

Synthesis and structure of liquid-crystalline side-chain polymers

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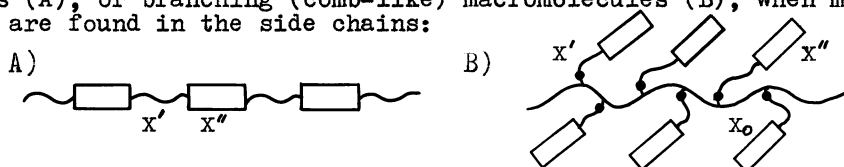
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Abstract - The synthesis, structure and some properties of thermotropic liquid crystalline polymers with side mesogenic groups are discussed. Approaches towards the synthesis of such systems are presented, as well as the data revealing the relationship between the molecular structure of the liquid-crystalline polymers and the type of mesophase formed. The structure of smectic, nematic and cholesteric mesophases as well as models of chain packing in them are analyzed. The possibility to affect the structure of a liquid-crystalline polymer by an electric field is demonstrated.

INTRODUCTION

A new scientific trend related to the synthesis and study of thermotropic liquid-crystalline (LC) polymers was formed and extensively developed in the field of chemistry and physics of high molecular weight compounds in the past decade (refs. 1-5).

The general approach towards the synthesis of such systems is incorporation of mesogenic fragments into macromolecules with formation either of linear systems (A), or branching (comb-like) macromolecules (B), when mesogenic groups are found in the side chains:



where x' and x'' are the lengths of flexible and rigid fragments, respectively, x_0 is the distance between points of branching, \bullet is the attachment bridge.

An important role in the both cases belongs to the length of flexible fragments (spacers) $-x'$, linking either mesogenic groups with each other (A) or separating mesogenic groups from the main chain (B). This above-mentioned pathway was the first time used in refs. (6-8) for the synthesis of LC comb-like polymers (refs. 6-7) and linear systems (ref. 8), it is currently universally adopted (ref. 5)*.

Liquid-crystalline side chain polymers are obtained either by synthesis of monomers containing LC (mesogenic) groups with their subsequent homopolymerization (Fig.1a) or by copolymerization with non-mesogenic (Fig.1b) or mesogenic compounds (Fig.1c), or by attachment of molecules of low molecular weight liquid crystals to the polymer chain via polymer-analogous reactions (Fig.1d). These methods open in fact unlimited possibilities for combinations of different mesogenic fragments within macromolecules (ref. 11).

Among synthesized LC comb-like polymers, those of acrylic and methacrylic series, containing various types of widespread mesogenic fragments of low-molecular weight liquid crystals (Schiff's base, cyanobiphenyl groups,

*There are some other pathways of obtaining linear LC polymers when "foreign" units distorting the initial regular structure of the polymer chain are incorporated (refs. 9,10).

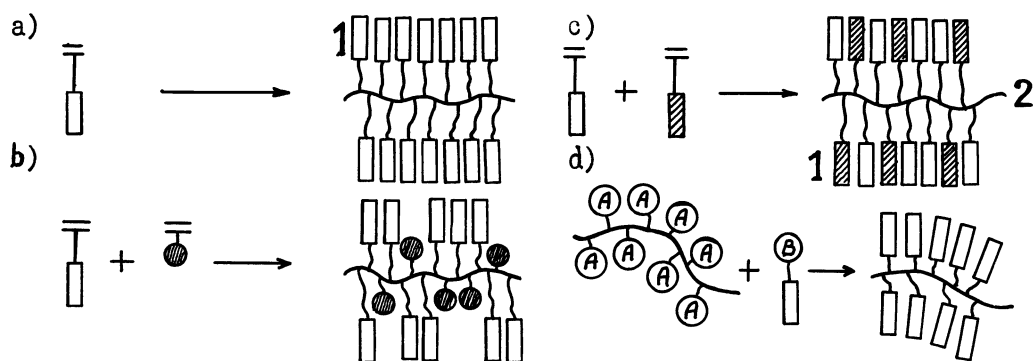


Fig. 1. Synthesis of LC polymers with mesogenic side groups
1-mesogenic groups; 2-main chain; A and B -functional groups.

esters of alkoxybenzoic acids, cholesterol esters etc.) occupy the central position. A great number of copolymers of mesogenic monomers with alkyl-acrylates and methacrylates were synthesized (ref. 12). Organoelemental LC compounds (linear and crosslinked polysiloxanes) (ref. 13), LC polymers with discotic molecules (ref. 14) as well as LC polymers containing a number of mesogenic groups in each monomer unit (ref. 15) were obtained.

Recently already several hundreds of LC comb-like polymers have been obtained and the possibilities given by synthesis are quite evidently far from being exhausted.

Therefore the number of "synthetic" papers increases, while that on studies of the structure and regularities of physico-chemical behavior of LC polymers is still very small, in particular, in comparison with the papers on studies of physical properties of low molecular weight liquid crystals.

This situation is, probably, explained by two reasons. The first is that the synthesis of thermotropic LC polymers is still more difficult than that of low molecular weight liquid crystals. Hence, small amounts of substances are available for researchers. The second is the consequence of the first - most synthesized LC polymers are available for polymer chemists and "synthesis" chemists. Without disparaging the merits of this group of researchers, it should be said that, this fact, naturally, restricts the use of the wide arsenal of physical methods of studies conventional for the low molecular weight liquid crystal researchers.

This paper presents the result of comb-like polymer structure studies and of some other studies carried out in general at Moscow State University; some of the data have been obtained in collaboration with the scientists of Kiev Institute of Chemistry of High Molecular Compounds of the Ukrainian Academy of Sciences.

PECULIARITIES OF MOLECULAR STRUCTURE OF THERMOTROPIC LIQUID CRYSTALLINE SIDE CHAIN POLYMERS

Let us start from the common peculiarities of the structure of LC polymers containing side mesogenic groups. The macromolecules of these polymers are of dual nature. On the one hand, they are carriers of "polymeric" properties determined by the main chain. On the other hand, the side mesogenic groups are carriers of mesomorphic properties. More complicated structure of LC polymers in comparison to that of low molecular weight crystals hampers studies of their properties and especially the interpretation of their physico-chemical behavior. As low molecular weight fragments are simultaneously carriers of liquid and crystal properties they are figuratively called centaur, and then attachment of these centaur to the polymer chain transforms them into peculiar polycentaur and the behaviour of these complicated hybrids cannot be always predicted and cannot be always explained.

First let us consider briefly the role of each of the fragments of the macromolecule, i.e. of the main chain, of the spacer, of the attachment bridge and of mesogenic fragments in LC state formation.

