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## Liquid Crystals

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# Kerr effect in solutions of carbosilane dendrimers with terminal mesogenic groups

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First results of investigations of electro-optical properties of liquid crystalline (LC) dendrimers in solution are presented. Measurements of electric birefringence (Kerr effect) and dielectric polarization of first generation carbosilane dendrimers with different ester linked terminal mesogenic groups (cholesteryl, cyanobiphenyl and 4-methoxyphenyl benzoate) have been carried out using dilute solutions in  $\text{CCl}_4$ . The results show that the dielectric polarization is proportional to the second power of the electric field in accordance with Kerr law. The Kerr constants calculated are close to those of the low molar mass analogues of the corresponding mesogenic groups. Thus the electric birefringence of the LC dendrimer solutions is mainly determined by the electro-optical properties of their terminal mesogenic groups oriented in the electric field independently of the main chain.

## 1. Introduction

At present, among a wide variety of branched compounds of low and high molar mass, dendrimers attract the increasing attention of researchers. Dendrimers are hyperbranched polymeric and oligomeric systems of regular structure. They can be obtained by the use of reiterative reactions for the controlled synthesis of molecules or molecular fragments [1]. Recently several papers devoted to the synthesis of dendrimers displaying thermotropic liquid crystalline (LC) properties have been published [2-6]. Such LC dendrimers are a new class of mesogen-containing LC compounds of high molar mass, studies of which are of considerable interest from both theoretical and practical points of view.

It was shown recently [3, 4] that one can synthesize LC dendrimers bearing almost any terminal mesogenic group. This opens up many possibilities for the preparation of new LC compounds obtained by controlled variation of the chemical structure and physical properties of the terminal fragments. Investigation of the

molecular characteristics of such dendrimers, the study of which has only just begun, seems to be a necessary step in understanding the nature and properties of the mesophases displayed.

This paper presents first results of electric birefringence (EB, Kerr effect) and dielectric polarization (DP) measurements for LC dendrimers in solutions in  $\text{CCl}_4$ .

Three types of LC dendrimer based on a carbosilane dendritic 'matrix' of the first generation, differing from each other in the chemical nature of the terminal mesogenic fragments, were investigated. EB and DP measurements for a number of low molar mass compounds, which are analogues of the polar mesogenic groups of the dendritic samples, were carried out in order to establish the influence of the dipole geometry of the mesogenic groups on the electro-optical properties of the LC dendrimers.

## 2. Experimental

### 2.1. Materials

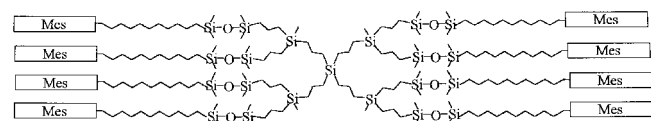
The samples of LC dendrimers, the synthesis of which has been published in [4], had the following chemical

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Table 1. Structural formulae and phase transition temperatures for the low molar mass analogues under study.

Sample	Structural formula	Temperatures of phase transitions/°C
M-1	<chem>C5H11-c1ccc(cc1)-c2ccc(cc2)C#N</chem>	Cr 22.5 N 35 I
M-1'	<chem>C7H15O-c1ccc(cc1)-c2ccc(cc2)C#N</chem>	Cr 54.5 SmA 75 I
M-2	<chem>C4H9O-COO-c1ccc(cc1)-COO-c2ccc(cc2)OC2H5</chem>	Cr 49 N 90 I
M-3	<chem>CH3-(CH2)8-COO-Chol</chem>	g 77 N* 87 I

structure:



where Mes : -COO-c1ccc(cc1)-c2ccc(cc2)C#N D-1

-COO-c1ccc(cc1)-COO-c2ccc(cc2)OC2H5 D-2

-COO-Chol † D-3

All the dendrimers investigated form smectic mesophases of different types [4].

