

Polymeric Liquid Crystals—Problems and Trends

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ABSTRACT: The problems of synthesis, structure and physico-chemical properties of synthetic liquid crystalline polymers whose macromolecules contain mesogenic fragments in the side chains are discussed. A detailed structural analysis of these polymers which form S_A , S_B , S_C , S_F , and other straight and inclined smectic phases is given, along with ferroelectric properties. Structural transformations in these polymers influenced by temperature and external mechanical and electrical fields cause polymorphism of liquid crystalline polymers including reversible transition from smectic to nematic phase. Conformational transitions and relaxational processes in nematic polymers by the action of an electrical field including phenomena of electrohydrodynamical instability and recording and storage of information are discussed. Attention is paid to the polymers of cholesteric structure which can be obtained by inducement of helicity due to the copolymerization of chiral monomers with comb-like systems for which nematic phase in polymeric state is typical. Optical properties of these polymers, degree of helicity, helix pitch and the wavelength of the selective reflection of the light can be regulated in wide limits using a synthetic approach, temperature, and electrical field influence.

KEY WORDS Liquid Crystals / Nematic / Smectic / Cholesteric / Helix
Pitch / Mesophase / Electrohydrodynamic Instability / Chiral Monomer /
Ferroelectric Properties / Spacer / Texture /

Up to-date physics and chemistry of polymeric liquid crystals is an intensively developing field of polymer science. Every year more than hundred new thermotropic polymeric liquid crystals are synthesized. The structure of liquid crystalline (LC) polymers and their behavior in outer fields, reology and the properties of LC solutions are studied. The theoretical aspects of the LC ordering are also developing. New applications of LC systems which combined the mechanical properties of polymeric materials and structure features of liquid crystals are being sought.

Based on the chemical structure of macromolecules thermotropic LC polymers can be divided into two groups: linear polymers containing alternating rigid and flexible fragments in the backbones and branched polymers car-

rying mesogenic groups in side chains.¹ A wide range of different mesomorphic structures is known to be formed by branched or so-called comb-like polymers. The variety of structures depends on the flexibility of the backbone, on the length and flexibility of the spacer and on the chemical nature of mesogenic fragments and attachment bridges.²

In this review we consider some structural peculiarities of LC polymers. The ferroelectric properties of chiral smectics and the optical properties of polymer side chain cholesterics are discussed in details.

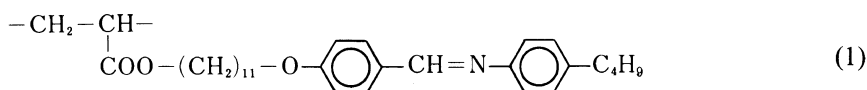
MESOPHASES OF POLYMERS WITH SIDE MESOGENIC GROUPS

Among the different mesophases of comb-

like polymers the smectic phase is the most typical one. This is related to the chemical binding of mesogenic groups by backbones. The latter should induce the layered structure formation. The wide range of backbones, spacers and mesogenic groups of different

chemical structures provide the formation of different LC phases. More than one hundred smectic comb-like polymers are known up to-date.³⁻¹⁴

Polymer 1 having the formula



below 90°C forms the smectic phase with the "fan-like" texture (Figure 1). There is an intensively sharp reflex at wide angles and a set of small angle maxima on the X-ray pattern of this polymer.⁸ For oriented samples the position of the splitted reflexes indicates the formation of the smectic phase with the ordered layers. The mesogenic groups are displaced normally to the layer plane. Such ordering is typical for the S_B phase of low molar mass liquid crystals. Between 90° and 140°C the position of splitted reflexes is the same but the wide angle maximum becomes more difused. This indicates the order disturbance within the layers and the S_A phase formation.

This example shows the dimorphism of the $S_B \rightarrow S_A$ type.

