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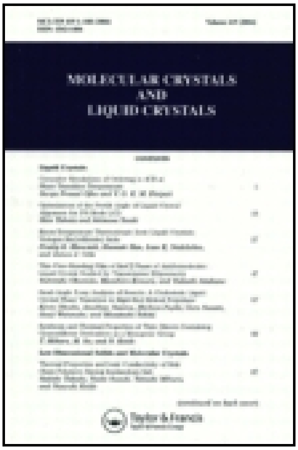

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Structural and Conformational Transformations in Comb-Like Liquid Crystalline Polymers

Valery Shibaev [a]

[a] Department of Chemistry, Moscow State University, Moscow, 119899, USSR

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STRUCTURAL AND CONFORMATIONAL TRANSFORMATIONS IN COMB-LIKE LIQUID CRYSTALLINE POLYMERS

VALERY SHIBAEV
Department of Chemistry, Moscow State University,
Moscow 119899, USSR

Abstract Structural and conformational transformations in comb-like nematic, smectic and cholesteric polymers under the action of external fields (mechanical, electric and magnetic) are considered.

INTRODUCTION

During the last years on the basis of comb-like polymers a wide variety of liquid crystal side chain polymers has been synthesized and investigated[1-6]. However even for these polymers many aspects of their structure and physical properties up-to-date are unknown. Therefore this paper will describe some our results concerning the structural and conformational transformations of liquid crystalline (LC) comb-like polymers in nematic smectic and cholesteric phases under the action of external fields (mechanical, electric and magnetic). In general these data have been obtained in the laboratory of chemical transformations of polymers at Moscow State University.

SOME PECULIARITIES OF LC COMB-LIKE POLYMERS RELATED TO THEIR MACROMOLECULAR NATURE

As far as the chain nature of macromolecules essentially affect all the properties of LC polymers first of all we briefly consider some new data concerning the role of the main chain in realization of LC state.

At present it's well known that the phase transition

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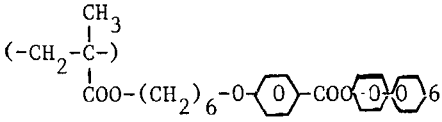
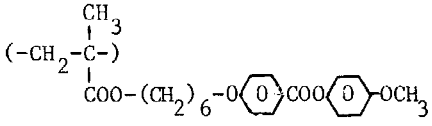
temperatures rise with increasing degree of polymerization (DP). There is a definite critical length of a polymer chain, starting from which the clearing temperature T_{cl} does not depend on DP. However, the relations between the critical DP and flexibility of the main chain of comb-like polymers are not so far clear.

Moreover recently we found that the type of mesophase also depends on DP (Figure 1). At the low values of DP only smectic F and nematic phases are formed; at higher values of DP the more complicated polymorphism is observed. It follows two important conclusions:

1) So far as the mesophase type depends on DP, the unfractionated samples of LC comb-like polymers can be considered as the mixture of the different types of mesophases. Using the unfractionated samples for investigations one can "lose" some types of mesophase.

What's perhaps why one and the same polymer can have the different types of mesophase and the transition temperatures (Table 1).

TABLE 1 The comparison of phase transition temperatures and mesophase types for one and the same polymer

Polymer	Phase transitions, °C			Ref.
	Glass	S → N	N → I	
	65-70	-	170-173	7
	132	164	184	8
	53	135	155	9
	95	-	105	10
	47	74 N/S	111	11

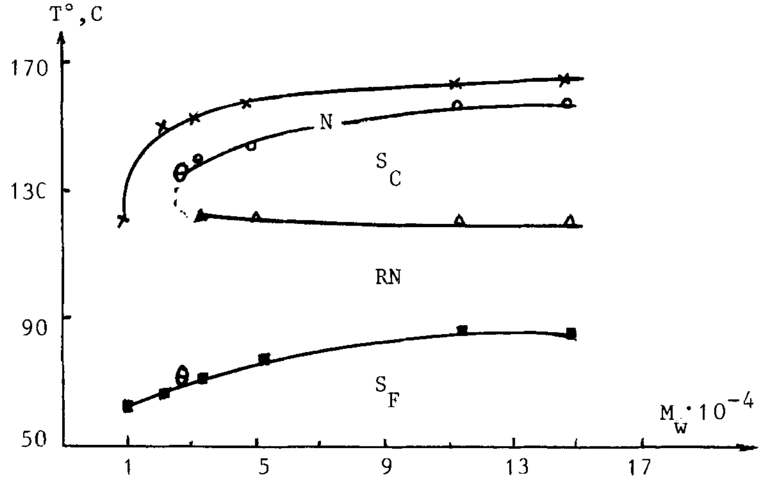
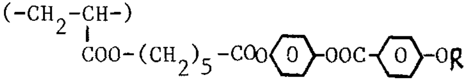
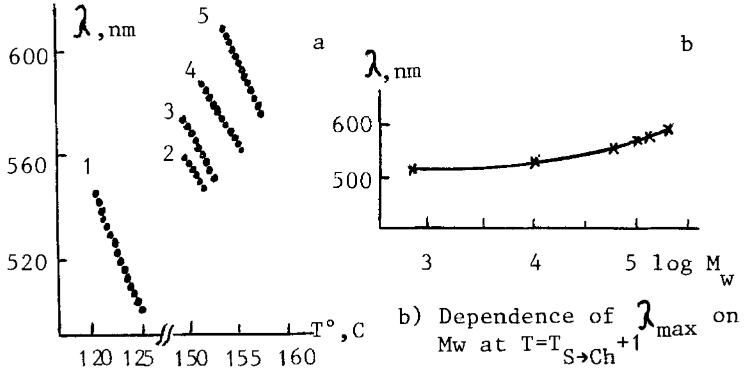


