

THERMOTROPIC LIQUID CRYSTALLINE POLYMERS IN ELECTRIC AND MAGNETIC FIELDS

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Abstract - A behaviour of thermotropic liquid crystalline polymers in the electric and magnetic fields is discussed. Experimental data are given on the orientation and relaxation processes, Frideriks effect, "guest-host effect", influence of molecular mass on the electrooptical properties of some LC polymers. Phenomena of electrohydrodynamic instability in such polymers are discussed, new structural transition induced by electric field is discovered, principles of thermoadressing and information recording using LC polymers are described.

INTRODUCTION

It is well known now, that polymers having mesogenic groups in backbones and in side branches of macromolecules can exist in the state equivalent following many features to the liquid crystalline (LC) state of low molecular compounds (Ref.1-5).

One of the significant proofs for LC state in polymers in their capability to orient when external electric and magnetic fields are applied. This is the quality of low molecular LC which provided so wide applications of these materials in electrooptic devices. Electro- and magnetooptics of LC is now well developed field of physics and technics.

As to electro- and magnetooptics of polymeric LC first publications appeared only 2-3 years ago. Here we shall give a first review of qualitative picture of phenomena observed with the analysis of similarity and differences in the behaviour of polymeric and low molecular LC in the external fields. Main attention will be paid to the researches carried out in our laboratory at the University of Moscow in 1980-1983.

Let us remind the main types of electro- and magneto optic phenomena known for low molecular LC and first of all for nematics.

The most of electro- and magneto optical effects are related to the reorientation of the director (or optical axis) of the macroscopic volume of the liquid crystal under the influence of the field or of the liquid's flow. The orientation is caused by the anisotropy of electrical and magnetic properties of liquid crystals such as dielectric and diamagnetic susceptibility and electric conductivity. Besides that the process of rearrangement depends on the initial orientation of a liquid crystal and its visco-elastic properties. The change of optical properties as a result of the reorientation process is already the consequence of the optical anisotropy of liquid crystals.

All known electro- and magneto optical phenomena can be divided into two main groups: field effects when deformation of liquid crystals by the external field is not related with the electric conductivity - and electrohydrodynamical instabilities (EHD), which are caused by the fluid's flow induced by the electric field. EHD instabilities occur in liquid crystals when impurity caused electric conductivity is high enough.

ORIENTATION PHENOMENA IN LC POLYMERS

The first positive results in the study of the electric field influence on LC polymers of comb-like structure have been reported in (Ref.6-8). The orientation in an electric field is the easier the higher is the constant dipole moment value and the polarizability anisotropy of molecules.

The dielectric anisotropy is the overall measure of both characteristics. It is equal to the difference of dielectric constants measured along the field direction and normally to it:

$$\Delta \epsilon = \epsilon_{\parallel} - \epsilon_{\perp}$$

Liquid crystals in which the constant dipole moment is directed along the long molecular axis are always characterized by positive dielectric anisotropy. Taking that into account two groups of scientists in USSR and BRD have synthesized some smectic and nematic polymers of acrylic and methacrylic series with nitrile group at the end of side chains. These polymers had cyandiphenyl (Ref.8-10), phenyl benzoate (Ref.6 & 11), and azomethyle (Ref.7 & 10) mesogenic side groups (Table 1).

The incorporation of the nitrile group provides the high positive value of the parallel component of the dipole moment in the side chain direction and, as a consequence, a high value of $\Delta \epsilon > 0$ (Ref.7). The orientation of the liquid crystal depends on the sign of $\Delta \epsilon$.

Application of low frequency electric field to the sample of a nematic polymer having the initial texture with the optical transmission, which is conditionally taken for 100%, results in a decrease of the transmission practically down to zero (Fig.1a).

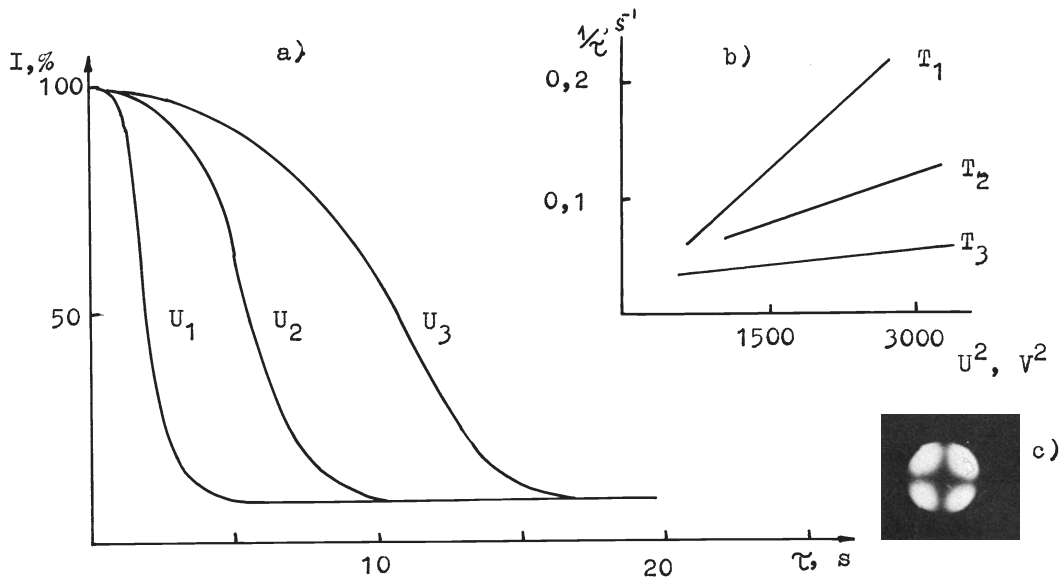


Fig. 1. Kinetics of the change of the optical transmittance (crossed polarizers) under the action of a.c. electric field for polymer comb-like nematics with $\Delta \epsilon > 0$; intensity $U_1(1) > U_2(2) > U_3(3)$ (a) and reciprocal rise time $(1/\tau)$ as a function of the voltage square at different temperatures $T_1(1) > T_2(2) > T_3(3)$ (b); conoscopic figure of the oriented polymer film (c).

