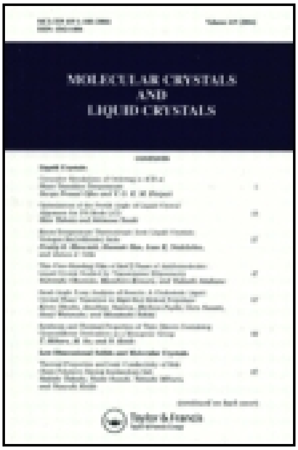

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Some New Physico-Chemical Aspects of Side Chain Liquid Crystal Polymers

Valery Shibaev [a]

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

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Some New Physico-Chemical Aspects of Side Chain Liquid Crystal Polymers

VALERY SHIBAEV

Department of Chemistry, Moscow State University, 119899 Moscow, Russia

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Some aspects of physico-chemical behaviour of thermotropic liquid-crystalline (LC) polymers with mesogenic side groups (comb-shaped polymers) are considered in connection with the peculiarities of their molecular structure. The relationship between molecular parameters, such as molecular weight and molecular weight distribution of LC polymers and their thermal and phase behaviour are examined. The unusual mesophase types formed by such polymers and dynamics of their orientation in magnetic field are analyzed. Thermo- and photooptical phenomena in comb-shaped LC polymers related to their potential application as optical data storage are described.

Keywords: side chain liquid crystal polymers, comb-shaped polymer, phase behaviour, thermorecording, photooptical phenomena

INTRODUCTION

Polymers with a comb-shaped structure were the first representatives of thermotropic liquid-crystalline (LC) polymers.[1–5] The initial attempts to create LC systems in which the molecules of low-molecular weight liquid crystals are incorporated in the side chain of the macromolecules were also primarily stimulated by the significant advances in the area of the investigation and especially the practical use of low-molecular weight liquid crystals.

However after the first unsuccessful attempts to solve this problem "in the head" by synthesis of polymets with mesogenic groups directly bound with the main chain (Figure 1a) no less than 5–6 years elapsed before it was proposed that so-called comb-shaped polymers[6] be used as the most convenient matrix for synthesis of LC polymers.[1–5] The chronology of the development of these investigations can be found in the literature.[5,7,8]

The presence of long side (usually aliphatic, or oxyaliphatic) branches in each monomeric unit is a distinctive feature of the structure of the comb-shaped macromolecules (Figure 1b). Many higher homologs of poly-*n*-alkyl acrylates, poly-*n*-alkyl methacrylates, poly-*n*-alkyl ethers and esters, poly-*n*-alkylstryenes etc., are among such polymers.

Study of the structure and physico-chemical properties of comb-shaped polymers in dilute solutions, gels and the solid state generalized in our publications[6,7,8] per-

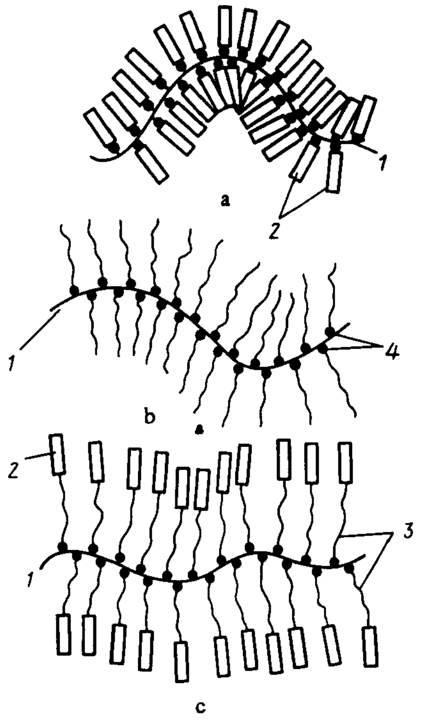


FIGURE 1 Schematic representation of the macromolecules of polymers with direct attachment of mesogenic groups to the main chain (a), with spacers (c) and the comb-shaped macromolecule (b): 1 = main chain; 2 = mesogenic group; 3 = spacer; 4 = attachment bridge.

mitted describing the structural features of this special class of branched polymer systems in detail within the framework of the so-called rotational-crystalline state, a variety of the LC state.[9]

The basic principle of the structure of the macromolecular systems which make it possible to obtain thermotropic LC polymers which side mesogenic groups consists of chemical attachment of mesogens to the aliphatic side branches of comb-shaped polymers (Figure 1c).[1-8]

The key to making comb-shaped LC polymers is the presence of a flexible connecting link (spacer) between the mesogenic group and its attachment point to the backbone. "Distancing" of the mesogenic groups from the backbone with a spacer (which is typically polymethylene type) gives the mesogenic groups relatively high autonomy with respect to the main chain, causing their cooperative interaction with the formation of mesophase.

Recently already several hundreds of LC comb-shaped polymers have been synthesized and the possibilities given by synthesis are quite evidently far from being exhausted. As regards the structure of such systems, it is overwhelmingly versatile. In the first studies published relatively simple polymeric systems were reported (Figures 1c, 2a).[10-14] However the series of reports that followed described comb-shaped polymers of sufficiently complex and even exotic structures. Figures 2a–j show the molecular structures of the major types of comb-shaped LC polymers, synthesized by today.

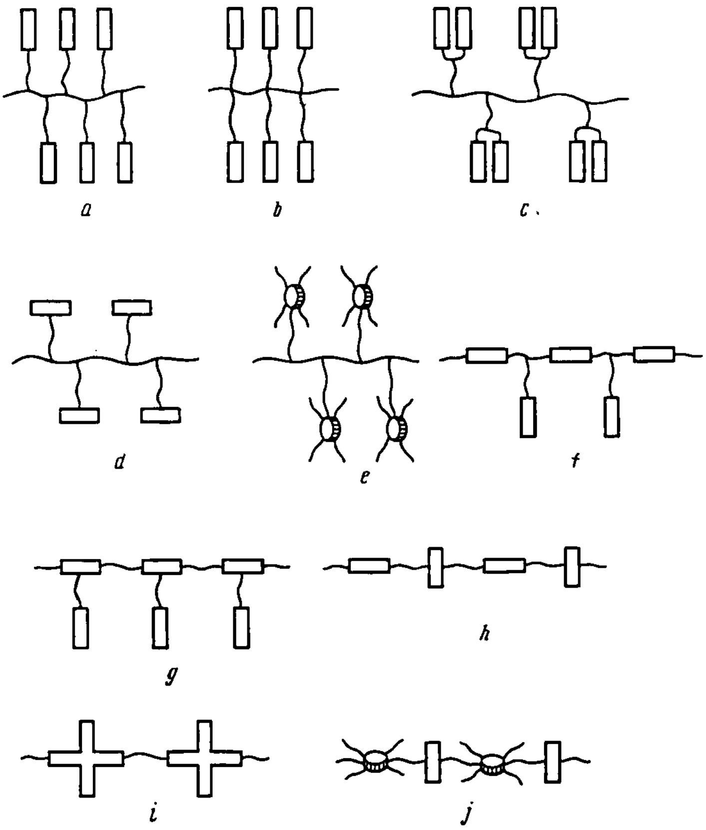


FIGURE 2 Schematic representation of macromolecules of LC polymers with mesogenic groups.

At the same time, in spite of the versatility of the types of molecular structure of LC comb-shaped polymers there are only some studies devoted to the detailed analysis of the structure and physico-chemical behaviour of such complex LC polymers as, for instance, those shown in Figures 2, b–g. The major piece of data was obtained for LC polymers incorporating a rod-like mesogenic fragment within each monomeric unit. However even these sort of LC polymers has not been studied sufficiently.

In other words today the art of synthesis of LC polymers is far ahead of the studies concerning their structure and physical properties in particular. That is why in this paper we would like to concentrate our attention on the consideration some physico-chemical aspects of comb-shaped LC polymers behaviour, reflecting our last experimental results obtained in general at Moscow State University; some of the data have been obtained in collaboration with the scientists of Humboldt University in Berlin.

Four main points will be presented here:

1) the relationship between molecular parameters of LC comb-shaped polymers (such as molecular weight and molecular weight distribution) and their thermal and phase behaviour;

2) some structural features concerning unusual types of mesophases of LC comb-shaped polymers;
3) dynamic of orientation of LC comb-shaped polymers in the magnetic field;
4) some aspects of thermo- and photooptical behaviour of LC polymers related to optical data storage.

INFLUENCE OF MAIN CHAIN AND SPACER ON THE PHASE BEHAVIOUR OF LC COMB-SHAPED POLYMERS

Despite the fact that the mesophase is formed by mesogenic groups and the type of mesophase is basically (although not always) determined by their chemical structure, the polymer backbone contributes essentially to the physico-chemical behaviour of LC polymers.