Figure 1. Phase transition temperatures of the polyacrylic polymer



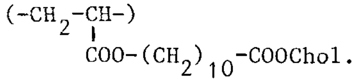
$(-CH_2-\underset{COO-(CH_2)_5-COO-C_6H_4-OOC-C_6H_4-OR}{\underset{|}{C}H}-)$

θ - unfractionated sample; RN - reentrant nematic phase



b) Dependence of λ_{max} on Mw at $T=T_{S\to Ch}+1$

Figure 2. a) Tempeature dependence of λ_{max} for the fractions of cholesteric polymer



$(-CH_2-\underset{COO-(CH_2)_{10}-COOChol.}{\underset{|}{C}H}-)$

$M_w = 1\cdot10^4$ (1); $6\cdot10^4$ (2); $12\cdot10^4$(3); $14\cdot10^4$ (4); $20\cdot10^{-4}$(5)

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2) DP essentially affects the miscibility of LC polymers with low molar mass liquid crystals. The use of unfractionated samples for these investigations can lead to the errors in identification of mesophase types.

The role of DP is still more clearly displayed in cholesteric polymers having the very delicate-balanced structure. The temperature dependence of the selective reflection wavelength λ_{max} for some fractions of the polymer in cholesteric phase is shown in Figure 2[12]. It is noteworthy that the range of selective reflection is shifted to the long wave length region with increasing molar mass of the polymer. In Figure 2b the characteristic wavelength at certain reduced temperature as a function of the molar mass is shown.

At time present it is very important to find the principal correlations between DP, molar mass distribution and other structural and physical properties of the different types of LC polymers. The ignorance of such relationships can lead to the erroneous conclusions concerning not only the temperature interval of LC state but the type of mesophases, their structural features etc.

ORIENTATION BEHAVIOUR OF LC POLYMERS

Nematic and Smectic Polymers

Let us consider the orientation of LC polymers under the action of mechanical field. The uniaxial stretching of polymers from the nematic mesophase is usually accompanied by the arrangement of the side mesogenic groups along the fibre axis. Another situation is realized under the orientation from the smectic A and C mesophases. In this case the planes of the smectic layers are arranged along the direction of the stretching. The orientation of the mesogenic groups depends on of the type of mesophase ; in S_A phase the mesogenic groups are disposed normally to the planes of smectic

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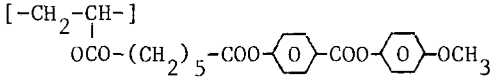
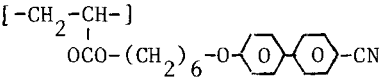
layers and in S_C phase they are tilted [1,13,14].

The majority of nematic LC comb-like polymers exhibit certain elements of layer ordering in the arrangement of the mesogenic groups. This type of packing is more close to cibotactic or smectic type due to of the main chain existence[1]. It is clearly seen from X-ray diffraction pattern of unoriented and oriented nematic polymer I (Figure 3)



(I)

The orientation under the mechanical shear from reentrant nematic RN and smectic mesophases also leads to completely different arrangement of the mesogenic groups. This is result from the comparison of dichroism of the polarization IR spectra and X-ray diffraction data of acrylic polymer[15]:



(II)

RN 83° S_A 118° N 134 I

In the RN phase the mesogenic groups are oriented along the shear direction, in S_A phase they are disposed perpendicular to the shear direction. From these data we can assume that in the RN and the S_A mesophases the different flow mechanism is realized. The values of activation energy of viscous flow (E_a) also reflect the different flow mechanism ($E_a \approx 90$ kJ/mole in RN phase; $E_a = 360$ kJ/mole in S_A phase). The deformation of LC polymer in RN phase is realized in general by displacement of the mesogenic groups. The flow of smectic polymers promotes the slipping of smectic layer and results in their disposition along the direction of the mechanical field. The E_a values in both the cases essentially

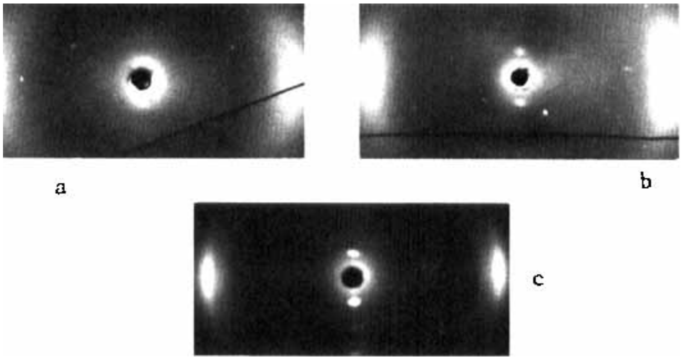


Figure 3. X-ray diffraction pattern of nematic polymer I; a) just after orientation from nematic phase; b) after 20 days; c) after 6 months.