The main chain

It is natural to start from the role of the main chain since it distinguishes polymer liquid crystals from low molecular weight liquid crystals:

a) First of all attachment of low molecular weight liquid crystals to the macromolecular chain increases the thermal stability of mesophase as it is seen in Fig.2. The interval of LC state, determined by the glass transition

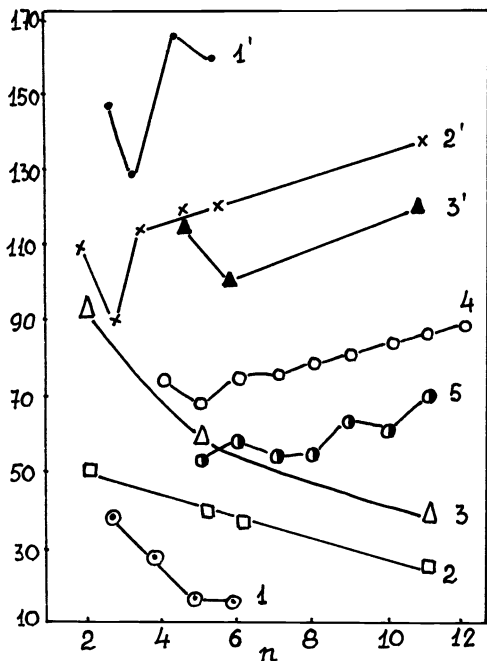
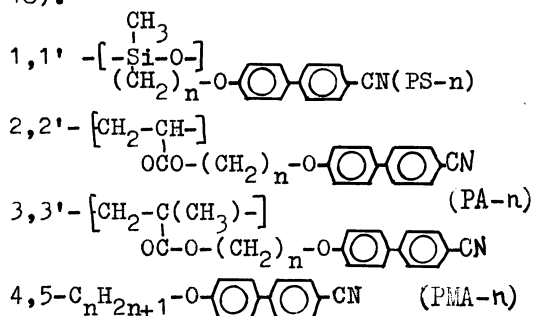


Fig. 2. Glass transition temperatures (1-3), clearing points (1'-3', 4) and melting temperatures (5) vs. number (n) of carbon atoms in the aliphatic substituent (refs. 16-18).



temperature (T_g) (the low limit) and the clearing temperature (T_{cl}), is much wider in the case of polymers than that in low molecular analogues.

b) The clearing temperature rises with increasing degree of polymerization (DP). It should be indicated that there is some critical value of DP starting from which T_{cl} does not depend on DP (Fig.3) (refs. 19-21). It is seen in figures 3a and 3b that DP_{crit} only slightly depends on the nature of the polymer main chain.

c) The main chain in LC polymers provides much higher viscosity of polymer mesophases which is 3-4 times as high as that of low molecular liquid crystals (refs. 13,22). This results in slowing down of all structural

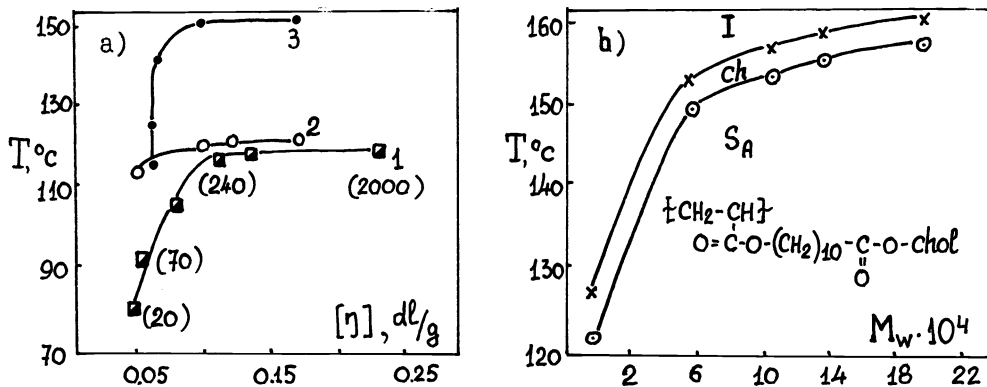
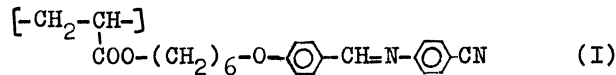


Fig. 3. Clearing points of biphenyl-cyano-containing polymers (a) and cholesterol-containing polymers (b) as a function of molecular weight: 1-PA-5; 2-PMA-5; 3-PA-11 (see symbols in legend to Fig.1) (in parentheses: P_w for fractions of PA-5) (refs.19-21).

rearrangements in thermotropic LC polymers. It is clearly seen in the table where the time of orientation, τ , in the electric field is given for polymer fractions with various degree of polymerization P_w (ref.21).



P_w	5-10	250	350	1200
τ, s	4	18	25	510

d) Just retardation of all structural and relaxation processes results in the appearance of a great number of nonequilibrium (metastable) states which may be often erroneously interpreted as equilibrium states. Reaching the equilibrium for LC polymer often requires a very long time (or T rise).

On the other hand, it is one of the most interesting specific features of LC polymers, allowing to affect the anisotropic liquid LC phase and to control its properties and to fix (by cooling below T_g) LC structure with inherent anisotropy of mechanical, optical, electric and other properties in a solid material (refs. 3-5,11-13).

e) The importance of the chain length is manifested at the studies of orientation of LC polymers. Recently at least two quite opposite orientations of mesogenic groups for one and the same polymer, depending on DP, were found (ref.23). Using the method of IR spectroscopy, authors (ref. 23) have calculated the value of the dichroic ratio R_{xy} for a number of the characteristic absorption bands of different polymer fractions in the process of the mechanical orientation.

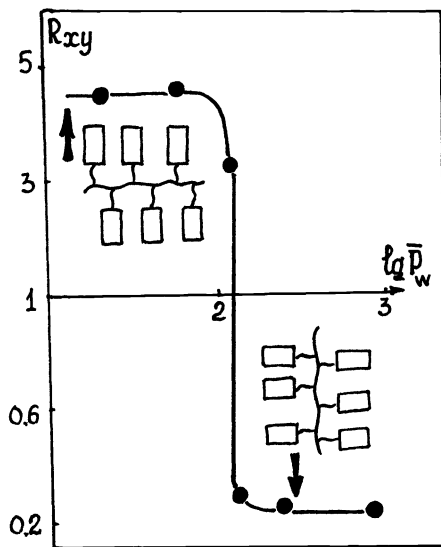


Fig. 4. Dichroic ratio as a function of P_w and schemes of mesogenic groups arrangement in PA-5 (ref. 23).

