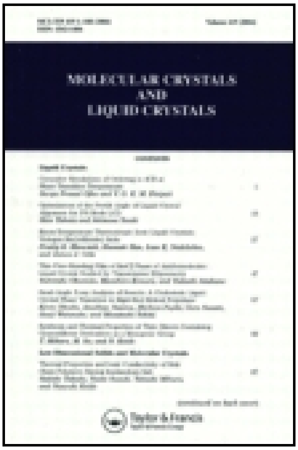

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On the Electrical Switching Properties of Polymeric Liquid Crystals

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On the Electrical Switching Properties of Polymeric Liquid Crystals[†]

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The properties of side chain polymeric liquid crystals in an electric field are described. The polymers investigated are (A) a polysiloxan-copolymer with Cl- and OCH_3-end groups in the mesogenic side chains and (B) a polyacrylic ester homopolymer with a CN-group in the mesogenic side chain.

Applying the Fréedericksz-effect, the rise times and the passive decay times are determined. With the two-frequency technique, the active decay time is also obtained. The order of magnitude for the active decay time is about one second. The active decay time is approximately constant in a temperature region about 15 K below the clearing point.

INTRODUCTION

Liquid crystalline side chain polymers show physical properties similar to those of low molecular liquid crystals. As a result of the polymeric main chain, the viscosity is comparatively high. The electrical properties of such systems are a point of interest. Recently a number of contributions[1–4] concerned with this problem and also with the dielectric properties[5,6] have appeared.

As a consequence of the comparatively high viscosity of liquid crystalline polymers, the response times are appreciably longer for this group of materials. Our experiments were based on the change of sign of the dielectric anisotropy; the active decay time has not previously been investigated in this way for liquid crystalline polymers.

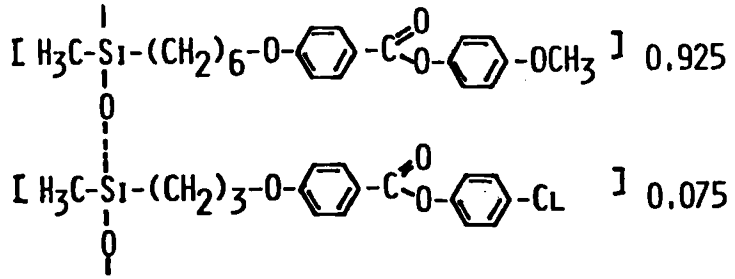
[†] Presented at the Ninth International Liquid Crystal Conference, Bangalore, December 6–10, 1982.

EXPERIMENTAL

Substances

The side chain polymeric liquid crystals investigated possess a substituted benzoic acid phenyl ester group with a polysiloxane (*A*) or a polyacrylic ester (*B*) backbone.

The investigated polymer *A* of the former type is a copolymer



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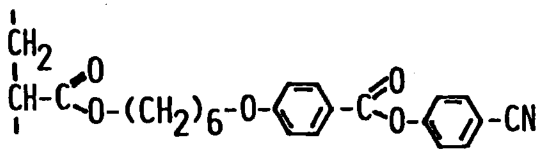
The polymer of type *B* is a homopolymer



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In the copolymer *A*, the flexible spacer in the side group with positive dielectric anisotropy, from the p-chlorosubstitution, consists of three CH_2-units, whereas the methoxy-substituted phenyl ester group with negative dielectric anisotropy possesses a spacer of 6 methylene groups. The degree of polymerization is approximately 95[4]. This polymer was kindly prepared by Dr. H. Finkelmann.

In the case of the homopolymer *B*, six methylene groups act as spacers. A positive dielectric anisotropy is found as a result of the cyano-group. The degree of polymerization is approximately 130.[7] This polymer was prepared in accordance with a procedure described elsewhere.[7] The polymer *A* exhibits smectic phases, whereas the polymer *B* only shows a nematic phase. The investigated temperature range was >65 K above the glass temperature of the respective compound.

Cell Preparation

The experiments start with the cell preparation for the polymer *A* which followed the known procedure for low molecular liquid crystals. The glass plates used were coated with a In_2O_3/SnO_2 layer as conductor and a foil of polyimide was employed as a distance spacer. The mounted cell was then cleaned carefully in an atmosphere of chloroform vapor. The distance of 24 μm between the glass plates was confirmed by interference measurements with monochromatic light using a spectrometer. The glass plates were subsequently rubbed by means of a styropor wheel to obtain a homogenuous orientation. The cell was filled using the capillary effect. For the filling procedure, the sample in question was heated above its clearing point (~400 K) for a period of approximately 5 h. Thereafter the cell was annealed some degrees below the clearing point for nearly two days. By means of this procedure, it was possible to eliminate the defects in the oriented film. The quality of the orientation was then confirmed by employing a polarizing microscope (LEITZ Orthoplan POL.) The orientation was sufficiently good for the measurements, but nevertheless was not perfect along the rubbing direction.