The substitution of the end group in the mesogenic group (butyl for nitryl) or the

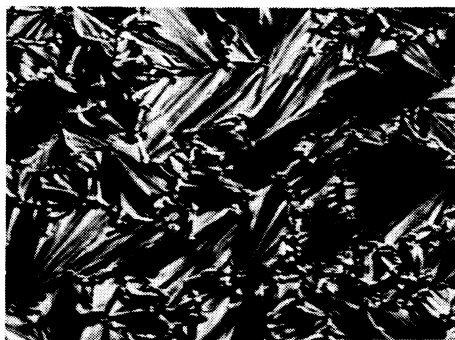
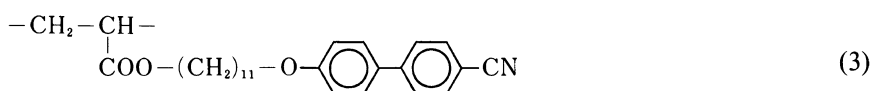
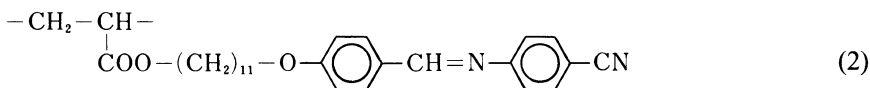


Figure 1. Optical microphotograph of smectic "fan-like" texture of polymer 1.

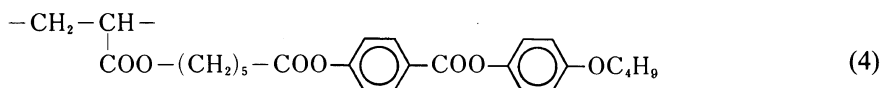
change of the mesogenic group as a whole (azomethyne for cyanobiphenyl) causes some other type of dimorphism: $S_C \rightarrow S_A$, which is observed in polymers having the general formula



In these polymers, the high temperature phase is the same as in the polymer mentioned above — S_A . But the low temperature phase is the S_C phase with the inclined arrangement of meso-

genic groups in nonordered layers.

Some other smectics are observed in acrylic polymers with phenyl-benzoate mesogenic groups.¹³ The X-ray pattern of the polymer



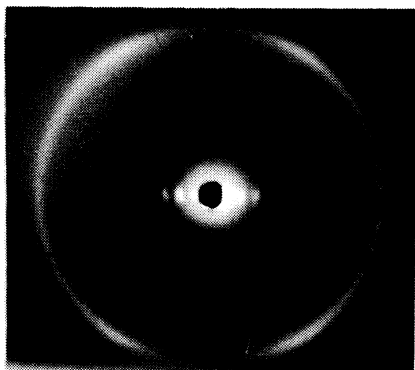


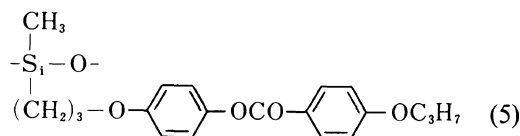
Figure 2. X-Ray texture diffraction pattern of polymer 4.

at room temperature consists of some small angle maxima and the sharp reflex at wide angles. The orientation of the polymer sample causes the splitting of the small angle rings into equatorial point-like reflexes. The wide angle reflex is split in to four arcs (Figure 2). This indicates the S_F -like inclined ordered structure of mesogenic side groups within the layer. Above 60°C the order is destroyed and the inclined S_C smectic phase is formed.

Thus, in carbonchain polymers with side mesogenic groups, one can see different smectic mesophases of S_A , S_B , S_C , and S_F types.

The highly ordered S_E phase is formed in a siloxane polymer with phenylbenzoic side

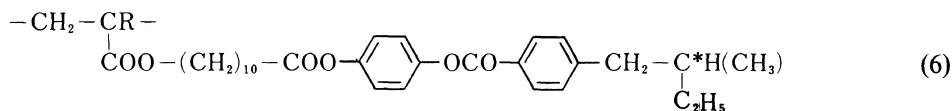
mesogenic groups:



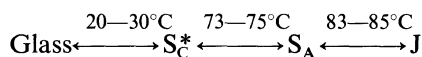
Besides small angle reflexes, there are two sharp wide-angle maxima in the X-ray pattern of this polymer. Being rather intensive, both small and wide angle reflexes are split in an oriented sample. The textured reflexes are displaced in two mutually perpendicular directions. Unlike the smectic S_B phase with the pseudohexagonal packing of mesogenic groups, the structure in the smectic S_E phase is orthorhombic.

Revealing ferroelectric properties is one of the interesting features of low molar mass liquid crystals of chiral smectic S_C^* type. It has been known that a smectic phase with chiral molecules having long axes tilted toward a layer plane has a dipole ordering. The only symmetry element of such structure is a polar two-fold axis along the layers and normal to the molecular tilt plane. Transverse dipole moment of chiral molecules determines the spontaneous polarization along this axis.