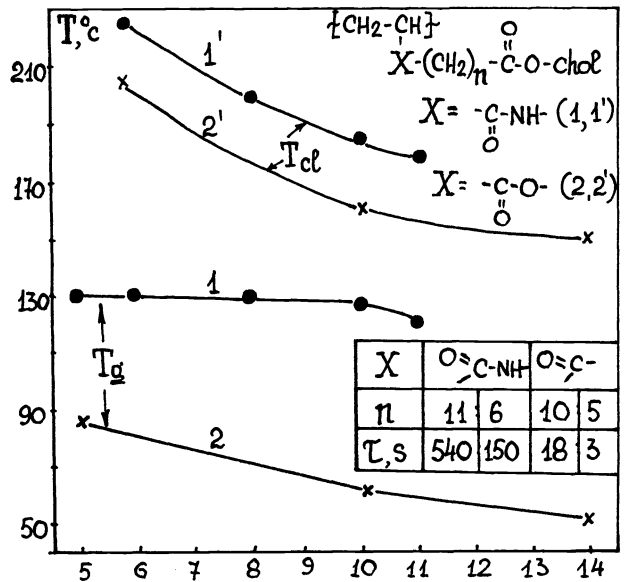


Fig. 5. T_g and T_{c1} vs. spacer length and relaxation time, τ , of dipole polarization in solution for cholesterol-containing polymers (refs. 28-29)

It is seen in Fig.4 that at small DP mesogenic groups are oriented in the direction of the force action, i.e. in the same direction as the molecules of low molecular weight liquid crystals. If some value of DP_{crit} is exceeded, quite opposite orientation is observed. Different orientations of mesogenic groups are, evidently, determined by the ratio of the rates of rearrangement of mesogenic groups and main chains under the action of the mechanical field affecting different structural elements of a polymer sample at different DP.

TABLE 1. Influence of the main chain flexibility on LC temperature interval for polymers with identical mesogenic groups (refs. 13, 18, 20, 24).

$R=O-\text{C}_6\text{H}_4-\text{C}_6\text{H}_4-\text{CN}$	$T_g, ^\circ\text{C}$	$T_{cl}, ^\circ\text{C}$	$R=O-\text{C}_6\text{H}_4-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-\text{C}_6\text{H}_4-\text{OCH}_3$	$T_g, ^\circ\text{C}$	$T_{cl}, ^\circ\text{C}$
$[-\text{CH}_2-\overset{\text{CH}_3}{\underset{\text{OCO}(\text{CH}_2)_6-\text{R}}{\text{C}}}-]$	55	S 100	$[-\text{CH}_2-\overset{\text{CH}_3}{\underset{\text{OC}-\text{O}(\text{CH}_2)_2-\text{R}}{\text{C}}}-]$	96N	121
$[-\text{CH}_2-\overset{\text{CH}_3}{\underset{\text{OCO}(\text{CH}_2)_6-\text{R}}{\text{C}}}-]$	35	S 125	$[-\text{CH}_2-\overset{\text{CH}_3}{\underset{\text{OC}-\text{O}(\text{CH}_2)_2-\text{R}}{\text{C}}}-]$	47N	77
$[-\overset{\text{CH}_3}{\underset{(\text{CH}_2)_6-\text{R}}{\text{Si}}}-\text{O}-]$	14	S 166	$[-\overset{\text{CH}_3}{\underset{\text{CH}_2-(\text{CH}_2)_2-\text{R}}{\text{Si}}}-\text{O}-]$	15N	61

f) It should be noted that the main chain flexibility affects the temperature range of LC phase (Table 1). As is seen from Table 1 when flexibility of the polymer backbone increases from polymethacrylates to polysiloxanes (a drop of T_g), an elevation of clearing temperature for polymers with oxycyanobiphenyl groups is observed, while for polymers with methoxyphenylbenzoate groups T_{cl} decreases. Different phase behavior of the two groups of polymers is, probably related to different types of mesophases formed by these two groups of polymers, however, the problem of the importance of the main chain flexibility in the formation of LC state of polymers and its effect on mesophase type and T_{cl} cannot be considered as completely elucidated.

Spacer-groups

a) The main function of a spacer is to provide autonomy in the behavior of side mesogenic groups. There is certain correlation between the main and side chains for polymers without spacers. This correlation disappears for comb-like polymers, especially when spacers become longer. That is clearly shown by the data of studies of birefringence in solutions and by the comparison of the values of optical anisotropy ($\alpha_1-\alpha_2$) and Kerr constant, K, (characterizing in fact the degree of binding of various structural units) (Table 2) (ref. 25). It is seen that "separation" of a mesogenic fragment from the main chain by "polymethylene bridge" consisting of 10 methylene units results in a drastic decrease in the correlation of side groups and backbone orientation.

b) The other not less important function of spacers is related to their plasticizing effect on polymer. Figs. 2 and 5 show that an increase in the

TABLE 2. Segmental anisotropy ($\alpha_1-\alpha_2$), the Kerr constant K and the number of monomer units in the Kuhn's segment ν (ref. 25).

No	Structure of the monomer unit	$(\alpha_1-\alpha_2) \cdot 10^{25} \text{m}^3$ (solvent)	$K \cdot 10^{10}$ ($\text{cm}^5 \text{g}^{-1}$) $\nu / (300)^{-2}$	ν
1.	$[-\text{CH}_2-\overset{\text{CH}_3}{\underset{\text{OC}-\text{O}-\text{C}_6\text{H}_4-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-\text{C}_6\text{H}_4-\text{OC}_{16}\text{H}_{33}}{\text{C}}}-]$	-3100(CCl_4)	-10	24
2.	Monomer of polymer 1	-	+0.21	-
3.	$[-\text{CH}_2-\overset{\text{CH}_3}{\underset{\text{OC}-\text{O}-\text{C}_6\text{H}_4-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-\text{C}_6\text{H}_4-\text{C}_9\text{H}_{19}}{\text{C}}}-]$	-2700(CCl_4)	$-(8.0 \pm 3.0)$	25
4.	$[-\text{CH}_2-\overset{\text{CH}_3}{\underset{\text{OC}-\text{O}-(\text{CH}_2)_{10}-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-\text{C}_6\text{H}_4-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-\text{C}_6\text{H}_4-\text{C}_4\text{H}_9}{\text{C}}}-]$	-90 (dioxane)	$-(0.8 \pm 0.2)$	26

spacer length results in the T_g shift towards lower temperatures.

c) The mesophase type can be greatly affected by the spacer group length. More than 4-6 methylene units in a spacer group give a possibility to transform the nematic mesophase to smectic one under other similar conditions.

d) The flexibility of a spacer group considerably affects the formation of LC mesophase (Table 3).