That demonstrates the change of the LC polymer orientation. The analysis of kinetic characteristics of the orientation process as a function of the electric field intensity (Ref.8) and the study of dielectric relaxation of the polymer 4b (Table 1) (Ref.12-15) permit to conclude that the effect under consideration is analogous to a Fredericks transition in low molecular nematics having positive $\Delta \epsilon$. In the case of comb-like polymers

TABLE 1. Mesophase type, glass (T_g) and clearing (T_{cl}) temperatures of some nitrile-containing LC polymers of comb-like structure

No	Y	Polymers m	X	$T_g, ^\circ\text{C}$	$T_{cl}, ^\circ\text{C}$	Mesophase type*
		$\left[\text{CH}_2 - \underset{\text{COO}}{\underset{ }{\text{C}}(\text{Y})} \right]_n - (\text{CH}_2)_m - \text{O} - \text{C}_6\text{H}_4 - \text{COO} - \underset{\text{C}_6\text{H}_4}{\text{C}} - \text{X}$				
1a**	CH ₃	6		60	213	S $\xleftarrow{203}$ N
	CH ₃	6	C ₆ H ₄ OCH ₃			
1b**	CH ₃	6		60	227	S $\xleftarrow{198}$ N
	CH ₃	2	C ₆ H ₄ OCH ₃			
1c**	CH ₃	2		70	195	N
	CH ₃	6	C ₆ H ₄ OCH ₃			
1d**	CH ₃	2		-	224	N
	CH ₃	2	C ₆ H ₄ OCH ₃			
2a	H	2	CN	62	93	N
2b	H	6	CN	25	109	N
2c	H	2	N=CH-C ₆ H ₄ CN	72	267	N
2d	H	6	N=CH-C ₆ H ₄ CN	35	211	N
		$\left[\text{CH}_2 - \underset{\text{COO}}{\underset{ }{\text{C}}(\text{Y})} \right]_n - (\text{CH}_2)_m - \text{O} - \text{C}_6\text{H}_4 - \text{C}_6\text{H}_4 - \text{CN}$				
3a	CH ₃	2		95	-	-
3b	CH ₃	5		60	121	S
3c	CH ₃	11		40	121	S
4a	H	2		50	112	N
4b	H	5		40	120	N
4c	H	11		25	145	S
		$\left[\text{CH}_2 - \underset{\text{COO}}{\underset{ }{\text{C}}(\text{Y})} \right]_n - (\text{CH}_2)_m - \text{O} - \text{C}_6\text{H}_4 - \text{CH}=\text{N} - \text{C}_6\text{H}_4 - \text{CN}$				
5a	CH ₃	6		35	125	S
5b	CH ₃	11		25	155	S
6a	H	6		20	158	N
6b	H	11		10	169	S
*) S- smectics						
* N- nematics						
**) copolymers						

it means the orientation of the side mesogenic groups.

The orientation induced by an electric field can be fixed on cooling the polymer below T_g . Such polymer film is characterized by the conoscopic figure presented in Fig.1C. It shows the optical equivalency of this system to an anisotropic uniaxial crystal with the axis direction coinciding with the electric field direction.

Thus a nematic polymer of comb-like structure can be oriented in an electric field like a low molecular nematic, in spite of the chemical binding of the mesogenic groups to the main chain.

The duration of the orientation process essentially depends on the polymerization degree P_w enhancing with its increase (Fig.2) (Ref.17 & 18).

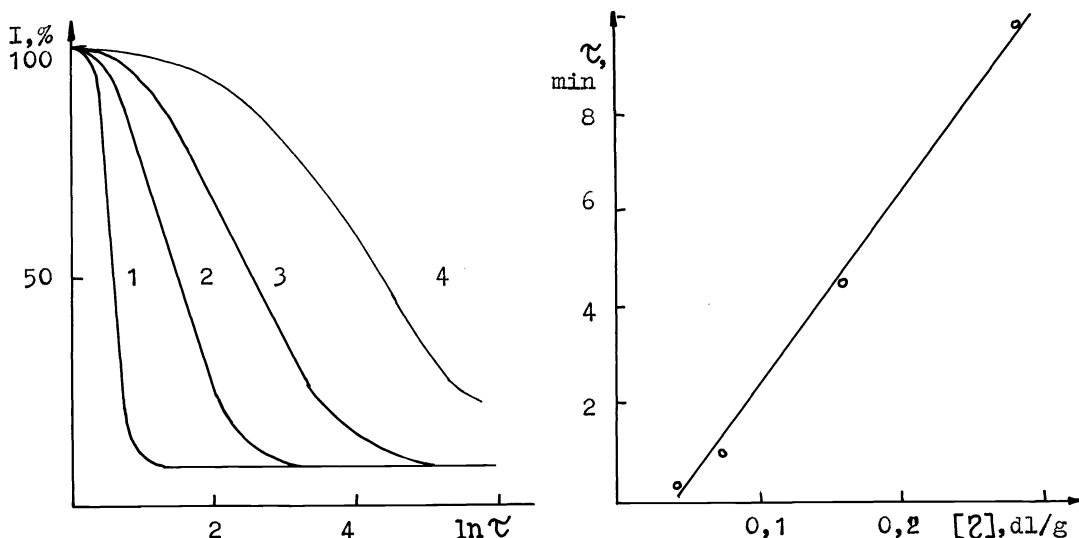


Fig. 2. (a) Optical transmittance as a function of time at the voltage $U = 100V$ ($f = 50 \text{ Hz}$) for the polymer 4b having polymerization degree P_w : 20 (1), 70 (2), 240 (3), 1200 (4) (film thickness $d = 12 \mu\text{m}$, $\Delta T = T_{cl} - T_{exp} = 3^\circ$).