For one of the polymers with the general formula



with the following phase transitions



we detected pyroelectric effects in the range of S_C^* phase existence.¹⁵ The temperature dependences of the pyroelectric coefficient γ and spontaneous polarization P_S calculated on integrating the curve $\gamma = dP_S/dT$ are presented at Figure 3.

The relaxation time τ of the spontaneous polarization is about $100 \mu\text{s}$ well below the $S_C^* \rightarrow S_A$ transition and reveals fast growth in the vicinity of this point reaching 1 ms. This attests the presence of the soft mode in molecular motions at the transition, similar to the ferroelectric soft mode in solid ferroelectrics near the Curie point. The large relaxation time in LC polymers which exceeds value for low molar mass ferroelectric liquid crystals

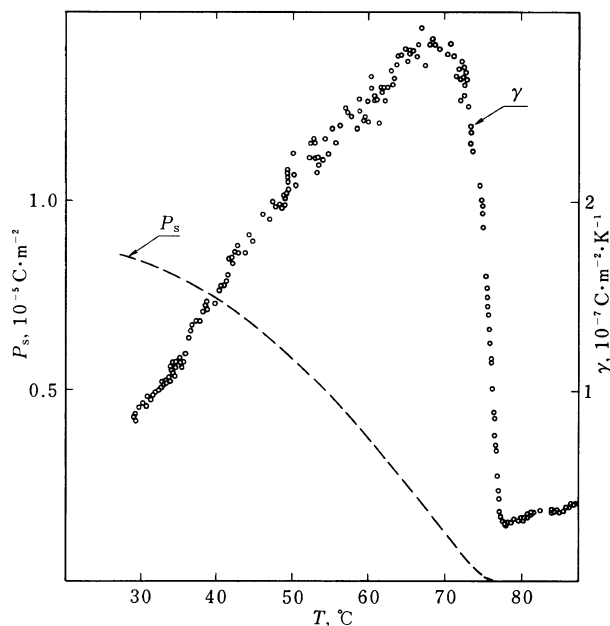


Figure 3. The temperature dependence of pyrocoefficient γ and spontaneous polarization P_s for polymer 6.

(LFLC) by two orders of magnitude seems to be connected with high viscosity of polymeric mesophase and with thermal disordering of the large molecular ensembles "tied" by polymeric chains instead of just single molecular groups.

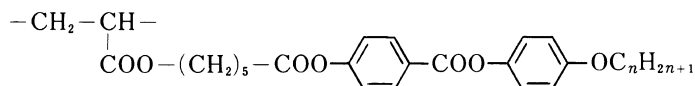
After switching off the external polarizing voltage and making short circuit of the cell electrodes, the pyroelectric response remains constant for more than 5 minutes. This is indicative of the small values of elasticity coefficients and the large values of viscosity coefficients as compared with usual LC.

The spontaneous polarization is preserved

in a wide temperature region including room temperature.

STRUCTURE OF NEMATIC POLYMERS

These have the same chemical structure as smectic polymers. But in contrast to smectic forming macromolecules they have as a rule shorter spacers and shorter alkyl substituents in mesogenic groups. As an example the polymers with phenylbenzoic mesogenic fragments may be considered

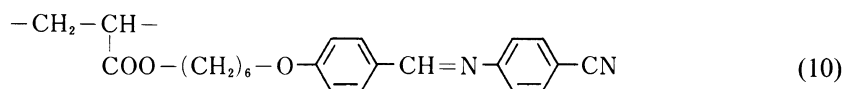
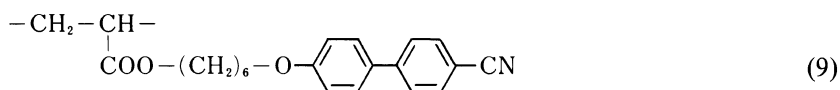


where $n=1(7)$ and $4(8)$.

While the first polymer is a nematic one, the second substance forms the smectic phases.