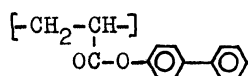
TABLE 3. Influence of the main chain and spacer flexibility on the phase state of polymers with identical mesogenic groups ($R = \text{---} \text{C}_6\text{H}_4 \text{---} \text{C}_6\text{H}_4 \text{---} \text{CN}$) (refs. 16,20,26)

No	Main chain	Side chain	Temperature of phase transitions °C
1.	$\left[\text{CH}_2 - \underset{\text{OC-O-}}{\underset{ }{\text{C}}}(\text{CH}_3) - \right]$	$-(\text{CH}_2)_2\text{-O-}(\text{CH}_2)_2\text{-OR}$	$T_g = 65^\circ$ No mesophase
2.		$-(\text{CH}_2)_5\text{-OR}$	$T_g = 65^\circ$ S120 I
3.	$\left[\text{CH}_2 - \underset{\text{OC-O-}}{\underset{ }{\text{CH}}} - \right]$	$-(\text{CH}_2)_2\text{-O-}(\text{CH}_2)_2\text{-OR}$	$T_g = 35^\circ$ No mesophase
4.		$-(\text{CH}_2)_5\text{-OR}$	$T_g = 40^\circ$ S120 I
5.	$\left[\begin{array}{c} \text{CH}_3 \\ \\ \text{---Si-O---} \\ \\ \text{CH}_2 \end{array} \right]$	$-(\text{CH}_2)_2\text{-O-}(\text{CH}_2)_2\text{-OR}$	$T_g = 5^\circ$ LC phase 60 I
6.		$-(\text{CH}_2)_5\text{-OR}$	$T_g = 14^\circ$ S166 I

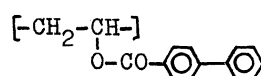
The attachment bridge

The attachment bridge connects a mesogenic group through a spacer with the main chain. It would have seemed that this small fragment is of no importance for the physico-chemical behavior of a macromolecule. Let us demonstrate, however, its importance by two examples only.

a) Below two polymers with identical mesogenic groups, but with different directions of ester groups are presented:



(II)



(III)

Polymer II forms a smectic mesophase with $T_{cl} \approx 200^\circ$, polymer III does not exist in LC state (ref.27).

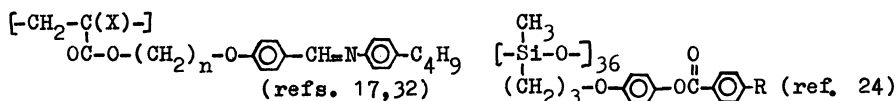
b) The other example (Fig.5) shows the effect of the formation of hydrogen bond between attachment bridges on transition temperatures and molecular mobility (refs. 28,29).

Thus, we attempted to show the role played by each of the structural elements of the macromolecule of LC polymer without considering the role played by a mesogenic group. But actually the situation is more complicated and the mutual influence of different structural elements and their contribution to the structure and behavior of macromolecules essentially aggravates the finding of general regularities in the properties of LC polymers. However, some theoretical studies concerning orientational ordering in the melt of linear and comb-like polymers with mesogenic groups (see types A and B macromolecules on the first page of this paper) and finding of the certain correlation between molecular structure (x_0 , x' and x'') of these polymers and their properties are already being developed (refs. 30-31).

Let us consider now the structure of smectic, nematic and cholesteric mesophases.

SMECTIC MESOPHASES

Most LC comb-like polymers form smectic mesophases. Previously, in structural studies of LC polymers, researchers considered that only A, B and C mesophases exist in polymers. Recently E, F, G mesophases and chiral smectics C* have been obtained (refs. 32-37). Examples of some types of mesophase polymorphism are listed in Tables 4 and 5.

TABLE 4. S_B and S_A - polymorphism of LC polymers

No	X	n	$S_B \rightarrow S_A$		$S_A \rightarrow I$		No	R	T_{GC}°	$S_B \rightarrow S_A$		$S_A \rightarrow I$	
			$T_{1,9}^{\circ}\text{C}$	$\Delta H_1, \text{J/g}$	$T_{\text{cl}}^{\circ}\text{C}$	$\Delta H, \text{J/g}$				$T_{1,9}^{\circ}\text{C}$	$\Delta H_1, \text{J/g}$	$T_{\text{cl}}^{\circ}\text{C}$	$\Delta H, \text{J/g}$
1	H	6	76	4.2	115	8.4	5	-OCH ₃	-	46(S _E)	10.7	169	4.4
2	H	11	90	6.7	149	11.3	6	-OC ₄ H ₉	65	79	7.7	179	5.2
3	CH ₃	6	77	3.3	115	7.9	7	-OC ₅ H ₁₁	43	52	1.0	177	6.0
4	CH ₃	11	86	5.0	140	12.5	8	-OC ₆ H ₁₃	75	115	2.7	176	10.8
							9	-OC ₈ H ₁₇	67	82	3.1	156	10.7

TABLE 5. Some types of smectic mesophases (refs. 19, 35-36)

No	Polymer	R	Type of mesophase and phase transitions, °C
1.	$[-\text{CH}_2-\text{CH}-]$ COO-(CH ₂) ₅ -COO-C ₆ H ₄ -COO-C ₆ H ₄ -OR	-C ₃ H ₇	$S_G \xleftarrow{60} S_C \xrightarrow{40} S_F$ 95 N 116 I
2.		-C ₄ H ₉	S_F 60 S_C 145 I
3.	$[-\text{CH}_2-\text{CH}-]$ COO-(CH ₂) ₅ -COO-C ₆ H ₄ -OOC-C ₆ H ₄ -OR	-C ₃ H ₇	S_F 60 N 120 I
4.		-C ₄ H ₉	S_F 70 N 135 I
5.	$[-\text{CH}_2-\text{C}(\text{CH}_3)-]$ OC-O-(CH ₂) ₁₀ -C(=O)-O-C ₆ H ₄ -OCO-C ₆ H ₄ -R	-OC ₇ H ₁₅	S_F 80 S_C 139 I
6.		$-\text{C}(=\text{O})-\text{O}-(\text{CH}_2)_2-\text{CH}(\text{CH}_3)-\text{C}_2\text{H}_5$	S_C^* 75 S_A 85 I

The character of the arrangement of mesogenic groups in mesophase (Fig.6) may be displayed by X-ray diffraction analysis. Side groups of adjacent macromolecules in smectics A are arranged, as a rule, parallel or anti-parallel to each other; packing with partial or full overlapping of side groups is also possible (Fig.7). Mesogenic groups form a one-layer or a two-layer packing. Depending on ordered or disordered arrangement of mesogenic groups in layers there are ordered smectics (B, E, I, F and G) and disordered smectics (A, C).