D-1: Glass (−24°C) SmC (50°C) SmA (90°C) I

D-2: Cr<sub>1</sub> (−4°C) Cr<sub>2</sub> (28°C) SmC (77°C) I

D-3: Glass (−15°C) SmA (100°C) I

Structural formulae and temperatures of the phase transitions of the low molar mass analogues investigated are given in table 1.

### 2.2. Techniques

Solutions of the LC dendrimers and the low molar mass analogues were prepared in tetrachloromethane of 'extra pure' quality at 20°C.

Dielectric coefficients were measured by the method of zero pulsation at a frequency of 700 kHz using a capacity meter E12-1 and a cylindrical titanium condenser having itself a capacity of 92.86 Pf.

Refractive indices of the solutions were determined using a refractometer IRF-23 and the line at 578 nm, corresponding to the wavelength of Hg.

The electric birefringence of the solutions of the LC dendrimers and the low molar mass analogues of their terminal mesogenic groups was measured by the compensatory method in rectangular pulsed and sinusoidal

fields [7]. The frequency range of 3–200 kHz was used. The Kerr cell was made from a glass tube with titanium electrodes soldered into it. The length of the electrodes was 2 cm in the path of the light beam and the gap between them was 0.05 cm. A thin mica plate having its own path difference of  $0.01 \times 2\pi$  was used as compensator.

### 3. Results and discussion

The concentration dependence of the increments in the dielectric coefficients ( $\epsilon_{12} - \epsilon_1$ ) and refractive indices ( $n_{12}^2 - n_1^2$ ) of the solutions of the LC dendrimers and the corresponding low molar mass mesogens are presented in figure 1. ‡ Using the magnitudes of the specific increments

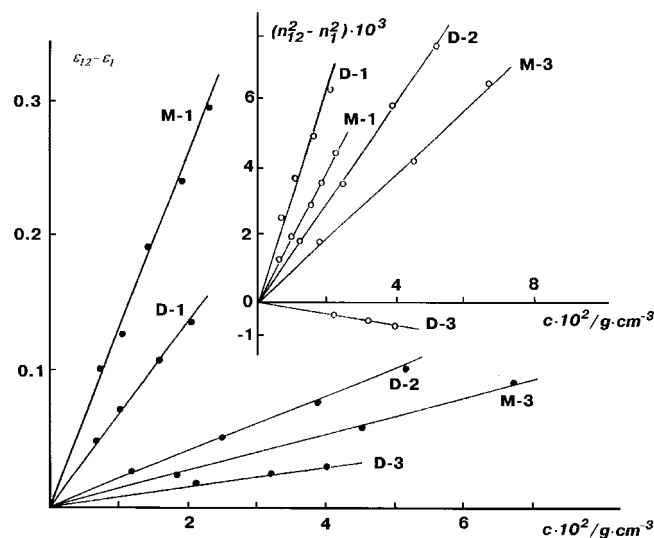
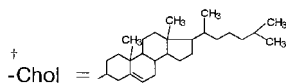


Figure 1. The concentration dependences of the increments in the dielectric coefficients ( $\epsilon_{12} - \epsilon_1$ ) and refractive indices ( $n_{12}^2 - n_1^2$ ) for the dendritic samples D-1, D-2 and D-3 and the low molar mass analogues M-1, M-2 and M-3 in their solutions in  $\text{CCl}_4$ .

‡ The index 12 corresponds to the dendrimer solution, and the indices 1 and 2 correspond to the solvent and solute, respectively.



of the dielectric coefficients  $(\epsilon_{12} - \epsilon_1)/c$  and those of the refractive indexes  $(n_{12}^2 - n_1^2)/c$  ( $c$  = concentration in solution), the values of the permanent dipole moments  $\mu$  for the compounds M-1, M-1' and M-3 were calculated according to the method of Guggenheim-Smith [8]:

$$\mu^2 = 27kT M_2 [(\epsilon_{12} - \epsilon_1)/c - (n_{12}^2 - n_1^2)/c] / 4\pi N_A \quad (1)$$

where  $k$  is the Boltzman factor,  $N_A$  is the Avogadro number,  $T$  is the absolute temperature and  $M_2$  is the molar mass of the solute.