(b) Rise-time of Frederics effect as a function of intrinsic viscosity of polymer 4b ($U = 100 \text{ V}$, $d = 12 \mu\text{m}$, $\Delta T = T_{cl} - T_{exp} = 3^\circ$).

The reverse process of the relaxation is also dependent on P_w . In (Ref.16) the relaxation have not been already observed in polymers with P_w of about 70 and higher. At the same time the values of rise-time and relaxation time, which have been reported by Ringsdorf *et al.* and given in the Table 2 for some CN-containing acrylic polymers, are commensurable with the kinetic characteristics of low molecular nematics. This fact permitted to predict the perspective of the usage of polymer liquid crystal as high speed responsible subjects. It can be supposed, however, that low rise and relaxation times observed in (Ref.11) indicate the extremely low polymerization degrees of polymers studied. Therefore the correct comparison of the properties of high and low molecular liquid crystals needs the exact indication of the molar mass of the corresponding polymer.

The orientation time depends on the temperature (Fig.3) (Ref.27). The study of the kinetics, which has been carried out in (Ref.19) for polymeric cyandiphenyl and azomethyne derivatives, has shown, that the curves of the change of the optical transparency (Fig.3) are related to the field included relaxation process and can be described by the equation given below:

$$1 - \theta = e^{-k\tau^n}$$

where θ - degree of completeness of the process; τ - time; k and n - constants ($n = 1$ in the wide temperature range and it doesn't depend on the polymerization degree).

The constant k which can be considered as a rate constant of the orientation process exponentially depends on the temperature. That permits to calculate the effective activation energy of the orientation process which is equal to 80-200 kJ/mol (Table 3). Any physical model of the orientation of the comb-like LC polymer corresponds to the real mechanism if it explains two experimental facts: the essential dependence of the orientation time on the main chain length (P_w) and the slight influence of the polymerization degree on the activation energy value for each polymer given. The latter is a strong argument in favour of the common mechanism of the orientation process in the range of molecular masses studied.

TABLE 2. Threshold voltage (U_0), rise (τ_1) and relaxation (τ_2) time of some comb-like LC polymers (Ref.11)
$$\left[\text{CH}_2 - \underset{|}{\text{CH}} \right]_n$$

$$\text{COO}-(\text{CH}_2)_m-\text{O}-\text{C}_6\text{H}_4\text{COO}-\text{C}_6\text{H}_4-\text{X}$$

X	$T_{\text{exp}}-T_g$	U_0, V	τ_1, s	τ_2, s	
CN	2	22	60	14	87
CN	6	76	5	3	3
N=CH-C ₆ H ₄ CN	2	84	23	3	3
N=CH-C ₆ H ₄ CN	6	120	4	1	4

Layer thickness - 20 μm , T_{exp} - temperature of the experiment

TABLE 3. Activation energy (E_A) and rise-time ($\tau_{1/2}$) of the orientation for polymeric azomethyne derivatives of different polymerization degree (P_w)
$$\left[\text{CH}_2 - \underset{|}{\text{C}} \right]_n$$

$$\text{COO}-(\text{CH}_2)_m-\text{O}-\text{C}_6\text{H}_4-\text{CH}=\text{N}-\text{C}_6\text{H}_4-\text{CN}$$

Polymer y	m	Mesophase type	P_w	$\tau_{1/2}, s$	$E_A, \text{kJ/mol}$
H	6	N	5-10	4	-
			250	18	97
			350	25	105
			1200	510	105
H	11	S	-	10	84
H (80 mole %) CH ₃ (20 mole %)	6	S	-	120	170

The value of the viscous flow activation energy ($E_A \sim 70-90 \text{ kJ/mol}$) of the nematic comb-like polymer 4b in the LC phase is close to E_A values given in the Table 3. One can suppose that the segments of macromolecules are involved in the orientational movement. The enhancing of the orientation time with the increase of the polymerization degree means, that the position of macromolecule as a whole is changed. But the process itself is caused by the tendency to orientation of side chains which form the LC phase with the positive value of $\Delta \epsilon$.

The activation energy of the orientation of the acrylic comb-like polymers of smectic structure is about the same value as in nematic systems (Table 3). This fact is not typical for low molecular smectics which are oriented more difficult in comparison with nematics. That is apparently related to the polymeric nature of substances studied. E_A depends not on the mesophase structure but on the mobility of main chains taking part in the orientational process.