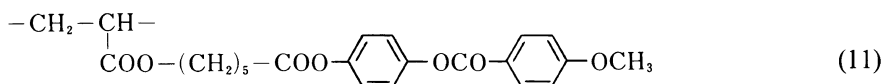
As it has been mentioned above in cyanobiphenyl and azomethyne containing polymers with 11 CH_2 -groups in the spacer, smectic

phases are formed. Preserving the chemical structure of the mesogenic group and the acrylic backbone one can obtain nematic polymers by shortening the length of the spacer (2–6 CH_2 -groups):

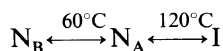


Nematic polymers form typical nematic-like optical textures—marble and shlieren texture with thread-like disclinations. There is only one diffused maximum at the X-ray pattern of a nematic polymer. But besides the usual nematic phase with the only orientation order-

ing of mesogenic groups we observed a new type of the nematic structure in polymers which has never been detected in usual liquid crystals. The X-ray pattern of the polymer given as



consists of only one sharp maximum at wide angles. This indicates the ordered hexagonal packing of mesogenic groups in the absence of the translations in the long axis direction. We have named it a nematic N_B phase. It precedes the usual nematic N_A phase



The orientation behavior of LC polymers strongly depends on the mesophase structure.¹³ Under mechanical stress the mesogenic groups of nematic polymers are arranged along the orientation axis. But the orientation of smectic polymers induces the orientation of smectic layers. The mesogenic groups are displaced normally (S_A, S_B, S_E) or inclined (S_F, S_C) to the orientation axis (Figure 4).

Smectic and nematic polymers can be slightly oriented in the orientation direction. Then in the fiber, the transition nematic—smectic takes place. In the inclined smectic phase the chevron structure with a certain angle between the layer plane and the fiber axis is formed.

Among polymeric liquid crystals the cholesteric polymers are of special interest. The unique optical properties of cholesteric liquid

crystals are related to the helix super molecular structure of the mesophase. Such a periodic structure selectively reflects the light. The wavelength of the light reflected depends on the dimensions of the helix pitch.¹⁶

The incorporation of the cholesterol-containing groups in the side chains of the comb-like polymers is one of the ways to synthesize cholesteric polymers. In Figure 5 the X-ray diffraction curves of some cholesterol-containing polymers in the smectic S_A and cholesteric phases are given. The cholesteric mesophase of low molar mass liquid crystals is well known to be represented as a combination of quasinematic layers which are turned at a certain angle. We have shown the cholesteric mesophase in polymers to have the smectic like structure. The schematic structure of polymer cholesterics is given in Figure 6. The side mesogenic groups are arranged in layers helically twisted along the axis normal to mesogenic groups. That is why any section normal to the twisting axis looks like the S_A structure element.

Cholesteric polymers selectively reflect the light. By varying the molar mass of a polymer¹⁷ one can regulate the temperature region and the range of the wavelengths (Figure