The significant feature of comb-shaped LC polymers in comparison with low-molecular weight liquid crystals consists in an essential increase of the mesophase thermostability of LC polymers. This is easy to see then comparing clearing temperatures of low-molecular weight alkoxycyanobiphenyls and of comb-shaped

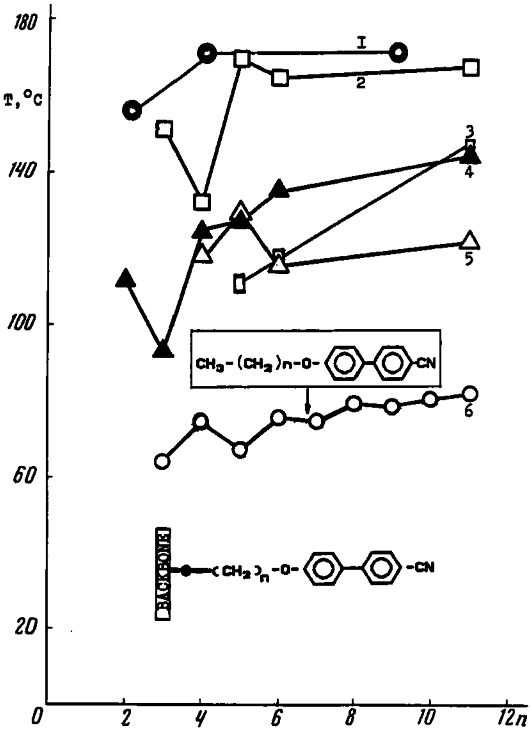


FIGURE 3 Dependence of T_{cl} on the number of carbon atoms *n* in the spacer for LC compounds: 1 = Poly-α-oxiranes(POX-*n*); 2 = Polysiloxanes(PSi-*n*); 3 = Polyvinyl ethers(PVE-*n*); 4 = Polyacrylates(PA-*n*); 5 = Polymethacrylates(PMA-*n*); 6 = Alkoxycyanobiphenyls. For POX-4 and POX-9 the values of melting points are shown.

polyacrylates, polymethacrylates, polysiloxanes, polyvinylethers and poly-α-oxiranes, containing the same cyanobiphenyl mesogenic groups[1-5] (Figure 3).

However when comparing polymeric and low-molecular weight liquid crystals one should bear in mind the following important point.

Owing to the specific features associated with methods of polymer synthesis (chain polymerization, polycondensation) polymers are always a mixture of macromolecules of different length, i.e. these systems are polydisperse. The macromolecules distribution function over their length, which is described by the ratio between the weight-average molecular weight $\bar{M}_w$ and the number-average molecular weight $\bar{M}_n$ may appear rather broad (ratio $\bar{M}_w/\bar{M}_n$ may reach several units in magnitude). The first table illustrates the effect of molecular weight distribution (MWD) on thermodynamic parameters of LC polyacrylic polymer.

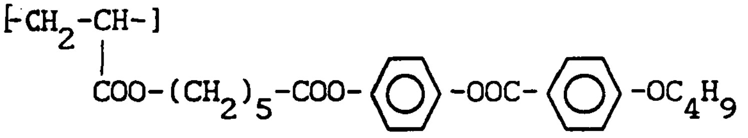
As is seen the two samples with close values of $\bar{M}_w$ but differing in polydispersity are essentially different with regard to the mesophases formed and the relevant clearing points. Moreover, when the MWD is broad not all LC phases characteristic of the given polymer are liable to be observed. Therefore sufficiently narrow fractions ($\bar{M}_w/\bar{M}_n$ < 1.2–1.3) should be used to ensure correct and reproducible results in the studies of LC polymers.

Separation and investigation of such sufficiently narrow fractions embracing a wide range of molecular-weight average made it possible to trace the more "delicate" effect of polymer chain length on the thermal properties of LC comb-shaped polymers.

Figures 4, 5 and 6 depict the plots of transition temperature versus average degree

TABLE I

Effect of molecular parameters of polyacrylic polymer



POLYMER I

on its phase transitions

Sample	$\bar{M}_w * 10^{-4}$	$\bar{M}_w/\bar{M}_n$	Phase transitions, ^{0}C
Fraction	3.95	1.2	S_F 68 RN 122 S_A 135 N 148 I
Unfractionated	4.10	2.9	S_F 70 N 140 I

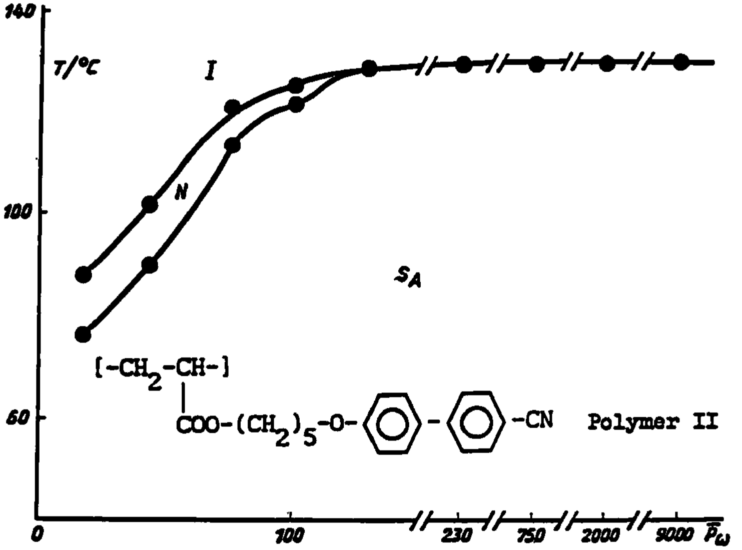


FIGURE 4 Phase transition temperatures of the fractions of LC Polymer II as a function of the degree of polymerization.

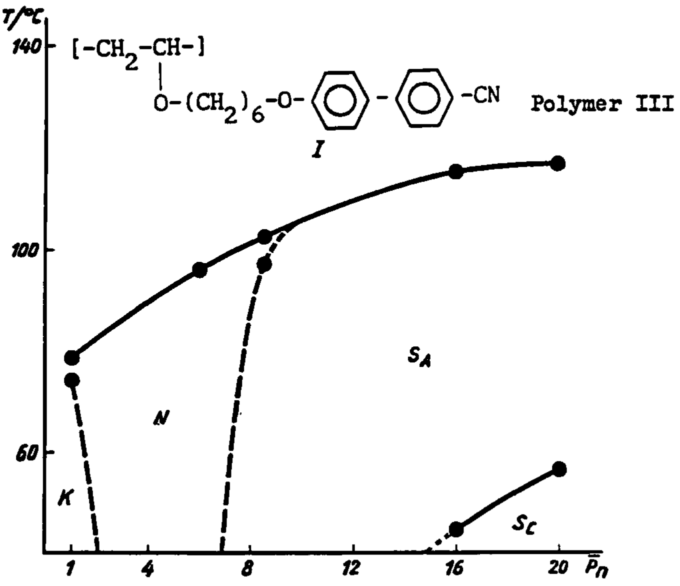


FIGURE 5 Phase transition temperatures of the fractions of LC Polymer III as a function of the degree of polymerization.

of polymerization (DP) for LC comb-shaped polymers with the different main chains. It follows at least two conclusions.

First, in all the cases the clearing temperature (T_{cl}) rises with increasing DP. It means that there is a definite critical value of DP starting from which values of T_{cl} don't depend on DP. It is also seen that the critical values of DP depend on the chemical structure of the main chain.

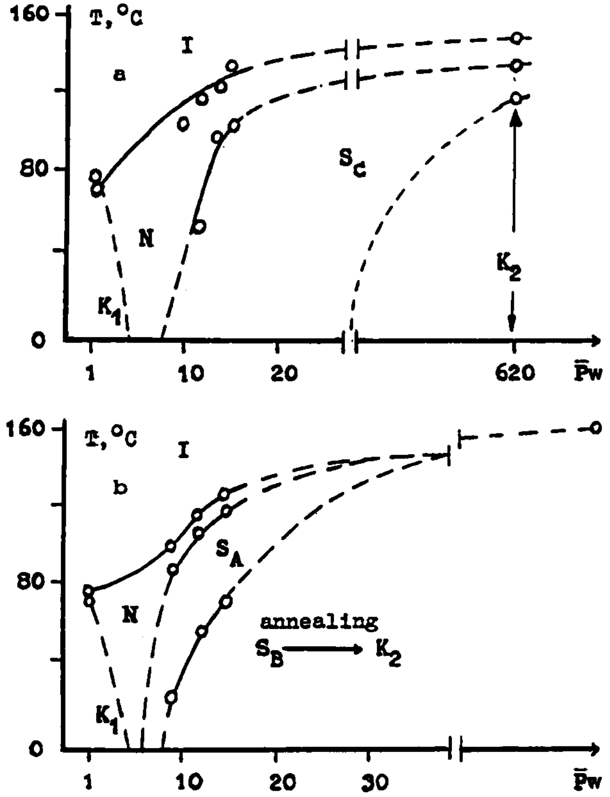
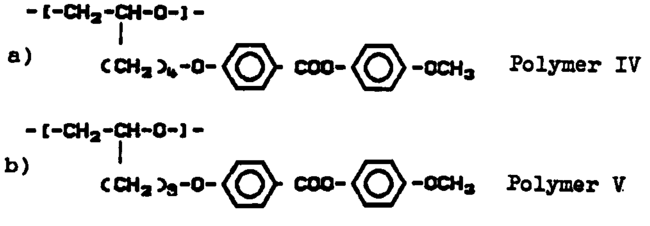


FIGURE 6 Phase transition temperatures as a function of the degree of polymerization for Polymer IV and Polymer V:



Second, it is more important that the mesophase type also depends on DP. In the case of cyanocontaining polyacrylates the low-molecular weight fractions have a nematic structure whereas the fractions with higher DP possess a smectic structure. More complex situation is observed for polyvinyl ethers and poly-α-oxiranes, which were synthesized by cationic polymerization in order to obtain the oligomers with a narrow molecular weight distribution.[17-19]

The fractions of these polymers allow to monitor the transition temperatures passing from the monomer to oligomers with very short chain and finally to polymers. As Figure 5 indicates the monomer forms crystalline and nematic phases. However oligomer with DP = 7 loses the ability to crystallize, retaining however the same mesophase type (*N*-type) as the monomer. The increase of DP (already at DP = 11) leads to S_A phase formation and moreover starting from 16 monomer units S_C phase also is formed.