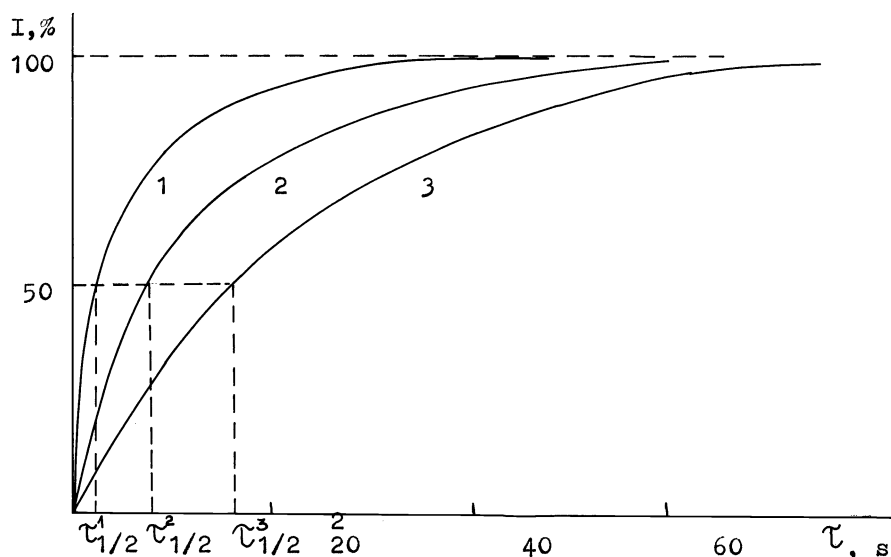


Fig. 3. Change of transparency of nitrile containing comb-like polymers during the orientation process at different temperatures: $T_1(1) > T_2(2) > T_3(3)$ ($\tau_{1/2}$ - time of 50% change of optical transmittance).

The increase of the orientation activation energy in copolymer with methacrylic units (Table 3) and the delay of the orientation in methacrylic homopolymers (Ref.19) confirm the decisive role of the main chains mobility and proves the participation of the main chain in the process of the orientation of comb-like polymer in an electric field.

Studying polymeric and low molecular liquid crystals from the viewpoint of the analogy in their electrooptical behaviour such useful characteristic of Frederics effect as threshold voltage must be considered. The use of some effective value of the threshold voltage (Ref.8) permits to establish some qualitative regularities. Taking for threshold voltage U_0^* the voltage at which no change of the optical transmittance during at least 15 min was observed we have studied the frequency dependence of $U_0^* : U_0^* = \psi(f)$ (Fig.4). The results obtained (Fig.4) are in a good agreement with the dependence of the threshold voltage of Frederics effect on the frequency of the electric field well-known for low molecular nematics.

The data given in Fig.4 show also the existence of the frequency corresponding to $\Delta\epsilon = 0$ at which the value U_0^* tends to infinity. Above this frequency for the dielectric anisotropy changes its sign as a result of the part of the orientational polarization. That is also confirmed by the increase of the relaxation process rate in the electric field of high frequency (Fig.5). After the field homeotropic orientation starts to relax (curve 2). At the repeated applying of the field (at $\tau = 135$ s) of increasing frequency (curves 3-6) the rate of orientation is going down (curves 3, 4). At frequencies above the critical value (in this case - 6 kHz) reorientation occurs, which is induced by the turn of mesogenic group in the direction normal to the field direction (curves 5, 6). This effect can be explained by the sign change of $\Delta\epsilon$ - effect known for low molecular nematics with a positive $\Delta\epsilon$, having a perpendicular component of the dipole moment. In this case specific features of the polymer are manifested themselves by the decrease of the $\Delta\epsilon$ sign change frequency. That can be related to the high viscosity of polymers. Beside this due to kinetic restrictions the orientation, which does not correspond to the $\Delta\epsilon$ sign at given temperature can be fixed in the polymer by its cooling below T_g .

"GUEST-HOST EFFECT"

The "guest-host" effect which is known in low molecular liquid crystals is detected also in polymers. The host role is played by LC polymer matrix and the pleochroic dye is a guest. Dye molecules are characterized by an

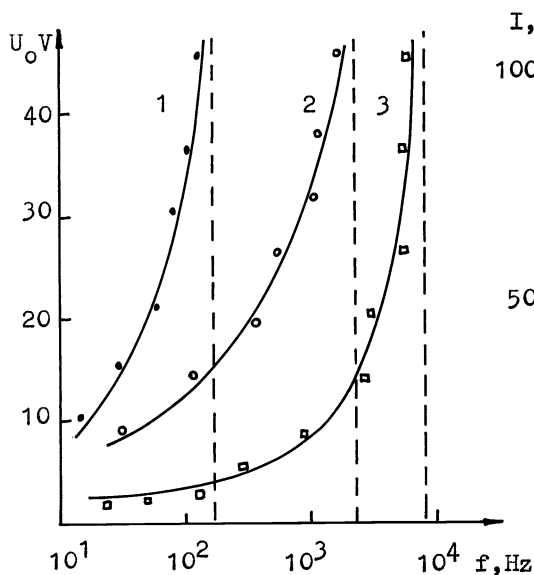


Fig. 4. Threshold voltage as a function of the electric field frequency for the polymer 4b: $\Delta T = 18^\circ$ (1), 13° (2), 9° (3).