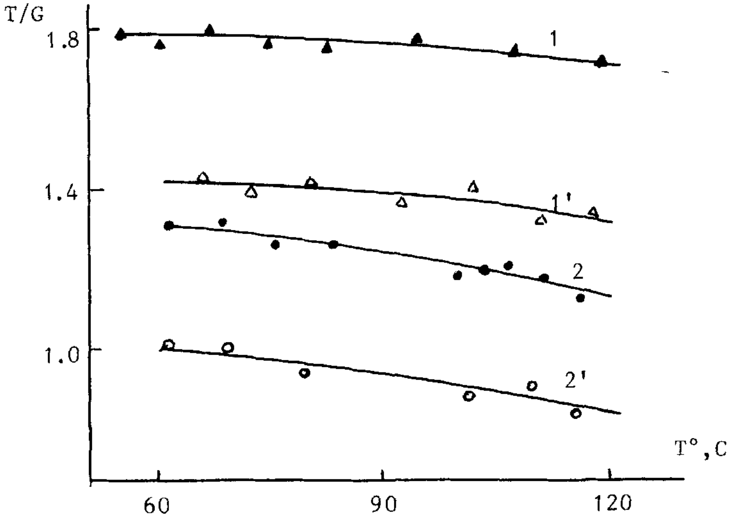


Figure 4. The change of trans-gauche ratio (T/G) of polymer IIIa (1,1') and IIIb (2,2') under the action an electric field (1,2 - E=0; 1',2'-E = 10^4V/cm).

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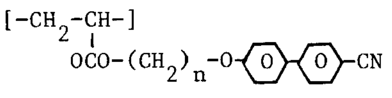
exceed the corresponding values E_a of low molar mass liquid crystals. It reflects the polymeric feature defined by the participation of the segments of macromolecules in the flow.

Unlike the mechanical stretching on which the character of the mesogenic groups orientation essentially depends on the mesophase type the structural type of mesophase doesn't signify under orientation in electromagnetic fields. In latter case the direction of the mesogenic groups orientation defined only by the field direction and the signs of $\Delta\varepsilon$ and $\Delta\chi$[16-18].

In studying the orientation of comb-like polymers a number of questions arise: whether the mesogenic groups are oriented independently on the polymeric chains, or the interaction of liquid crystalline domains with external field affects the position and conformation of the main chains. What is the molecular mechanism of all the structural transformations involving the main chains, spacers and mesogenic groups?

Let us consider the participation of these structural fragments in the orientational processes.

Using the data of infrared spectroscopy the trans-gauche isomer ratio of methylene spacers for two LC polymers have been estimated. In Figure 4 the trans-gauche ratio for two LC polymers with the different length of spacer



(III)

n = 5 (IIIa)
n = 6 (IIIb)

before and after orientation in LC state as a function of temperature is shown.

It is seen that the electric field leads to the decreasing of trans-gauche ratio for both the polymers. It means that the

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process of orientation is accompanied with increasing the concentration of gauche-isomers. In other words the methylenic chains are slightly twisted, that is the conformational change of spacers takes place in the electric field.

In spite of the torsion of the spacers under the orientation the electric and magnetic fields stimulate the high orientation of the mesogenic groups.

Moreover we have even observed the essential change of the polymer structure under an action of the magnetic field. The unoriented polyacrylate IIIa (n = 5) is characterized by sibotactic nematic structure (Figure 5, curve 1). The correlation length in the direction of the long axes of mesogenic groups $\xi_{\parallel}$ is in the range 30 to 35 Å. However after the orientation of LC polymer in electric ($E = 10^5$ V/cm) and magnetic (H = 1.88 T) fields X-ray scattering curve shows the intensive low angle reflex (Figure 5, curve 2). The longitudinal correlation length increases up to 3000 Å. Such a high value of the correlation length is characteristic of high ordered smectics.

Thus the orientation of LC polymers in electric and magnetic fields stimulates the additional structural changes. On the one hand, the degree of orientational order of spacers gets worse, on the other hand the longitudinal order of mesogenic groups increases to a marked degree.

