Cholesteric and other phases in thermotropic liquid crystalline polymers with side chain mesogenic groups

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<u>Abstract</u> – A new field of physical chemistry of macromolecular compounds – physical chemistry of synthetic liquid-crystalline polymers, particularly, comb-like polymers with mesogenic side-groups is considered. The classification of mesophase types of such polymers is given and the dependence of its structure on the chemical constitution of monomeric units is analized. The approaches to creation of liquid crystalline polymers with definite interval of existance and of mesophase type are demonstrated. Particular attention is paid to the structure and the optical properties (selective reflection of light) of cholesteric polymers. The formation of an intramolecular liquid crystalline structure in solutions of polymers with mesogenic side groups is discussed.

INTRODUCTION

Thermotropic liquid crystalline (LC) polymers belong to relatively novel class of lquid crystalline compounds. First attempts to create thermotropic polymeric liquid crystals have been undertaken some fifteen years ago (refs. 1 - 8).
The study of both thermotropic and lyotropic LC polymers is directly related to the solution of practical problems connected with the creation of polymeric materials endowed with pre-assigned properties. Thus, for instance, the use of the LC state anisotropy in the processing of polymeric materials proves to be highly promising for the production of ultra-strong high-modulus fibers and films (refs. 9 - 13).
At present, at least three types of thermotropic LC polymers can be considered. These are (i) melts of some linear crystallizable polymers; (ii) the polymers containing the mesogenic groups within the backbone chains, and (iii) the polymers with side chain mesogenic groups (ref. 14).
The present paper deals with the LC polymers with mesogenic groups within the side branchings of macromolecules. We emphasize the most significant and principal questions relating to some aspects of the synthesis of nematic, smectic and cholesteric LC polymers and some features of their structure.

SYNTHESIS OF LIQUID CRYSTALLINE POLYMERS WITH SIDE CHAIN MESOGENIC GROUPS

The main pathway to obtain polymers with side chain mesogenic groups involves the synthesis of monomers followed by either their homopolymerization, or copolymerization with other mesogenic or nonmesogenic compouns (Fig. 1) (refs. 14 - 18). An alternative method, that is the addition of molecules of low molar mass liquid crystals to a polymeric chain by means of polymer-analogous reactions, is used so far at seldom, and quite a few LC polymers were synthesized by this method (refs. 19 - 21).
The length of the side chain connecting the mesogenic group with the back-bone chain (the spacer) is of extremely high significance for the realization of the LC state. The point is that the attachment of the mesogenic groups directly to the backbone chain (with no spacer) not necessarily leads to the formation of the LC polymer. This is accounted for by the notable steric hindrance imposed on the packing of mesogenic groups by the backbone chain, and, as a consequence, most polymers turned out to be amorphous. The attachment of mesogenic groups to the side branching of the so-called comb-like polymers, i.e. the polymers having long aliphatic branchings, allows

to lower essentially the limitations imposed on the packing of mesogenic
groups by the backbone chain, as compared to the polymers with the mesogenic
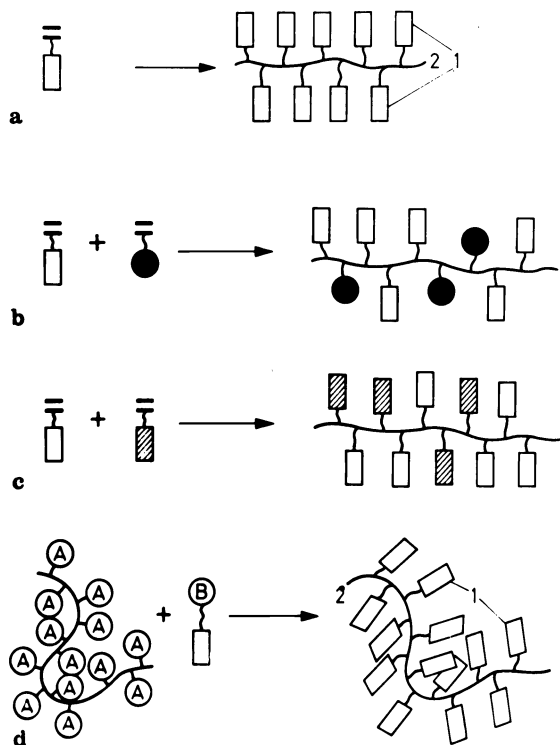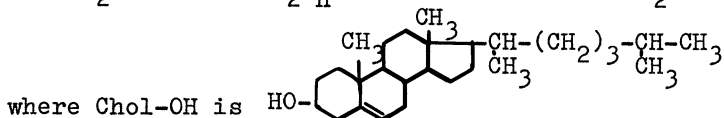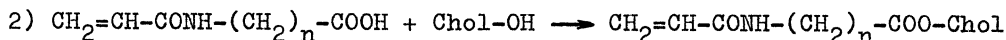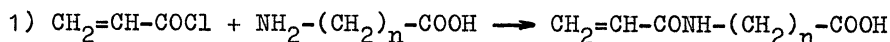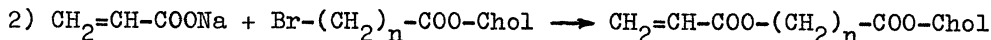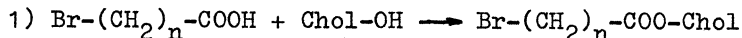groups directly attached to the backbone chain.