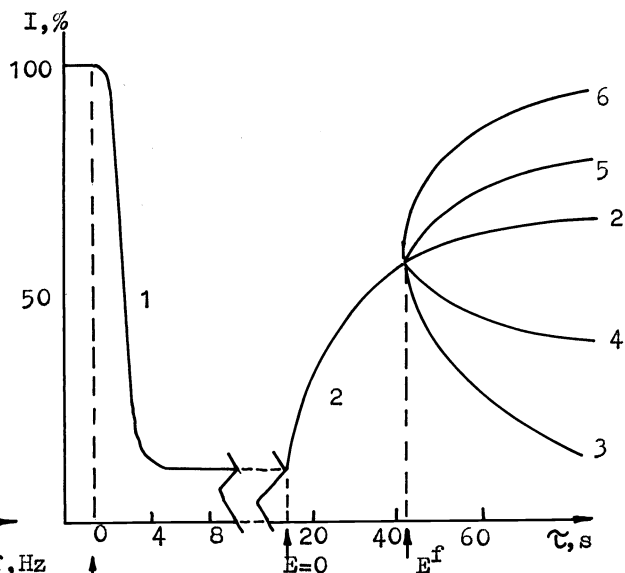
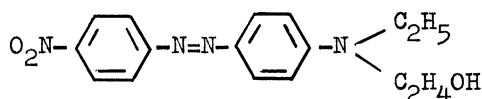


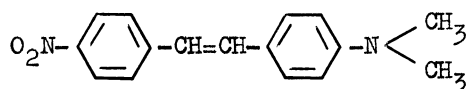
Fig. 5. Optical transmittance as a function time upon application of an electric field ($U = 80V$, $\Delta T = 2^\circ$) of different frequency 50 Hz(1), 1kHz(2), 5kHz(3), 7kHz(4), 20 kHz(5) and relaxation upon switching the field off (2).

elongated form with the absorption oscillator, directed along the long molecular axis. Dye can be incorporated in polymer either mechanically (Ref.21,22) or by chemical binding of guest molecules with polymer matrix (Ref.23).

The incorporation of 1-2% by weight of the low molecular azo-dyestoff (Ref.21)



or of styrene-derivative (Ref.22)



has been shown not to change polymer mesophase structure. Electric field induces an alignment of a guest dye (Fig.6) in a host polymer which results in a change of colour of the polymer film as a function of the dye type, $\Delta \epsilon$ sign and the external field parameters. The experimental data given in (Ref.21-23) indicate the possibility of the creation of indicators with controlled colour characteristics.

"Guest-host" effect can be used for the determination of the order parameter S of the liquid crystal. The values of S estimated by comparative absorption measurements of comb-like nematic polymers with low molecular dyes are about 0.3-0.5 (Ref.21 & 22).

Thus the compatible compositions of LC comb-like polymers with the pleochroic dye stuff can be obtained. This fact in combination with the "guest-host" effect makes possible to vary the colour characteristics of polymeric films and to obtain quantitative information about the orientational order of the LC polymer.

INFLUENCE OF MAGNETIC FIELD ON LC POLYMERS

As it has been already mentioned above the Fredericks effect can be induced both by electric and magnetic fields. Due to the anisotropy of the diamagnetic susceptibility the LC polymers as well as low molecular liquid crystals are able to be oriented in magnetic field. This fact has been demonstrated in NMR experiments with comb-like polymers containing deuteriosubstituted phenyl esters of p-hydroxybenzoic acid as mesogenic groups and with cyandiphenyl-containing polymers (Ref.25). The latter have been synthesized and studied in our laboratory. The orientation in magnetic field has been shown by proton magnetic resonance ($^1\text{H NMR}$) experiment and by X-ray analysis. The transition from the isotropic melt to the LC phase is accompanied by the change of the narrow singlet (Fig.7a) into a partially resolved triplet, which is typical for oriented liquid crystal (Fig.7b).

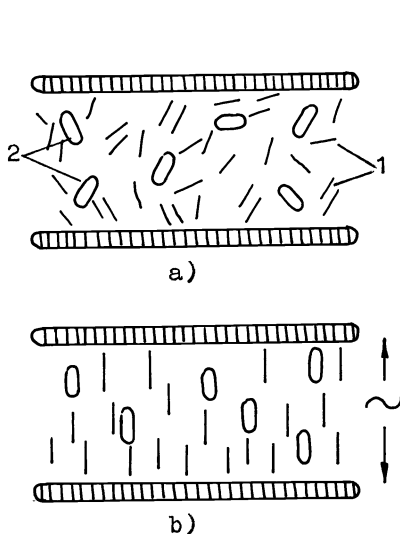


Fig. 6. "Guest-host" effect in an electric field $U = 0$ (a) and $U \neq 0$ (b): 1 - mesogenic groups, 2 - dye molecules.

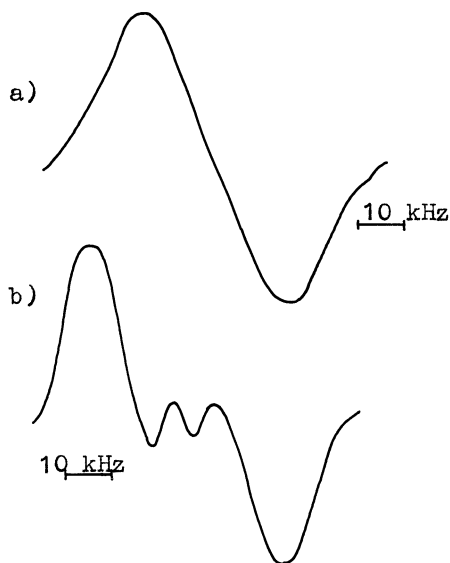


Fig. 7. $^1\text{H NMR}$ spectra of the polymer 4b at different temperatures: in isotropic melt (a) 120° and in LC phase, 80° (b).

As well as in the case of electric field the orientation of side mesogenic groups along the magnetic field direction has been confirmed by X-ray data.

The order parameter S can be calculated from the splitting constant of side components of a partially resolved triplet which arise from a direct dipole-dipole interaction of the benzene ring protons.

The value $S = 0.45$ is in a good agreement with the S values which are obtained by other methods (Ref.21-23,26).