A specific feature of smectics A and C is the presence of a wide diffuse halo in X-ray diagrams at wide angles and ordered smectics are characterized by a narrow reflex at wide angles (Fig.8a). The transformation of an

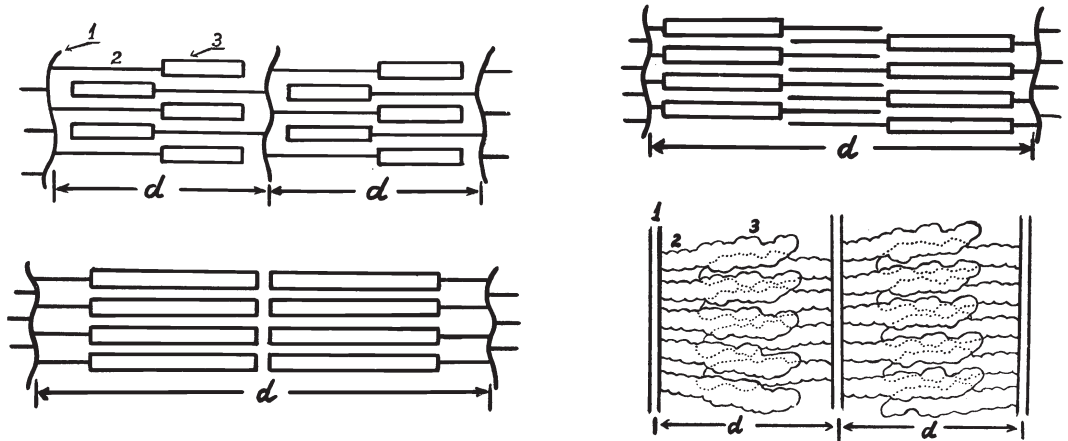
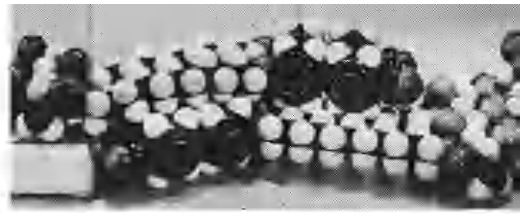


Fig. 6. Schemes of side chains packing of macromolecules in S_A -mesophase of oriented LC polymers. 1 - main chain; 2 - spacer; 3 - mesogenic group.



(a)



(b)

Fig. 7. Molecular models of layer packings of macromolecules in S_A -mesophase with partial (a) and full (b) overlapping of side branchings (ref. 33).

ordered state to disordered one is manifested as the first order transition with a small heat effect.

In tilted smectics (S_C and S_F) mesogenic groups are arranged at some angle to the main chain of macromolecules, in such a way that either dense hexagonal packing of side groups (S_F) or their disordered arrangement (S_C) can be formed in the plane perpendicular to the long axes of mesogenic groups (ref. 19).

The most ordered character of arrangement of mesogenic groups is typical of S_E and S_G mesophases (Table 4, Fig.8 b,c). There are two-three distinct reflexes at wide angles in their X-ray patterns. Polymers of S_E type form an orthorhombic cell with the orthogonal arrangement of mesogenic groups (Table 4, polymer 5), while monoclinic cell of S_G phase is characterized by tilted arrangement of side branches (Table 5, polymer 1) (refs. 19,38).

A specific feature of LC polymers is coexistence of various types of mesogenic group packing (one layer, two layer and with partial or full overlapping of mesogenic fragments) within a smectic mesophase (ref. 5).

The analysis of intensity, I , of small angle periodicity for smectic polymers makes possible the calculations of one-dimensional correlation functions $\chi_1(x)$

$$\chi_1(x) = \frac{\int s^2 I(s) \cos(sx) ds}{\int s^2 I(s) ds}$$

where $s=2\sin\theta/\lambda$, θ is a half of the scattering angle, λ is the wavelength (ref. 34).

That permits to estimate the thickness of the smectic layer, d , sizes of smectic ordered regions ("layer packs"), L , and the parameter of disordering

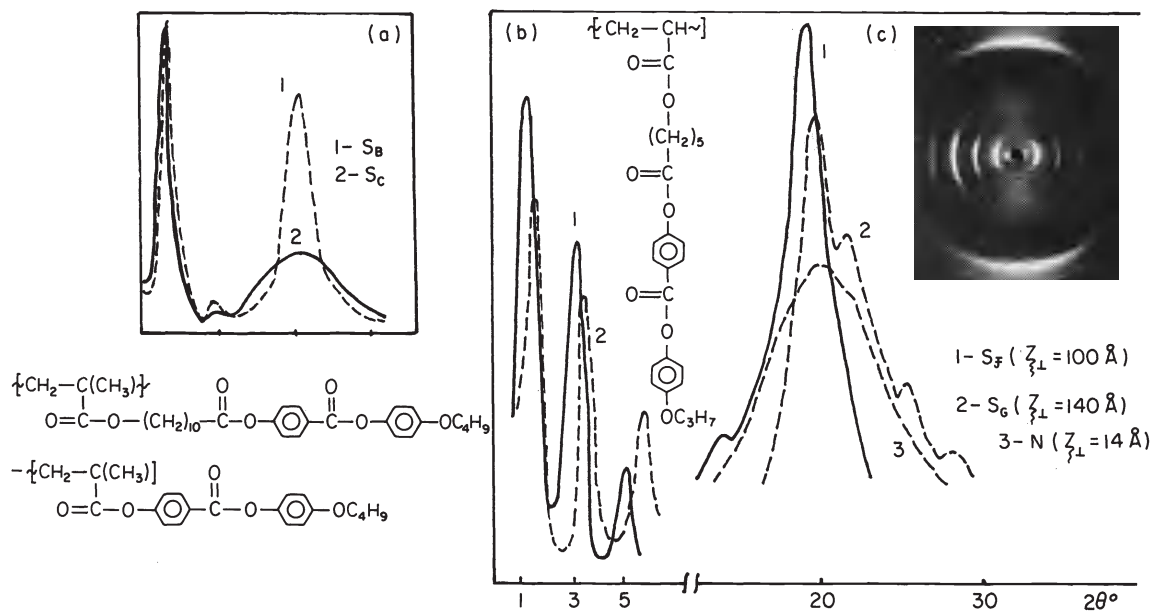


Fig. 8. X-ray diffraction curves of LC polymers (a,b) and X-ray diagram of polymer 5 (Table 4) (c) (refs. 19,38).

of layer packing:

$$g^2 = d/\pi^2 [\beta_{\text{exp}}^2 - 1/L^2]^{1/2}$$

where β_{exp}^2 is the integral width of the diffraction maximum, d - is the thickness of a smectic layer.