Fig. 1. Synthesis of LC poly-
    mers with mesogenic side
    groups: (a) – homopolymeri-
    zation; (b) – copolymeriza-
    tion of mesogenic and non-
    mesogenic monomers; (c) –
    copolymerization of mesoge-
    nic monomers; (d) – poly-
    mer-analogous reaction;
    1 – mesogenic groups;
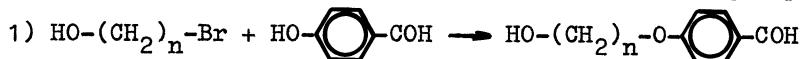   2 – main chain;
    A,B – functional groups

There are several methods to build the monomer molecules with the mesogenic
groups parted from the reactive double bond by the flexible spacer.
The first method is as follows: initially aminocarboxylic acid, which methy-
lene chain will now serve as a spacer, is attached to the reactive acrylic
or methacrylic group, and then the mesogenic groups (cholesterol fragments
for instance) are attached to the terminal carboxyl group (ref. 8):

1) $CH_2=CH-COCl + NH_2-(CH_2)_n-COOH \longrightarrow CH_2=CH-CONH-(CH_2)_n-COOH$

2) $CH_2=CH-CONH-(CH_2)_n-COOH + Chol-OH \longrightarrow CH_2=CH-CONH-(CH_2)_n-COO-Chol$
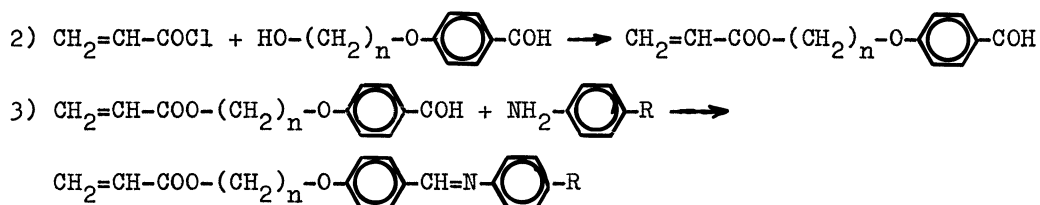
where Chol-OH is

There is an alternative method, i.e. initially the spacer is attached to the
mesogenic group, and then follows the reaction with acrylate or methacrylate
to give the monomer (ref. 22):

1) $Br-(CH_2)_n-COOH + Chol-OH \longrightarrow Br-(CH_2)_n-COO-Chol$

2) $CH_2=CH-COONa + Br-(CH_2)_n-COO-Chol \longrightarrow CH_2=CH-COO-(CH_2)_n-COO-Chol$

In those cases when it is troublesome to carry out the reaction with already
available mesogenic group, as is, e.g., the case for Schiff bases, the mono-
mer can be synthesized as follows. First, the spacer is attached to the
fragment of prospective mesogenic group, then to obtain thus far non-mesoge-
nic monomer, and finally the required mesogenic monomer is prepared by the
reaction with the other fragment of the mesogenic group (ref. 24):

1) $HO-(CH_2)_n-Br + HO-\bigcirc\!\!\!\bigcirc-COH \longrightarrow HO-(CH_2)_n-O-\bigcirc\!\!\!\bigcirc-COH$

2) $CH_2=CH-COCl + HO-(CH_2)_n-O-\langle\bigcirc\rangle-COH \longrightarrow CH_2=CH-COO-(CH_2)_n-O-\langle\bigcirc\rangle-COH$

3) $CH_2=CH-COO-(CH_2)_n-O-\langle\bigcirc\rangle-COH + NH_2-\langle\bigcirc\rangle-R \longrightarrow$

$CH_2=CH-COO-(CH_2)_n-O-\langle\bigcirc\rangle-CH=N-\langle\bigcirc\rangle-R$

Up to date, some hundred new LC polymers with various side mesogenic groups have been synthesized (refs. 14,17).

THE STRUCTURE OF SMECTIC POLYMERS

In the polymers with side mesogenic groups the spacer provides the suffici-
ent autonomy of the backbone chain and side mesogenic groups. If there was
the total autonomy then the structure of polymer would be completely deter-
mined by that of mesogenic groups, i.e. the polymers with the nematogenic
or smectogenic groups would produce the nematic or smectic mesophase, respec-
tively, whereas the chiral mesogenic groups would lead to the LC polymers of
cholesteric or chiral smectic type. As a matter of fact this is not the case.
The total autonomy cannot be achieved, and thus the structure of the polymer
is determined not only by its mesogenic groups, but also by the chemical
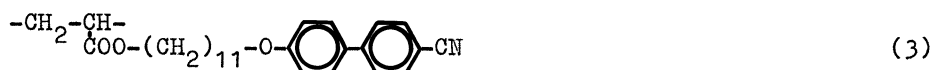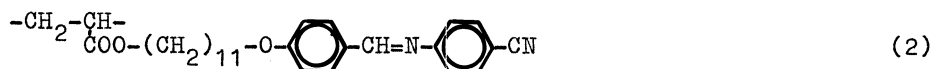structure of the spacer and backbone.
Fig. 1 shows that the backbone chain induces the layer ordering in the arra-
ngement of mesogenic groups. That is why the most abundant mesophase type
for such polymers is the smectic one. Presently, more than a hundred of
comb-like polymers are known to form the smectic mesophase (refs. 14 - 17,
23, 25 - 30). Now we consider several types of smectic mesophases which can
occur in polymers.
The polymer (1) of the following structure

$$-CH_2-\underset{\underset{COO-(CH_2)_{11}-O-\langle\bigcirc\rangle-CH=N-\langle\bigcirc\rangle-C_4H_9}{|}}{CH}- \tag{1}$$
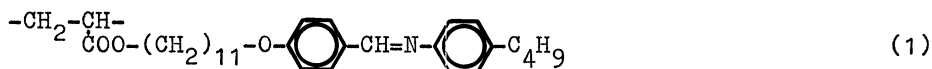
forms below 90°C the smectic phase featuring a fan-shaped texture. An X-ray
pattern of the polymer shows an intensive narrow reflection at wide angles
and a series of low-angle reflections. The orientation results in the arc-
shaped splitting of all reflections, with the low-angle reflections being
transformed into the equatorial and the wide-angle ones into the meridional
arcs (Fig. 2a). Such a character of X-ray patterns indicates the formation
of the smectic phase with the ordered layers, in which mesogenic groups are
arranged normally to the layer plane (ref. 30). This ordering is typical of
the smectic S_B phase for low molar mass liquid crystals (ref. 31). Within
the temperature range between 90 and 149°c the general character of the ref-
lection arrangement is pertained but the wide-angle reflection becomes dif-
fuse (Fig. 2b). This fact indicates that the order in layers is destroyed,
and, hence, is typical of the smectic S_A phase. Thus, the smectic dimorphism
S_B - S_A is found in the polymer (1). The structure of these phases is shown
in Fig. 3.
If the butyl group in the mesogenic group of the above polymer is substitu-
ted by the nitrile one (the polymer (2)) (ref. 32), or the azomethyne meso-
genic group is substituted by the cyanodiphenyl one, leaving unaffected the
backbone acrylate chain and the spacer of 11 methylene units (the polymer
(3)) (ref. 28), one arrives at the other type of dimorphism.

