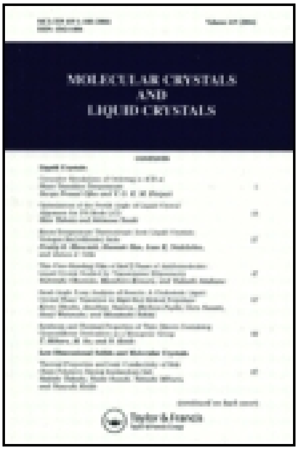

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Analysis of Reorientational Processes in Liquid Crystalline Side Chain Polymers Using Dielectric Relaxation, Electro-Optical Relaxation and Switching Studies

R. Birenheide [a] , M. Eich [a] , D. A. Jungbauer [a] , O. Herrmann-Schönherr [a] , K. Stoll [a] & J. H. Wendorff [a]

[a] Deutsches Kunststoff-Institut Darmstadt Schloßgartenstr. 6, 6100, Darmstadt, FRG

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Analysis of Reorientational Processes in Liquid Crystalline Side Chain Polymers Using Dielectric Relaxation, Electro-Optical Relaxation and Switching Studies

R. BIRENHEIDE, M. EICH, D. A. JUNGBAUER, O. HERRMANN-SCHÖNHERR, K. STOLL and J. H. WENDORFF

Deutsches Kunststoff-Institut Darmstadt Schloßgartenstr. 6, 6100 Darmstadt, FRG

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Reorientational processes were investigated for liquid crystalline side chain polymers, displaying a nematic phase, by means of dielectric relaxation, electro-optical relaxation and switching studies. The results on the dynamical responses were analyzed in terms of the appropriate theories, i.e., in terms of the Landau de Gennes phenomenological approach (electro-optical relaxation), the continuum approach (switching) and the extended Debye approach (dielectric relaxation).

The main results of such an analysis are that the three different models yield dynamical quantities such as the viscosities and the response times, which are consistent with respect to each other. This leads, first of all, to the conclusions that the basic process controlling all three phenomena is the reorientational motion of the mesogenic unit about the short axis and secondly that the rotational process is controlled in the case of side chain polymers by fluctuations rather than by small step rotational diffusion.

Keywords: liquid crystalline polymers, dielectric relaxation, electro-optical relaxation, optical switching

I. INTRODUCTION

This paper is concerned with a quantitative analysis of those dynamical properties of liquid crystalline phases which are related to reorientational processes. The particular properties which will be considered are the dielectric relaxation, the switching and, in addition, the electro-optical relaxation (Kerr relaxation). These properties will be considered for the case of liquid crystalline side chain polymers displaying a nematic phase.

The reorientational motions taking place in liquid crystalline systems have been reported to display frequently features which differ strongly from those characteristic of normal fluids.[1–6] It is, for instance, a particular property of liquid crystalline systems that the reorientational motion about the short axis is—in comparison to the corresponding motion about the long axis—considerably slower.[3–6] One typically observes time scales which differ by up to two orders of magnitude in comparison to those found for the same rotation taking place in nonliquid crystalline systems having the same viscosity. A second feature characteristic of liquid crystalline systems is the occurrence of strong correlations for the reorientational motions already in the isotropic state and particularly in the liquid crystalline state as far as the reorientation about a short axis is concerned.[7-9]

These specific aspects of the reorientational motions occurring in liquid crystalline systems give rise to a very distinct behavior of the dielectric relaxation, of the electro-optical relaxation and of the switching properties.[3-15] Each of these phenomena related to the reorientational motions has been analyzed theoretically on the basis of a different approach. The dielectric relaxation, for instance, has been treated in terms of an extended Debye theory, which takes the coupling of the reorientational motions to the anisotropic surroundings into account[3-6]; the Kerr relaxation process in terms of the phenomenological theory of phase transitions proposed by Landau and adapted to liquid crystalline systems by de Gennes[7-9] and finally the switching properties on the basis of a continuum theory, taking elastic and viscous properties of the fluid states into account.[15-18] So far it has never been discussed, to our knowledge, whether these three different approaches lead to results which are consistent with respect to each other. This is the content of the present paper.

II. THEORETICAL AND EXPERIMENTAL CONSIDERATIONS

a) Kerr relaxation studies

The Kerr relaxation experiment consists in applying an electrical field to the macroscopically isotropic fluid state and in the determination of the optical birefringence resulting from the induced reorientational motions of the molecules. The Kerr law states that the induced birefringence increases linearly with the square of the applied field E:

$$\Delta n = \lambda B E^2 \tag{1}$$

where B is the Kerr constant and λ the wavelength of the light.[7,8] The dynamical aspect of the Kerr relaxation is investigated by determining the time evolution of the birefringence after switching the field on or off. Both the Kerr constant and the Kerr relaxation time are usually rather weak functions of the temperature as far as normal fluids are concerned. This is, however, not the case for liquid crystalline fluids in the isotropic melt in the neighborhood of a nematic phase.

The theoretical treatment of the static and dynamic electro-optical properties of the isotropic phase in the neighborhood of the nematic phase is based on the simple phenomenological Landau theory of phase transitions, as proposed by de Gennes.[9] The free energy density $F(T,S)$ in the vicinity of this transition is expressed according to this treatment as a function of the nematic order parameter S as:

$$F(T,S) = F_o(T) + (a(T)/2)\,S^2 - (b(T)/3)\,S^3 + (c(T)/4)\,S^4 + \ldots \tag{2}$$

The coefficient of the quadratic term $a(T)$ is expressed as

$$a(T) = a_o (T - T^*)^\gamma; \quad (\gamma = 1, \text{ mean field approximation}) \qquad (3)$$

where T^* is a hypothetical second order phase transition. The assumption is that this second order phase transition temperature is located just below the first order phase transition temperature which happens at a temperature T_{ni}. The expansion coefficients are available from macroscopical properties such as the heat of fusion ΔH, the difference between T^* and T_{ni} and the jump of the nematic order parameters ΔS_{ni} at the phase transition.

The coefficient a_o is given by:

$$a_o = 2\Delta H / T_{ni}(\Delta S_{ni})^2 \qquad (4)$$

The phenomenological theory may also be used to express the dependence of the Kerr constant B on the temperature:

$$B(T) = (\Delta n^o \Delta\epsilon^o \epsilon_o)/(3\lambda a_o (T - T^*)) \qquad (5)$$

where Δn^o and $\Delta\epsilon^o$ are the anisotropy of the refractive index and of the dielectric constant respectively corrected for $S = 1$.

The phenomenological approach can also be taken in order to derive an expression for the relaxation time characteristic of the electro-optical response. The prediction on its temperature dependence is:

$$\tau = 3\eta (T)/(2 a_o (T - T^*)) \qquad (6)$$

where η is the viscosity which controls the time scale of reorientational motions.

The prediction thus is that the Kerr relaxation is characterized by the occurrence of pretransitional effects leading to a divergence both of the Kerr constant B and of the Kerr relaxation time at the characteristic temperature T^*. The divergence both of the Kerr constant B and of the relaxation time are caused by the divergence of the correlation length for reorientational motions. Using a molecular statistical approach one may express this divergence by a correlation parameter g_2 which is directly related to the pair correlation function and which is defined as:

$$g_2 = 1 + \sum_{j=2}^{N} (1/2) \langle 3 \cos^2 \theta_{1j} - 1 \rangle \qquad (7)$$

where θ_{ij} is the angle between the long axes of the molecules 1 and $j \cdot g_2$ represents, to a first approximation, the number of mesogenic units which reorient in a correlated fashion and it can be calculated from the expression:

$$g_2 = (45\, N\, k\, T)/((n^2 + 2)^2\, a_o (T - T^*)) \qquad (8)$$

where N is the number of units per unit volume.