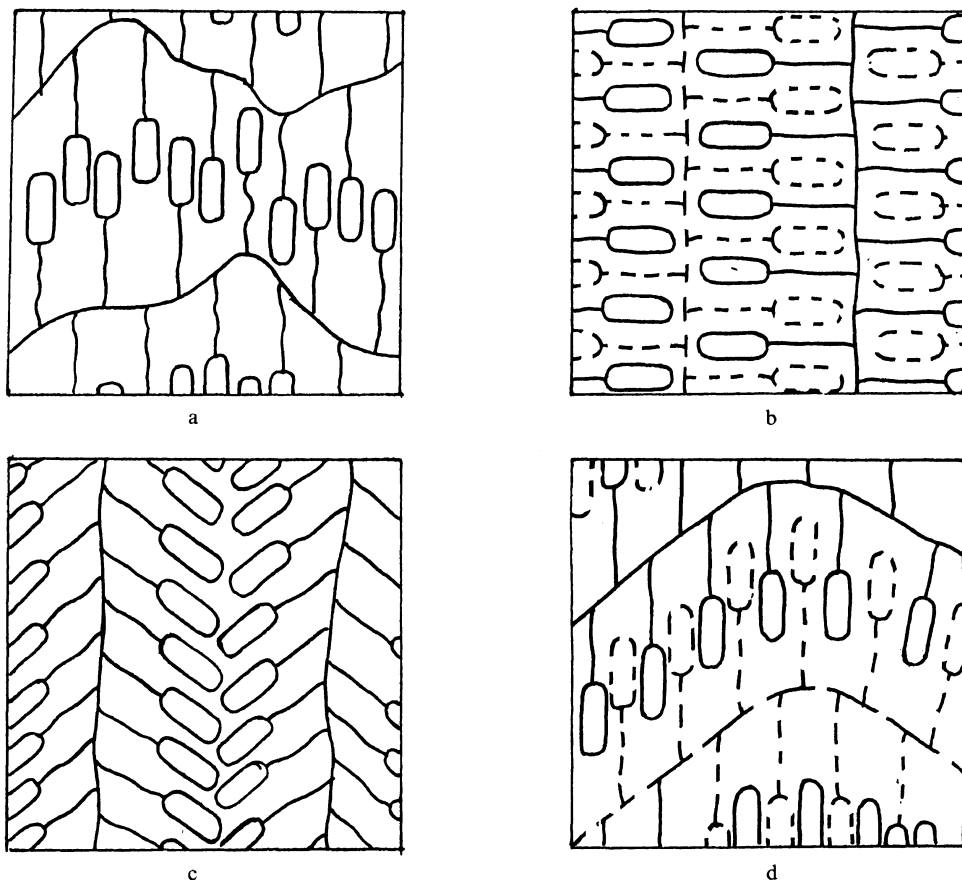


Figure 4. Schemes of macromolecular packing of oriented polymers in nematic N_A and N_B (a), smectic S_A and S_B (b), S_C and S_F (oriented in S_C) (c) and S_F (oriented in N_A) (d) phases.

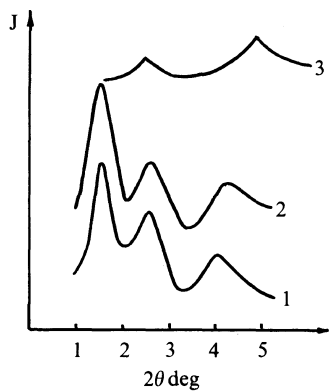
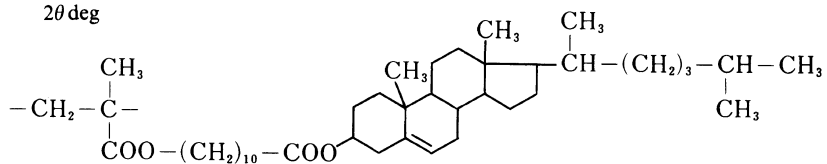


Figure 5. Small-angle X-ray diffraction curves of polymer



in $S_A(1,2)$ and $\text{Ch}(3)$ phases at 20(1), 90(2), and 140°C(3).

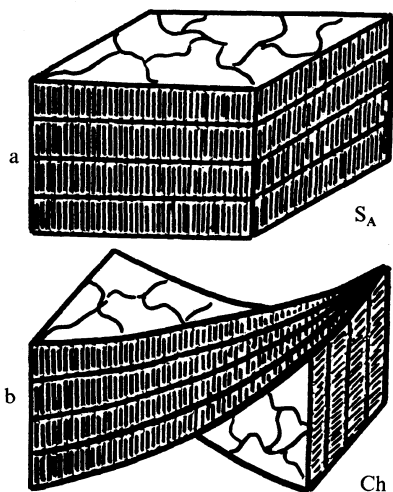


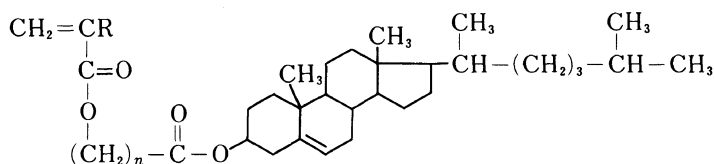
Figure 6. Schemes of arrangement of mesogenic groups in S_A (a) and cholesteric (b) phase of polymers.

7).

The copolymerization of nematogenic and cholesterol-containing comonomers is very useful for the creation of cholesteric copolymers with regulated optical properties.¹⁸⁻²⁰ The introduction of cholesterol-containing units in the macromolecules of nematic polymers induces the cholesteric twisting. An important characteristic of induced twisted structure is the rotation power A

$$A = \frac{dP^{-1}}{dX_{ch}} \quad \text{at } X_{ch} \ll 1$$

where X_{ch} , the content of the chiral additive;
 P , helix pitch.