The close (although more unusual) dependence has been observed for poly-α-oxiranes with *p*-methoxyphenyl benzoate mesogenic groups and spacer length n = 1–4, 9 (Figure 6a,b). All oligomers starting with n = 2 form LC phases and the ordering degree of mesophases increases with increasing DP. For oligomers with four and nine methylenic groups in spacer S_C and S_B phases were observed respectively. However the further increase of DP favours the crystallization of polymers with higher DP. Thus the crystallization of the side chains of these poly-α-oxiranes with high DP essentially restricts to the temperature range of the mesophase existence and sometimes prevents from LC phase formation. Such behaviour of LC comb-shaped poly-α-oxiranes probably is explained by the different conformations of the flexible main chains of the oligomers and high molecular weight fractions as well as the different contribution on terminal groups of oligomers and high-molecular weight fractions to the formation of the diverse structural types responsible for the temperature transitions. The determination of both backbone conformation and an evaluation of energy and entropy contributions of the main structural units of macromolecules to the thermodynamic behaviour of comb-shaped polymers is one of unsettled question in this field.

An important consequence ensues from the data above presented. When elaborating on assignment of a set of phases and definite phase transition temperatures to a distinct polymer sufficiently narrow fractions of a polymer have to be examined, yet with the average DP exceeding a certain threshold value above which the clearing temperature is independent of DP (Figures 3–6). Only such data can be used to establish correlations between chemical structure of comb-shaped polymers and their mesomorphic properties.

Neglecting the reliability established dependences between molecular weight characteristics of LC polymers and their thermal and structural properties may lead to serious errors in assessing thermostability and even the mesophase type.

On the other hand the possibility of the variation of both the temperature range and the type of mesophase by means of the change of DP of comb-shaped polymers can be used at their practical application. The point is that the orientational behaviour of LC polymers in electric and magnetic fields essentially depends on molecular weight and the orientation time decreases with decreasing DP. In this sense the advantages of oligomers for their usage in electrooptics for fast-acting devices are evident.

Another, a not less important feature associated with the polymer chain mediated phenomena in LC polymers is related to the effect of the backbone flexibility on mesophase thermostability, i.e. on the clearing temperature.

As is seen from Figure 3 in going from poly-α-oxiranes (maximum of main chain flexibility) to polymethacrylates (minimum of main chain flexibility) with the same mesogenic groups the tendency to decrease in T_{cl} with decreasing flexibility of the polymer backbone is observed. That means the thermostability of LC phases essentially increases with increasing the flexibility of the main chain. However the tendency to the crystallization observed for polysiloxanes and to the greater degree for poly-α-oxiranes bring to nothing the advantages of these polymers from the LC phase formation point of view.

The effect of the spacer length (reflected its flexibility) on the transition temperatures and phase behaviour of LC polymers is illustrated by Figure 7 and Table II. As in the case of comb-shaped polymers without mesogenic groups,[6–8] an increase in the length of the aliphatic bridge (spacer) results in a decrease in the glass transition temperatures (Tg). As Figure 7 shows by altering the spacer length in the homologous series of polyacrylates with cyanobiphenyl mesogenic groups it is thus possible to affect the Tg, i.e. to change the lower temperature boundary of the LC state.

Another equally important function of the spacer group is its effect on the type of mesophase. It is usually possible to pass from the nematic to the smectic mesophase by increasing the number of methylene units in the spacer while all other parameters of the polymers (including DP) remain the same (Figure 7).

The odd-even effect of spacer length should be also taken into consideration.[20]

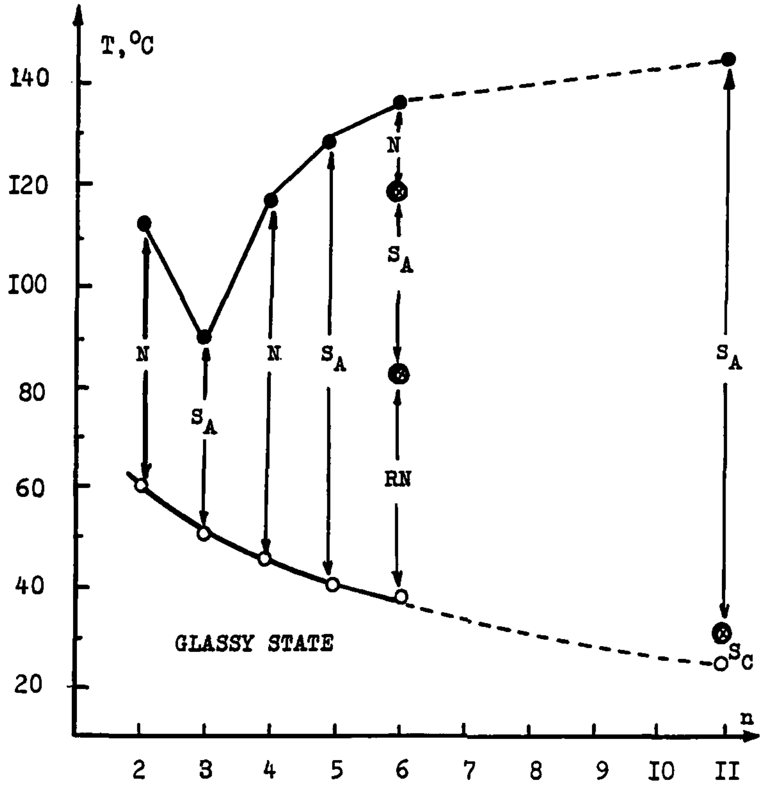


FIGURE 7 Phase transition temperatures as a function of spacer length of LC polyacrylic polymers:

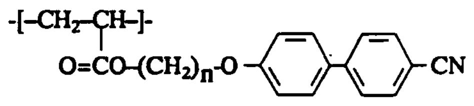
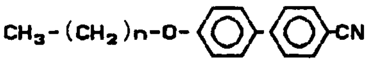
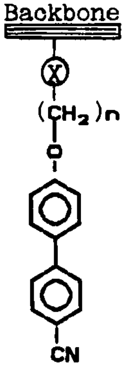


TABLE II

Influence of the main chain structure and spacer length on the phase state of the cyanobiphenyl containing LC polymers

LC compound		Spacer length,n					
		2	3	4	5	6	11
		(N)	(N)	(N)	N	N	S_A
LC polymers Backbone 	PMA	no	-	S_A	S_A	S_A	S_A
	PA	N	S_A	N	S_A	RN,S_A,N	S_C,S_A
	PVE	no	N	N	S_A,N	-	S_A
	POX	N	S_A	K,N	-	-	S_A
	PSi	-	S_A	S_A	S_A	S_A	S_C,S_A

no - no mesophase; Backbone : PMA - polymethacrylates; PA - polyacrylates; PVE - polyvinyl ethers; POX - poly-α-oxiranes; PSi - polymethylsiloxanes

As is seen from Figure 7 the formation of the nematic phases is easier when the spacer contains an even number of carbon atoms (*n* = 2, 4) than an odd number of atoms. Moreover the reentrant nematic phase can be realized for a spacer containing six carbon atoms.

The odd-even effect can be probably explained by the different placement of the mesogenic groups in relation to the backbone[21] due to the diverse conformation of the side groups. Eventually the odd-even effect should vanish with increasing spacer length and starting from seven carbon atoms in the spacer probably only the smectic phases can be formed (Figure 7).