The important parameters which can be derived from of the Kerr relaxation studies and which will be compared with the dynamical parameters coming out from the other theoretical approaches introduced above are the relaxation time τ, the viscosity η and the correlation parameter g_2.

b) Switching studies

The switching experiments consist in inducing first of all a homogeneous or homeotropic texture within a thin liquid crystalline film. The texture is distorted by applying a magnetic or an electric field and the variations of the optical properties resulting from these distortions are measured. The theoretical treatment of the static and dynamical aspects of the switching properties are based on a continuum approach. A set of elastic constants K_{ii} is used to describe the variation of the free energy density g due to distortions of the director field distribution $\mathbf{n}^{10-18}$:

$$g = 0.5\,(K_{11}\,(\text{div}\,\mathbf{n})^2 + K_{22}\,(\mathbf{n}\,\text{rot}\,\mathbf{n})^2 + K_{33}\,(\mathbf{n} \times \text{rot}\,\mathbf{n})^2) \tag{9}$$

where the constants K_{11}, K_{22} and K_{33} represent splay, twist and bend distortions. The application of this general theory on the elastic properties of liquid crystalline phases to the case of switching experiments leads to the predictions that threshold values exists for the applied field and that no distortions occur for applied fields smaller than these threshold values given by:

$$U_o = \pi\,(K_{ii}/\epsilon_o\Delta\epsilon)^{1/2},\; H_o = (\pi/d)\,(K_{ii}/\Delta\chi)^{1/2} \tag{10}$$

The dynamical aspects of the switching are controlled by the viscous properties of the fluid state, which again may be represented by a set of viscous coefficients η_i within the framework of a hydrodynamic theory of anisotropic fluids.[10-18] These viscous coefficients represent various modes of flow and reorientational processes. The application of both the elastic and the hydrodynamic theory to the case of switching behavior leads to the following predictions on the characteristic time scale of the switching for the case of switching off the field (decay):

$$\tau_d = (d^2/\pi^2)(\eta_s/K_{ii}) \tag{11}$$

and for the case of switching on the field (rise):

$$\tau_r^{-1} = \tau_d^{-1}\,((U/U_o)^2 - 1) \tag{12}$$

where τ_r is the switching time in the presence of the applied field and τ_d the decay time in the absence of the electrical field. The important dynamical parameters are the switching time τ_d and the absolute value of the viscosity η_s. We will consider these quantities below in more detail.

c) Dielectric relaxation studies

The peculiar features of the rotational motions in liquid crystalline systems manifest themselves particularly in the dielectric relaxation properties. It is known, for instance, that the dielectric properties of liquid crystals are strongly influenced by the occurrence of reorientational motions of the rod-like molecules about the long and short axis. The first process is known to happen very rapidly with a characteristic relaxation time of the order of 10^{-9} s. Only those dipolar configurations which have a component perpendicular to the chain long axis contribute to the dielectric relaxation in this case. The second process, usually called the δ-process takes place on a much longer time scale. The relaxation time is typically of the order of $10^{-6} - 10^{-8}$ s. It is the longitudinal component of the total dipolar configuration which contributes to the dielectric properties in this case. The presence of these two kinds of reorientational motions gives rise, for instance, to changes of the sign of the dielectric anisotropy as a function of the frequency at constant temperature or as a function of the temperature at constant frequency.

The discrepancy between the absolute value of the two relaxation times does not result from the anisotropy of the geometrical shape of the molecules. The axial ratio is of the order of 4. The reason for the difference in time scale is that the rotational motion about a short axis couples to the anisotropic surrounding which exists in liquid crystalline phases and to a certain extent also in the isotropic phase in the neighborhood of the liquid crystalline phase.

The slowing down of the reorientational motion in anisotropic fluids has been treated theoretically by Meier, Saupe and coworkers.[3-5] They were able to show that one can predict such a shift of the time scale of the reorientational process by taking the anisotropic potential barrier for reorientational motion into account. They defined a retardation factor g_n by:

$$\tau_{DK} = \tau_o g_n \tag{13}$$

where the relaxation time τ_o corresponds to the one expected from the Debye equation:

$$\tau_o = \xi_o/kT \qquad (\xi_o \text{ friction coefficient}) \tag{14}$$

The retardation factor was expressed as:

$$g_n = \exp\left((q/kT) - 1/(q/KT)\right) \tag{15}$$

where q is the height of the nematic potential barrier. This barrier is frequently found to be of the order of 8–25 kJ/mole, giving rise to a retardation factor of the order of 100. The theory predicts that the reorientational motion about the long axis is not hindered by the presence of the anisotropic surrounding, just on the contrary. The prediction is that it should occur on a slightly shorter time scale than the one calculated from the Debye equation. The quantity which will be analyzed in some detail below is the absolute value of the relaxation time resulting from the reorientational motion about the short axis.

III. EXPERIMENTAL

The studies were performed on side chain liquid crystalline polymers displaying at high temperatures an isotropic phase and at lower temperatures a nematic phase. This was apparent from X-ray scattering studies as well as from optical studies. The chemical structures of these polymers which we have named PBiCN and PBPCN are displayed in Figure 1. The average chain length *n* of the polymer PBiCN amounts to 14 and that of the polymer PBPCN to 22, as calculated from the number average molecular weight. The ratio of the weight to the number average molecular weight was about 1.2. The calorimetric investigations were performed with a DSC 4 (Perkin Elmer) calorimeter. The Kerr relaxation studies were done with an experimental set-up, constructed by us. Details of the set-up have been published previously.[8,19,20] In each of the experiments described below we checked whether the induced birefringence depended linearly on the square of the electric field (Kerr law) as required by theory. The dielectric measurements were carried out in the range between 100 Hz and 1 MHz, using a Hewlett-Packard Impedance Analyzer HP 4192. The thickness of the samples within the capacitor was about 25 μm. The temperature could be varied between −190°C and 200°C.

IV. RESULTS AND DISCUSSIONS

a) Electro-optical investigations

The application of an electric field to the liquid crystalline side chain polymers within the isotropic melt gives rise to a saturation value of the induced birefringence Δn which increases linearly with the square of the amplitude of the electric field E_o, as expected from the Kerr law. This is shown for the particular case of the

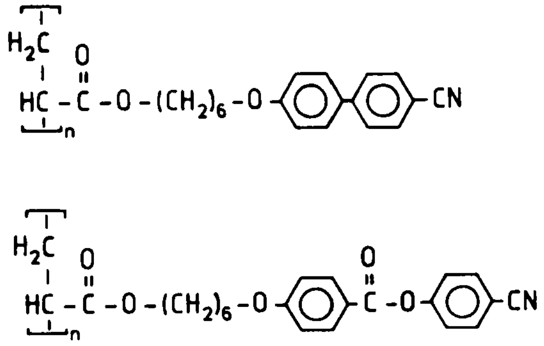

FIGURE 1 Chemical structures of the liquid crystalline side chain polymers studied.