$$-CH_2-\underset{\underset{COO-(CH_2)_{11}-O-\langle\bigcirc\rangle-CH=N-\langle\bigcirc\rangle-CN}{|}}{CH}- \tag{2}$$

$$-CH_2-\underset{\underset{COO-(CH_2)_{11}-O-\langle\bigcirc\rangle\langle\bigcirc\rangle-CN}{|}}{CH}- \tag{3}$$

The high-temperature phase of these polymers is the same as in the polymer
(1), while the low-temperature phase has a tilted disordered arrangement of
mesogenic groups within the layers, that is, represents the smectic S_C phase.
The other type of smectic polymorphism is observed for the comb-like poly-
mers with acrylic backbone chains and phenylbenzoate mesogenic group. An
X-ray pattern of the polymer (4) (ref. 29) at room temperature shows the

low-angle reflections and a narrow wide-angle reflection (Fig. 2c).

$$-CH_2-CH-\\ \quad\ COO-(CH_2)_5-COO-\langle\bigcirc\rangle-COO-\langle\bigcirc\rangle-OC_4H_9 \qquad (4)$$

Upon orientation the low-angle rings are splited into the equatorial point
reflections, while the wide-angle reflection is splitted into 4 arcs. This
fact indicates the tilted ordered arrangement of mesogenic groups in layers,
typical of the smectic S_F phase. Increasing the temperature within the 60 -
145°C range destroys the order in the layers to give the S_C phase (Fig. 2d).
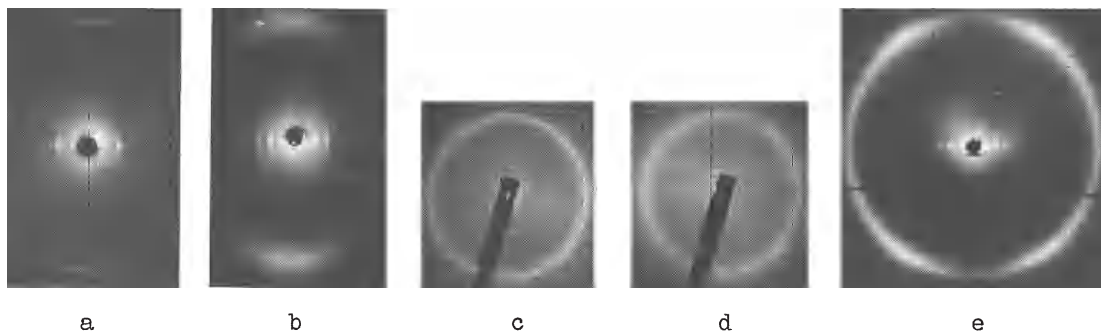The structure of the S_F and S_C phases is shown in Fig. 3.

Fig. 2. X-ray diagrams of polymer (1) in oriented S_B(a) and S_A(b)
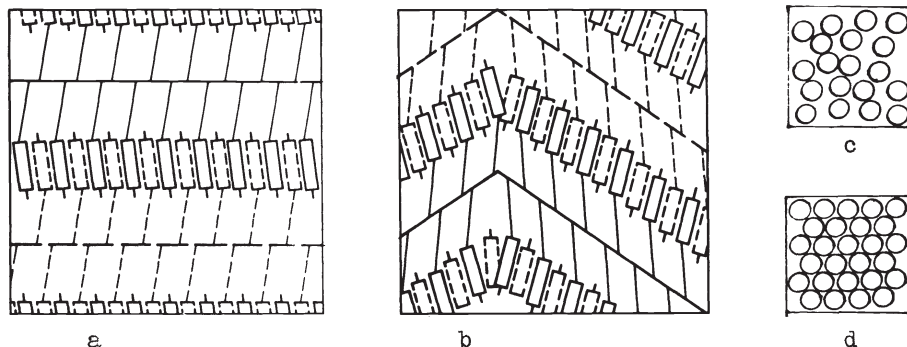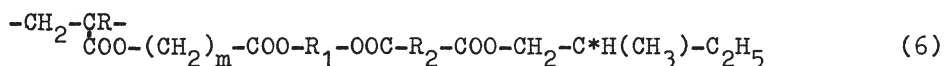phases and polymer (4) in S_F(c), S_C(d) and in oriented S_F(e)^A pha-
ses.

Fig. 3. Schemes of molecular packing in smectic phases.
Arrangement of macromolecules with mesogenic groups in S_A(a),
S_B(a), S_C(b) and S_F(b) phases.
Packing of the mesogenic groups in plane, perpendicular to long
axis of side groups in S_A(c), S_C(c), S_B(d) and S_F(d) phases.

Thus, the smectic phases S_A, S_B, S_C and S_F are all observed in the polymers
with the carbon-chain backbone and various mesogenic groups. The highly-or-
dered smectic phase S_E is formed in the polymer with the siloxane backbone
chain and phenylbenzoate mesogenic groups (the polymer (5)):

$$\begin{array}{c} CH_3\\ -Si-O-\\ (CH_2)_3-O-\langle\bigcirc\rangle-OOC-\langle\bigcirc\rangle-OC_3H_7 \end{array} \qquad (5)$$
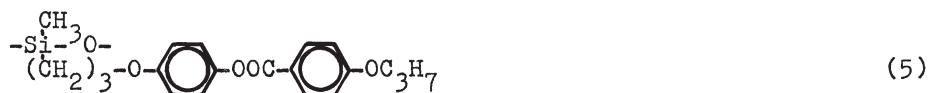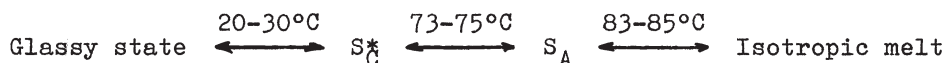
An X-ray pattern of this polymer shows together with intensive low-angle re-
flection the presence of 2 narrow wide-angle reflections. Upon orientation
the low- and wide-angle reflections break up into mutually perpendicular di-
rections (Fig. 4) (ref. 33). In contrast to the S_B phase with the pseudohe-
xagonal packing of mesogenic groups , that of the S_E phase is orthorombic.
One of particular features of the low molar mass liquid crystals of the chi-
ral smectic S_C^* type is their ferroelectric properties. It is known that the
smectic phase with chiral molecules, whose longer axes are inclined to the