The correlation function $\gamma_1(x)$ decreases with increasing x due to accumulation of paracrystalline distortions by an exponential law:

$$\gamma_1(x) = \gamma_0 \exp(-2x/\xi)$$

where ξ is the correlation length characterizing the distance at which the correlation of arrangement of layers is practically constant. Fig.9 shows one-dimensional correlation function for smectic polymers without spacers.

The values of L , ξ and g and of long spacings d for some LC polymers and low molecular weight analog are listed in Tables 6 and 7.

As is seen from Fig.9 and the data listed in Table 6, the sizes of ordered regions (ξ_{\parallel}) in the direction of the long axes of mesogenic groups of comb-like smectic polymers are in the range 300 to 500Å. These values of ξ are much smaller than those for low molecular weight liquid crystals. At the same time the short lateral packing of intralayer mesogenic groups (ξ_{\perp}) of LC polymers is very similar to that for low molecular weight smectics.

A specific feature of polymer smectics is the presence of LC microregions of some hundreds of nanometers in size. That follows from the analysis of curves of small angle scattering. In addition to sharp small angle maxima, corresponding to layered structure, powerful zero-angle scattering is observed (ref. 34). Its intensity is 2 to 4 orders higher than that of the small-angle peaks. Above mentioned microregions are aggregates of some layered packs without positional order between them. The layered packs themselves consist of a number of closepacked planar layers with positional order in their packing.

Among polymer smectics the chiral smectics, C*, are of greatest interest, since they manifest ferroelectric properties (Table 5, polymer 6) (Fig.10a). In this case an ordered state of dipoles is formed due to the presence of chiral centres in side groups and tilting of mesogenic fragments to the plane of the smectic layer. This ordered state leads to a spontaneous polarization. At the transition from S_A phase into S_C phase spontaneous polarization P_s appears and is retained in the polymer at cooling lower than

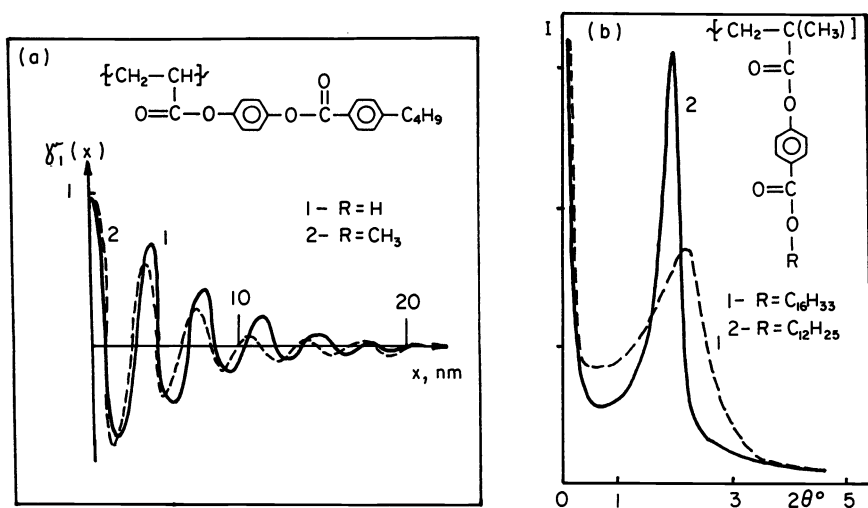


Fig. 9. a- One-dimensional correlation functions $\gamma_1(x)$; b- small angle X-ray scattering curves (ref. 34)

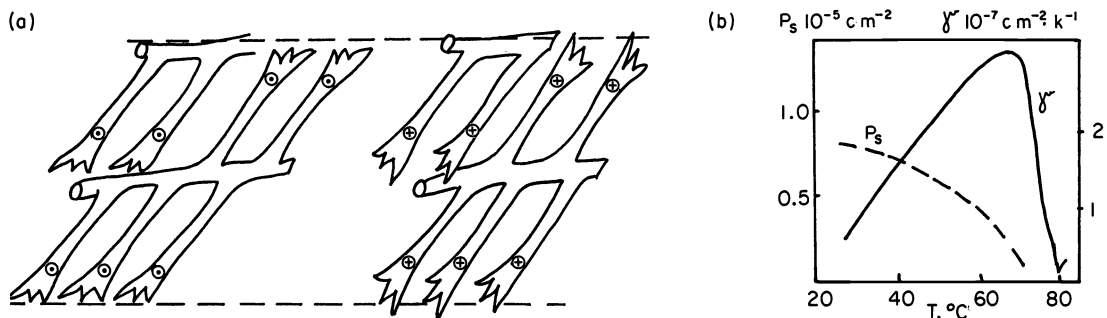


Fig. 10. a- Schemes of dipole ordering of side mesogenic groups for chiral smectic S^* . b- Temperature dependence of spontaneous polarization, P_s , and pyrocoefficient, γ , for chiral polymer 6 (Table 5) (refs. 35,36).

TABLE 6. Some structural parameters of LC polymers (refs. 34,37)

No	Polymer	Type of mesophase	$d, \text{\AA}$ small angles	$L, \text{\AA}$	$\bar{\eta}, \text{\AA}$	$g, \%$
1.	$[-CH_2-\overset{CH_3}{\underset{ }{C}}-]$ $COO-C_6H_4-O-C(=O)-C_6H_4-OC_nH_{2n+1}$	S_C	38	230	40	16
2.	$n=9$	S_A	41	200	42	17
3.	$[-CH_2-\overset{CH_3}{\underset{ }{C}}-]$ $COO-(CH_2)_{10}-COO-C_6H_4-O-C(=O)-C_6H_4-OC_4H_9$	S_A	46	550	130	11
4.	$n=16$	S_B	32	680	160	6

TABLE 7. The comparison of some structural parameters of low molecular weight liquid crystals and LC polymers (ref. 38).