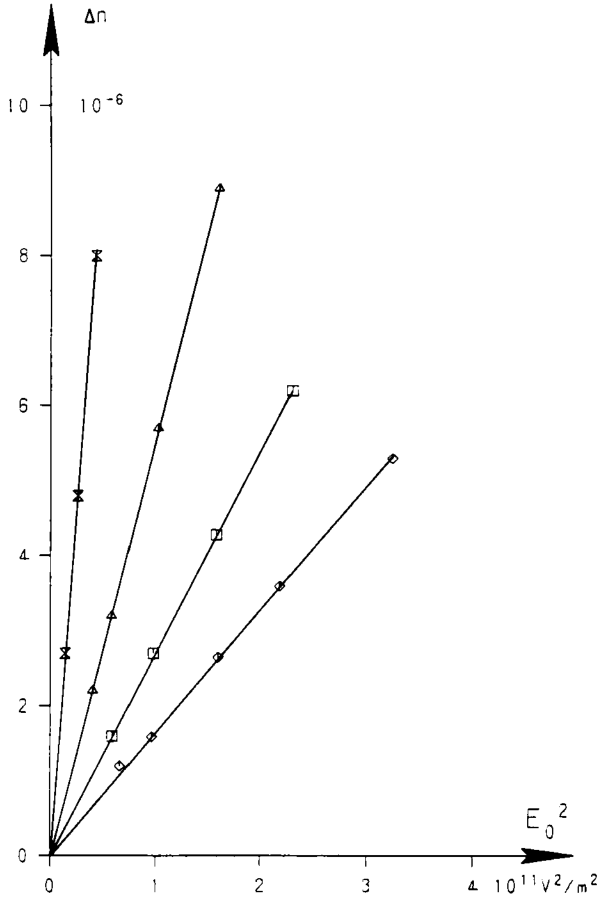

FIGURE 2 Dependence of the induced birefringence on the electric field for the polymer PBiCN (X $T = 383.15$ K, Δ $T = 383.65$ K, □ $T = 384.25$ K, ◇ $T = 388.05$ K).

polymer PBiCN in Figure 2. The slopes of the lines are directly correlated with the absolute value of the Kerr constant B and its sign. The sign is positive in all cases, due to the presence of the strong longitudinal CN-dipole; and the Kerr constant is found to depend strongly on the temperature. This is shown in Figure 3. The Kerr constant seems to diverge in the neighborhood of a temperature of 383 K. A plot of the inverse of the Kerr constant versus the temperature, which is shown in Figure 3 reveals that the Kerr constant behaves as predicted on the basis of the phenomenological theory:

$$B \sim (T - T^*]^{-\gamma} \tag{16}$$

and that the critical exponent is 1. The characteristic temperature is found to be 382.7 K which is about 0.3 K below the first order phase transition temperature

T_{ni}. The latter temperature is available from calorimetric experiments but is also evident from the Kerr relaxation studies. The samples turn turbid below this temperature so that no Kerr relaxation data can be obtained below this temperature. Similar results are obtained for the polymer PBPCN where the characteristic temperature T^* amounts to 388.65 K, which is 1.0 K below T_{ni}.

The discussion was limited so far to the saturation values of the induced birefringence. In the following we will consider the dependence of the induced birefringence on the time after switching the field on and off. Figure 4 gives an example. It displays the stepwise variation of the electrical field and in principle the corresponding variation of the intensity of the light at the photodiode which is directly related to the induced birefringence. Characteristic results obtained at various temperatures are displayed in Figure 5 for the case of the polymer PBiCN. The logarithm of the reduced birefringence is found to increase linearly with the time. This suggests that the Kerr relaxation behaves as a single exponential process.

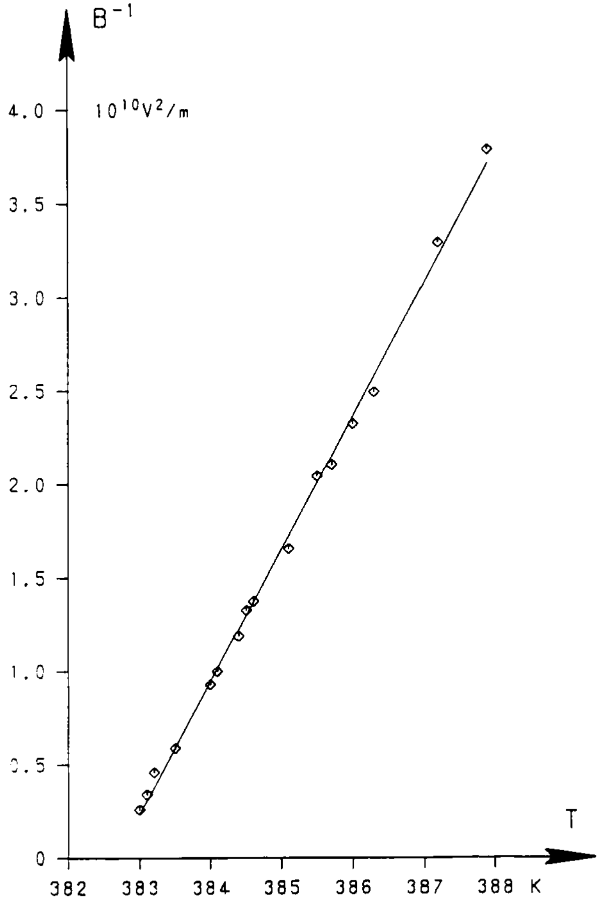

FIGURE 3 Variation of the inverse of the Kerr constant B with the temperature for the polymer PBiCN.

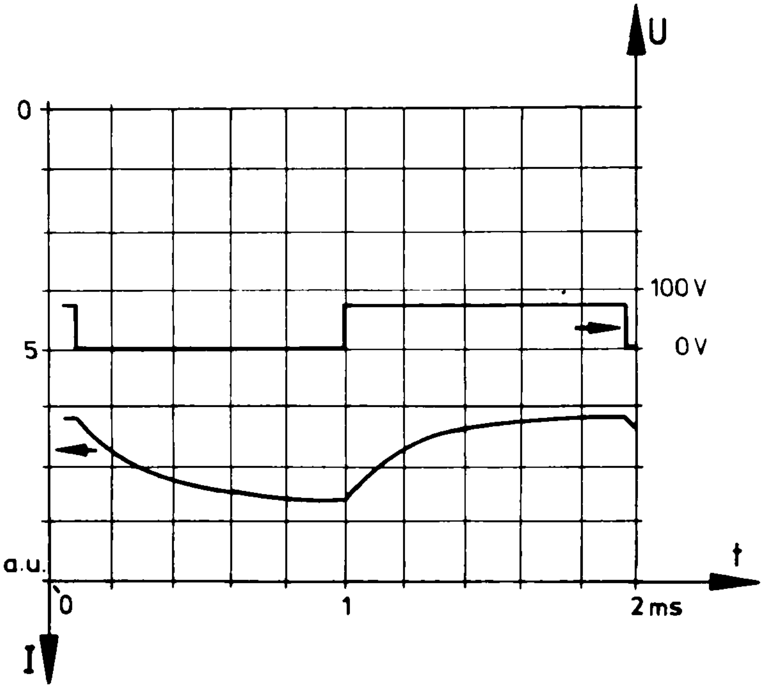

FIGURE 4 Variation of the intensity I of the light passing through the Kerr relaxation set-up due to the switching-on and switching-off of the field.