layer plane, has an ordered arrangement of dipoles. The only symmetry element for such a structure is a polar two-fold axis lying within the layer plane and normal to the plane of molecule inclination. In this case there can occur a spontaneous polarization along that axis which is determined by the transversal dipole moment of the chiral molecules.
For one of the polymer of general formula (6)

$$-CH_2-\underset{\underset{\displaystyle COO-(CH_2)_m-COO-R_1-OOC-R_2-COO-CH_2-C*H(CH_3)-C_2H_5}{|}}{CR-} \qquad (6)$$

which displayed the following transitions

$$\text{Glassy state} \xleftrightarrow{20-30°C} S_C^* \xleftrightarrow{73-75°C} S_A \xleftrightarrow{83-85°C} \text{Isotropic melt}$$

we have revealed the pyroelectric phenomenon within the region of the chiral smectic S_C^* phase existence (ref. 34). The temperature dependences of the pyrocoeffitient γ and spontaneous polarization P_s, calculated by integrating the curve γ (T), are shown in Fig. 5.
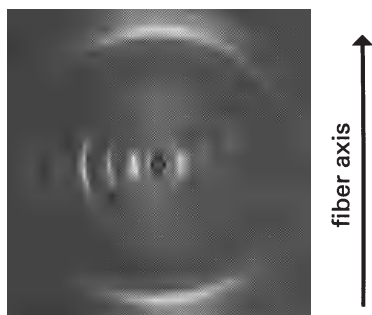

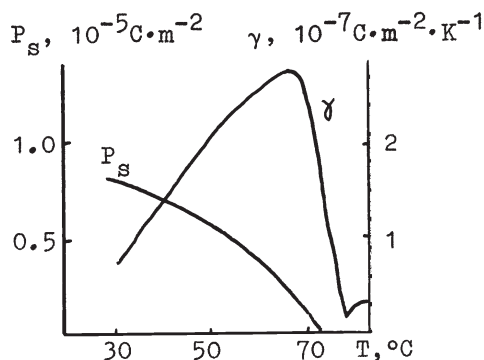Fig. 4. X-ray diagram of oriented polymer (5) in S_E phase

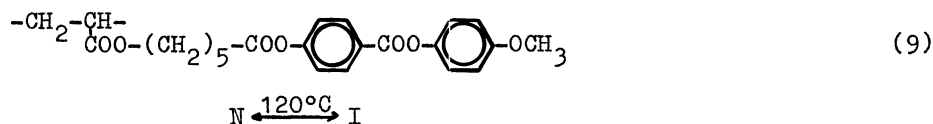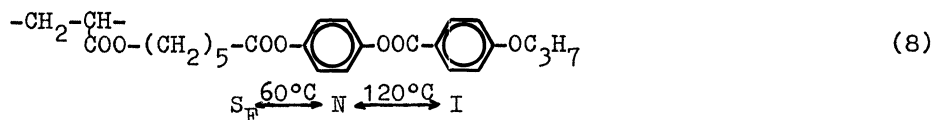Fig. 5. The temperature dependence of pyrocoefficient γ and spontaneous polarization P_s for polymer (6)
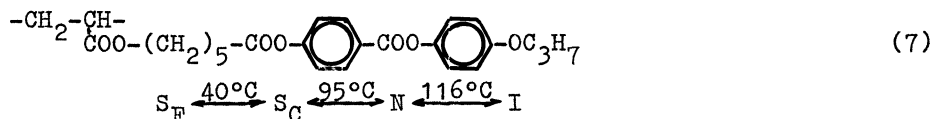
The relaxation time of spontaneous polarization τ is $\sim$100 μs well below the S_C^* - S_A transition point, but increases sharply nearly the latter point up to $\sim$1 ms. This fact indicates the presence of the soft mode for molecular motion in this transition, similar to the ferroelectric soft mode in solid ferroelectrics near the Curie point. The large relaxation time for the polymeric LC ferroelectric, which is two orders of magnitude as great as that for the low molar mass ferroelectric liquid crystals, seems to be related to the greater viscosity of the polymeric mesophase and to the thermal disordering not of separate mesogenic groups, but rather of large ensembles "entangled" by polymeric chains.
After the external polarizing field was switched off and the cell electrodes were made short circuit, the pyroelectric responce remains constant for more than 5 min., hence indicating the low elastisity modulus and veryhigh viscosity coefficient as compared to those of low molar mass liquid crystals.
The spontaneous polarization was preserved within the broad temperature range, at room temperature in particular.
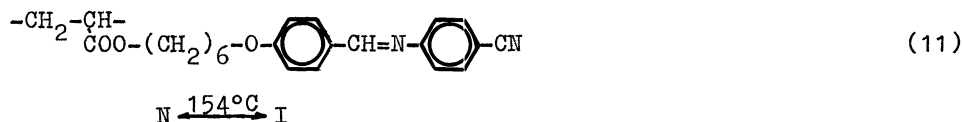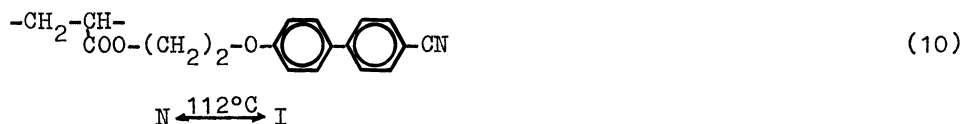
THE STRUCTURE OF NEMATIC POLYMERS

Now let us consider the polymers forming the nematic mesophase. The structure of these polymers is similar to that of smectic polymers, but, as a rule, with shorter spacers and shorter alkyl substituents in mesogenic groups. Thus, the above-mentioned polymer (4), having phenylbenzoate mesogenic group and 4-carbon terminal substituent, gives rise to smectic phases. The polymers (7) and (8), having phenylbenzoate mesogenic group and 3-carbon terminal substituents, form both smectic and nematic phases (ref. 29).
For the polymer (9), having a 1-carbon terminal substituent, only nematic

phase is observed (ref. 29).