As for the main chain conformation of comb-like polymers, then how it follows from the experimental works of westgerman and french scientists, the backbone conformation in the oriented nematic and smectic mesophases has rather an anisotropic form. Our neutron scattering investigations of the partially deuterated polysiloxane have also shown some anisotropic conformation of its macromolecules in magnetically oriented nematic phase. In Table 2 are listed all

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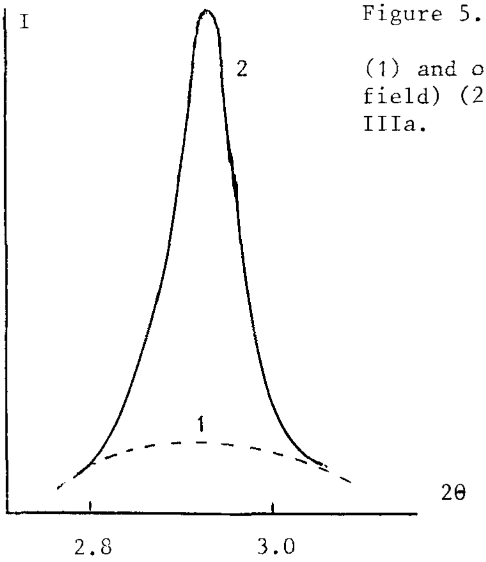

Figure 5. X-ray scattering curves of unoriented (1) and oriented (in magnetic field) (2) samples of polymer IIIa.

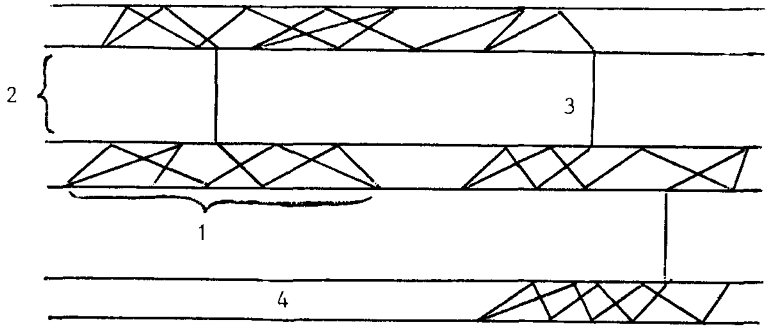

Figure 6. Conformational model of the comb-like macromolecule backbone. 1 - Quasi-two-dimensional subcoil; 2 - mesogenic groups layers; 3 - crossing (tie) segments (defects) ; 4 - intermediate layers.

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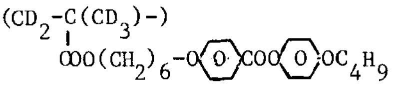
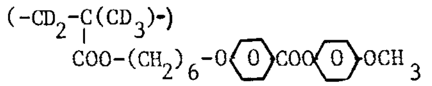
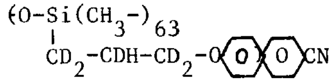
the up-to-date results obtained for different LC comb-like labelled polymers by small angle neutron scattering method (SANS)[20-22].

TABLE 2 The values of the radii of gyration, Rg, $R_{\parallel}$ and $R_{\perp}$ (in Å) of labelled LC polymers

Polymer	Isotropic melt	Nematic		Smectic		Ref.
	Rg	$R_{\perp}$	$R_{\parallel}$	$R_{\perp}$	$R_{\parallel}$	
	61±5	65±5	59±5	86±9	22±3	20
	92	120	94	-	-	21
	13	-	-	16	10	22

The values of two projections of the radius of gyration measured with the scattering vector parallel ($R_{\parallel}$) and perpendicular ($R_{\perp}$) to the axis of orientation are shown. The macromolecule coils are shaped like an oblate rotational ellipsoid the short axis of which is parallel to the director (axis of orientation). These results show that the main chain have anisotropic conformation both in the nematic and the smectic mesophases. The anisotrophy parameter for nematics is around 1.1-1.6 and a ≈ 4 for smectic.

Using these data D.Svetogorsky and Kunchenko from Joint Institute for Nuclear Research in Dubna have suggested the new structural model of main chain conformation in smectic phase of comb-like polymers (Figure 6)[23]. The macromolecular

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chain in the smectic phase is divided into quasi-two-dimensional coils randomly placed in different smectic layers, formed by mesogenic groups. The two-dimensional subcoils are connected with each other by a number of tie segments crossing of the layers. They can be considered as defects of the smectic phase. The model allows to estimate the number of defects from the radii of gyration of the macromolecule (Rg, $R_{\perp}$, $R_{\parallel}$) which is measured by neutron scattering method.

Let us consider some kinetic features of orientation of LC polymers forming the RN phase, that allows to understand better the mechanism of conformational transformations[15,17].

It's well known that on cooling the nematic and smectic polymers the rise time τ increases with decreasing temperature. Another situation is observed for LC polymers having the RN phase (Figure 7). At first the values of τ increase with decreasing temperature and then values of τ drastically fall. The time falling with decreasing temperature is connected with $S_A \longrightarrow$ RN transition. It is worthy of attention that the values of time orientation in RN and N phases separated by around 60°, are equal. It means the mobilities of the mesogenic groups in these phases are very close. The maximum on the curves tends to the increase with decreasing of electric voltage while the peak position practically doesn't depend on voltage. It is of interest that the rise of orientation time τ into the wide temperature interval precedes to RN $\longrightarrow S_A$ transition. Such a behaviour of LC polymer can be explained by the pretransition phenomena, determined by the appearance of new mesophase nuclei. Usually these phenomena occur nearly of phase transition mesophase-isotropic melt for low molar mass liquid crystals.