In order to achieve better oriented displays, the results of the experiments described were obtained with a cell whose glass plates (SIEMENS AG) were coated with a polyimide film. The thickness of this cell was 13 μm. Likewise this cell was filled by means of the capillary effect and prepared in the same manner as described above. For a better filling procedure the cell was cut off at one of the corners. The orientation of this cell was of a high quality, as indicated by observations using the conoscopic technique.

The viscosity of the polymer *B* is appreciably higher than of *A*. In this respect the filling by means of the capillary effect was not possible. Because of this, the sample was carefully applied onto the glass plate and then heated for some time above its clearing point in order to allow the trapped air to escape. These glass plates were coated only with In_2O_3/SnO_2 and had a polyimide spacer. The cell was thereafter mounted and fixed with the help of a spring. The thickness of the cell was again approximately 24 μm. To obtain a better as well as more uniform orientation the cell was tempered for nearly two days at 5–10 K below the clearing point. The quality of the display after the tempering was acceptable for the measurements that followed.

Apparatus

The experimental set-up in Figure 1 is comparable with one described previously.[8] The optic axis of the planar cell, prior to switching, forms an angle ϕ of 45° with the E-vector of the incident light. The light source consisted of a He–Ne laser (Coherent 80–2HP). It was polarized by means of a Polarizing Microscope (Leitz Orthoplan POL). The intensity of the transmitted light was registered by means of a photo-diode and recorded

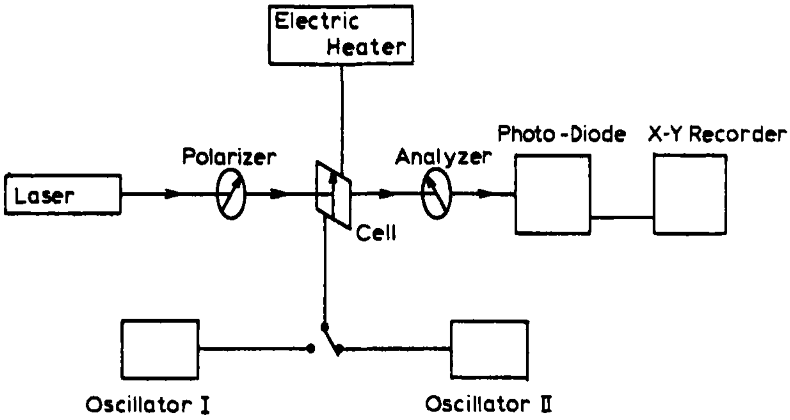

FIGURE 1 Experimental set-up.

with an X-Y-writer. Two oscillators were employed for the purpose of generating the appropriate electric field, i.e., one for the low frequency region and the other for the high frequency field. The voltage was constantly monitored during the experiments. Different heating modes were employed to raise the temperature of the cells. Thus the 13 μm-cell (sample A) was heated by means of the Mettler Hot-stage FP 52 in conjunction with the control unit FP 5. For all other cells of thickness 24 μm a heating-cell was used for the same purpose.

The temperature of the latter cells was measured with a calibrated Cr-NiCr-thermocouple. The drift in temperature was not in excess of ±0.5 K.

RELATIONS

The intensity function of a planar cell[9] is given by

$$I = I_p \sin^2 2\phi \sin^2\left(\frac{1}{2}\delta\right) \tag{1}$$

with

$$\frac{1}{2}\delta = \frac{\pi d}{\lambda}\Delta n\langle\cos^2\varphi\rangle_d \tag{2}$$

$\overline{\varphi}$ is defined as

$$\overline{\varphi} = \text{arc cos}\sqrt{\langle\cos^2\varphi\rangle_d} \tag{3}$$

Here I_p is the intensity of the transmitted polarized light from the laser. ϕ is the angle between the optic axis and the vector of the electric field of the incidental light, which in this case was 45°. The phase difference is denoted by δ and the thickness of the cell by d. $\Delta n = n_e - n_0$, and the wavelength λ of the light from the He-Ne laser is 632.8 nm. φ is the angle between the optic axis and the glass plates of the planar cell.