$$-CH_2-CH- \\ \quad COO-(CH_2)_5-COO-\bigcirc-COO-\bigcirc-OC_3H_7 \qquad (7)$$

$$S_F \xrightarrow{40°C} S_C \xleftarrow{95°C} N \xleftarrow{116°C} I$$

$$-CH_2-CH- \\ \quad COO-(CH_2)_5-COO-\bigcirc-OOC-\bigcirc-OC_3H_7 \qquad (8)$$

$$S_F \xleftarrow{60°C} N \xleftarrow{120°C} I$$

$$-CH_2-CH- \\ \quad COO-(CH_2)_5-COO-\bigcirc-COO-\bigcirc-OCH_3 \qquad (9)$$

$$N \xleftarrow{120°C} I$$

The polymers with cyanodiphenyl and azomethyne mesogenic groups and the spa-
cer of 11 methylene units form, as it was already shown, smectic phases. Ta-
king a shorter spacer of 2 − 6 methylene units (and leaving unaffected the
mesogenic group and the acrylate backbone) gives rise to the nematic poly-
mers (10) and (11) (refs. 24, 32).

$$-CH_2-CH- \\ \quad COO-(CH_2)_2-O-\bigcirc\bigcirc-CN \qquad (10)$$

$$N \xleftarrow{112°C} I$$

$$-CH_2-CH- \\ \quad COO-(CH_2)_6-O-\bigcirc-CH=N-\bigcirc-CN \qquad (11)$$

$$N \xleftarrow{154°C} I$$

The nematic polymers show the textures which are typical of nematic liquid
crystals, i.e. marbled, schlieren, threaded. The X-ray patterns of nematic
phases of polymers show the presence of only one diffuse maximum (Fig. 6a).
And besides the usual nematic phase with just orientational order in the ar-
rangement of mesogenic groups, we have found in polymers a new type of the
nematic ordering (ref. 29), which was not observed in low molar mass liquid
crystals. An X-ray pattern for the polymer (12) of the following structure

$$-CH_2-CH- \\ \quad COO-(CH_2)_5-COO-\bigcirc-OOC-\bigcirc-OCH_3 \qquad (12)$$
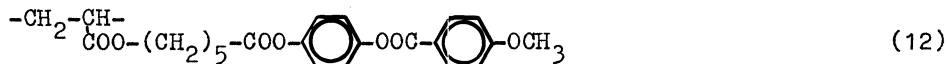
shows one narrow wide-angle reflection with no low-angle reflections (Fig.
6b). Such a character of the X-ray pattern indicates the ordered hexagonal
packing of the side mesogenic groups with no translational order in the di-
rection of their long axes (Fig. 7). This new type of the nematic structure
may be denoted as the nematic N_B phase, which in the considered polymer pre-
cedes the usual nematic N_A phase

$$N_B \xleftarrow{60°C} N_A \xleftarrow{120°C} I$$
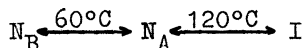
One of peculiar features of the smectic and nematic polymers is their beha-
viour upon the uniaxial orientation (ref. 29). Under the action of a mecha-
nical field on nematic polymers it is the mesogenic groups that are arranged
along the orientation axis, not the backbone chains, i.e. there occurs a
concerted turning of the LC domains formed by the mesogenic groups (Figs.
6a and b). In the case of the smectic polymers it is the smectic layers that
are arranged along the orientation axis, while the mesogenic groups are ar-
ranged either normally to them (the smectics S_A, S_B, S_E (Figs. 2a,b and 4))
or at some angle (the smectics S_F, S_C (Fig. 2e[A])). The[B] polymers that form
both smectic and nematic mesophases (the polymer (8)) are readily orientable
in the nematic phase, with the mesogenic groups being oriented along the ori-

entation axis, and then, in fibers, the nematic – smectic transition takes place (Fig. 8). If the mesogenic groups in the smectic phase are tilted to the layer then the chevron-like structure is originated, with the smectic layers being situated at some angle to the fibre axis.
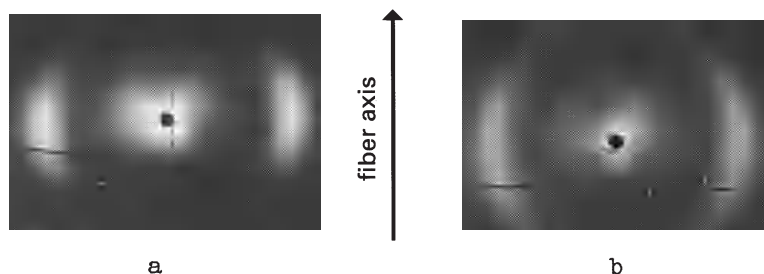

Fig. 6. X-ray diagrams for polymer (9) in oriented N_A phase (a) and for polymer (12) in oriented N_B phase (b)
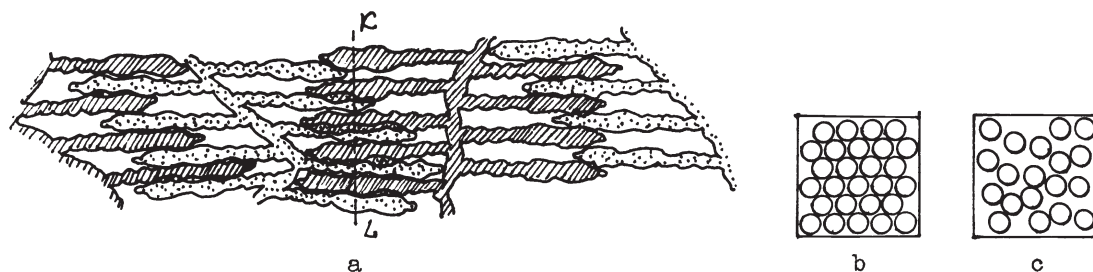

Fig. 7. Scheme of macromolecular packing in nematic phases. Arrangement of macromolecules with mesogenic groups framed by Van der Waals radii (a); packing of mesogenic groups in N_B(b) and N_A(c) phases within the KL plane, which is normal to long axes of side branchings.
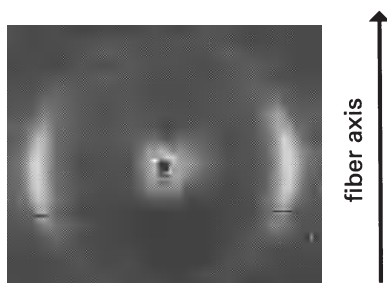

Fig. 8. X-ray diagram for polymer (8) in S_F phases, oriented in the nematic state.