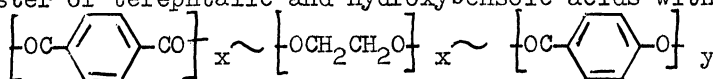
If the orientation in electric field has been observed only for polymers of comb-like structure, the magnetic field induces the orientation of linear polymers having mesogenic groups in main chains also (Ref.27-29).

Studying the orientation properties of linear polymers in external fields the question arises: how many units are included in a LC domain, which is oriented in the field? That is not clear yet, so the oligomer fraction consisting of 10-20 and even 30 monomeric units can't be regarded as equivalent model of polymer chains. It is possible, that the transition to polymers with higher polymerization degrees can be accompanied by the change of the mechanism of orientation in magnetic field.

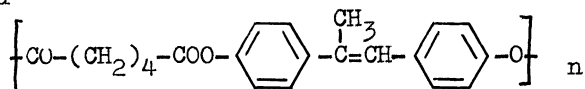
ELECTROHYDRODYNAMICAL INSTABILITIES IN LC POLYMERS

The second group of effects is related with the appearance of electrohydrodynamical (EHD) instabilities in polymers. The formation of instability patterns such as Kapustin-Williams domains in two different linear polymers:

copolyester of terephthalic and hydroxybenzoic acids with ethylene glycol

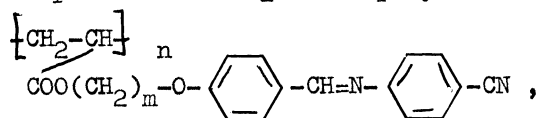


and polyester synthesized from 4,4'-dihydroxy- α -methylstilbene and adipic acid



has been reported by Krigbaum et al. (Ref. 30-32). This fact indicates that these polymers form the LC phase of nematic structure with negative dielectric anisotropy ($\Delta\epsilon < 0$) and positive conductivity anisotropy ($\Delta\sigma > 0$). Unlike low molecular liquid crystals the times of the domain structure formation in LC polymers are about many tenths of minutes. That is undoubtedly related to the high viscosity of polymer melts.

As to comb-like nitrile-containing polymers the formation of domains in these systems has not been observed as it could be expected in polymers with high positive $\Delta\epsilon$. At the same time an applying a.c. electric field to homeotropic oriented films of polymers



where $m = 6.11$

induces the intensive "boiling" of LC melts resulted in the sharp distortion of the optical transparency (Ref. 18 & 19). That seems to be an EHD process of dynamic scattering mode (DSM) type. Data shown in Fig. 8 indicate that the appearance of DSM in polymer liquid crystals essentially depends on the temperature. With the increase of the electric field frequency the DSM region becomes narrower: the lower limiting temperature T_{EHD} is shifted to the higher temperatures (at higher frequency the increased ions mobility for flow of liquid is needed).

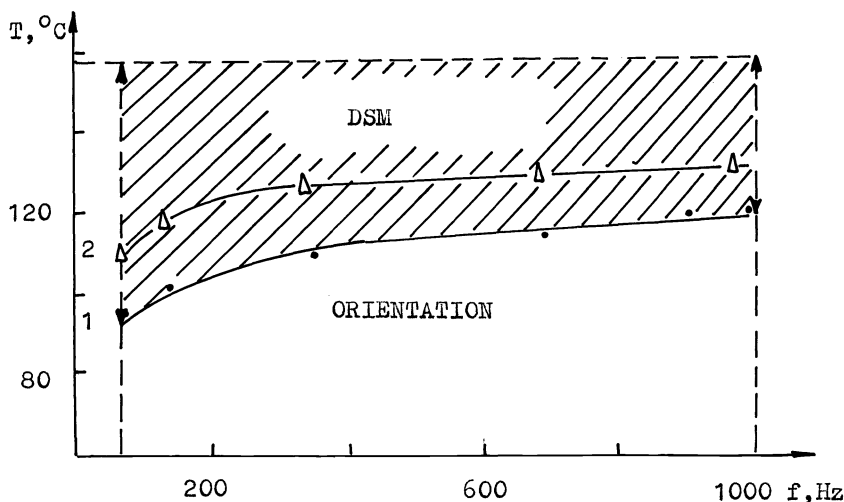


Fig. 8. Temperature of the appearance of EHD instability in homeotropically oriented films of polymers 6a(1) and 6b(2) as a function of the electric field frequency ($U = 200$ V, $d = 12 \mu\text{m}$)

At lower temperature in the high frequency field the ions oscillate only and that doesn't prevent the homeotropic orientation.

Such type of the frequency dependence of T_{EHD} (Fig. 8) permits to realize the two-frequency switching of optical characteristics of polymer films. At the given temperature T (where $T_{\text{EHD}}^1 < T < T_{\text{EHD}}^2$) one can change the

regime of homeotropic orientation to an electrohydrodynamic one by variation of the electric field frequency (Ref.19) (Fig.9).