Intensity maxima occurred at π, 3π, 5π, etc., and minima at 2π, 4π, 6π, etc. The intensity trace of polymer A is given as an example in Figure 2. The thickness d of the cell was determined by the interference method using a Cary-spectrometer which was described previously.[8]

The birefringence Δn for sample A was determined with a Leitz-Jelley-Microrefractometer as sketched in Figure 3. The Δn-value for polymer B at 376 K was obtained from Eq. 2.

The threshold voltage for a planar cell is given by

$$U_0 = \pi\left(\frac{k_{11}}{\varepsilon_0 \Delta\varepsilon}\right)^{1/2} \quad \text{for} \quad \Delta\varepsilon > 0 \tag{4}$$

and

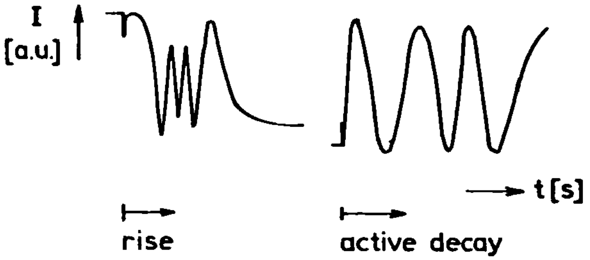

FIGURE 2 Intensity as a function of time for rise and active decay (polymer A).

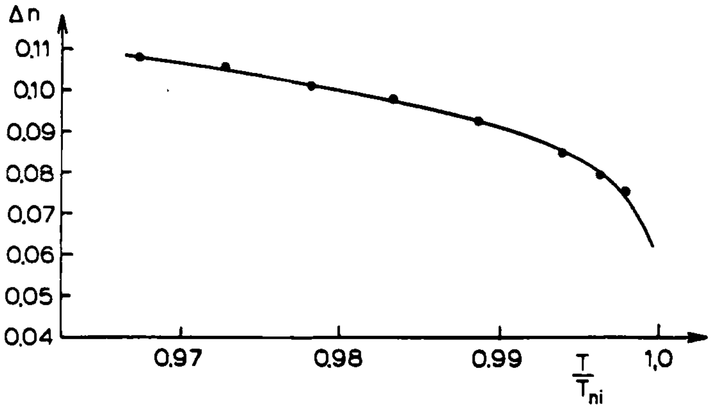

FIGURE 3 Birefringence as a function of temperature (polymer A).

$$U_0^+ = \pi\left(\frac{k_{11}}{\varepsilon_0|\Delta\varepsilon|}\right)^{1/2} \quad \text{for} \quad \Delta\varepsilon < 0 \tag{5}$$

k_{11} is the splay elastic constant.

The time constant relations[10] for a planar cell are:

rise time

$$\frac{1}{t_r} = \frac{1}{t_d^0}\left[\left(\frac{U}{U_0}\right)^2 - 1\right] \tag{6}$$

active decay time

$$\frac{1}{t_d} = \frac{1}{t_d^0}\left[\left(\frac{U}{U_0^+}\right)^2 + 1\right] \tag{7}$$

passive decay time

$$\frac{1}{t_d^0} = \left(\frac{\pi}{d}\right)^2 \cdot \frac{k_{11}}{\eta_1} \tag{8}$$

where η_1 is a viscosity parameter. The rise time is defined as the time required to change from $\overline{\varphi} = 0.2$ to $\overline{\varphi} = 1.0$, and the converse applies to the decay time. These values of $\overline{\varphi}$ are approximately equivalent to the time scale with $I = 10\%$ to $I = 90\%$ in the TN-cell.

RESULTS AND DISCUSSION

The frequency of the dielectric isotropy f_0 was determined by two independent methods. One method ($m1$) makes use of the results from a plot of the active decay time as a function of the applied frequency based on Eq. 7. From Eq. 5, with $\Delta\varepsilon = 0$, one obtains U_0^+ as ∞ and consequently $t_d = t_d^0$; this is demonstrated in Figure 4. the other method ($m2$) is based on an extrapolation of the rise time in the frequency dependent sector. This is roughly equivalent to an extrapolation of U, where U_0 is a function of the frequency. We believe that the former method is more accurate, as it is independent of $\Delta\varepsilon$ with its relatively broad range within which its sign changes.

It should be mentioned that all the f_0 values obtained by means of this method are somewhat higher as shown in Figure 5.