THE STRUCTURE AND OPTICAL FEATURES OF CHOLESTERIC POLYMERS

A separate class of the LC systems is formed by the polymers with the cholesterol-containing side groups (refs. 6 – 8, 14 – 16, 36 – 38). Low molar mass cholesterol esters form the liquid crystalline cholesteric phase which is characterized by the helical structure. The helix pitch of this structure is usually of the order of the visible light wavelengths, so the cholesteric liquid crystals reflect selectively visible light. The reflected light has either left or right-hand circular polarization depending on the sign of the cholesteric helix. The helix pitch is highly sensitive to various external effects and this property finds wide application in different devices.
The cholesterol-containing polymers of the acrylic and methacrylic series of general formula

$-CH_2-CR-$
$CO-X-(CH_2)_n-COO-Chol$, whre R=H or CH_3; X=NH or O and n=2 – 14
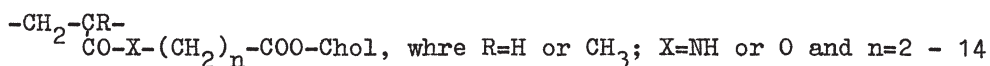
were synthesized in (refs. 18, 36, 37).
All the cholesterol-containing polymers form mesophase within the broad tem-
perature range. X-ray patterns of these polymers in the wide-angle region
show just a diffuse halo corresponding to a spacing of 0.58 - 0.62 nm. The
uniaxial orientation increases the intensity of the halo in the meridional
direction. In the low-angle region a series of intensive reflections is obser-
ved which transform to equatorial arcs upon the uniaxial orientation. Such a
pattern of the reflections intensity is defined primarily by the normal ar-
rangement of the side groups with respect to the backbone chains. The positi-
on of the low-angle reflections depends on the length of the methylene spa-
cer connecting cholesterol to the backbone chain. This fact indicates the
formation of the layered structures with the layer thickness defined by the
length of the side mesogenic groups. The structure of the polymers is shown
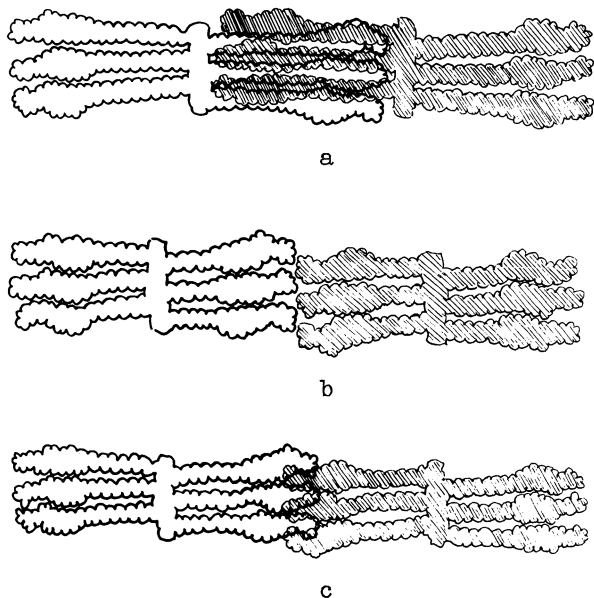schematically in Fig. 9.

a

b

c

Fig. 9. Schemes of macromole-
cular packing of cholesterol-
containing polymers:
a) one-layer
b) two-layer
c) intermediate
Shaded molecules are within
the plane parallel to the
Figure plane.

Depending on the length of the spacer there can be formed a one layer pack-
ing with the mesogenic groups being antiparallelly arranged in such a way
that the cholesterol groups of one macromolecule are surrounded by the methy-
lene chains of the neighboring macromolecules. The short spacers give rise
to the two-layer packing with mesogenic groups being arranged in parallels.
An intermediate packing in which the aliphatic parts of the cholesterol gro-
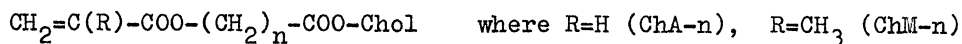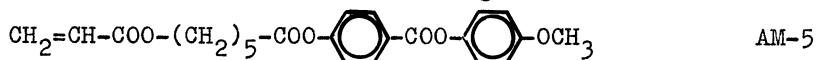ups overlap is also possible.
As is known a typical feature of the cholesteric liquid crystals is their
ability to reflect light selectively and, as a consequence, to display cir-
cular dichroism. In fact, for a series of cholesterol-containing polymers in
the UV-region there was observed the maximum of reflection and circular di-
chroism (ref. 38).
Thus, the cholesterol-containing homopolymers of the acrylic and methacrylic
series form both smectic and cholesteric mesophases, the latter reflects se-
lectively the light in the UV-region.
In order to obtain the cholesteric polymers having the ability to reflect
visible light the property of the nematic liquid crystals to untwist the he-
lix of the cholesteric mesophase is usually employed.
Wide opportunities provide copolymerization of cholesteric monomers with ne-
matogenic ones (refs. 39, 40). At present, a large number of copolymers
which reflect selectively visible light has been synthesized on the basis of
nematogenic and cholesterol-containing monomers (refs. 17, 40, 41).
As an example let us consider the copolymers of the nematogenic monomer AM-5
with various cholesterol-containing monomers

$$CH_2=CH-COO-(CH_2)_5-COO-\bigcirc-COO-\bigcirc-OCH_3 \qquad \text{AM-5}$$

$$CH_2=C(R)-COO-(CH_2)_n-COO-Chol \qquad \text{where } R=H \text{ (ChA-n)}, \quad R=CH_3 \text{ (ChM-n)}$$