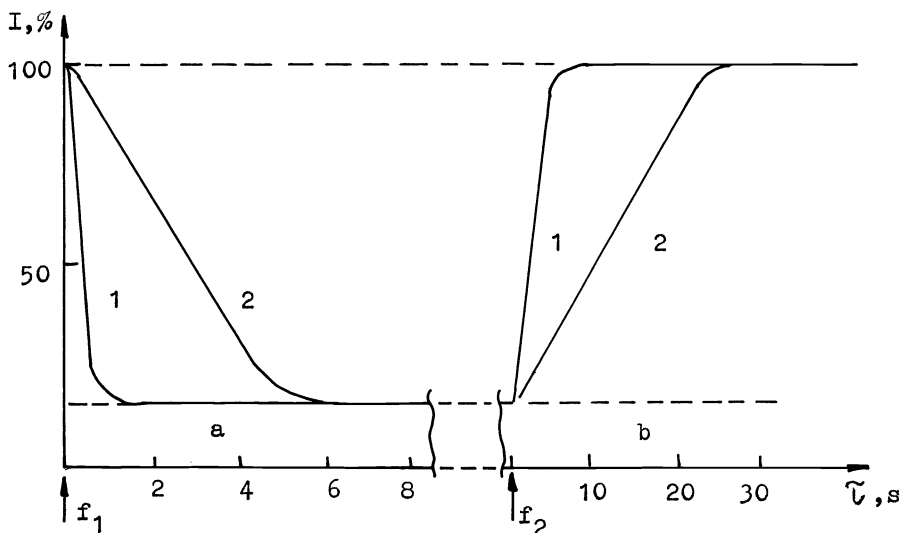


Fig. 9. Kinetics of the change of the transparency of polymers 6a(1) and 6b(2) at the discrete switching of the field frequency ($U = 250$ V, $d = 12 \mu\text{m}$, $T = 125^\circ\text{C}$; 400 Hz (1a), 4 kHz (1b), 200 Hz (2a) and 1 kHz (2b))

By switching on the low frequency field the initial homeotropic oriented film with the high transparency starts to scatter the light due to EHD instability. The transparency is 5-6 times decreased. The use-time of DSM in polymers exceeds the time of the orientation process and depends on the field frequency. As in linear systems DSM process in comb-like polymers manifests itself at high temperature at which the viscosity the LC melt is not too high. If in the polymer with $P_w \approx 100-200$ EHD process takes place in the temperature range wide enough, DSM in the polymer with $P_w \approx 1500$ in an electric field (at $f = 50$ Hz) appears only several degrees below T_{c1} and manifests itself very poorly.

Domain structure formation in linear polymers can be explained in the framework of the classical Carr-Helfrich-Williams mechanism (Ref.32 & 33). In nitrile-containing polymer Schiff's bases ionic current impurity conductivity results in DSM effect. As far as the value of $\Delta \epsilon$ is positive and high enough, the EHD instability in CN-containing polymers can't be described with the mechanism mentioned above. The process seems to have the isotropic mechanism typical for isotropic liquids (Ref.34).

COOPERATIVE STRUCTURE TRANSITION IN LC POLYMERS INDUCED BY THE ORIENTATION IN EXTERNAL FIELD

In this part of the paper one peculiar effect observed for the first time and unknown for low molecular analogues is discussed (Ref.35 & 36). The homeotropic oriented structure of some LC comb-like polymers has been shown not to be fixed on cooling below T_g . Being cooled the polymer film oriented in an electric field undergoes stepwise change of the orientation which results in the sharp appearance of the birefringence. As an example the dependence of the optical transmittance measured in crossed polarizers versus temperature for the polymer 6a (Table 1) is given in the Fig.10. The study of the structure and dielectric characteristics have shown that the observed change of optical properties is related with the cooperative structure transition. This transition also occurs both in electric field and when the electric field is switched off at the temperature $10-15^\circ$ above the transition temperature. The transition takes place only in preliminary oriented polymer, and the field creates this orientation. The transition temperature decreases with the increase of the field intensity (Fig.11). Such dependence means, that the homeotropic structure is stabilized by the field, and the transition itself is caused by the "internal", thermodyna-

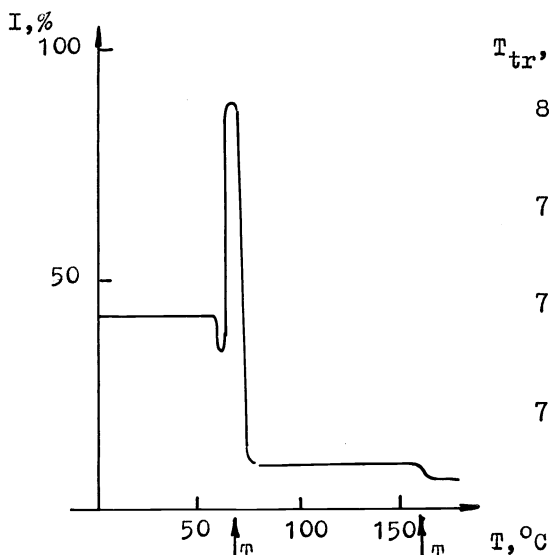


Fig. 10. Change of optical transmittance of the polymer 6a with the temperature ($U = 200$ V, $d = 12$ μ m, crossed polarizers)

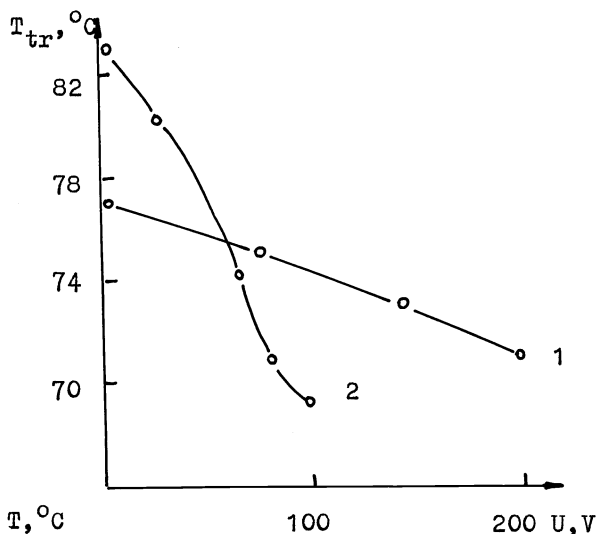


Fig. 11. Temperature of the structure transition as a function of electric field voltage for the polymer 6a (1) and its copolymer with methylmethacrylate (2)

mical properties of the polymer. This effect is observed only in polymers of nematic structure, in smectic polymers the homeotropic orientation is known to be stabilized below T_g .