However the chemical nature of the main chain also has an affect on the mesophase type of LC comb-shaped polymers. Table II summarizes a series of polymers with the different backbones but with identical mesogenic groups. The Table demonstrates the influence of structure of backbone and spacer length on the mesophase types of five series of comb-shaped polymers with cyanobiphenyl mesogenic groups synthesized by us. (As a rule the samples with DP exceeded their critical DP have been used.) In addition the data concerning the mesophase types of low-molecular weight alkoxycyanobiphenyl liquid crystals are also included in Table II. As is seen practically almost all alkoxycyanobiphenyls preferentially form the nematic mesophase independently on the length of alkyl "tail"; only an increase of alkyl "tail" length till eleven leads to the smectic phase formation. The situation is more complicated for comb-shaped polymers. The majority of comb-shaped polymers presented in Table II form the smectic type of mesophase. It is interesting to note that an exstence of methyl group in monomeric units stimulate the smectic phase formation independently on the spacer length (see polymethacrylates and polymethylsiloxanes). With respect to other LC polymers included in Table II, it is thus still relatively difficult to establish a direct correlation between the type of mesophase and their molecular structure.

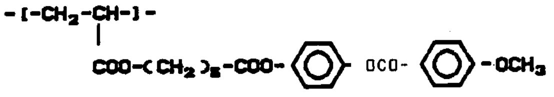
The features of the structure of comb-shaped LC polymers mentioned above (molecular weight and MWD) and the mutual effect of the individual structural elements of the macromolecules (main chain, spacer, mesogenic group and linkage which joins a mesogenic group or spacer to the main chain) significantly complicates the detection of common features in their physico-chemical behaviour.

It is of no doubt that experimental studies in this field and the ensuing accumulation of relevant data are the necessary stages in investigations of the thermal properties and phase behaviour of comb-shaped LC polymers. The outcome of this work should be the compilation of LC polymers with strictly identified physical characteristics within a Handbook similar to "Flussige Kristallen in Tabellen"[20] widely used by researchers working in the field of low-molecular weight liquid crystals.

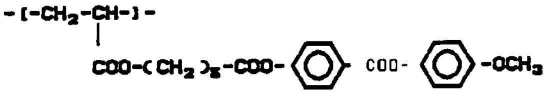
SOME STRUCTURAL PECULIARITIES OF LC COMB-SHAPED POLYMERS

Comb-shaped LC polymers in which all of the mesogenic side groups are joined in a single structurally organized ensemble by the main chain most frequently form a smectic type of mesophase.[8,21] Previously, in structural studies of LC polymers only A, B, C, F smectics were observed. Recently G, H, E, I, J smectics, reentrant nematic phases (RN), chiral S^*_C and N* as well as blue phases were also discovered.[22-24] Practically speaking in the case of LC comb-shaped polymers the same LC phases typical to low-molecular liquid crystals are realized. These structural types of LC polymers have been already comprehensively considered in the literature.[8,22-24] At the same time the nematic structure are more rarely found among LC comb-shaped polymers. Here we would like to consider only two examples concerning some unusual types of mesophases discovered by us some time ago. The first one is related to nematic mesophase, the second one to cholesteric polymer.

The structural studies of two acrylic comb-shaped polymers with close structure:



POLYMER VI



POLYMER VII

revealed their different mesogenic group packing.

For Polymer VI at a temperature below 60° the x-ray patterns are quite unusual for the low-molecular weight nematic liquid crystals. At wide scattering angles a single sharp reflex corresponding to the interplanar distance of 0.44 nm is observed; the small-angle reflexes are absent (Figure 8).$^{25-26}$ Such a pattern indicates that a nematic structure of the polymer with the ordered hexagonal arrangement of mesogenic groups displaying no periodicity along their long axes is formed. Correlation length in the direction perpendicular to the long axes of mesogenic groups $\xi_\perp$ was calculated to be 7.0 nm. At temperature above 60° a sharp reflection transforms to a diffuse halo (Figure 8) characteristic of common nematic structure. Correlation length decreases: $\xi_\perp = 1.5$ nm (80°). To distinguish between these two phases a conventional nematic phase was denoted as the N_A phase, whereas the hexagonally ordered one as the N_B phase, according to the following scheme:

$$N_B \xrightarrow{60°C} N_A \xrightarrow{120°C} I$$

It is quite notable that the LC Polymer VII with a similar structure, differing only in orientation of the ester group between two benzene rings forms only an

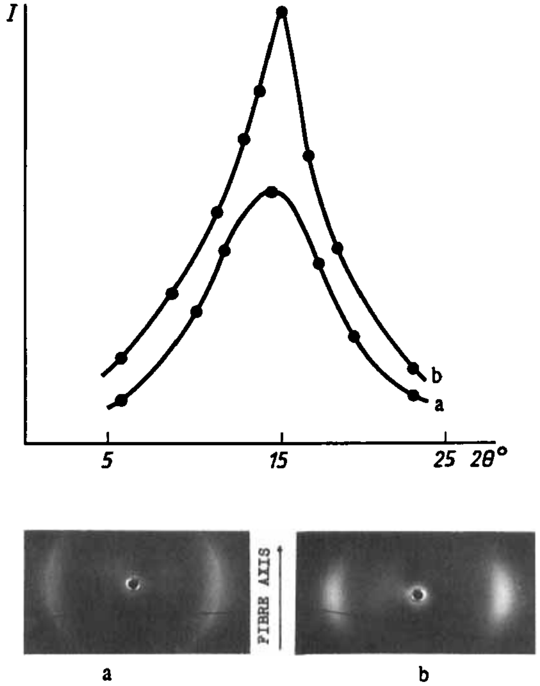
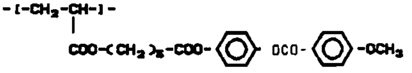


FIGURE 8 X-ray diffraction curves and x-ray diffraction patterns of Polymer VI in N_A (a) and N_B (b) mesophases.



$$-[-CH_2-CH-]- \quad | \quad COO-(CH_2)_5-COO-C_6H_4-OCO-C_6H_4-OCH_3$$

(VI)

ordinary nematic mesophase N_A which passes into an isotropic melt at the same temperature as Polymer VI

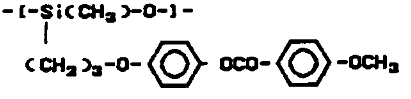
$$N_A \xrightarrow{120°C} I$$

This behaviour is characteristic of unfractionated Polymer VI. However the fractions of Polymer VI of the different molecular weight are characterized by different thermal behaviour. An increase of DP leads to the disappearance of N_B phase and only N_A phase can be detected. The influence of the molecular weight and MWD on the phase transitions of the polymer fractions of Polymer VI is shown below:

Polymer VI

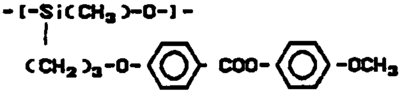
$\bar{M}_w \times 10^4$	$\bar{M}_w/\bar{M}_n$	Phase transitions, °C
0.5	1.10	N_B 45 N_A 117 I
1.5	1.05	N_B 50 N_A 128 I
3.5	1.10	N_A 137 I
2.6	1.10	N_A 138 I

The orientation of the ester group, similar to Polymer VI (in comparison to the opposite orientation in Polymer VII) apparently causes the more ordered arrangement of the mesogenic groups, which also follows from a comparison of a series of polysiloxanes with identical mesogenic groups[27]:



POLYMER VIII

N 60° I



POLYMER IX

S 112° I

Polymer VIII forms only the nematic phase, while Polymer IX forms the smectic type of mesophase.

The reasons for this difference should be looked for in the character of the conformational state of the mesogenic fragments, which results in different anisotropy of the polarizability of the side groups of the polymer in consequence of which the diverse replacement of mesogenic groups in respect to backbone is realized. This is confirmed by the difference in the temperature dependence of dipole moments μ, found by us for example for Polymer VI and Polymer VII (Figure 9).

Another example concerns with cholesteric phase. As is well-known the cholesteric phase in comb-shaped polymers is formed by an incorporation of chiral centres

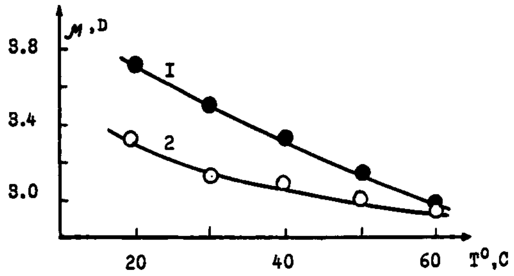


FIGURE 9 Temperature dependence of the dipole moments of Polymer VI (1) and Polymer VII (2); the dipole moments were measured in benzene solutions of polymers.

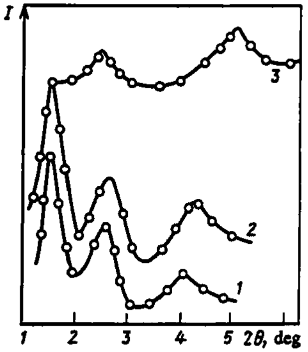
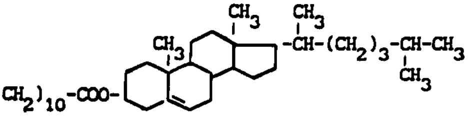
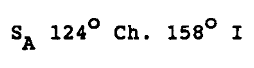


FIGURE 10 Small-angle diffraction patterns of Polymer X in the smectic (1, 2) and cholesteric (3) phases at temperatures of 25 (1), 90 (2) and 140°C (3).