Increasing the fraction of the nematic monomeric units in copolymers leads
to the shift of the wavelength of the selective reflection to the long-wave
region, which means the untwisting of the cholesteric helix. The formation
of the cholesteric mesophase in copolymers can be considered also as the in-
dusing of the helical structure in the nematic polymer under the action of
chiral colesterol-containing units. A useful characteristic, which is widely
used in studying optical properties of the induced cholesteric mesophase in
nemato-cholesteric mixtures, is the helical twisting power (HTP) of a chiral
additive

$$HTP = \frac{d\rho}{dx_{ch}}$$

where x_{ch}- molar fraction of chiral additive. Taking into account that $\lambda_R = nP$
(n is the average refractive index, P is the helix pitch) and assuming
$n = const$ the latter expression can be written as

$$HTP = n \frac{d\lambda_R^{-1}}{dx_{ch}}$$

i.e. HTP is determined by the slope of λ_R^{-1} as a function of x_{ch}.
Fig. 10 shows the dependence of λ_R^{-1} on x_{ch} for a series of cholesteric copo-
lymers. As can be seen from this Figure, the copolymers of the same nemato-
genic monomer and different cholesterol-containing monomers have the value
of the HTP which is close to that for the mixtures of low molar mass chole-
sterics and nematics, namely, cholesteryl propionate and p-buthoxybenzylide-
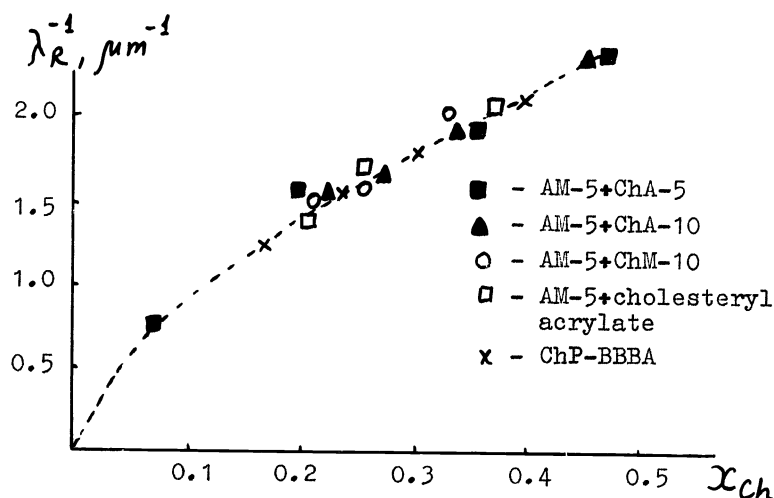ne-p-buthylaniline (ChP-BBBA).

Fig. 10. Dependence of λ_R^{-1} on the molar frac-
tion of cholesteric component for copoly-
mers and for mixtures of low molar mass li-
quid crystals.

■ – AM-5+ChA-5

▲ – AM-5+ChA-10

○ – AM-5+ChM-10

◻ – AM-5+cholesteryl acrylate

x – ChP-BBBA

Now let us consider the influence of the temperature on the helix pitch of
the mesophase of cholesteric copolymers. For low molar mass cholesterics in
the region far from phase transitions the helix pitch is,as a rule, slightly
dependent on the temperature. A sharp dependence on temperature is observed
near the point of transition tothe smectic mesophase, provided the latter
exists. The copolymers of AM-5 and ChA-5 give rise to the cholesteric meso-
phase only, and the helix pitch for these copolymers is defined by their com-
position and is slightly dependent on temperature within the whole range of
the mesophase existence (Fig. 11). Weak dependence of the helix pitch on the
temperature is observed also for the copolymers AM-5 with ChA-10 and AM-5
with ChM-10 for low concentrations of cholesterol-containing units. Increa-
sing the concentration of the latter enhances their tendency to form layer
structures, i.e. smectogenety, in consequence the helix pitch in the copoly-
mers containing more than 30 mol.% of ChA-10 or ChM-10 units sharply increa-
ses with decreasing of temperature (Fig. 11).
A significant feature of polymeric systems is their ability to pass to the
glassy state. This property allows one to fix the cholesteric mesophase with
a definite helix pitch within a glassy film. Since all comb-like cholesteric
polymers form the left-hand helix, they reflect the left-hand circular com-
ponent and transmit the right-hand one, and thus, they are transformers of
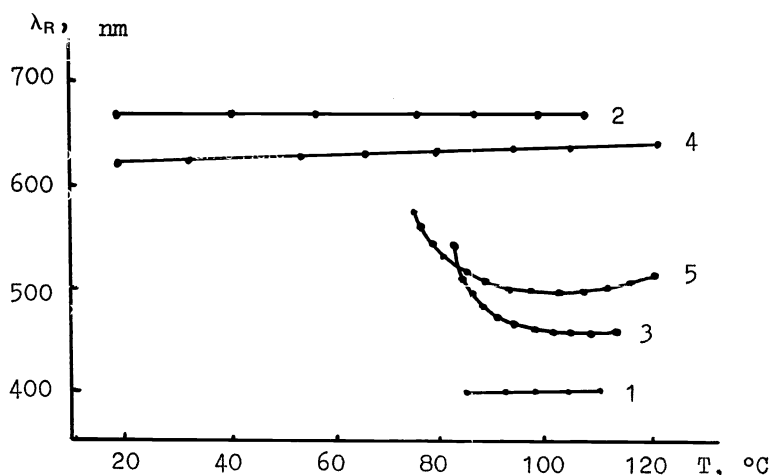the plane-polarized light into the circular- polarized one.

Fig. 11. Temperature dependences of λ_R for copolymers of AM-5
    with 20 mol.% of ChA-5 (1), with 28 mol.% of ChA-10 (2),
    with 39 mol.% of ChA-10 (3), with 22 mol.% of ChM-10 (4)
    and with 33 mol.% of ChM-10 (5).