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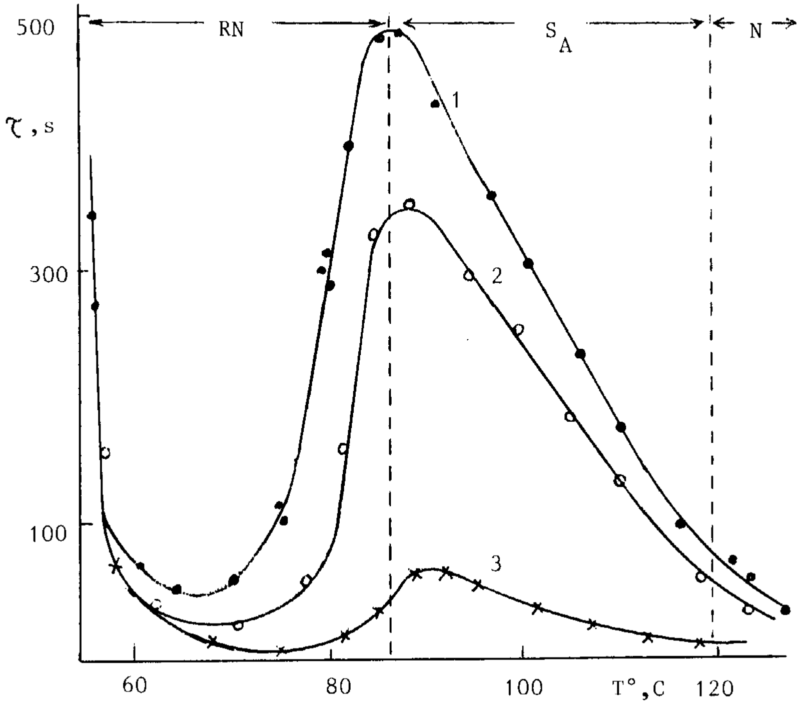

Figure 7. Temperature dependence of orientation time τ for polymer II under the action of electric field: 1 - E= 50 kV/cm; 2 - E= 60 kV/cm and 3 - E= 90 kV/cm

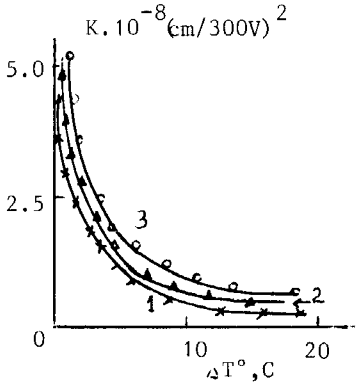

Figure 8. Kerr's constant as a function of ΔT for the polymer II(1) and the liquid crystals IV(2) and V(3).

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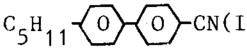
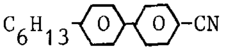
We also observed these pretransitional phenomena studying of LC comb-like polymer II and low molar mass liquid crystals with identical mesogenic groups

 (IV) and  (V)

$C_5H_{11}-C_6H_4-C_6H_4-CN$ (IV) and $C_6H_{13}-C_6H_4-C_6H_4-CN$ (V)

using the electric birefringence (Δn) method [24]. Figure 8 shows the Kerr's constant (K) as a function of $\Delta T = T_{cl} - T_{exp}$. It is seen that the values of K of all the compounds are positive in an isotropic melt range and then strongly increase with decreasing of ΔT. It means that the mesogenic groups of polymer and the molecules of liquid crystals are oriented in the same way along the electric field direction. The rise of the values of K with decreasing temperature corresponds to the nuclei mesophase formation. It follows, that the main chains don't essential affect the fluctuations of the orientational order in isotropic melt. Consequently the best orientation conditions of LC polymers in electric and magnetic fields are realized in the pretransitional range (a little bit above T_{cl}) where the high mobility of the mesogenic groups is successfully combined with existence of the ordered mesophase nuclei[19],

Analysis of the orientational behaviour of LC comb-like polymers in magnetic and electric fields have allowed to estimate a number of orientational characteristics such as the twist viscosity coefficient γ_1, and activation energies of the orientation process E_a[17,25]. The values of γ_1 obtained for polymers II and IIIa in the RN phase are shown below:

Polymer II, $\gamma_1 = 5{,}8 \cdot 10^5$ poise
Polymer IIIa, $\gamma_1 = 15 \cdot 10^5$ poise (DP = 380)

These values for both the polymers are of nearly the

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same magnitude as the shear viscosity (η_{sh}) at the same temperature ($\eta_{sh} = 5\cdot10^5$ poise, 70°C). In the case time the values of γ_1 exceeds the γ_1 of low molar mass liquid crystals by 5-6 orders of magnitude.