(X)

in the side chain.[28,29] Let us consider the structure of one of cholesterol-containing Polymer X having the following phase transitions:



POLYMER X

S_A 124° Ch. 158° I

As is seen this polymer forms the smectic and the cholesteric phases. In the smectic phase x-ray diffraction patterns are characterized by the presence of several small angle reflexes (Figure 10). Two types of packing of side cholesterol groups were observed to coexist in the structure of layers. One of the types corresponds to the antiparallel packing, so that the cholesterol groups of one macromolecule are surrounded by the methylene chain of the neighbouring macromolecules (single-layer packing) (Figure 11a). The other type of packing involves the partially over-

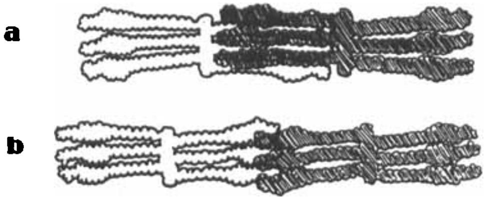


FIGURE 11 Schemes of the packing of the side groups of cholesterolcontaining Polymer X in the S_A-phase.

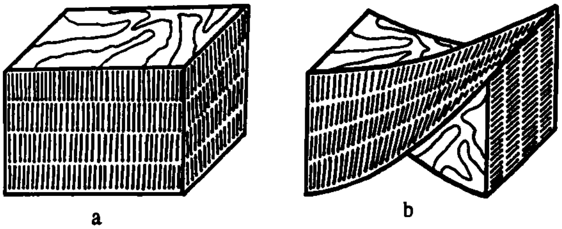


FIGURE 12 Schemes of the layered packing of the side groups and arrangement of the layers in the S_A-phase (a) and the cholesteric phase (b) of Polymer X.

lapping of alkyl "tails" of the cholesterol groups (Figure 11b). The schemes of packing of the side groups are analogous to the packing of mesogenic groups in the smectic A phase as shown in Figure 12a. The transition to the cholesteric mesophase changes the character of x-ray diffraction pattern in comparison to the S_A phase, however the presence of small-angle maxima indicates preservation of the layered order in the arrangement of the side groups (Figure 10, curve 3).

The chlolesteric mesophase of low molecular-weight liquid crystals is usually considered as a twisted nematic phase. The cholesteric mesophase of the polymer just considered (and also other ones) possesses a pronounced layered order, and hence this mesophase cannot be regarded as a twisted nematic one. The cholesteric mesophase of polymers in this case can be considered as follows (Figure 12b). At low temperatures a smectic mesophase type S_A is formed; in the region of the $S_A \rightarrow$ Chol transition there occurs a twisting of the smectic layers in such a way that each section perpendicular to the axis of twisting represents a structure typical of the S_A phase. It means that the cholesteric mesophase in LC polymers has the layer-like structure (layered cholesteric). It is interesting to note that a little bit later the close structure have been found for some low-molecular weight cholesterics.[30] This structure was called helical smectic.

However a number of examples of unusual mesophase types, probably is not limited to the structural types mentioned above. Our preliminary data show that the chiral S_F^* and N_B^* mesophases also can be observed.[31]

One of the important scientific results of studying the structure and properties of LC polymers is that a much larger number of different phases and structures than for low-molecular weight liquid crystals is apparently characteristic of them. Figure 2 demonstrates a number of structural varieties of LC polymers and at present new types of LC comb-shaped polymers are synthesized and studied. Much valuable structural information concerning new unusual types of mesophase of such polymers can be hoped for.

DYNAMICS OF ORIENTATION OF NEMATIC COMB-SHAPED POLYMERS

It is well-known that a magnetic field is a very powerful method of creating an oriented structure and controlling the properties of LC polymers.[8,22]

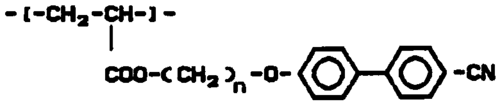
On the other hand the study of orientation processes-gives us very essential information concerning mechanism of director reorientation and allows to calculate a number of physical parameters of LC polymers such as order parameter S, rotation viscosity coefficient γ_1, anisotropy of magnetic susceptibility $\Delta\varepsilon$, the characteristic times of director orientation etc. Broad line NMR spectroscopy proved to be a powerful tool in these studies.[32-34]

We consider here some recent data concerning dynamics and mechanism of director reorientation in comb-shaped LC polymers with different molecular weight. The polymers under investigations are shown in the Table III.

For our investigations we have used NMR-spectrometer MSL-90 equipped by a specially designed goniometer providing the precision of angular displacement of

TABLE III

Molecular characteristics and phase transitions of comb-shaped LC polymers studied by NMR method



Polymer	DP	Phase transitions, °C
Polymer XI	560	N 123.4 I
n = 4	830	N 124.7 I
	2500	N 125.2 I
Polymer XII	35	RN 72 S_A 106 N 119 I
n = 6	70	RN 79 S_A 123 N 128 I
	140	RN 82 S_A 129 N 133 I
	280	RN 84 S_A 133 N 138 I

0.06° as well as Tesla BS-487B spectrometer. Using the NMR technique it appears to be a relatively simple task to create good orientational structure in a rather large sample (~5 mm) by a magnetic field of high intensity. Moreover the "quality" of the orientational structure is permanently monitored since it is directly related to the line shape of the NMR spectrum.

NMR spectroscopic studies are aimed at finding the director reorientation model for LC comb-shaped polymers and comparison these results with classical monodomain director reorientation model for low-molecular weight liquid crystals. Also an influence of the molecular weight on mechanism and some characteristics of director reorientation are discussed.

First of all we consider the monodomain model of director reorientation. This model and experimental technique are presented below.

An initial orientational structure similar to that of the monodomain is first created (Figure 13). That is a nematic monocrystal. This structure is formed by slowly cooling the sample in the magnetic field of a spectrometer from the isotropic melt to the nematic phase. One can see that director and direction of the magnetic field coincides. The line shape of the spectra of such aligned structures are described as *F*(*w*, *o*) (see Figure 14).

On the second stage sample is rapidly turned around the axis perpendicular to

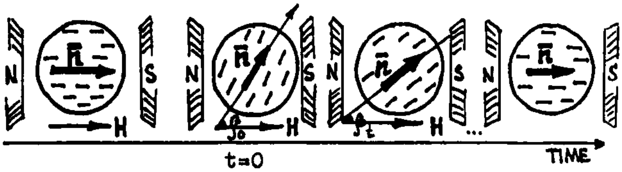


FIGURE 13 Schematic representation of monodomain reorientation of the LC director *n̄* in the magnetic field.

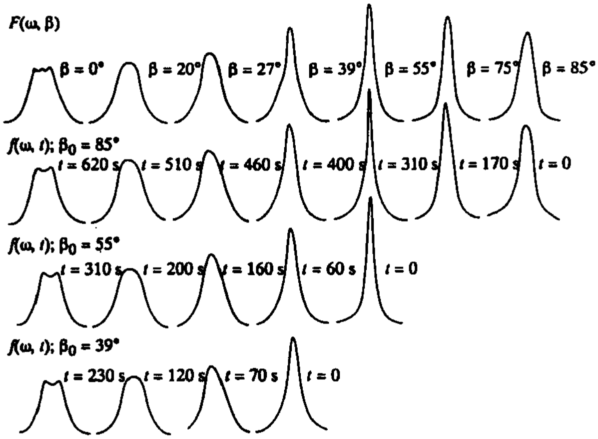


FIGURE 14 Comparison of the angular dependence of ^{1}H NMR spectra of comb-shaped Polymer XII (DP = 280) in RN phase with the spectra registered at the indicated moments of time in the course of reorientation started at different initial director orientation with respect to the direction of the magnetic field.

the field director to make a certain angle β_o between the sample director and the external field. Simultaneously, the time count starts ($t = 0$) (Figure 13).

After that NMR spectra $f(w, t)$ are registered during the course of time of the relaxation of the angle β_o to zero value; the director is relaxed to an equilibrium state parallel to the field.

The spectra will change according to the angle β, giving us the information on the time dependence of the angle $\beta - F(w, \beta)$.

Figure 14 shows angular and time dependence of the spectral line shape for one of the polymers investigated in nematic state. As is seen the spectra registered at a certain angle β coincide with corresponding spectra registered at the indicated moments of time ($f(w, t) = F(w, \beta)$). It means that we can affirm that reorientation proceeds via the same states as when the sample as a whole is rotated by the angle β. In other words the orientational structure is retained during the reorientational process and this equality should be valid. It corresponds to monodomain orientation.

Quantitatively the monodomain model is based on the following assumptions and equations.