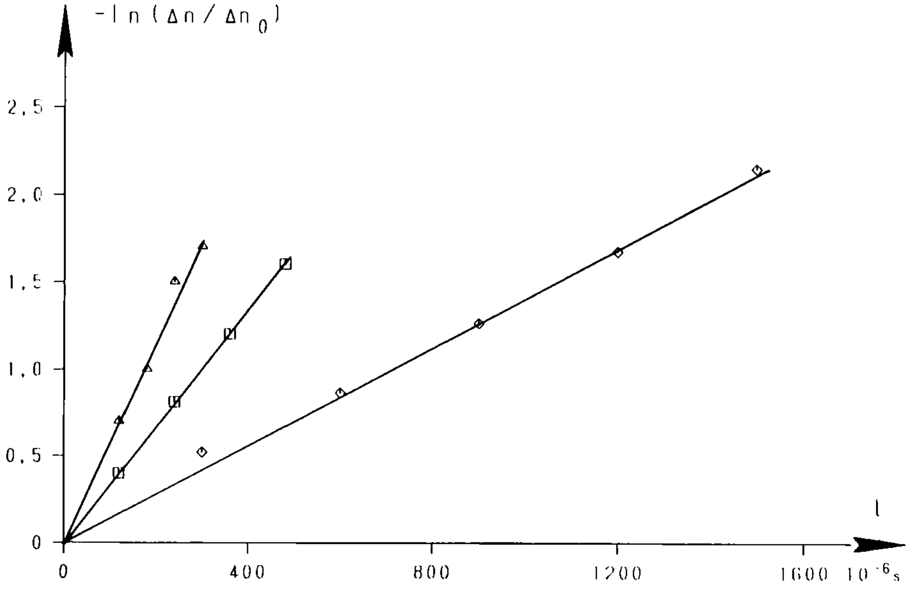

FIGURE 5 Variation of the electrically induced birefringence with time for the polymer PBiCN (△ T = 383.65 K, □ T = 384.25 K, ◇ T = 388.05 K).

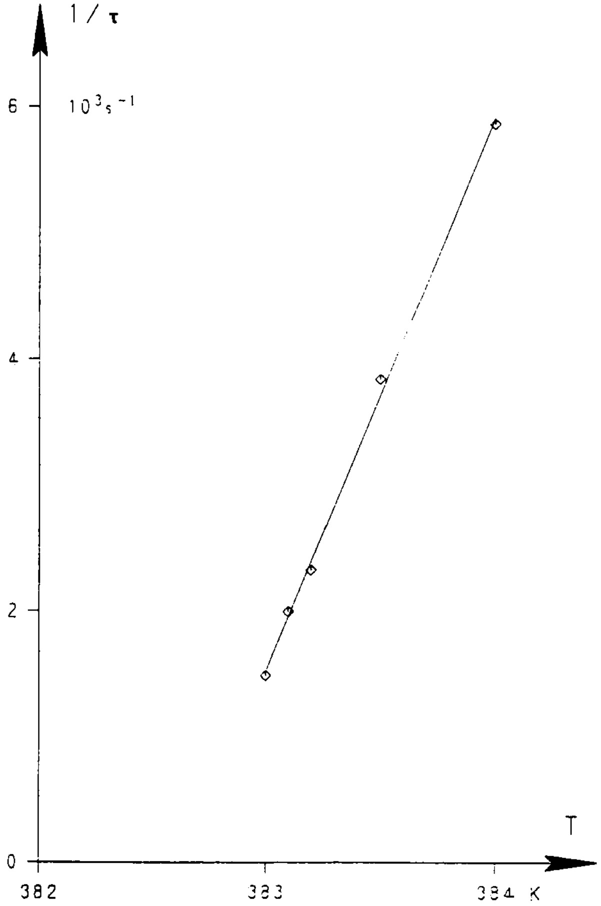

FIGURE 6 Variation of the inverse of the Kerr relaxation time (decay) with temperature for the polymer PBiCN.

The observation is that the magnitude of the relaxation time is identical for the rise and the decay for both polymers studied and that it depends for the rise and decay only on the temperature but not on the magnitude of the electric field (as it does in the case of switching, as we will see below). The relaxation time is found to increase strongly with decreasing temperature and to diverge at the temperature T^*, as expected from the theoretical treatment. This is shown in Figure 6 again for the case of the polymer PBiCN.

In the following we will analyze the data obtained for both polymers within the framework of the phenomenological theory introduced above. Using the values on the transition temperatures, the heat of fusion and of the jump of the order parameter S at the transition we are able to calculate the important coefficient a_o from equation 4:

$$a_o = 2\Delta H/(T_{ni}\,(\Delta S_{ni})^2)$$

TABLE I

Results of the electro-optical studies

	Polymer PBPCN	
	$T^* = 388.65$ K; $T_{ni} = 389.65$ K	
$a_o = 7.3\ 10^4$ J/Km^3		(from thermodynamic data)
$a_o = 7.6\ 10^4$ J/Km^3		(from electro-optical data)
	$\tau_{\text{Kerr}}\ (T^* + 2\text{K}) = 0.2\ 10^{-3}$ s	
	$g_2\ (T + 2\text{K}) = 123$	
	$\eta\ (T^* + 2\text{K}) = 19.5$ Ns/m^2	
$\Delta H = 1.25$ *J*/*g*		$E_a = 154$ kJ/mole
	Polymer PBiCN	
	$T^* = 382.7$ K; $T_{ni} = 383$ K	
$a_o = 2.1\ 10^5$ J/Km^3		(from thermodynamic data)
$a_o = 2.0\ 10^5$ J/Km^3		(from electro-optical data)
	$\tau_{\text{Kerr}}\ (T^* + 1.3\text{K}) = 0.17\ 10^{-3}$ s	
	$g_2\ (T^* + 1.3\text{K}) = 85$	
	$\eta(T^* + 1.3\text{K}) = 40.5$ Ns/m^2	
$\Delta H = 1.2$ *J*/*g*		$E_a = 225$ kJ/mole

The results are given in Table I. This value agrees quite well with those characteristic of low molar mass systems and side chain polymer systems reported in the literature. We will test in the following whether this value is consistent with the one which may be derived from the Kerr relaxation results according to Equation 5:

$$a_o = \Delta n^o \Delta\epsilon^o\ \epsilon_o/(3\lambda B(T)\ (T - T^*))$$

Values on the anisotropy of the refractive index and of the dielectric constant were available from dielectric relaxation studies on macroscopically oriented samples (see below) and from optical studies on monodomains, including dichroitic studies in the UV-range.[28] Figures 7–9 represent characteristic results for the polymer PBPCN. Using these quantities we obtain values for a_o which agree very well with the value given above. This is obvious from Table I. So the treatment is at least consistent in this respect.

Next we will analyze the Kerr relaxation times in order to obtain the basic dynamical quantity viscosity which controls the reorientational motions. Using the experimentally obtained values for the Kerr relaxation time and for a_o we are able to calculate the viscosity. The values are also given in Table I. These viscosity data will later-on be compared with the one obtained from the switching experiments.

The Kerr relaxation data reported above allow to calculate also the correlation parameter g_2 from Equation 8. Its absolute value and its dependence on the temperature are displayed in Figure 10 for the particular case of the polymer PBiCN. Similar values are obtained for the polymer PBPCN (see Table I). It is apparent that g_2 diverges as the temperature T^* is approached and that g_2 is of the order of 100 in the neighborhood of first order phase transition T_{ni}. Similar values were reported for low molar mass and for other side chain liquid crystalline polymers.