The Arrhenius energy of activation from the plot $\ln f_0$ *vs* $1/T$ was calculated for *A* and amounted to 190 kJ/mol (method $m1$) and for *B* and amounted to 200 kJ/mol (method $m2$). When comparing these results with the activation energy of low molecular liquid crystals, it becomes clear that

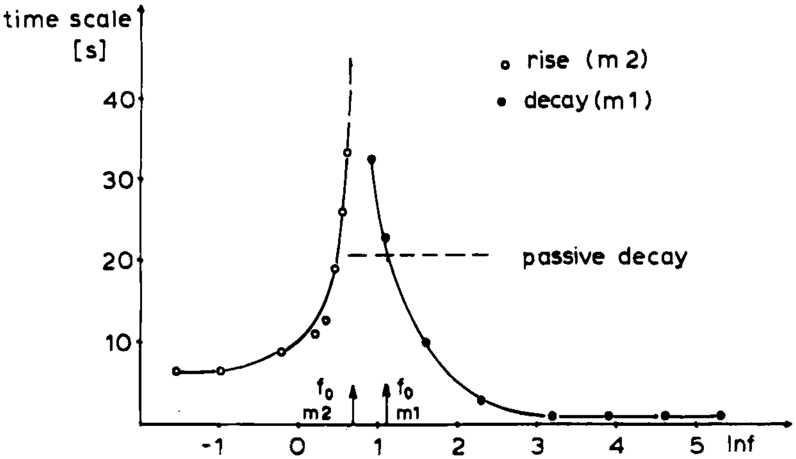

FIGURE 4 Evaluation of f_o. Method (*m*1): *f* is equal to f_o if t_d is equal to t_d^o; the passive decay time is determined independently. Method (*m*2): *f* is equal to f_o if U_o approaches infinity. If *U* is still equal to U_o, having high absolute values, then f_o can be extrapolated roughly from the rise time *vs*. frequently plot. The presented times are values between two extremes. *f* is given in kHz.

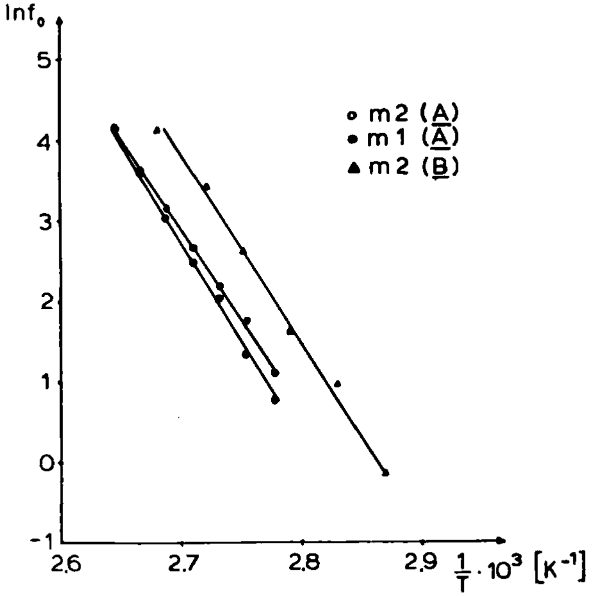

FIGURE 5 ln f_o *vs* $1/T$ for polymer *A* and *B*.

the greater energy of this relaxation process in polymers is due to their higher viscosity.

The threshold voltages were determined by an indirect method from a plot of $1/t_r$ as a function of U^2 (Figure 6). The passive decay time which was used for this plot was determined as described above.

The direct measurement of the threshold voltage is somewhat less accurate as it depends upon the relatively broad range of the response time. When all the determined times are injected into equations 6–8, it can be seen that these relationships are also valid for polymeric side chain liquid crystals.

All results as described above for polymer *A* and *B* are summarized in Table I and Table II, respectively.

Table I demonstrates the strong temperature dependence of the rise time and also the temperature dependence of the threshold voltage and passive decay time. The temperature dependence of the threshold voltage reflects the temperature dependence of the ratio $k_{11}/\Delta\varepsilon$, while the temperature dependence of the passive decay time reflects the temperature dependence of the ratio η_1/k_{11}.