Twisting moment imparted by the magnetic field to the magnetically anisoptropic groups is expressed by

$$M_{\text{twist}} = \tfrac{1}{2}\cdot\Delta\chi H^2\cdot\sin 2\beta \tag{1}$$

Viscous friction moment is given by

$$M_{\text{vis}} = \gamma_1\cdot d\beta/dt \tag{2}$$

Monodomain reorientation of the LC director in the magnetic field implies the equality of the twisting moment M_{twist} and moment arising from viscous friction M_{vis}.

$$\gamma_1\cdot d\beta/dt + \tfrac{1}{2}\cdot\Delta\chi H^2\cdot\sin 2\beta = 0 \tag{3}$$

This equation is transformed to Equations (4–6)

$$2\tau\, d\beta/dt + 2\sin 2\beta = 0 \tag{4}$$

$$\tau = \gamma_1/\Delta\chi H^2 \tag{5}$$

$$\tan\beta = \tan\beta_o\cdot\exp(-t/\tau) \tag{6}$$

where H is the magnetic flux density of the field, β is the angle between the LC director and the magnetic field, $\Delta\chi = \chi_{//} - \chi_{\perp}$ is anisotropy of magnetic susceptibility, γ_1 is the rotational viscosity coefficient of the LC polymer, τ is the characteristic time of director realignment and $\beta_o = \beta_{t=0}$ is the initial angle between the director and the field.

So using the Equation (6) we can verify or reject the monodomain model. In addition we can also evaluate the values of γ_1 for LC polymer with different degree of polymerization.

Figure 15 shows the semilogarithmic plots of the director relaxation kinetics for the comb-shaped polymers in the different phase states according to the Equation (6).

One can see the good linearity of the ln tan $\beta(t)$ versus t for the Polymer XII in RN mesophase and Polymer XI in nematic phase.

The difference between these two polymers is displayed only in the values of characteristic time of director realignment. In the nematic state $\tau = 94$s (DP = 560) in the RN state $\tau = 12$ h(DP = 280).

These results show that reorientation of the LC director in nematic and RN phases of these two polymers actually occurs by the mechanism of monodomain orientation.

So the monodomain model was shown to be valid for describing reorientation in comb-shaped polymer nematics a wide range of degree of polymerization and temperatures.

However in the case of Polymer XII, forming nematic, S_A and reentrant phases monodomain reorientation in nematic phase wasn't observed (Figure 15b).

Correlation of the angle and time dependences of the spectrum line shapes is very poor and this results in deviation from linearity—of dependence of tg β as a function of time. Such a complicated dynamics is probably explained by the pre-

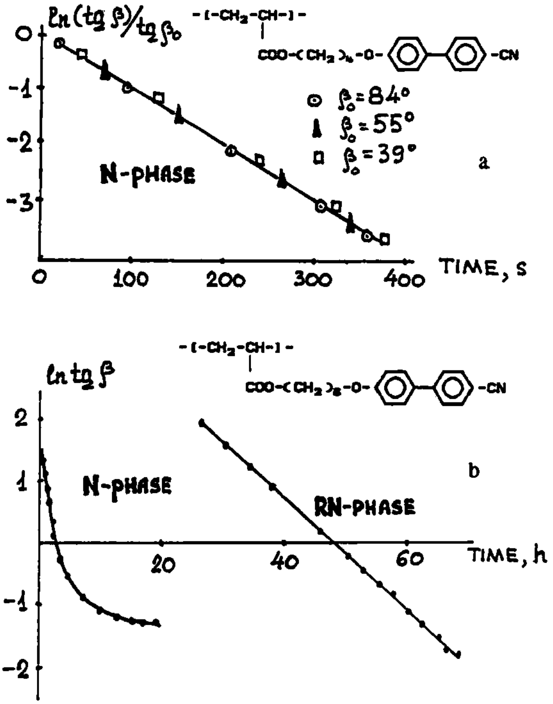


FIGURE 15 Semilogarithmic plot of the director relaxation kinetics for Polymer XI (DP = 560) in nematic phase (a) as well as Polymer XII (DP = 280) in nematic and reentrant nematic (RN) mesophases (b).

transitional phenomena nearly the phase transition nematic-smectic A phase. In this case probably some smectic phase nuclei are formed in N phase and mechanism of the director orientation is not sufficiently clear.

Based on the monodomain model for Polymer XI some physical parameters of LC polymer fractions were estimated from these NMR experiments.

Figure 16 shows the temperature dependence of order parameters S, which were estimated from the dublet splitting of the PMR-spectra. It is seen that all experimental data for three fractions of Polymer XI are described by one and the same curve. It means that values of order parameter in nematic phase of LC polymer don't depend on DP in the broad range of molecular weights.

Table IV summarized the coefficients of rotational viscosity for the same fractions of nematic Polymer XI at the different temperatures.

It is seen that these values essentially increase with increasing DP and decreasing temperature. Using these data the temperature dependence of ratio γ_1/S for all

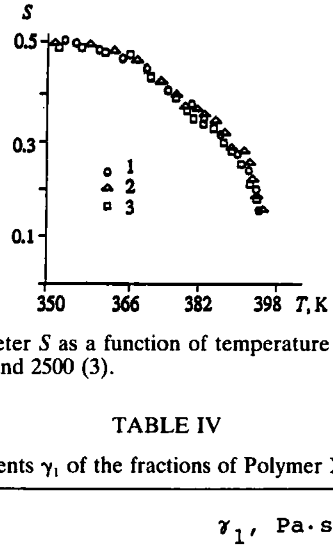


FIGURE 16 The order parameter S as a function of temperature for polymer fractions of Polymer XI with DP = 560 (1), 830 (2) and 2500 (3).

TABLE IV

Rotational viscosity coefficients γ_1 of the fractions of Polymer XI at different temperatures

DP	γ_1, Pa·s				
	T, K=	392	383	368	357
560		$9.6\cdot10^2$	$4.8\cdot10^3$	$7.2\cdot10^4$	$2.6\cdot10^5$
830		$1.8\cdot10^3$	$1.5\cdot10^4$	$2\cdot10^5$	$1.4\cdot10^6$
2500		$1.6\cdot10^4$	$2.2\cdot10^4$	$7.2\cdot10^5$	10^7

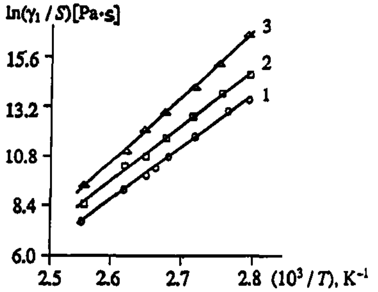


FIGURE 17 Temperature dependence of γ_1/S ratio in the Arrhenius coordinates for the polymer fractions of Polymer XI with DP = 560 (1), 830 (2) and 2500 (3).

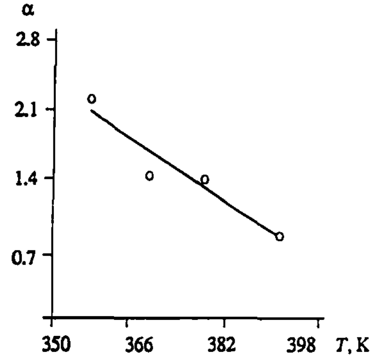


FIGURE 18 Temperature dependence of the exponent α in equation $\gamma_1 = DP^{\alpha}$ for Polymer XI.

polymer fractions was plotted (Figure 17). This dependence obeys the Arrhenius low, that permits estimating the apparent activation energy values E, which are listed below:

DP	E, kJ/mol
560	160
830	195
1500	240

These values are abnormally high and rise with increasing DP. These results provide evidence that the director orientation is controlled by the high viscosity of the LC polymer despite of monodomain character of orientation.

Of special interest are the dependence of the coefficients of rotational viscosity (Table IV).

Using the expression $\gamma_1 \sim DP^{-\alpha}$ the exponents α were estimated from Table IV and these values of α are plotted against temperature in Figure 18.

One can see from this figure that values of α rise linearly with decreasing temperature. The small values of α ~ 0.8–2.2 may indicate that the chain length of the Polymer XI is smaller than a certain critical length corresponding to the appearance of a spatial network of chain entanglements in polymer. It is interesting to note that α-values are essentially less as compared with the same values of some main chain LC polymers.

LIQUID CRYSTALLINE COMB-SHAPED POLYMERS AS OPTICAL INFORMATION RECORDING MEDIA

Comb-shaped LC polymers as optical information recording media have attracted much attention in the last few years.[35-49] Goal of these investigations is a creation of the new materials for optical data storage and reversible optical recording. Several articles and book chapters have been published describing the potential application of side chain liquid crystal polymers in optical data storage.[39,43,46] Here we briefly summarized some of our results concerning thermorecording and photorecording on oriented LC polymeric films.

Thermorecording

The use of LC polymers for thermooptical recording of information was first demonstrated in the works of Russian scientists from Moscow State University.[35-37] They have used the polyacrylic Polymer II (see Figure 4) which was readily oriented in the electric field. The principle of information recording is the following. A transparent film of such homeotropically oriented polymer is illuminated by a laser beam which creates local regions of overheating. At these sites LC polymer melts passing into an isotropic melt and its orientation is destroyed. Cooling the sample, for example through simple displacement of the laser beam leads to the formation on the transparent film of a strongly light-scattering polydomain texture, that corresponds to recording a certain bit of information. Illumination of the polymeric film with a defocused laser beam allows the recorded image to be projected onto a screen. This type of recording is usually called "thermal recording" or "thermal addressing."