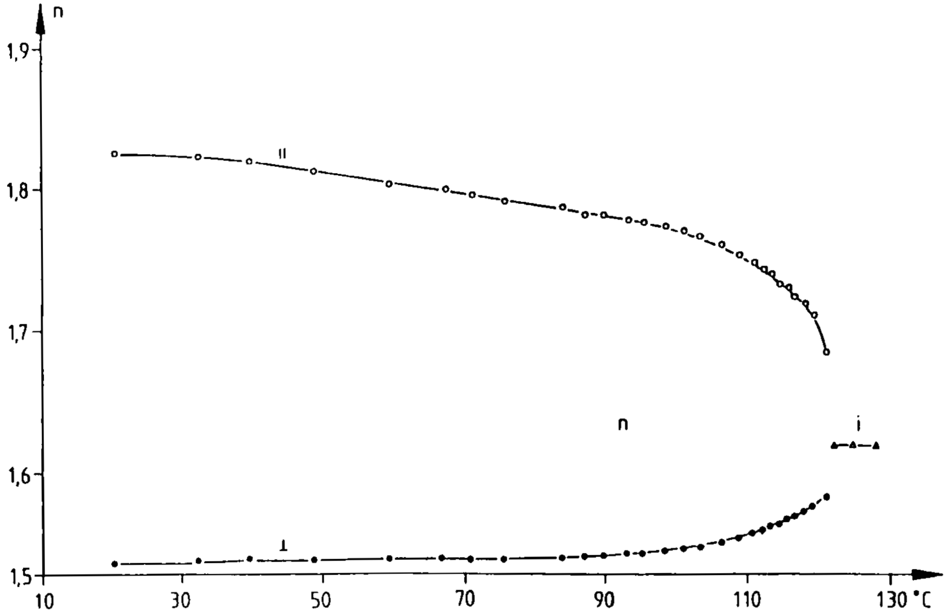

FIGURE 7 Variation of the ordinary and extraordinary refractive index with temperature for the polymer PBPCN.

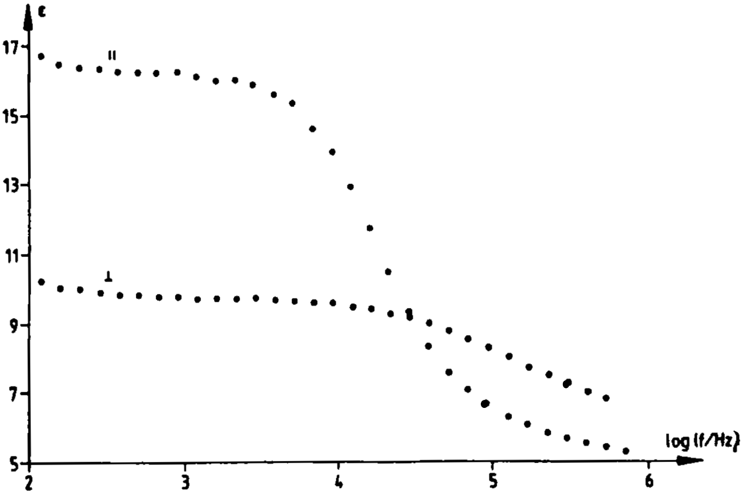

FIGURE 8 Variation of the dielectric constant parallel (∥) and perpendicular (⊥) to the director with the frequency (T = 373 K) for the polymer PBPCN.

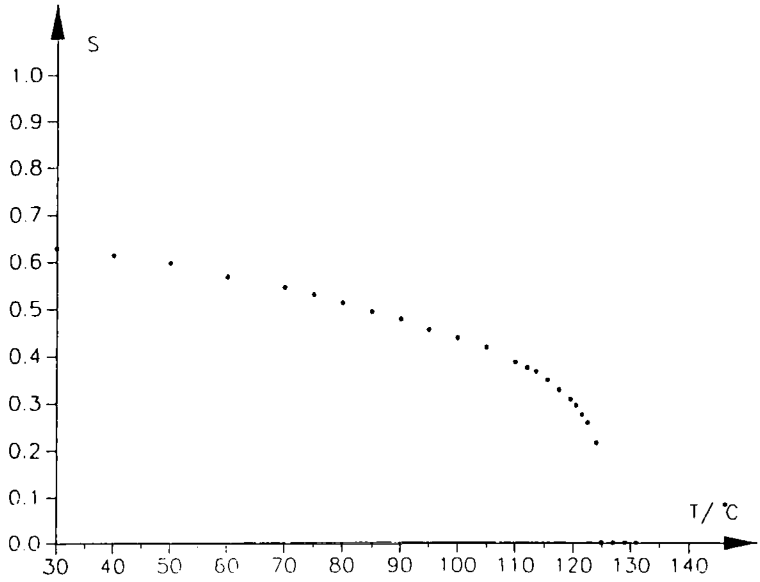

FIGURE 9 Variation of the nematic order parameter S with the temperature for the polymer PBPCN, as obtained from dichroitic investigations.

This value will be used later-on again when considering the results of the dielectric relaxation studies.

b) Investigations on the switching behavior

The switching behavior of the side chain polymers considered here were determined both in the presence of magnetic as well as of electrical fields. Figure 11 gives an example for the dependence of the capacity of a thin film having a homogeneous texture and consisting of the side chain polymer PBiCN on the applied magnetic field. The capacity could be used in this case to monitor the director reorientation in the film due to the presence of the longitudinal CN dipole. These results allow, in principle, the calculation of the threshold field, for instance. Similar results are obtained if an electrical field is applied and the induced variations of the director field are determined by optical means.

The following discussion will concentrate on the results obtained on the dynamical response due to the switching on and switching off of the field. Figure 12 gives an example for the dependence of the switching times, which are available from these experiments, on the square of the applied field. Parameter is the temperature.

Based on the Equation 12 given above:

$$\tau_r^{-1} = \tau_d^{-1} \left((U/U_o)^2 - 1 \right)$$

we expect that the inverse of the characteristic switching times increases linearly with the square of the electric field, becomes zero for the case that the field

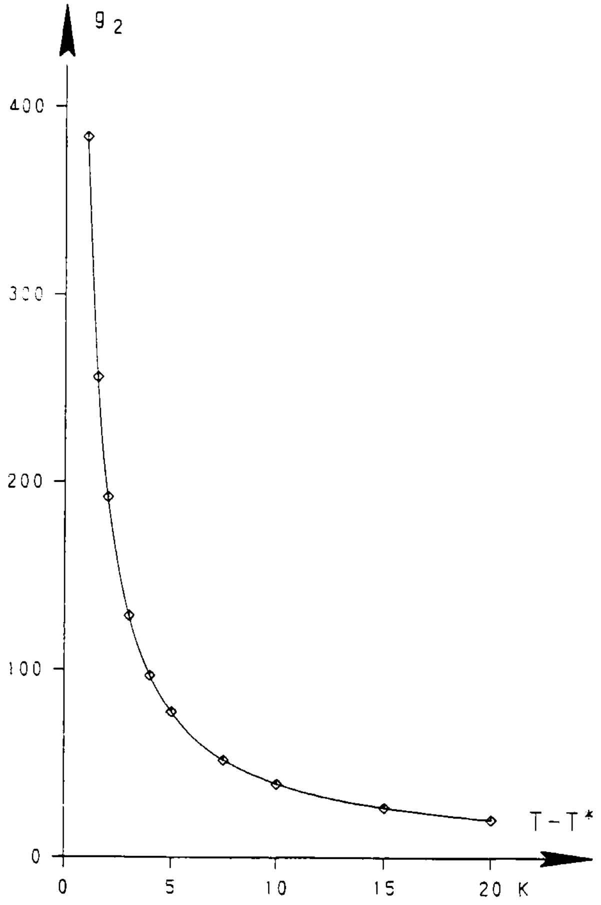

FIGURE 10 Variation of the correlation parameter g_2 with the temperature for the polymer PBiCN.

corresponds to the threshold field and corresponds to τ_d^{-1} for $U = 0$. The results shown in Figure 12 can be used to obtain, first of all information on the threshold field and thus on the elastic coefficient K_{11}. The results are displayed in Table II for the two polymers considered here. The finding is that the elastic constants are of the same order of magnitude as observed for low molar mass systems and other side chain polymers.[5,14,21,22]