THE FORMATION OF INTRAMOLECULAR STRUCTURE IN
CHOLESTEROL-CONTAINING POLYMERS

The chain structure of macromolecules of the LC polymers leads to the forma-
tion of a principally new type of mesophase - the intramolecular mesophase
at the level of a single macromolecule. This effect is displayed most clear-
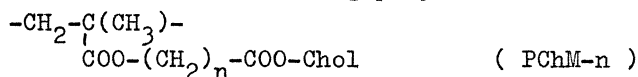ly in the cholesterol-containing polymers.

$$-CH_2-\underset{|}{C}(CH_3)-$$
$$COO-(CH_2)_n-COO-Chol \qquad\qquad (PChM-n)$$

Fig. 12 shows the temperature dependence for the radius of gyration $(\bar{R}^2)^{1/2}$,
intrinsic viscosity $[\eta]$, specific optical rotation $[\alpha]$ and relaxation
time τ (characterizing the intramolecular mobility) for one of cholesterol-
containing polymers (PChM-10) in heptane solution.
It is easily seen from this Figure that sharp change of all the above para-
meters takes place within the temperature region 40 - 60°C.
The decrease in $(\bar{R}^2)^{1/2}$ and $[\eta]$ result from the formation of compact struc-
ture. The latter is substantiated also by the decrease in the intramolecular
mobility (the increase in the τ). The internal structure of the globule
can be inferred from the polarimetry data. It can be seen that the $[\alpha]$ va-
lues for temperatures below 40°C are essentially greater than those resul-
ting from the intrinsic molecular activity of the cholesterol group (the da-
ta for the monomer, which are unaffected within the whole temperature range,
are also listed). High optical activity (roughly of the order as observed
for the polymer at 20°C) is characteristic for liquid crystals of the choles-
teric type. All the results show unambiguously that below 40°C the choleste-
ric liquidcrystalline globules are formed.
Analysing the relationships shown in Fig. 12 allows to distinguish two sta-
ges in the observed transition. At the first stage (60-50°C) there occurs ce-
rtain reduction in size of the molecule and decrease in the intramolecular
mobility. The $[\alpha]$ values are almost unaffected. This is the transition "a
coil - an isotropically liquid globule", with random arrangement of mesoge-
nic groups in the latter. The second stage (below 50°C) is characterized by
the sharp drop of the intramolecular mobility and sharp increase in $[\alpha]$.
This fact indicates the transition "isotropically liquid globule - liquid
crystalline globule of the cholesteric type" with the mesogenic groups pac-
ked,in a dense helical structure.
The mechanism of formation of globule with the intramolecular cholesteric
structure is clearly manifested in studying the fractions of the polymer
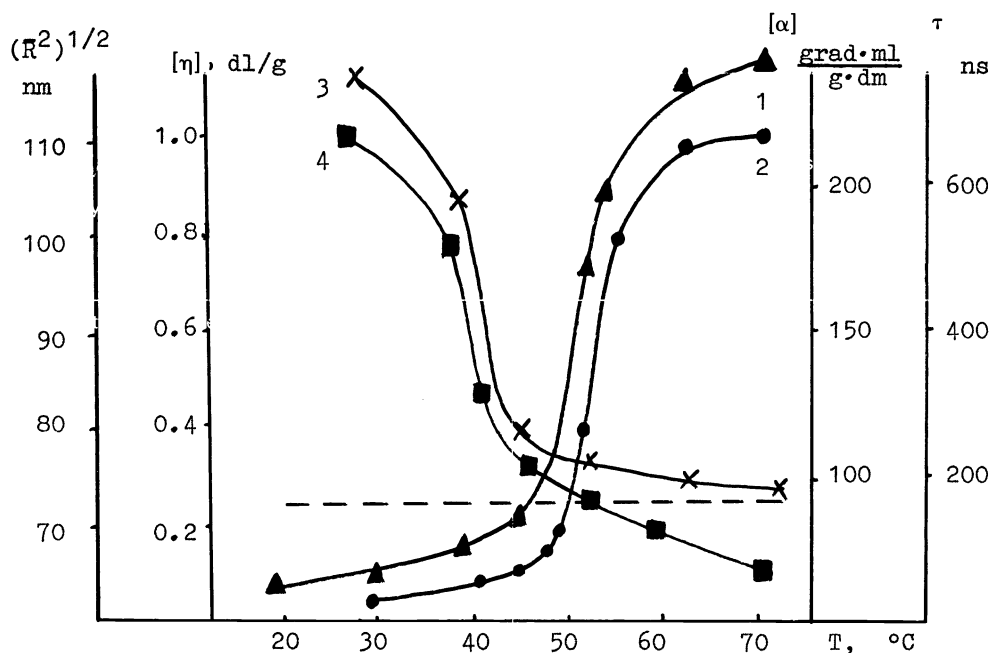with different molar mass.

Fig. 12. Temperature dependences for $(\bar{R}^2)^{1/2}$ (1), $[\eta]$ (2),
[α] (3) and τ (4) for PChM-10 in heptane solution.
Dotted line - [α] for monomer ChM-10.

For the high-molecular sample ($\bar{M}_w=6.6 \cdot 10^6$- the molar mass is unaffected with
in the whole temperature range, i.e. the LC globules consist of a single ma-
cromolecules (Fig. 13). The formation of the LC globule for the macromolecu-
les of molar mass less than $1.5 \cdot 10^6$ is accompanied by the effective growth
of the molar mass, i.e. the association of macromolecules takes place. These
results show that the formation of the intramolecular mesophase requires a
definite critical content of mesogenic groups, which for the polymer consi-
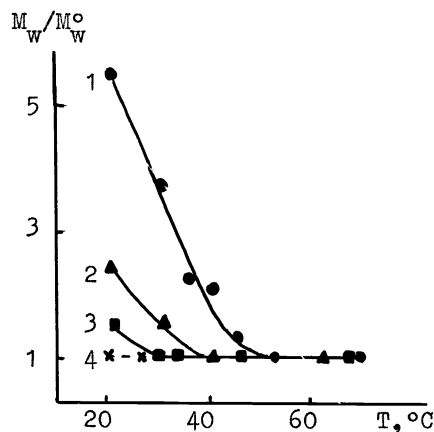dered amounts to ~ 3000.

Fig. 13. Temperature dependence for
changes in PChM-10 molar mass in
heptane solution (M_w/M_w^o) for frac-
tion $M_w^o=0.35 \cdot 10^6$(1); $0.73 \cdot 10^6$ (2)
$1.5 \cdot 10^6$ (3); $6.6 \cdot 10^6$ (4)

Thus wide variety of types of structural arrangements in thermotropic LC po-
lymers and possibility to change this structure give chance to regulate pro-
perties of these very promissing and interesting polymeric materials.

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