis* isomerization of azodye-fragments on exposure to laser irradiation. These cholesteric materials possessed quite high photosensitivity varying in the interval of $10^{-2} - 10^{-3}\,cm^2/J$ with high diffraction efficiency from 10 to 38%.

In our studies together with Ukrainian scientists we have shown possibility of using a mixture of nematic comb-shaped acrylic polymer [77] with a light-sensitive chiral dopant as an effective material for optical data storage. Laser-induced *trans-cis* isomerization of the dopant taking place in this material stimulated shift λ_{max} of the film from green to red spectral region by 100 nm.

An important advantage of polymer cholesterics is the possibility of producing thin polymeric films and coatings with unusual optical properties. The "Silicon Wacker" Company (Germany) has already tooled-up for the small-scale production of decorate papers, the upper layers of which is made of oligomeric cholesteric liquid crystals based on siloxanes.

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[3]These data are considered and discussed in details in the book [76].

Today, the synthetic successes in developing a great variety of chiral LC polymers opens up wide interesting perspectives for their applications in the high-tech field of optics and electrooptics, including the creation of polarizers, reflective color filters, scattering displays, notch filters and different holographic elements.

It is important to emphasize in animate Nature cholesteric films for a long time existed. A vivid example of this is the observed ability of the outer coat of a number of beetles to rotate the plane of polarization of light and selectively reflect the circularly polarized light [78]. The main "building material" of the insectan outer wing is a natural aminopolysaccharide-chitin a rigid polymer from which a frozen cholesteric mesophase, separated by a fibrillar nematic layer of the same polymer, is formed. The use of this principle for creating synthetic multilayer polymeric materials with unusual optical properties would definitely be interesting.

Acknowledgements

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