Figure 19 gives example of the recording of geometrical figures on the film of Polymer II (the negative imprint obtained by S. Kostromin, I. Yakovlev and V. Motygin is shown). The laser recorded information is preserved for a long time if the sample is cooled below glass transition temperature. As far as the rate of

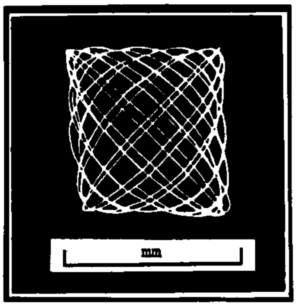


FIGURE 19 Typical example of thermo-optical recording on a homeotropically oriented film of Polymer II. Film thickness 30 μm, laser power 2.6 mW, scanning speed 10 mm/s.

disalignment of LC polymers having sufficiently high degree of polymerization (DP ~ 200–2000) is very small even near the glass temperature, that permits to use the LC polymers as film-matrix for information recording. The introduction of a dye of the anthraquinone series into Polymer II (see Figure 4) and the use of a laser beam with $\lambda = 1.06\ \mu m$ allowed information recording to be undertaken with high contrast (1:120) and quite good resolution of the order 100 lines/mm at the scanning rate of the laser beam ~0.45 cm/s.

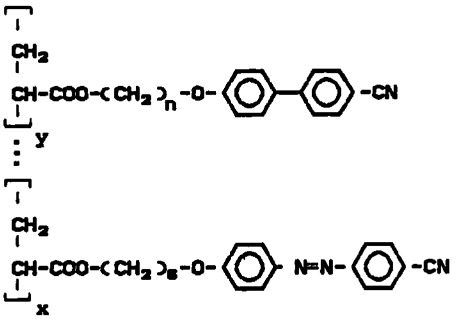
Taking into account also the publications of British scientist led by Coles[40,41] and McArdle,[43] concerning the thermorecording on the oriented films of side chain polysiloxanes one can consider these LC comb-shaped polymers as the perspective polymer materials for archival memory. Their properties are of interest for long-term storage of recorded data.

Photooptical Recording

Another method of information recording concern with photooptical recording. This principle of information recording (for the first time realized by Eich and Wendorf[38,39]) is based on a photo-induced change in birefringence in a homeotropically or planary oriented thin films of comb-shaped LC polymers containing chemically bound molecules of a dye undergoing conformational changes on exposure to a laser beam. The cause of the appearance of birefringence is, for example, the photo-generated trans-cis isomerization of the azobenzene fragments of the side groups inducing local reorientation of the mesogenic groups of the polymer. The phase image of the object is a consequence of spatial modulaton of birefringence and change in the refractive index relative to the vector of polarization of the incident light.

Let us consider some aspects of photooptical behaviour of LC comb-shaped polymers concerning the induced birefringence appearance in the field of laser radiation. The part of these data has been obtained by us in the collaboration with scientists from Humbolt University in Berlin.

We have used a series of acrylic and methacrylic copolymers containing cyanobiphenyl mesogenic groups and cyano-azobenzene dye molecules.



COPOLYMERS I

Some characteristics of copolymers I are shown below:

Copolymer	X, mol%	n	Tg°C	Phase transitions, °C
Cop I-1	20	5	40	S_A 104 N 110 I
Cop I-2	40	5	35	S_A 106 N 110 I
Cop I-3	20	4	42	N 106 I

The polymer samples were placed between two conductive glass plates separated by the spacer film amounted to circa 10 μm. A homeotropic orientation was achieved by applying an electric field in LC state. A planar orientation was achieved by using the special planary electrooptical cell and by annealing the polymer within the cell at a temperature within the nematic phase for a sufficiently long time.

Linearly polarized green light of an argon laser (λ = 514.5 nm, power density P = 20–300 mW/cm^2) was directed on the certain part of LC cell containing the planary or homeotropically oriented LC polymer sample. This laser beam (writing beam) induced the photo-optical effect.

For observation and registration the induced optical effects the same part of the sample was illuminated by the red He/Ne-laser (λ = 632.8 nm; power density has been varied from 10 to 100 mW/cm^2; reading beam). The intensity of the reading beam, passed through the LC film was registrated by photodiode and registration system.

Let us consider what happens under the laser irradiation of LC copolymer, containing azobenzene fragments. Azobenzene molecules are able to display a trans-cis conformational change due to the interaction with laser beam irradiation; these changes can be easily proved by study of UV spectra.[48] After illumination for different time interval the content of trans-form decreases and the content of cis-form increases. Azobenzene fragments are transformed from an elongated rod-like and thus mesogenic shape, into a bend and thus nonmesogenic shape. The appearance of cis-isomers locally perturbs the mesogenic side chain ordering, changing the optical properties of LC film; in other words induced birefringence Δn_{ind} appears.

Typical curves of laser-induced birefringence Δn_{ind} as a function of irradiation time under the action of a "writing" beam are presented in Figure 20 at room temperature ($T < T_g$) and above glass transition of LC polymers. Switching-on the laser, optical anisotropy is induced within the initially homeotropic (or planar oriented) films. During the first period of irradiation the increase of birefringence proceeds quickly and becomes smaller on continued irradiation. Several points are of interest.

a) It is clearly seen that the higher concentration of dye molecules the higher Δn_{ind} independently on the temperature.

b) The values of Δn_{ind} in LC state are circa one order of the magnitude higher as compared to the glassy state. That means that the photoinduced process is much more effective in the visco-elastic state than in the hard glassy matrix. Moreover the limited values of Δn_{ind} are achieved more quickly in LC state.

c) After switching off the laser beam a small decrease of primary induced birefringence Δn_{ind} takes place and stable values of birefringence (δn_{st}) are preserved in the glassy state. These stable values of Δn_{st} are "frozen" in the LC film and remain constant for prolonged time (for several months).

Another situation is realized for LC polymers above their glass transition tem-

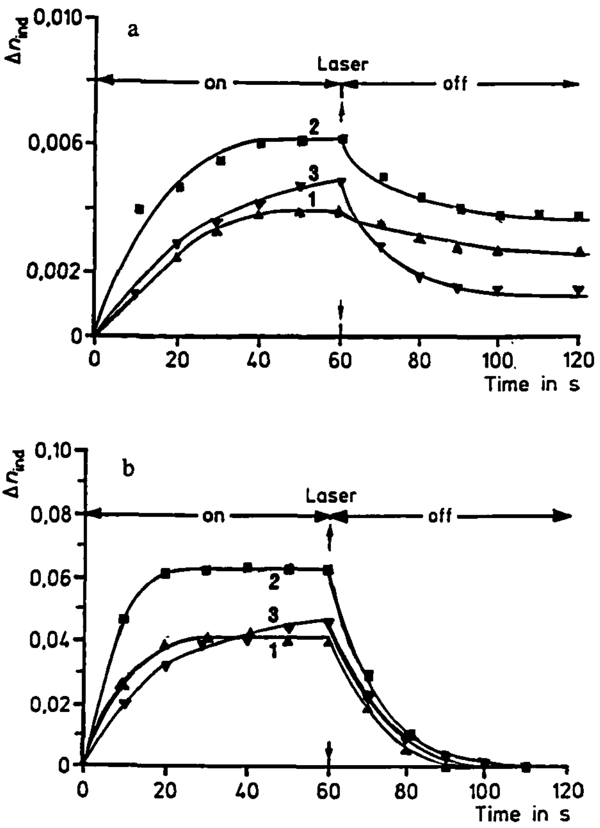


FIGURE 20 Time dependence of laser-induced birefringence Δn_{ind} in homeotropic films of copolymers Cop. I-1 (1), Cop. I-2 (2) and Cop. I-3 (3) on irradiation (power density of laser beam, P = 200 mW/cm^2) followed by relaxation. Temperature: a) 20°C and b) 70°C.