The values  $\mu$  for the M-1 and M-1' samples, determined by the above mentioned method, were in good agreement with the values of dipole moments calculated for these compounds earlier [9].

The dependences of EB ( $\Delta n$ ) on the second power of the electric field  $E^2$  for the solutions of all the samples under investigation were approximated by the straight lines coming from the origin of the coordinate system (figure 2). This fact is an accordance with Kerr law. The value of the specific Kerr constant  $K_C = \Delta n/E^2 c$  was determined from the difference in the slopes of the dependences  $\Delta n = f(E^2)$  for the solution (with a certain concentration,  $c$ ) and the pure solvent. Kerr constants  $K$  for the dendrimers, calculated from the dependences

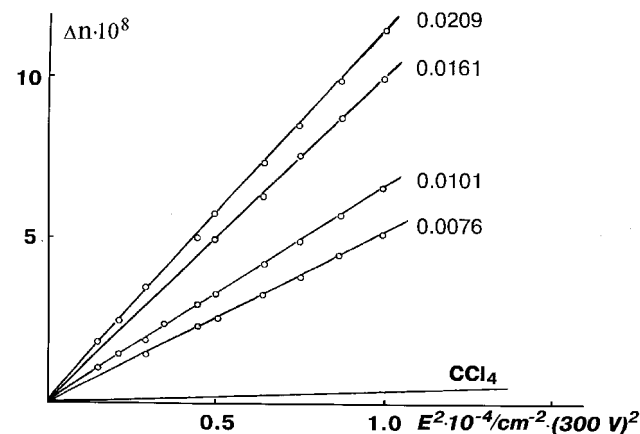


Figure 2. The dependences of the electric birefringence  $\Delta n$  on the second power of the electric field  $E^2$  for solutions of dendrimer D-1 in  $\text{CCl}_4$ . Concentrations in solutions are given in  $\text{g cm}^{-3}$ .

$\Delta n = f(E^2)$ , measured in rectangular pulsed and sinusoidal electric fields, coincided within the limits of the experimental error. The absence of a concentration dependence of the constant  $K_C$  for the LC dendrimers and their low molar mass analogues allowed us to assume the average from the experimental scatter of values for  $K_C$  to obtain the values of their specific electro-optical constants  $K = \lim_{c \rightarrow 0} K_C$  (see tables 2 and 3 and figure 3).

It is well known that the value of the Kerr constant  $K$  characterizes the electro-optical properties of the isolated molecule. For compounds consisting of molecules which have axial symmetry of their optical and dielectric properties and have a dipole moment  $\mu$ , directed at an angle  $\beta$  to the axis of their maximum optical polarizability, the Kerr constant  $K$  is determined

Table 3. Specific dielectric, optical and electro-optical characteristics of the dendrimers in tetrachloromethane solution.

Sample	$(\epsilon_{12} - \epsilon_1)/c$ $/\text{g}^{-1} \text{cm}^{-1}$	$(n_{12}^2 - n_1^2)/c$ $/\text{g}^{-1} \text{cm}^{-1}$	$K \times 10^{10}$ $/\text{g}^{-1} \text{cm}^5 (300 \text{ V})^{-2}$
D-1	6.9	0.32	5.96
D-2	1.9	0.16	0.09
D-3	0.7	-0.19	0.04

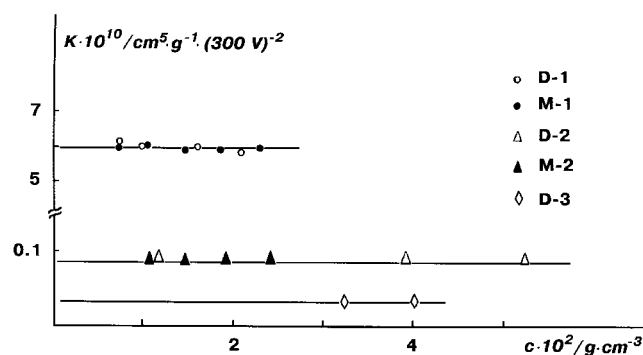


Figure 3. The concentration dependences of the specific Kerr constants  $K$  of dendrimers D-1, D-2, D-3 and of the low molar mass analogues of their terminal mesogenic groups (samples M-1 and M-2) in solution in  $\text{CCl}_4$ .