The detailed molecular mechanism of the effect mentioned above is not yet clear. One can suppose that the transition is related with the change of the conformational state of main chain in sites of the attachment of side mesogenic groups oriented in an electric field.

THERMORECORDING ON LC POLYMERS

Discussing the possibilities of practical use of electro-optical effects in polymeric liquid crystals, it can be concluded that these systems can't compete with low molecular ones in cases where the high speed of response is needed. At the same time the polymeric state of liquid crystals leads to the creation of new optical materials with properties which can be regulated with the aid of external field in LC phase and then can be fixed in the glass state.

This has been tested for the registration and the optical reflection of information. At the first time the usage of LC polymers for this purpose has been reported by the team of researcher from Moscow State University.

The principal LC scheme of the recording of information on the oriented layer of the LC polymer is given in Fig.12 (a-c).

On the transparent film of the homeotropically oriented LC polymer (Fig. 12a) the regions of local overheating are created with the aid of laser beam. In these local regions the liquid crystal passes over to an isotropic melt and the homeotropic orientation is destroyed (Fig.12b). Instead of transparent monodomain homeotropic texture a polydomain texture that scatters light is formed which stays on cooling (Fig.12c). In such a way some information can be recorded on the transparent film and may be "wipped off" by an electric field applying. Such type of recording is usually called as thermorecording or thermoaddressing. For thermorecording it is necessary for an oriented state to be stable in the absence of an electric field for a rather long time, i.e. the orientation relaxation rate should be sufficiently low. The low molecular nematics don't satisfy this requirement. As in the smectic state the homeotropic texture is stable enough the "smectic — nematic" transition is mainly used in thermorecording low molecular LC devices.

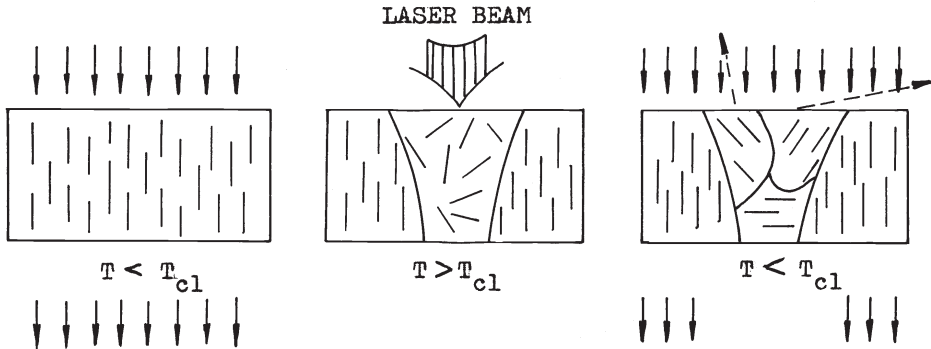


Fig. 12. Scheme of thermorecording using the film of the homeotropically-oriented nematic LC polymer: a) transparent layer of the liquid crystal, b) local heating of the sample above the T_{c1} , c) frozen transparent layer of the liquid crystal with the opaque regions.

As it has been shown above the relaxation rate of nematic polymers of high polymerization degree ($P_w \sim 200-2000$) is very low even in the vicinity of the T_{c1} . The property permits to use LC polymer as film-matrixes for the information recording. The recording can be realized with the action of focused laser beam on the homeotropically-oriented sample at the temperature closed to T_{c1} . On subsequent illumination of polymeric film by an unfocused laser beam the contrast dark spots are projected on screen corresponding to zones of a focused beam action. Fig.13a shows the letters recorded on the film of polymer 4b. The recorded symbols are completely "wiped off" in 2-3 s by an alternating electric field (Fig.13b).



Fig. 13. Polymeric film in illuminated light: a - transparent film with the laser-recorded letters, b - this film after applying an electric field.

The laser recorded information can be kept for a long time if the sample is cooled below T_g . This property of LC polymers can be used for the long-term keeping of recorded information. From this viewpoint LC polymers

differ beneficially from low molecular liquid crystals because the time of the recorded information keeping in devices with low molecular liquid crystals in most cases is limited by several days only. All this shows the possibilities of the usage of the LC state for the active control over the structural-optical properties of polymer materials.

CONCLUSIONS

Thus, the behaviour of polymeric and low molecular liquid crystals has many common features. It must be stressed out that this similarity is rather qualitative. The quantitative characteristics are differed strongly: in polymers one can find the sharp increase of the time of all processes and its dependence on the molecular mass, the strong temperature dependence of the orientation time caused by the high values of activation energy.

Results obtained during the short time from the very beginning of electro-optical study demonstrate the examples of new properties of polymeric liquid crystals: the possibility of the freezing of oriented structure and its stabilization in the absence of the field due to the glass transition and high relaxation times within the LC phase.

The study of electro- and magneto-optical properties of polymers starts only. The possibilities of the searching and study in this field are not yet completed. At the same time the well known regularities of the behaviour of low molecular liquid crystals are a good basis for the study of more complicated polymer systems. One of the main tasks for future is the creation of a physical model of polymeric LC which embraces the role of the backbone in the conditions of external fields action and serves the background for the "continuity" of oriented polymeric LC phase. It should be important to know also to what degree the apparatus developed for low molecular LC is good enough for quantitative description of polymeric LC.

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