From the above considerations it follows that the director reorientation in LC phase is governed by the polymer viscosity. In other words the main chain fragments are most likely involved in the orientational process. This assumption is supported by the high values of E_a estimated by us and of the activation energy of rotational viscosity for magnetically-oriented polysiloxane polymer, obtained by the french researchers[26] (Table 3).

TABLE 3 Activation energy (E_a) and rise time (τ) of the orientation for LC polymers with different DP[17].

Polymer	P_w	τ, s	E_a,kJ/mole	Mesophase type
Polymer IIIa	70	0,5	180	N,S
	140	0,8	170	S
	550	3,0	170	S
	2000	14,4	-	S
Polymer IIIb	5-10	4,0	-	N
	250	18,0	97	S
	350	25,0	100	S
	1200	512.0	100	S

It is seen that E_A values are higher than the known values of activation energies for the rotational viscosity of low molar mass nematics. ($E_a \approx$ 35-50 kJ/mole). It is interesting to note that E_A values slightly depend on the DP. This fact indicates that the mechanism of the orientation process

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is unaffected on changing the DP by 1-2 orders of magnitude. Moreover the values of E_a of LC polymers in smectic and nematic phases are the same order of magnitude. At the same time the values of E_a are close to E_A for segmental processes inherent for the polymers of respective structure.

All the polymers presented in the Table 3 have the flexible main polyacrylic chains. In addition the polysiloxane polymer with mesogenic groups, studied by french scientists[26] is also characterized by the activation energy around 100 kJ/mole. However, the incorporation of 20-50 mole % of methacrylic units into the main chain leads to the increasing of the E_a values up to 220-230 kJ/mole. The increase of the activation energy in copolymer with methacrylic units confirm the decisive role of the main chains mobility. It's essentially that values of activation energy are close to the values of E_A of viscous flow for polymer nematics and smectics respectively.

The decrease of E_a values with the lengthening of the spacer in the series of polymers (III) explained by plasticizing effect also indicates to the essential role of the backbone (and the spacer) in the orientational process:

Polymer III, n	3	4	5	6	11
Type of mesophase	S	N	S,N	S	S
E_a, kJ/mole	360	240	180	100	85

Cholesteric polymers

Let us consider the structural transformations in comb-like LC cholesterics under the action of the electric field. Except our data[27,28] up to date this question haven't been studied, because the most of cholesteric polymers described

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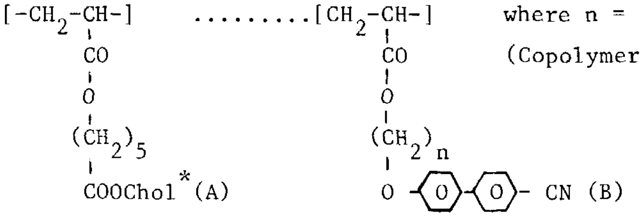
in literature are characterized by the insignificant small value of $\Delta\varepsilon$. The dielectric anisotropy is the main origin of the structural transformations occurring in an electric field on LC polymers including the cholesteric polymers. What is why the cholesteric copolymers with high value of $\Delta\varepsilon$ have been synthesized by us:



where n = 4 and 5

(Copolymers 4,5; 5,5)

Cholesterol containing units provides the helicoidal twisting of the polymer structure and the CN-biphenyl containing comonomer provides the positive anisotropy of dielectric susceptibility, $\Delta\varepsilon$, required for orientation process in an electric field.

Figure 9 shows the changing of the optical properties of the planar-oriented cholesteric film as a function of the electric voltage. The initial sample has the planar orientation of mesogenic groups and the cholesteric helix axis is normal to the film plane. The sample selectively reflects the red light. An electric field induces the untwisting of the helix. In this case the optically active planar cholesteric texture transforms into the uniaxially oriented homeotropic texture. This process is rather a complicated and consists at least of two stages.

At the first stage the transition from the planar texture to the confocal turbid texture takes place. λ_{max} is shifted to the short wave range. The helix axises are tilted to respect of the film plane.

The second stage is connected with the untwisting of

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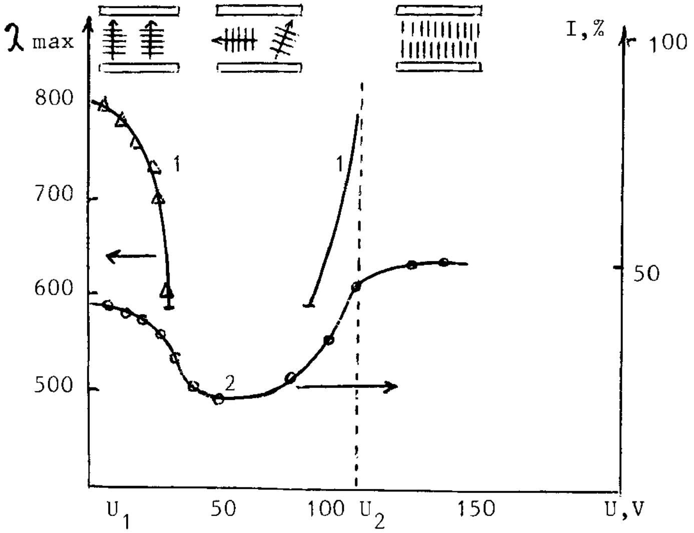

Figure 9. Change of optical properties (λ_{max} and transparency) of cholesteric copolymer 5.5 (A:B = 28:72) under the action of electric field.