Inserting equations 4 and 8 into 6, there follows:

$$\frac{1}{t_r} = \frac{1}{\eta_1 d^2}(U^2\varepsilon_0\Delta\varepsilon - \pi^2 k_{11}) \tag{9}$$

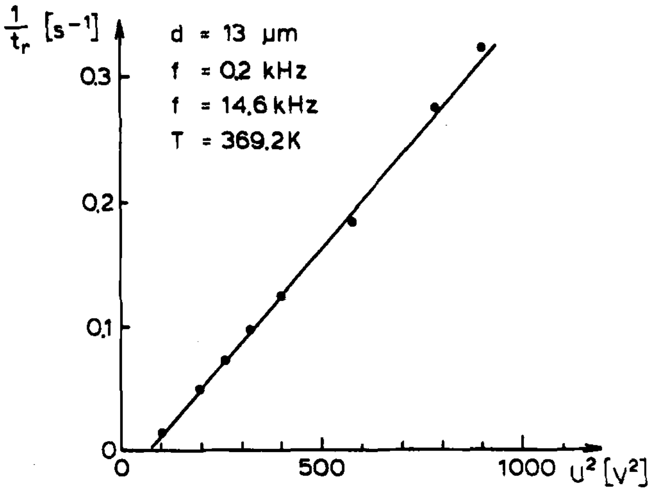

FIGURE 6 Reciprocal rise time as a function of U^2 for polymer *A*. Analogous relations are also valid for the decay times.

TABLE I

Time constants and related values for polymer *A*
$T_{ni} = 381$ K, $f = 0.2$ kHz $< f_0 <$ 200 kHz,
$d = 13$ μm voltage as r.m.s.

						15 V	30 V
T[K]	f_0[kHz]	U_0[V]	U_0^+[V]	Δn	$t_d^0[s]$	$t_d[s]$	$t_r[s]$
360.2	3.1	13.3	3.9	0.119	96.7	6.2	23.4
363.2	5.8	9.8	4.0	0.114	57.7	3.8	7.0
366.2	9.0	8.9	4.5	0.110	44.5	3.7	4.4
369.2	14.6	7.3	4.2	0.107	38.2	2.9	2.5
372.2	23.6	6.8	4.6	0.101	26.5	2.3	1.4
375.2	38.5	5.5	5.1	0.095	21.8	2.2	0.78
378.2	66.0	4.2	6.0	0.084	19.5	2.6	0.39

TABLE II

Time constants and related values for polymer *B*
$T_{ni} = 406$ K, $f = 0.2$ kHz $< f_0 <$ 600 kHz,
$d = 24$ μm voltage as r.m.s.

						15 V	30 V
T[K]	f_0[kHz]	U_0[V]	U_0^+[V]	Δn	$t_d^0[s]$	$t_d[s]$	$t_r[s]$
376.0	5.4	1.7	6.6	0.131	1 660	254	1.4

Because η_l depends exponentially on the temperature, the viscosity is the most important factor for the temperature dependence of the rise time.

For the active decay time and for U_0 the temperature dependencies are smaller. In the temperature region from 363 K to the clearing point, the active decay time is about 3 sec for the experimental conditions used. From the observation that the decay time is rather constant in this temperature range, we conclude that there is a compensation of the temperature dependence of the single parameters.

From capacitance measurements,[11] values for *A* are determined to be $\Delta\varepsilon_{\text{static}} = 0{,}07$ (372 K, $U_0 \sim 6.8$ V). From this we can approximate the elastic constant k_{11} to $3 \cdot 10^{-12}$ *N*. This is in reasonable agreement with the elastic constants for low molecular liquid crystals[12] at the same reduced temperature. From this, using Eqs. 6 to 8, the viscosity η_l can be estimated to $10^3 - 10^4$ cP for polymer *A* using the applied experimental conditions. This viscosity coefficient is 10^2–10^3 times higher than analogous values for low molecular liquid crystals, but $\sim 10^3$ times lower than for non-mesogenic polymers. It should be mentioned here that the viscosity is approximated by the conditions $\overline{\varphi}$ changing between $\overline{\varphi} = 0.2$ and $\overline{\varphi} = 1.0$.

The threshold voltages in Table I are in good agreement with data for a very similar copolymer.[4]

By changing from the polysiloxane copolymer A to the polyacrylic ester homopolymer B the threshold voltage is lowered, probably because of the low concentration of the polar chloro-substituted group in A. The rise times of A and B are nearly the same, but the active decay times and the passive decay times are very much different. This may be caused by the different elastic constants and mostly by the very markedly different viscosity. In particular, the viscosity of B is estimated to be about 20 times higher than the analogous value for A.

Acknowledgments

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