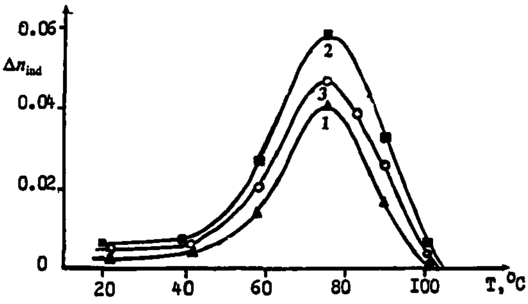


FIGURE 21 Temperature dependence of the Δn_{ind} of copolymers: Cop. I-1 (1), Cop. I-2 (2) and Cop. I-3 (3). (Irradiation time 60 s).

peratures. In the visco-elastic state (Figure 20b) the induced birefringence drastically falls down to zero within 60s after switching off the laser, i.e. the samples of LC polymers relax completely to their initial state due to the mobility of the mesogenic side groups. Figure 21 shows the values of induced birefringence, as a function of temperature for LCP copolymers I-1, I-2 and I-3 on 60s of irradiation time. In the glassy state the values Δn are only slightly dependent on temperature. However, above glass temperature a considerable increase of induced birefringence to values one order of magnitude higher occurs. Maxima of inducing efficiency were achieved for all polymers at temperatures about 70–80°C. Further rising temperatures cause a lowering of order and thus the decrease of the birefringence to be induced.

d) It is interesting to compare the LC polymers with the same content of azobenzene groups of 20 mol.% but different types of mesophases (Figure 20). The values of induced birefringence of the smectic copolymers I-1 and I-2 gradually increase during the first period and become constant after 20s in the visco-elastic state and after 40s in the glassy state. At the same time the other time dependence of Δn_{ind} is observed for copolymer I-3, having nematic structure. (Figure 20a,b, curves 3.) In the glassy state as well as in the nematic state the values of Δn_{ind} have tendency to increase at 60 s and even at 600 s irradiation time to much higher values of the induced birefringence.

Thus a comparison of three samples of azo-benzene containing LC polymers demonstrates that not only the content of photochromic moieties but also the type of mesophase influences the efficiency of the process.

Based on the results obtained by optical measurements[46–49] we have suggested the following picture of photooptical behaviour of LC comb-shaped polymers.

In initial state all azobenzene fragments and mesogenic groups are oriented homeotropically. After the illumination by laser beam trans-cis isomerization takes place and geometry of the dye molecules are changed. In addition azobenzene side groups are reoriented in such a way that the long axes of the azobenzene groups and the plane of polarization of laser beam would be perpendicular. It causes probably small local change of the orientation of neighbouring mesogens. The degree of such reorientation is controlled by free volume fluctuations. The values of induced birefringence are approximately 0.006–0.008 for homeotropic orientation and one order of the magnitude higher for planar orientation.

Another situation is realized in LC state above glass transition temperature. In this case the photoinduced process is much more effective in the mobile LC phase than in the glassy state. It is probably explained by the cooperative reorientation of the majority of mesogenic fragments in the fluid LC state. With the result that higher values of laser-induced birefringence are observed ($\Delta n_{\text{ind}} \sim 0.06$–$0.08$) for homeotropic orientation.

After switching off the laser beam the induced birefringence falls down to stable values (Δn_{st}) in glassy state and to zero in the LC state. The latter is explained by the high mobility of side chains and thermal cis-trans back relaxation. As is seen from the right part of curves in Figure 20b the induced birefringence relaxes completely to the initial state. Namely this feature prompts the method decreasing Δn_{st} that is the erasing procedure of image.

There exist at least two methods of erasure. The first one is heating of the sample above Tg. Figure 22 shows the temperature dependence of stable values of birefringence. These values of Δn_{st} were attained after irradiation by laser beam and relaxation of Δn_{ind} at 20°C (see Figure 20a). It is seen, that the Δn_{st} values are

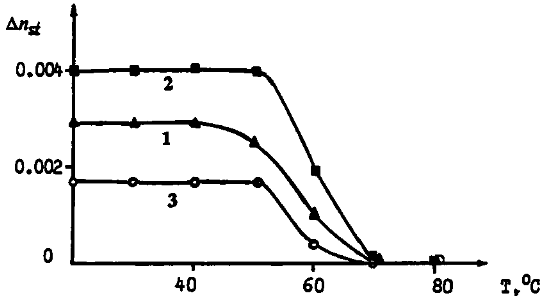


FIGURE 22 Temperature dependence of the Δn_{st} of copolymers: Cop. I-1 (1), Cop. I-2 (2) and Cop. I-3 (3).

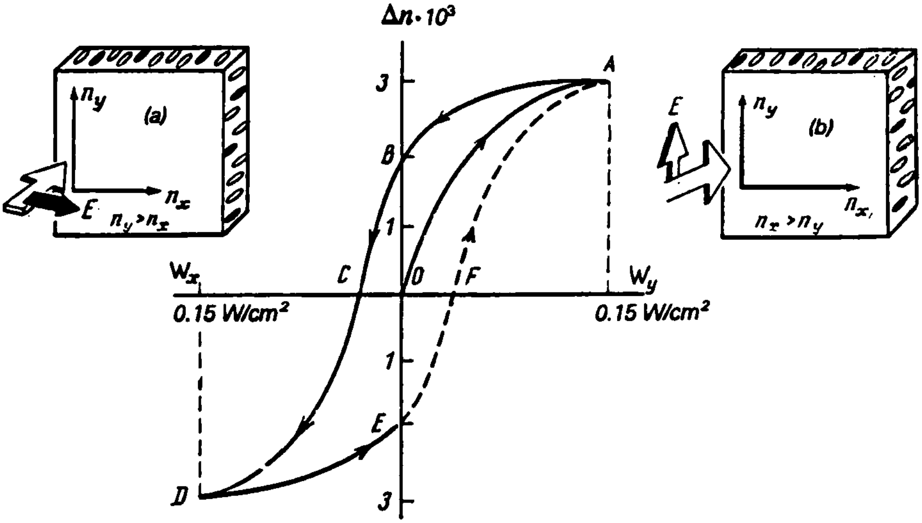


FIGURE 23 Change in induced birefringence Δn on successive irradiation of the homeotropically oriented sample of LC Copolymer I-1 with the laser beam for different polarization of it; a) and b) schematic representation of the LC cell; E = direction of polarization of laser beam.

nearly constant in the glassy state, however, above Tg the loss of any stable birefringence is observed. As a matter of fact it corresponds to erasure process of image.

However there exist the more interesting and promising method of erasure. This method consists in the illumination of LC film with recorded information by the laser beam with polarization plane opposite to the initial polarization plane of the writing beam.

Detailed study of the laser-induced change in Δn_{ind} for different polarization of the laser beam revealed the possibility of using this method for reversible information recording on thin films of LC comb-shaped polymers.

A generalized diagram of the information recording is given in Figure 23. At the centre of the figure change in induced birefringence Δn_{ind} of the homeotropically oriented film on exposure to a laser beam as a function of its power density for a different direction of polarization of the beam is shown. The left part of the figure corresponds to a power density of the laser beam with a polarization plane parallel to x and the right part of the figure to the opposite direction of polarization. The corresponding refractive indexes of the film are denoted as n_x and n_y (Figure 23a,b).

After illumination of the cell with polarized light always increase in the refractive index of the film in the direction perpendicular to the polarization plane of the laser beam is observed. Thus, for the case "a" $n_y > n_x$ and for the case "b" $n_x > n_y$.

At the first stage of information recording with increase in the power density W the Δn_{ind} value rises according to curve OA reaching its maximum value point A. The curve AB corresponds to some "relaxation" of the Δn_{ind} values. This may be related both to the reversibility of the trans-cis transition in the dye molecules and to relaxation of the thermal fluctuations induced by the action of the laser beam. At point B a stable value of Δn is reached, however it sharply falls with change in the direction of polarization of the writing beam—the process of erasure of the recording occurs. However if laser illumination of the films is continued rise in Δn (curve CD) is again observed (in this case $n_y > n_x$) and rerecording of information takes place. Then after "relaxation" Δn (curve DE) again changing the direction of polarization of the laser beam one may erase (curve EF) and again record information (curve FA).

In other words one may "stroll" along the loop carrying out recording-erasure, i.e. making a reversible optical recording of information. It is important to emphasize that one may in this way obtain any Δn values lying in the interval Δn_{max} and Δn_{min} which allows the whole "scale of greyness" to be realized. An example of recording of a test pattern is shown in Figure 24. Preliminary experiments showed that the LC comb-shaped polymers retain good reproducibility and stability, show high cyclicity, quite high photosensitivity ($\sim 10^{-2}$ J/cm^2) and high spatial resolution ($\sim$3000 lines/mm).

Thus, the possibility of inducing anisotropic structure order in polymer LC films with such parameters changing over the volume of the sample as birefringence and orientation of the polarization plane of an ordinary beam make it possible to undertake both phase and polarization recording. There is no doubt that further scientific and parallel applied investigations of comb-shaped LC polymers will lead

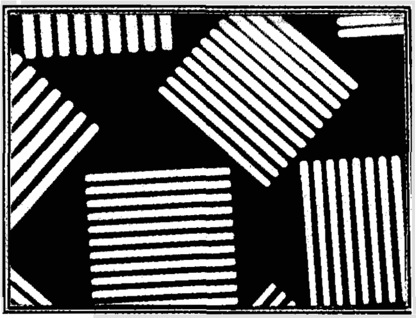


FIGURE 24 Photomicrograph of a film of LC Copolymer I-1 obtained with use of the test pattern. Film thickness 20 m, distances between strips 5 μm.

not only to widening of our knowledge on LC compounds, in general, but also to the creation of qualitatively new polymeric materials with functional significance.

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