The results displayed in Figure 12 allow also to determine the decay relaxation time τ_d and thus the viscous coefficient η_s on the basis of Equation 11. The results are also displayed in Table II. The viscous parameters are found to vary quite rapidly with the temperature. This is apparently due to the temperature dependence of the basic reorientational process which seems to be thermally activated. This is obvious from a plot of η versus $1/T$ shown in Figure 13 for the two polymers, yielding a straight line. The activation energies which are obtained from this plot amount to about 150 kJ/mole in the case of the polymer PBPCN and to about 225

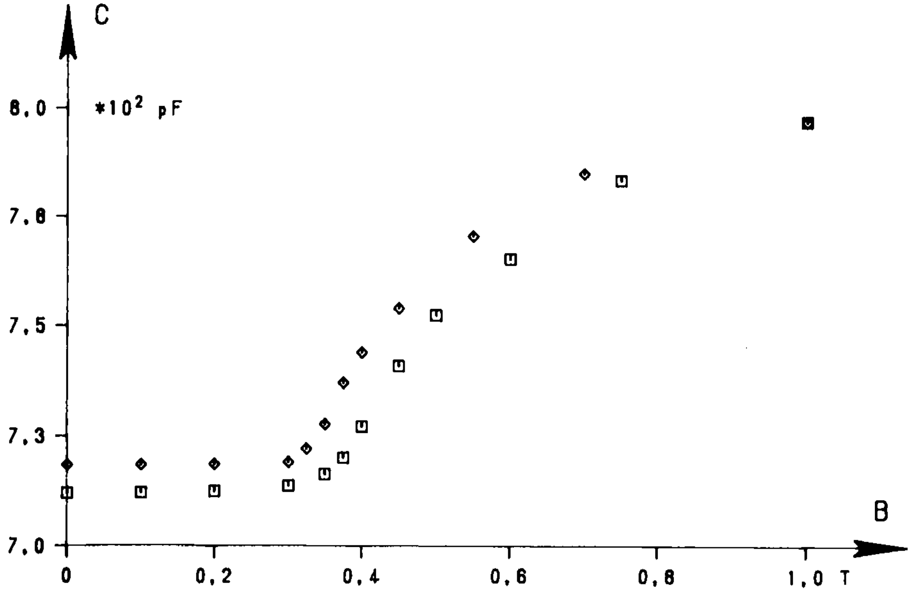

FIGURE 11 Variation of the capacity of a PBiCN-film with homogeneous texture in the presence of a magnetic field (□ T = 373.15 K, ◇ T = 380.95 K).

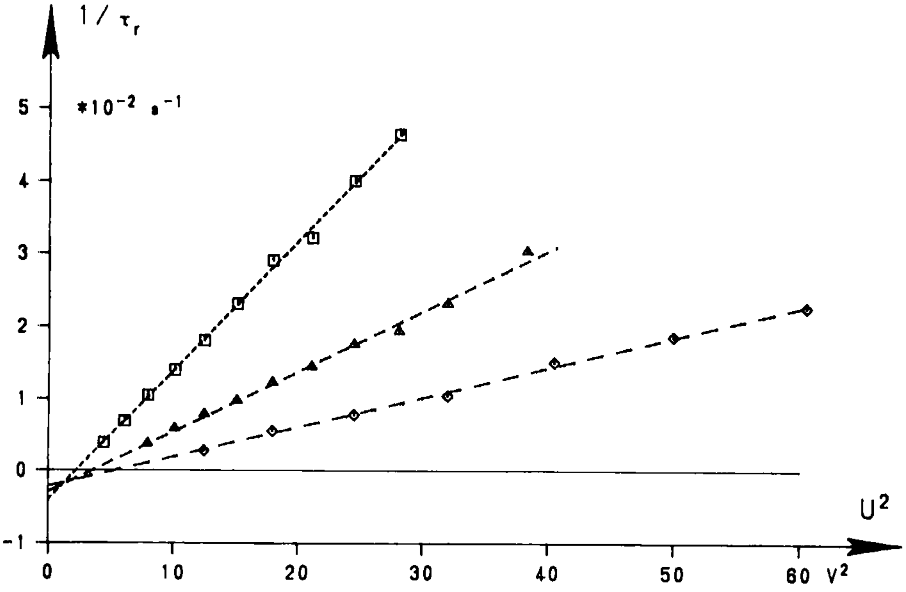

FIGURE 12 Dependence of the switching time (rise) on the applied electric field for the polymer PBiCN (◇ T = 373.15 K, △ T = 375.75 K, □ T = 380.95 K).

TABLE IIa

Results on switching studies

Polymer PBPCN	
$T = 358.3$ K	
	$K_{11} = 26.3\ 10^{-12}$ N $\eta_s = 1414$ Ns/m^2 $\tau_d = 5340$ s
$T = 363.8$ K	
	$K_{11} = 19\ 10^{-12}$ N $\eta_s = 681$ Ns/m^2 $\tau_d = 3420$ s
$T = 378.4$ K	
	$K_{11} = 11.6\ 10^{-12}$ s $\eta_s = 91$ Ns/m^2 $\tau_d = 900$ s

kJ/mole for the polymer PBiCN. This quantity will be discussed below in more detail.

c) Dielectric relaxation studies

The side chain polymers display in principle three different kinds of relaxation processes:

i) a high frequency secondary process within the glassy state which is connected with internal motions of the molecules. The activation energy is of the order of 60 kJ/mole.

ii) a glass relaxation process at intermediate frequencies, characterized by an effective activation energy which varies with the temperature and the magnitude of which is in the range of 250 to 400 kJ/mole. It is usually characterized by a broad distribution of relaxation times.

TABLE IIb

Results on switching studies

Polymer PBiCN	
$T = 373.15$ K	
	$K_{11} = 25.10^{-12}$ N $\eta_s = 342$ Ns/m^2 $\tau_d = 450$ s
$T = 375.75$ K	
	$K_{11} = 13\ 10^{-12}$ N $\eta_s = 139$ Ns/m^2 $\tau_d = 350$ s
$T = 380.95$ K	
	$K_{11} = 7.1\ 10^{-12}$ N $\eta_s = 56$ Ns/m^2 $\tau_d = 260$ s

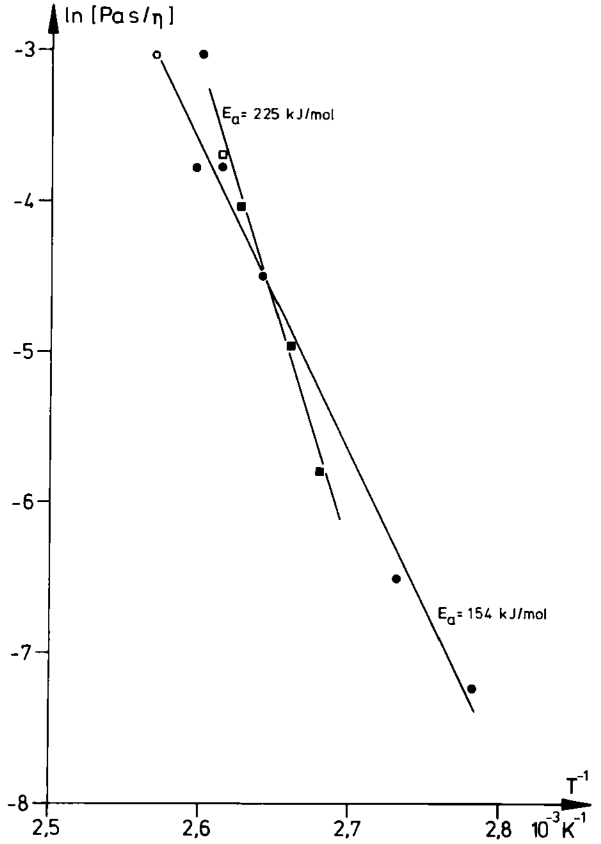

FIGURE 13 Variation of the viscosity obtained from the switching experiments with temperature (○□ viscosity obtained from Kerr relaxation studies) for the polymers PBiCN ■ and PBPCN ●.

iii) The δ low frequency process, due to the reorientational motion of the mesogenic groups about the short axis. This process displays usually a very narrow distribution of the relaxation time spectrum.