$R = \text{H}$, $n = 5$ (ChA-5); $R = \text{H}$, $n = 10$ (ChA-10); $R = \text{CH}_3$, $n = 10$ (ChM-10)

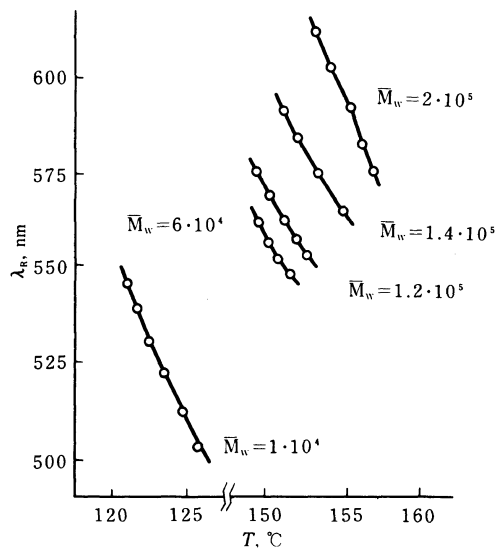
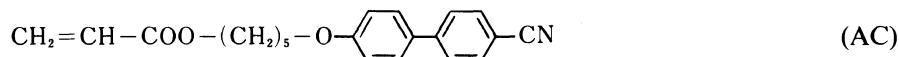
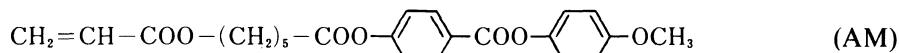


Figure 7. Temperature dependence of λ_R for the fractions of polymer: 1, $\bar{M}_w = 1 \times 10^4$; 2, $\bar{M}_w = 6 \times 10^4$; 3, $\bar{M}_w = 1.2 \times 10^5$; 4, $\bar{M}_w = 1.4 \times 10^5$; 5, $\bar{M}_w = 2.0 \times 10^5$.

Considering λ_R to be equal nP (n -refractive index, $n = \text{const}$) one can write

$$A = n \left(\frac{d\lambda_R^{-1}}{dX_{ch}} \right)$$

The twisting rotation power characterizes the ability of a nematic matrix to be twisted under the influence of a chiral additive and the twisting force of chiral additive.

In Figure 8 the dependence of λ_R^{-1} as a function of chiral units content in copolymers based on

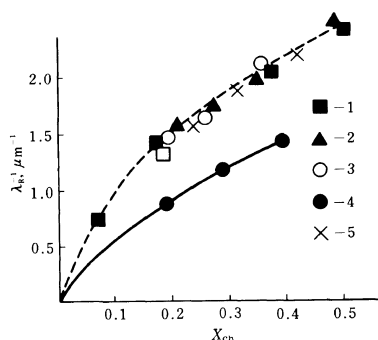


Figure 8. Dependence of λ_R^{-1} on the molar fraction of cholesterol-containing component for copolymers AM:ChA5(1), AM:ChA-10(2), AM:ChM-10(3), AC:ChA-5(4) and for cholesteryl propionate/*p*-butoxybenzylidene-*p*-butylaniline mixture (5).

is given. The twisting rotation power is the same for a wide set of copolymers on the base of nematogenic monomer with different cholesterol-containing monomers. It is about $10 \mu\text{m}^{-1} \text{mol}^{-1}$. Thus the twisting ability of a nematic matrix seems not to depend on the cholesteric monomer structure. The geometrical configuration of the cholesterol group and the molar optical rotation being the same for monomers used are the decisive factors. The value of the rotation power for the set of copolymers studied coincides with its value for the mixture of low molar mass liquid crystal-*p*-butoxybenzylidene-*p*-butylaniline and cholesterylpropionate. In the latter system, there is no specific interaction and the chirality arises only from the cholesterol fragment.

The rotation power is changed with variation of the nematic matrix. In smectogenic matrices with cyanobiphenyl mesogenic groups it is lower (about $8 \mu\text{m}^{-1} \text{mol}^{-1}$).

Causing the smectogenity, the strong lateral interactions between the mesogenic groups hinder helix twisting in such systems. One can see that the rotation power of the mixture of cholesterol propionate and *p*-butoxybenzylidene-*p*-aminobenzonitrile has the same value as the rotation power of smectogenic copolymers.

For the copolymers AM-5: ChA-10 with

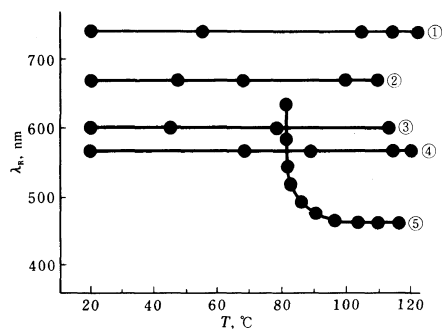


Figure 9. Temperature dependence of λ_R for copolymers AM:ChA-10, containing 17(1), 21(2), 24(3), 28(4), and 39(5) mol% of ChA-10 units.