Table 2. Characteristics of the low molar liquid crystals (LCs)—analogues of the terminal mesogenic groups of the dendrimers.

Sample	$(\epsilon_{12} - \epsilon_1)/c$ $/\text{g}^{-1} \text{cm}^{-1}$	$(n_{12}^2 - n_1^2)/c$ $/\text{g}^{-1} \text{cm}^{-1}$	$\mu(\beta)$ $/D$ (deg)	$K \times 10^{10}$ $/\text{g}^{-1} \text{cm}^5 (300 \text{ V})^{-2}$
M-1	13.2	0.19	5.1 (0)	5.84
M-1'	11.2	0.15	5.2 (10)	6.71
M-2	—	—	2.6 (55)	0.09
M-3	1.36	0.10	2.4 (62)	-0.04

by the following expression [7]:

$$K = \frac{\pi N_A (n_1^2 + 2)^2 (\epsilon_1 + 2)^2 \rho_1}{1215 k T n_1 M_2} \Delta b \times \left[ 2\Delta a + \frac{\mu^2}{kT} (3 \cos^2 \beta - 1) \right] \quad (2)$$

where  $\Delta b$  and  $\Delta a$  represent the optical and dielectric anisotropy of the molecule, respectively.

The sign of the Kerr constant depends on the value and direction of the dipole moment  $\mu$  of the molecule. For non-polar molecules ( $\mu = 0$ ) the Kerr constant is always positive because the signs of  $\Delta b$  and  $\Delta a$  coincide. In the case of polar molecules ( $\mu \neq 0$ ), when the first part in equation (2) can be neglected, EB is positive when  $\beta < 54.74^\circ$  and negative when  $\beta > 54.74^\circ$ . In general the sign of  $K$  is determined by the set of  $\beta$ ,  $\Delta b$  and  $\Delta a$  values.

Formula (2) has been used for the evaluation of the angle of the dipole moment  $\mu$  of the molecules M-1' and M-3 to the axis of their maximum optical polarizability (see table 2). In this case it was taken that  $\Delta a \approx \Delta b$  and that the anisotropy of maximum optical polarizability for M-1' is  $\Delta b = 160 \times 10^{-25} \text{ cm}^3$ , as for the compound  $\text{C}_8\text{H}_{17}\text{O-Ph-Ph-CN}$  [9]; the value  $\Delta b = 112 \times 10^{-25} \text{ cm}^3$  [10] was used for M-3.

The values of the dipole moment  $\mu$  and of its angle to the axis of maximum optical polarizability for the molecule M-2 were determined in [11]. Although the compound M-2 is not the complete structural analogue of the terminal groups of D-2, nevertheless estimation of the value and the direction of the dipole moment for the mesogenic groups of D-2, obtained from the dipole moments of individual functional groups [12], gave us values of  $\mu = 2.6 \text{ D}$  and  $\beta = 54^\circ$ , which are close to the values of  $\mu$  and  $\beta$  for M-2. The optical anisotropy of the molecule M-2 and the terminal fragment of D-2 can then be considered as the same to a sufficient degree of accuracy. Kerr constants of cyanobiphenyl and oxycyanobiphenyl are in fact mainly determined by the contribution of the dipole component, that is almost 50 times greater than the contribution of the deformational polarizability of molecule. On the contrary, the constant  $K$  for M-2 and M-3 mainly depends on the values of the latter effect. In the case of M-2, this is caused by the proximity to zero of the dipole contribution (the angle  $\beta$  is practically coincident with the critical value of  $54.74^\circ$ ). In the second case, both constituents of the effect are comparable. Therefore the reason for the change in values of the constant  $K$  in the series of compounds from M-1 to M-3 is the difference in the chemical structure and the parameters of the dipole geometry of the mesogenic compounds modelling the polar terminal groups of the LC dendrimers.