It is the last process which we will consider in the following in some detail since it is controlled by reorientational motions about the short axis.

Figure 14 shows for the case of the polymer PBPCN the variation of the dielectric constant and of the tan δ with the temperature at a given frequency of 10^5 Hz and Figure 15 the activation diagram obtained from these results. Similar results were reported in the literature both for the PAcrylat as well as for the polymer PBiCN.[23,24,27] It is obvious that the rotational motion is thermally activated and that the activation energy is independent of the temperature. We are particularly interested in the activation diagram of the δ process and in the absolute scale of the relaxation time in the temperature range neighboring the nematic isotropic transition temperature. These values are given in Table III for the two polymers considered here. These data agree quite well with the ones reported in the literature.[21-25,27]

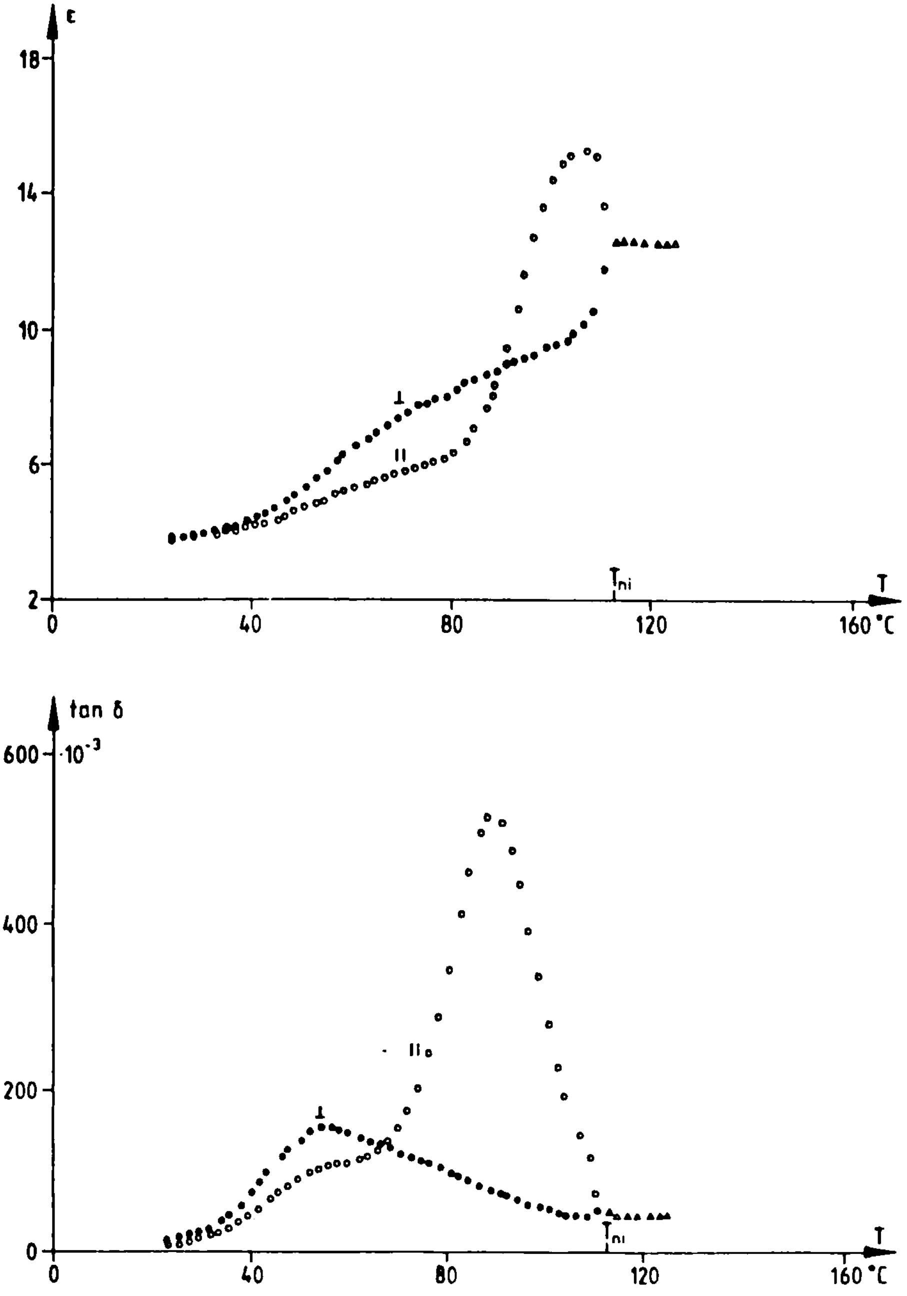

FIGURE 14 Variation of the dielectric constant parallel (||) and perpendicular (⊥) to the director (a) as well as of tan δ parallel and perpendicular to the director (b) with temperature at a frequency of 10 KHz for the polymer PBPCN.

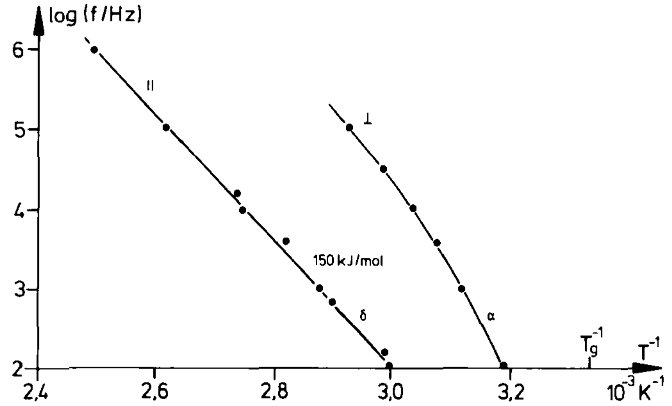

FIGURE 15 Activation diagram for the polymer PBPCN obtained from dielectric relaxation studies.

V. COMPARISON OF THE RESULTS OBTAINED BY THE DIFFERENT METHODS

In the following we will discuss whether the sets of data on the dynamical properties of the side chain polymers obtained from dielectric relaxation, from electro-optical relaxation and from the switching studies are consistent with each other. Each of the sets of data were obtained within the framework of a different theoretical concept but on identical polymer systems, possessing thus, for instance, the same average chain length and chain length distribution.