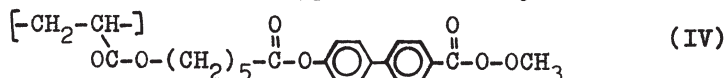
No	LC compounds	Type of mesophase	$D, \text{\AA}$, wide angles	$d, \text{\AA}$, small angles	$\bar{\eta}_I, \text{\AA}$	$\bar{\eta}_{III}, \text{\AA}$
1.	$C_6H_{13}O-C_6H_4-C_6H_4-CN$	N	4.51	22.0	28	80
2.	$C_8H_{17}O-C_6H_4-C_6H_4-CN$	S_A	4.49	32.6	29	>500
3.	$[-CH_2-\overset{CH_3}{\underset{ }{C}}(X)-]$ $COO-(CH_2)_5-O-C_6H_4-C_6H_4-CN$	S_A	4.49	32.0	27	500
	$X=H$	S_A	4.53	31.0	26	500
	$X=CH_3$	S	4.38	31.0	25	390
4.	$[-\overset{CH_3}{\underset{ }{Si}}-O-]$ $(CH_2)_3-O-(CH_2)_2-O-C_6H_4-C_6H_4-CN$					

T_g (ref. 36) (Fig.10b).

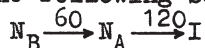
NEMATIC MESOPHASE

This type of mesophase is typical of LC polymers with short alkyl substituents in a mesogenic fragment and shorter (than in smectics) spacer length (Table 5, polymers 1,3,4). Nematic polymers form characteristic optical textures as marble, schlieren etc. X-ray patterns of nematic polymers show only one diffuse maximum in the range of wide angles and, as a rule, small angle reflexes are absent. The presence of the main chain, however, often leads to the appearance of some weak elements of layers ordering, showing a sibtactic character of nematic polymers. The short lateral packing of mesogenic group ($\frac{1}{2}$) of nematic polymers is much smaller as compared to smectics and usually presents 12-14Å. It is interesting to note that increasing the DP of nematic polymers leads to the formation of optical textures resembling to a greater extent the fan textures of smectic phases.

Rather an unusual structural nematic type was recently found for a polymer (ref. 19):



The X-ray pattern of this polymer shows only one sharp reflex at wide angles (4.4Å) and no small angle reflexes. This type of pattern indicates an ordered hexagonal ordering of mesogenic groups and the absence of the translational ordering in the direction of their long axes. This type of mesophase is designated as N_B phase which precedes the conventional nematic phase N_A according to the following scheme:



In nematic polymers mesogenic groups are arranged along the orientation axis by the action of mechanical orientation, i.e. a coordinated rotation of LC domains formed by mesogenic groups takes place. This differs nematic polymers from smectics where smectic layers are arranged along the orientation axis and mesogenic groups are positioned either perpendicularly to them (smectics S_A, S_B, S_E) or at an angle (smectics S_C, S_F).

The fact that nematic and some smectic polymers are readily oriented upon application of electric and magnetic fields is used for controlling LC polymer structures in mesophase and for obtaining polymeric materials with the required optical properties (refs. 39-41). This is demonstrated below by two examples.

a) Orientation in the mesophase upon application of an electric field of various frequency permits to obtain polymeric films with various structures by cooling the polymer below T_g . The initial and final (homotropic) orientations of mesogenic groups are shown in Fig.11a (A and B).

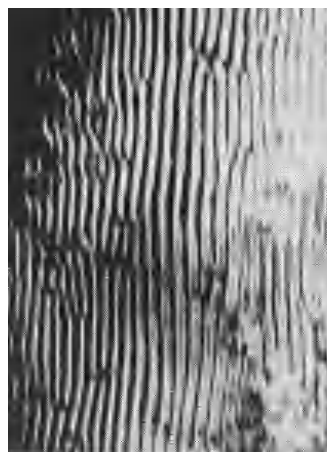
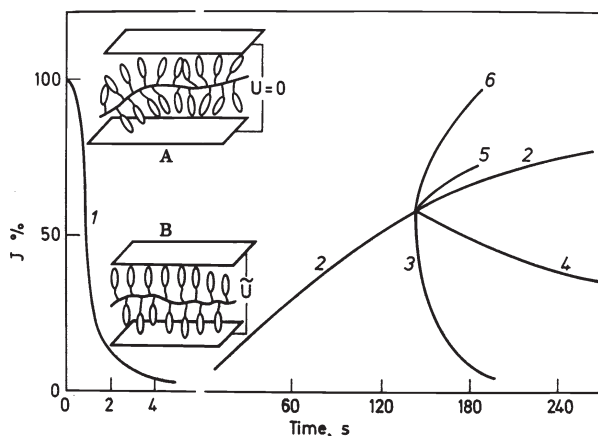


Fig. 11. a - Optical transmittance as a function of time upon application of an electric field ($U=80V$) of various frequency 50Hz (1), 1KHz (3), 5KHz(4), 7 KHz (5), 20KHz (6) and relaxation upon switching the field off (2) for polymer 4 (Table 3); b - domain structure of a nematic polymer obtained upon application of an electric field (refs. 39-40)

b) Using the regime of electrohydrodynamic instability (EHD) in polymer LC phase, polymeric films can be obtained with "frozen" regular and controlled domain structure (of the type of Williams domains) (Fig.11b). This reveals interesting perspectives for controlling the structure and optical properties of polymeric films.

CHOLESTERIC MESOPHASE

Cholesteric mesophase is observed in cholesterol containing homopolymers or in polymers containing chiral groups in side branches (ref. 42) (Table 8). A convenient method for obtaining a cholesteric mesophase is copolymerization of chiral and nematogenic monomers. In this case a nematic mesophase is "twisted" and as a result a broad range of copolymers with varied cholesteric helix pitch can be obtained (refs. 4,5,13,43-45).

X-ray patterns of cholesterol containing polymers (polymers 1-4, Table 8) display a wide diffuse halo at wide angles (5.8-6.2Å) and a number of intensive small angle reflexes showing the formation of layer structures. Depending on the spacer group length ($n \geq 10$) one-layer packing may be formed, where mesogenic groups of adjacent macromolecules are antiparallel (Fig.6a). In the case of short spacer groups ($n \leq 5$) two-layer packing is observed (Fig.6c); an intermediate type of packing with overlapping of aliphatic fragments of cholesterol tails is also possible (Fig.6d). The types of layer packing considered actually correspond to smectic mesophase, formed at temperatures lower than that of smectic-cholesteric transition (Table 8). Elevation of temperature, however, does not cause considerable changes in the character of packing of mesogenic groups. It is seen in Fig.12, where temperature dependence of structural parameters of polymers 2 and 4 (Table 8) are shown. The small angle reflexes $d_1 - d_3$ are retained (though their intensity $I_1 - I_3$ decreases dramatically) and simultaneously the distances between side branches D are increased. The correlation lengths \bar{L}_1 have sufficiently high values, comparable with the similar values of \bar{L}_1 for smectics, showing a high degree of ordering of mesogenic fragments within layer structures, even in a cholesteric mesophase. And only above T_{cl} a complete disturbance of the layer ordering is observed.