The change in Kerr constant  $K$  on passing from D-1 to D-3 closely correlates with the difference in the absolute values of  $K$  in the series of corresponding low molar mass compounds (see tables 2 and 3). Nonetheless the value of  $K$  for D-1 is a little smaller than  $K$  for M-1', and the values of  $K$  for D-3 and M-3 have different signs. This fact may be caused by the influence of the organosilicon dendritic 'matrix' ('core') on the electro-optical properties of the LC dendrimers. The linkage of the mesogenic fragments of the dendrimers in a united molecular system does not allow us to exclude *a priori* the possibility of some weak correlation in their orientation under the influence of the electric field. In this case, in the way that it takes place for molecules of the linear alkoxy-cyanobiphenyls having 12  $\text{CH}_2$  groups in the main chain, the value of the Kerr constant for D-1 could be smaller than  $K$  for the compound M-1' [13]. In addition, the presence of the rather long spacer between the organosilicon dendritic 'core' and the terminal mesogenic groups can have an influence on the parameters of the dipole geometry of the mesogenic fragments and lead to a change in the contributions of the dipole and deformational parts of the effect.

Nevertheless, the consideration mentioned above is of only a qualitative nature. For quantitative studies it is necessary to measure EB and DP for solutions of dendrimers with different spacer lengths. On the whole, taking into account the identity of the chemical structure of the organosilicon dendritic 'core' of all the dendrimers in question, we can summarize by saying that the EB of the solutions of the LC dendrimers is defined by the electro-optical characteristics of the terminal mesogenic fragments orienting independently of each other in the electric field. This conclusion is confirmed by the results of DP measurements of their solutions. The dependences of the increments in the dielectric coefficients for the samples of D-1, M-1 and D-3, M-3 on the weight fraction of the mesogenic fragments in solution coincided (figure 4).

The experimental data presented above show that the electro-optical properties of the molecules of the LC dendrimers under consideration,† of their low molar mass analogues, as well as of comb-shaped polymers with mesogenic groups linked to the main chain via flexible aliphatic spacers, are in general identical. One can assume that in the case of comb-shaped liquid crystalline polymers, as in the case of LC dendrimers, the freedom in the orientation of the mesogenic groups

† The referee has requested that it be pointed out that the dendrimers under consideration are somewhat equivalent to side group LC polymers (comb-shaped LC polymers), whereas other known LC dendrimers are more equivalent to main chain LC polymers and that dendrimers of the latter type would not behave so much like their low molar mass analogues.

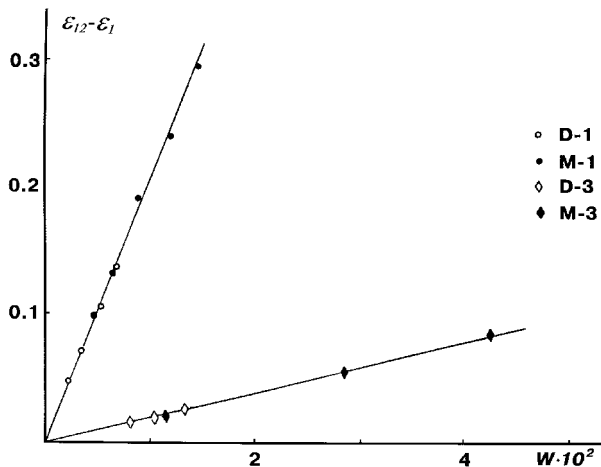


Figure 4. The dependence of increments in the dielectric coefficients of solutions in  $\text{CCl}_4$  of D-1 and M-1, as well as D-3 and M-3, on the weight contribution  $W$  of mesogenic groups in the solution.

is one of the most important factors influencing the capability of these compounds to form the thermotropic liquid crystalline state [14].

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