ChA-10 unit content less than 30 mol%, the cholesteric helix pitch does not depend on the temperature (Figure 9). It is preserved below the glass transition temperature also. The latter permits obtaining the polymeric glasses which selectively reflect light of designated wavelength.

Another temperature dependence of the helix pitch is observed in copolymers containing more than 30 mol% cholesterol units. These copolymers show the tendency to form layered structures. The stronger the layer order in copolymers decreases with temperature the bigger is the helix pitch. This induces the shifting of the selective reflection into the long wave region.

The reverse character of the temperature dependence is observed in cholesterol- and CN-biphenyl containing acrylic copolymers (Figure 10). With the decrease of temperature, the helix pitch slightly decreases according to the increase of the order parameter. These copolymers are typical cholesterol systems without any elements of the layered order.

Thus we have discussed two ways to control the optical properties of cholesteric copolymers: 1) the change of the chemical structure of the comonomer and the variation of its content in the copolymer and 2) the temperature influence.

Another method of governing the optical properties of systems mentioned is using the

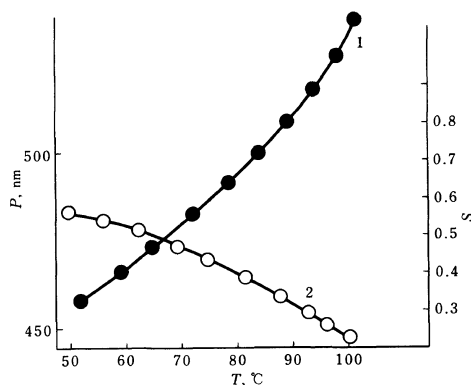


Figure 10. Temperature dependence of $\lambda_R(1)$ and order parameter $S(2)$ for copolymer AC:ChA-5 (79:21).

outer fields, in particular, the electric field.

The wavelength of selective reflection depends on the copolymer composition. With the decrease of the content of cholesterol containing units, it is shifted to the long wave region. The incorporation of CN-biphenyl-containing units provides the high positive dielectric anisotropy of copolymers and as a result, the structure transition in an electric field.

Application of an electric field to the planary oriented layer of the cholesteric copolymer with the helix axis being normally oriented to the layer plane (Figure 11) induces change of its optical properties. The increase of the voltage at its low values is accompanied by the shift of the selective reflection wavelength into the short wave region. At the same time the decrease of the optical transparency of the sample down to a certain value takes place. The subsequent voltage enhancement induces the new growth of transparency (Figure 11).

What is the explanation to this phenomenon?

At low voltage due to the positive dielectric anisotropy the orientation of the helix axis is varied. It leaves its position being normal to the layer plane for the parallel one. From the optical viewpoint this initial process corresponds to the inclined incident of light onto a

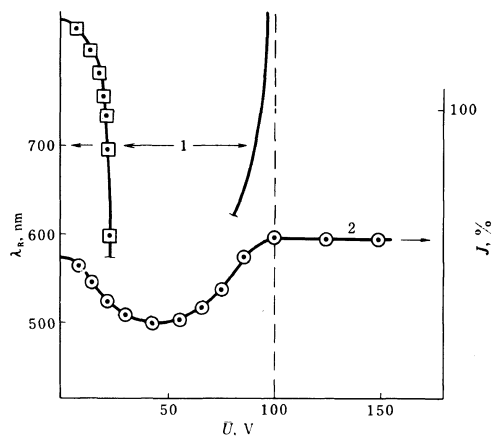


Figure 11. $\lambda_R(1)$ and the optical transparency (2) as a function of the electric field voltage for copolymer AC:ChA-5 (72:28).

cholesteric planar texture. This results in the shift of the selective reflection maximum into the blue region. The homogeneity of the sample is simultaneously disturbed and the confocal opaque texture is formed.

The more intensive change of the structure proceeds with subsequent voltage increase. Instead of cholesteric confocal texture the optically transparent homeotropic texture is formed.

The optical uniaxiality of the latter is the feature of nematics or orthogonal smectics. The X-ray data show that the side mesogenic groups in the homeotropically oriented sample are oriented along the field direction. This means the untwisting of the cholesteric helix as a result of the dielectric interaction between the polymer and an electric field.