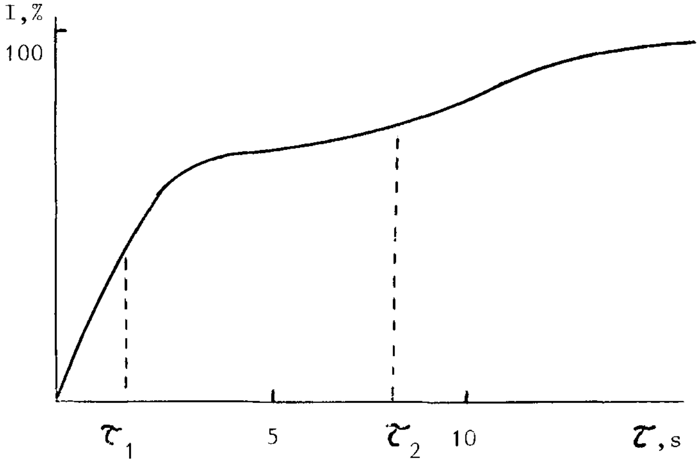

Figure 10. Kinetics of the untwisting of cholesteric helix of copolymer 5,5.

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the cholesteric helix. The λ_{max} drastically increases and the transparency also increases. X-ray and optical conoscopic data show the formation of the smectic structure. In other words the phase transition cholesteric ⟶ smectic takes place, unlike cholesteric ⟶ nematic transition typical for low molar mass liquid crystals. It is defined by the specific feature of comb-like polymers, having the tendency to the layer ordering of the mesogenic groups under the action of external fields.

Specific macromolecular nature of LC cholesterics permits to freeze the colour of polymeric cholesterics on any stage of untwisting of the helix by cooling of polymer films below T_g. However this is only true for copolymers having the comonomer B with the spacer length $n = 5$. These oriented copolymers keep the smectic structure induced by the electric field for a long time.

On the contrary the oriented copolymers with the comonomers unit B and the spacer length $n = 4$ don't keep the smectic structure after cooling. The cooling of these copolymers induces in the narrow temperature interval the structural transition: smectic A ⟶ RN phase [28]. Transition temperatures depend on the electric voltage and on the copolymer composition. The transition isn't observed for copolymers containing more than 30 mole % cholesteryl groups and smectic structure induced by electric field can be freezed by cooling of the samples below T_g.

Thus using the electric field for orientation of polymer cholesterics one can induce the unusual structural transformations unknown for low molar mass liquid crystals.

$$\mathrm{Ch} \xrightarrow{T_1} S_A \xrightarrow{T_2 < T_1} \mathrm{RN}$$

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Taking into account the critical electric field (threshold voltage U_2) of the untwisting of helix, the twist elastic constant K_{22} of comb-like copolymers have been determined from formula

$U_2 = \pi^2$ d/ 2P $(4\pi K_{22}/\Delta\varepsilon)^{1/2}$, where d - is the sample thickness, P - pitch of helix. The values of $K_{22} = (7-9)\cdot 10^{-7}$ dyne are practically not depend on DP and are of nearly the same magnitude as for the low molar mass liquid crystals.

Thus in spite of the existence of backbones in comb-like macromolecules the twist and splay elastic constants [29] of the polymeric liquid crystals are defined by the interaction of the mesogenic groups. In the same time the chain structure of LC cholesterics essentially affect the kinetics of their electrooptical behavior, accompanied by structural and conformational transformations.

Figure 10 shows the kinetics of the helix untwisting. In the figure the optical transmittance as a function of time is shown. One can see also two stages of this process. Both the stages of orientational process have the threshold electric voltages, values of which strongly depend on the copolymer composition, showing the essential role of dielectric interaction of LC polymers with electric field. The values of orientation time on the first stage (τ_1) don't practically depend on DP whereas the values of τ_2 corresponding to the untwisting time of helix increase with increasing of DP (Table 4).

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TABLE 4 Some parameters of orientational process of cholesteric copolymers (U = 130 V)

Copolymers 5,5,mole % A	T°,C	P_n	τ_1, s	τ_2, s	E_a kJ/mole (for τ_2)
17	95	60	1.0	1.0	-
		230	1.0	4.5	-
21	82	50	1.0	16	240
		60	-	-	200
		80	1.5	97	200
		160	1.0	138	200

As far as the time of untwisting of helix exponentially rises with decreasing of temperature the effective activation energy of the process of the helix untwisting have been estimated (see the values E_a in Table 4). You can see that the values of E_a slightly depend on DP. These values are very high and comparable with the values of activation energy of the viscous flow controlled by the mobility of the macromolecule segments. It is likely that the helix untwisting is accompanied by the regrouping of the separate chain segments of macromolecules.