Table IV displays a comparison of the viscosities obtained from the Kerr relaxation studies on the basis of the phenomenological Landau de Gennes treatment and from the switching experiments, on the basis of the continuum theory. Figure 13 displays the temperature dependence of the viscosity data obtained from the switching studies and the electro-optical relaxation studies for the two polymers. The data obtained from the switching and the Kerr relaxation studies fit nicely on the same line. So, the finding is that the two different approaches yield results on dynamical quantities which are consistent with each other. The activation energies obtained from this plot agree very well with those obtained from dielectric relax-

TABLE III

Results of dielectric relaxation studies

Polymer PBPCN
$(T^* + 2\text{K}) = 1.6\ \mu\text{s}$ $E_a = 150$ kJ/Mole
Polymer PBiCN
$(T^* + 1.3\ \text{K}) = 2\ \mu\text{s}$ $E_s = 143$ kJ/Mole

TABLE IV

Comparison of the dynamical data, obtained by electro-optical and dielectric relaxation as well as by switching experiments

Polymer PBPCN

$\eta_s\ (T = 380\ \mathrm{K}) = 43.0\ \mathrm{Ns/m^2}$ (switching)
$\eta(T = 391\ \mathrm{K}) = 19.5\ \mathrm{Ns/m^2}$ (electro-optical)
$\tau_{\mathrm{Kerr}}/g_2 = 1.63\ \mu\mathrm{s}$
$\mathrm{DK} = 1.60\ \mu\mathrm{s}$

Polymer PBiCN

$\eta_s(T = 381\ \mathrm{K}) = 56.0\ \mathrm{Ns/M^2}$
$\eta(T = 384\ \mathrm{K}) = 40.5\ \mathrm{Ns/m^2}$
$\tau_{\mathrm{Kerr}}/g_2 = 2\ \mu\mathrm{s}$
$\tau_{DK} = 2\ \mu\mathrm{s}$

ation studies in the case of the polymer PBPCN (150 kJ/mole in both cases) and less well for the polymer PBiCN (150 versus 220 kJ/mole). So to a first approximation we conclude that the basic reorientational process controlling the dielectric, Kerr and switching behavior is the reorientational motion of the mesogenic units about the short axis and we conclude that the dynamics of this rotation may be influenced by the neighborhood of the glass transition process since this tends to shift the activation energy to larger values.

We will continue the discussion by considering the Kerr relaxation times and the viscosities deduced from the electro-optical relaxation data on the basis of the phenomenological theory (Table I) and we will compare these quantities with the ones obtained from the other experimental methods, namely switching studies (Table II) and dielectric relaxation studies (Table III).

It is important to point out that in general the relation between the relaxation time τ_{DK} obtained from the dielectric relaxation studies and the relaxation times $\tau_{\mathrm{Kerr},d}$ and $\tau_{\mathrm{Kerr},r}$ obtained from the Kerr relaxation studies in the absence (decay) and the presence (rise) of the electric field depends on the nature of the reorientational motion involved.[25] The prediction of the theory is that all three different relaxation times agree, in the absence of correlated motions, if the reorientation happens by fluctuations:

$$\tau_{DK} = \tau_{\mathrm{Kerr},d} = \tau_{\mathrm{Kerr},r}$$

so that in the case of correlated motions one obtains:

$$\tau_{DK} = \tau_{\mathrm{Kerr}}/g_2$$

On the other hand, theory predicts for the case of rotational diffusion that the rise and decay times may be different and that:

$$\tau_{DK} = 3\ \tau_{\mathrm{Kerr},d}$$

for uncorrelated motions and

$$\tau_{DK} = 3\,\tau_{\mathrm{Kerr},d}/g_2$$

for correlated motions provided that the reorientation happens by rotational diffusion, i.e. by small steps.

The observation reported above was that the rise and decay times observed in the Kerr relaxation experiments agreed in all cases, which indicates that the reorientation happens by fluctuations. This is in agreement with the predictions of the Landau de Gennes approach, which is in principle a fluctuation approach. So we may apply the equation:

$$\tau_{DK} = \tau_{\mathrm{Kerr}}/g_2$$

The results are shown in Table IV. It is obvious that the relation given above holds exactly for both polymers, i.e., that the data on the reorientational dynamics obtained by the two methods are consistent with each other. We were able to show in previous publications that this holds for a large variety of different polymers.[26]

The main conclusions which can be drawn are that the three different models yield dynamical quantities such as rotational viscosities and response times, which are consistent with respect to each other. This leads, first of all, to the conclusions that the basic process controlling all three phenomena is the reorientational motion of the mesogenic unit about the short axis and secondly that the rotational process is controlled in the case of side chain polymers by fluctuations rather than by small step diffusion. It has to be pointed out that we have investigated in principle viscosities related to reorientational motions. However, at temperatures close to the isotropic transition temperature most viscosity parameters tend to become of equal magnitude. It is therefore not surprising that the viscosities found by the experiments described above also agree with those observed by shear experiments.

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References

1. P. A. Egelstaff, "An Introduction to the Liquid State," Academia Press, New York, London (1967).
2. K. Kohler, "The Liquid State," Verlag Chemie, Weinheim (1972).
3. G. Meier and A. Saupe, *Mol. Cryst. Liq. Cryst.*, **1**, 515 (1966).
4. W. Maier and G. Meier, *Z. Naturforschung*, **16 a**, 470, 1200 (1961).
5. H. Kelker and R. Hatz, in "Handbook of Liquid Crystals"; Verlag Chemie: Weinheim, 1980.
6. A. J. Martin, G. Meier and A. Saupe, *J. Chem. Soc. Symp. Farad. Soc.*, **5**, 119 (1971).
7. D. A. Dunmur, "Molecular Electro-Optics," S. Krause, Ed.; Plenum Press: New York, 1981.
8. M. Eich, K. H. Ullrich and J. H. Wendorff, *Polymer*, **25**, 1271 (1985).

9. P. G. De Gennes, "The Physics of Liquid Crystals"; Clarendon Press: Oxford, 1975.
10. L. M. Blinow, "Electro-optical and Magneto-optical Properties of Liquid Crystals," Wiley Interscience, New York (1983).
11. G. Baur, A. Stieb and G. Meier, "Liquid Crystals and Ordered Fluids 2," Plenum Press, New York (1974), p 645.
12. G. Baur, A. Stieb and G. Meier, *Appl. Phys.*, **6**, 309 (1975).
13. W. H. De Jeu, "Physical Properties of Liquid Crystalline Materials"; Gordon and Breach: New York.
14. A. Ciferri, W. R. Krigbaum and R. B. Meyer, Ed., "Polymer Liquid Crystals"; *Material Sci. Ser.*; Academic Press: New York (1982).
15. M. Gordon and N. A. Plate, Ed., "Liquid Crystalline Polymers I, II, II," *Adv. Polym. Sci.*, 59–61; Springer Verlag: Heidelberg (1984).
16. F. C. Frank, *Disc. Farad. Soc.*, **25**, 19 (1958).
17. F. M. Leslie, In "Adv. Liquid Crystals," G. H. Brown, Ed.; Academic Press: New York (1979).
18. J. L. Eriksen, *Arch. Mat. Mech. Anal.*, **10**, 189 (1982).
19. K. H. Ullrich and J. H. Wendorff, *Mol. Cryst. Liq. Cryst.*, **313**, 361 (1984).
20. M. Eich, K. H. Ullrich and J. H. Wendorff, *Progr. Colloid Polym. Sci.*, **69**, 94 (1984).
21. H. Pranoto and W. Haase, *Mol. Cryst. Liq. Cryst.*, **98**, 299 (1983).
22. N. A. Plate, *Pure Appl. Chem.*, **56**, 403 (1984).
23. R. Birenheide, Master-Thesis TH Darmstadt (1987).
24. W. Haase, H. Pranoto and F. J. Bormuth, *Ber. Bunsenges. Phys. Chem.*, **89**, 1229 (1985).
25. M. S. Beevers, D. A. Elliot and G. Williams, *Polymer*, **21**, 279 (1980).
26. R. Birenheide, M. Eich, B. Endres, H. Hirschmann, O. Herrmann-Schönherr and J. H. Wendorff, Vol. 17, Freiburger Arbeitstagung Flüssigkristalle (1987).
27. R. Zentel, G. R. Strobl and H. Ringsdorf, *Macromolecules*, **18**, 960 (1985).
28. M. Eich, PhD-Thesis, TH Darmstadt (1987).