This is how the field induced phase transition takes place. This transition in low molar mass liquid crystals is known to be interpreted as cholesterics—nematics transition. But in the comb-like polymer, the untwisted structure differs considerably from that of usual liquid crystals. There are some small angle maxima in the X-ray patterns of the copolymer subjected to the action of electric field. This indicates the layered smectic-like ordering of mesogenic

groups in the untwisted polymer cholesterics. Unlike the low molar mass cholesterics in comb-like polymers, an electric field induces cholesterics—smectics transition.

The helix untwisting process is characterized by the threshold voltage U_0 . At a voltage higher than the threshold one the helix pitch becomes infinitely large. The threshold voltage does not depend on the molar mass of the polymer. The corresponding experiments have been done for polymers having the polymerization degree of about 50—150.

Taking into account the threshold character of the untwisting process and using the equation given as

$$u_0 = \frac{\pi^2 d}{P_0} \left(\frac{4\pi K_{22}}{\Delta\varepsilon} \right)^{1/2}$$

where P_0 , helix pitch and $\Delta\varepsilon$, dielectric anisotropy, the elasticity constant K_{22} was estimated. Being not dependent on the polymerization degree the value K_{22} obtained ($\sim 9 \times 10^{-7}$ dyn) is in good agreement with that known for low molar mass mixtures of nematics and cholesterics.

Thus in spite of polymeric backbones which chemically bind mesogenic groups, the elastic properties of polymeric liquid crystals completely depend on the interaction of mesogenic groups.

But the chain structure of comb-like cholesterics contributes to the kinetics of the field induced process. On the kinetics curves of the optical transparency change, one can see both stages of the process (Figure 12). The time of the texture transformations at the first stage slightly depends on the polymerization degree. At the same time the lengthening of the polymer chain is accompanied by strong growth of the helix untwisting time at the second stage of the process (Figure 12). The untwisting time exponentially increases with the decrease of the temperature.

The high value of the activation energy E_A (~ 200 kJ mol $^{-1}$) being not dependent on the polymerization degree is characteristic for a

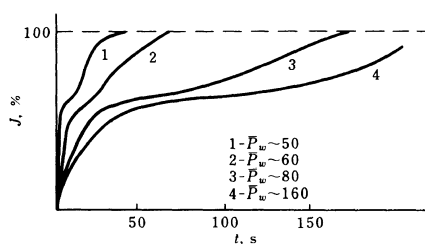


Figure 12. Kinetics of the untwisting of cholesteric helix.

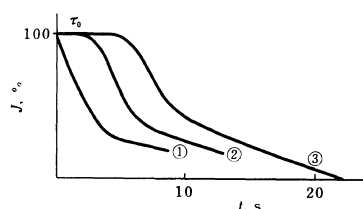


Figure 13. Relaxation transition (smectic) nematic \rightarrow cholesteric (initial voltage 120 V(1), 140 V(2), 160 V(3)).

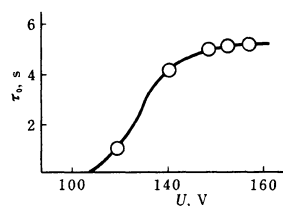


Figure 14. Induction time as a function of the initial voltage.

big set of relaxation processes in acrylic polymers which are controlled by the segmental movement of polymer chains.

The process discussed above is reversible. On switching off the field the system relaxes to an initial state. The curve of the transparency change (Figure 13) reflects the course of the relaxation process. Its S-like shape indicates the first stage of relaxation as a nucleation type process. Structure defects arise in the homeotropically oriented layer of the smectic liquid crystal during the induction time (τ_0). The consequent twisting of the cholesteric pitch begins at these places. The induction time strongly depends on the voltage at which the untwisting has proceeded. At the relatively low voltage in the macroscopically oriented sam-

ples, the twisted area seems to be preserved. In such a case, the induction period cannot be seen (Figure 13, curve 1). With voltage enhancement, the number of defects decreases. This is accompanied by the increase of τ_0 . At the limit voltage (Figure 14) this so called "memory time" preserves its constant value. The strong dependence τ_0 on the temperature should be stressed. This permits increased memory time by cooling the sample below the glass transition temperature and memorizing the structure created by the field in the polymeric film.¹

So it can be seen that polymeric LC provides a wide variety of structures and their optical properties can be regulated in the outer fields.

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