TABLE 8. Cholesteric homopolymers and copolymers (refs. 44,45).

No	Polymer	n	Phase transitions, °C	
1.	$[-CH_2-C(CH_3)-]$	5	Tg85 S190 Chol 210	
2.	$OC-O(CH_2)_nCOOChol$	10	Tg60 S124 Chol158	
3.	$[-CH_2-CH-]$	5	Tg55 S*- Chol218	
4.	$OC-O(-CH_2)_nCOOChol$	10	Tg35 S140 Chol148	
		mol% <i>A</i>	$\lambda_{max, nm}^{**}$	
5.	$\begin{array}{c} \text{CH}_2 \\ \\ \text{CH}-\text{C}(=\text{O}) \\ \\ \text{O} \end{array}$	28	$S_A 100$	Chol118 I 710
6.	$\begin{array}{c} \text{CH}_2 \\ \\ \text{CH}-\text{C}(=\text{O}) \\ \\ \text{O} \end{array}$	31	$S_A 98$	Chol110 I 510
7.	$\begin{array}{c} \text{CH}_2 \\ \\ \text{CH}-\text{C}(=\text{O}) \\ \\ \text{O} \end{array}$	40	$S_A 80$	Chol96 I 480
8.	$\begin{array}{c} \text{CH}_2 \\ \\ \text{CH}-\text{C}(=\text{O}) \\ \\ \text{O} \end{array}$	55	$S_A 85$	Chol104 I 420

* Polymer 3 forms monotropic mesophase; ** at $T = T_{S-Chol} + 40^\circ C$

A helical structure of cholesteric mesophase determines its unique feature, namely, selective light reflection (λ_{max}) in an IR-, UV- or a visible part of the spectrum. Varying the composition of cholesteric copolymers, it is possible to control the value of λ_{max} which is related to the helix pitch, P , by the relationship $P = n\lambda_{max}$ where n is the average refractive index (Table 8).

If a copolymer forms only a cholesteric mesophase then, as a rule, the helix pitch has a weak temperature dependence over the whole temperature range. A drastic temperature dependence of P , (determining the high selectivity of cholesterics) is observed near the cholesteric-smectic transition. Since cholesterol containing polymers are characterized by layer ordering,

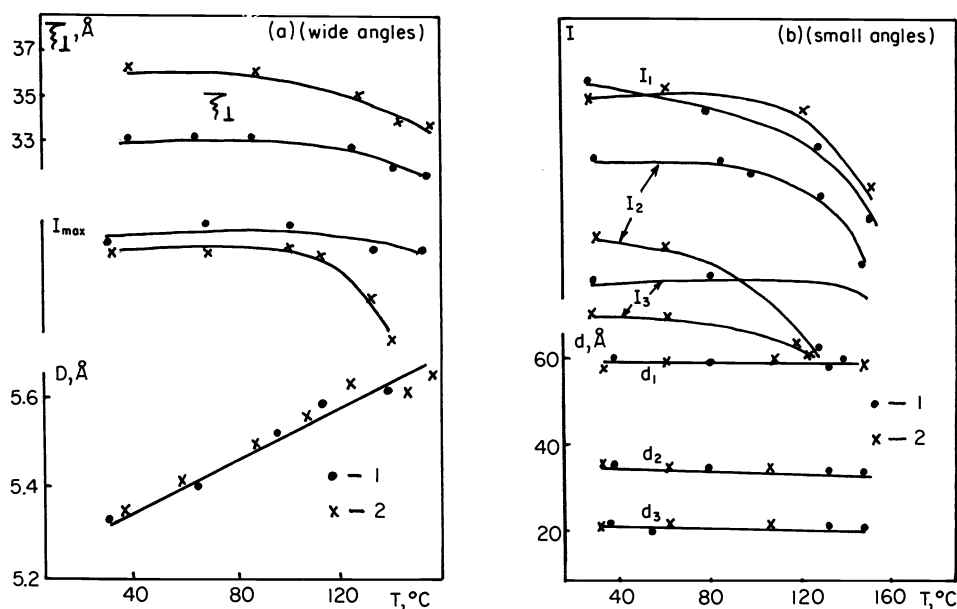


Fig.12. Temperature dependence of structural parameters calculated from X-ray diffraction curves at wide (a) and small (b) angles of polymers 2(1) and 4(2) (Table 8).

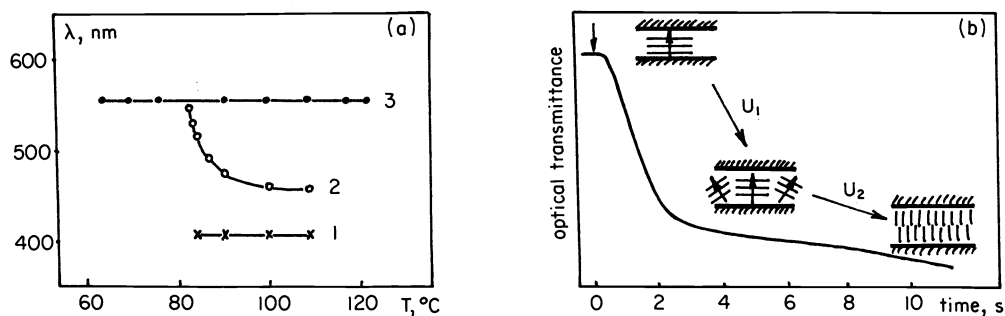


Fig. 13. a - Temperature dependence of λ_{max} for copolymer cholesterics consisting of a nematogenic monomer and cholesterol containing (Chol) monomer units with different contents of Chol. b - Kinetic curve of two-stage process "untwisting" of cholesteric helix of LC polymer cholesteric.

the introduction of cholesterol containing monomer units into macromolecules of a nematic polymer, increasing the trend to the formation of layer structures, results in the appearance of strong helix pitch temperature dependence (Fig.13a).

Specific macromolecular nature of LC polymers permits to "freeze the colour" of polymeric cholesterics by cooling their films below T_g . Using an electric field it is possible to deform and untwist the cholesteric helix and as a result the colour of polymeric films is changed (Fig.13b).

Thus, LC polymers with side mesogenic groups behave in many respects as low molecular weight liquid crystals. Simultaneously the specific polymer nature of these compounds permits to obtain and fix a number of new (or intermediate) structures due to the action of external fields on the mobile anisotropic LC phase with the following freezing of these structures in a solid state.

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