Thus on the base of the electrooptical date one can suppose that the processes of orientation of nematic and smectic polymers and the helix untwisting of cholesteric polymers are kinetically controlled by the movement of the macromolecule segments involved in the orientational process. In the same time the elastic constants of LC polymers are defined by the interaction of the mesogenic groups. Such a dual nature of LC comb-like polymers predetermines all their

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specific structural and physical features. Namely this peculiarity allows to affect the anisotropic mobile LC phase and to control its different properties and finally to fix (by cooling below T_g) LC structure in the solid state with inherent anisotrophy of mechanical, optical and other properties.

REFERENCES

1. V.P. Shibaev, N.A. Plate, Advances in Polymer Science, 60/61, 173 (1984).
2. H. Finkelmann, G. Rehage, Advances in Polymer Science, 60/61, 99 (1984).
3. M. Engel, B. Hisgen, R. Keller, W. Kreuder, B. Reck, H. Ringsdorf, Pure and Appl. Chem., 57, 1009 (1985).
4. O. Herrmann-Schonherr, J. Wendorff, H. Ringsdorf, P. Tschirner, Makromol.Chem., Rapid Commun., 7, 791 (1986).
5. C. Hsu, V. Percec, Polym. Bull. 17, 49 (1987).
6. E. Hessel, H. Finkelmann, Polym.Bull., 14, 375 (1985).
7. P. Davidson, P. Keller, A. Levelut, J. Physique, 46, 939 (1985).
8. H. Finkelmann, H. Ringsdorf, W. Siol, W. Wendorff, in Mesomorphic order in polymers, ACS Symposium series N 74 (Washington D.C.), 22 (1978).
9. J. Frenzel, G. Rehage, Makromol. Chem., 184, 1685 (1985).
10. H. Finkelmann, H. Ringsdorf, J. Wendorff, Makromol. Chem., 179, 273 (1978).
11. R. Zentel, J. Wu, Makromol. Chem., 187, 1727 (1986).
12. Ya.S. Freidzon, Ye.G. Tropsha, V.P. Shibaev, N.A. Plate, Makromol. Chem., Rapid Commun., 6, 625 (1985).
13. V.P. Shibaev, N.A. Plate, Pure and Appl. Chem., 57, 1589 (1985).
14. N.A. Plate, Ya.S. Freidzon, V.P. Shibaev, Pure and Appl. Chem. 57, 1715 (1985).
15. A.L. Smolyansky, Z.A. Roganova, P.V. Talroze, S.G. Kostromin, T.I. Gubina, V.I. Revva, V.P. Shibaev, Vysokomol. Soedin., 28B, 323 (1986).
16. N.A. Plate, R.V. Talroze, V.P. Shibaev, Pure and Appl. Chem. 56, 403 (1984).
17. N.A. Plate, R.V. Talroze, V.P. Shibaev, in Polymer Yearbook, (Elsevier Publ.), 195 (1985).
18. V.P. Shibaev, R.V. Talroze, Zehn arbeiten über flüssige kristalle, Martin-Luther Universität, Halle-Wittenber, Halle, p. 96 (1986).

19. A.L. Smolyansky, Z.A. Roganova, R.V. Talroze, L.A. Kazarin, S.G. Kostromin, Crystallography, 32, 265 (1987).
20. P. Keller, B. Carvalho, J. Cotton, M. Lambert, F. Moussa, G. Pepy, J. Physique Lett., 46, L1065, (1985).
21. R.G. Kirste, H.G. Ohm, Makromol. Chem., Rapid Commun., 6, 179 (1985).
22. S.G. Kostromin, A.B. Kunchenko, Y.M. Ostanevich, D.A. Svetogorsky, V.P. Shibaev, Preprint of the Joint Institute for Nuclear Research, Dubna (JINR), 14-87-361 (1987); submitted in Liquid Crystals.
23. A.B. Kunchenko, D.A. Svetogorsky, J. Physique, 47, 2015 (1986).
24. E.I. Rjumtzev, M.A. Agafonov, V.N. Tzvetkov, V.P. Shibaev, S.G. Kostromin, Dokl.Akad.Nauk SSSR, 288, 1156 (1986).
25. M.V. Piskunov, A.N. Olonovsky, L,B. Stroganov, R.V. Talroze, V.P. Shibaev, N.A. Plate, Dokl. Akad.Nauk SSSR, 290, 1396 (1986).
26. C. Casagrande, M.V. Veyssie, C. Weill, H. Finkelmann, Mol.Cryst.Liq.Cryst., 92 (Letters), 49 (1983).
27. R.V. Talroze, I.A. Korobeinikova, V.P. Shibaev, N.A. Plate, Dokl.Akad.Nauk SSSR, 290, 1164 (1986).
28. I.A. Korobeinikova, R.V. Talroze, V.P. Shibaev, N.A. Plate, Vysokomol.Soedin., A29, 1037 (1987).
29. M.F. Achard, G. Sigand, F. Hardouin, C. Weill, H. Finkelmann, Mol.Cryst., Liq.Cryst. 92 (Letters), 111 (1983).

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