

Pretransitional phenomena in the isotropic melt of a mesogenic side chain polymer

M. Eich, K. Ullrich and J. H. Wendorff

Deutsches Kunststoff-Institut, D-6100, Darmstadt, West Germany

and H. Ringsdorf

Institut für Organische Chemie D-6500 Mainz, West Germany

(Received 13 July 1983; revised 4 November 1983)

Pretransitional phenomena were characterized for a mesogenic side chain polymer using electric birefringence studies. The magnitude of the induced birefringence and its relaxation time were found to diverge in the isotropic melt as a hypothetical second order phase transition into the nematic phase is approached. The results are interpreted in terms of the Landau-de Gennes theory of the nematic phase transition.

(Keywords: liquid crystalline polymer; electrically induced birefringence; pretransitional phenomena; Landau-de Gennes model; orientation of nematic polymers; order parameter fluctuations)

INTRODUCTION

In most atomic or molecular systems the transition from the crystalline solid state to the isotropic melt takes place in one step (at the melting temperature). This transition is characterized by the simultaneous destruction of the positional and the orientational long range order. Consequently only a short range order exists in the high temperature phase.

In certain cases, however, the transition from the crystalline to the isotropic fluid state occurs stepwise, involving one or more intermediate phases. Molecules, which are characterized by elongated molecular shapes, may exhibit liquid crystalline phases i.e. nematic, cholesteric or smectic phases, including specific modification of these phases. In this paper we will be concerned only with the nematic phase. This phase is characterized by a short range positional order while at the same time displaying a long range orientational order. The orientational order is expressed in terms of the scalar order parameter S which is defined as

$$S = \frac{1}{2} \cdot \langle 3 \cos^2 \theta - 1 \rangle \quad (1)$$

where θ is the angle between the locally preferred direction and the molecular long axis. The order parameter is zero in the isotropic fluid state, but it increases during the transition from the isotropic to the nematic phase. Thus a first order phase transition occurs. This transition, however, has some of the features of a second order phase transition. For this reason, this particular transition has often been described as being only 'weakly' first order. This indicates that the discontinuities in the first derivative of the Gibbs free energy at the transition are small (in comparison to the corresponding values of the isotropic to crystalline transition). Pretransitional effects also occur.

We know that a characteristic property of a second order phase transition is the occurrence of strong fluctuations of certain thermodynamic parameters (such as the relevant order parameter) and the divergence of certain thermodynamic properties in its neighbourhood. Pretransitional effects related to order parameter fluctuations have been observed in the isotropic fluid state close to the nematic transition for low molecular weight systems¹.

Effects of this kind have recently met with considerable interest, including the fluid state of chain molecules. It has been assumed, for instance, that due to the anisotropic shape of chain molecules strong orientational correlations may occur in the melt of chain molecules. This is indicative either of the presence of a nematic phase or of a hypothetical, low temperature nematic phase, occurring in a temperature range below the actual crystallization temperature. In fact, results on the depolarized light scattering of several n-alkane melts have been successfully interpreted in terms of a low temperature nematic phase². The experimental data at higher temperatures were interpreted in terms of pretransitional effects³.

For this reason, we became interested in such pretransitional effects in polymers, known to show a nematic-isotropic phase transition⁴. We selected a side chain polymer, the side chain of which carries a mesogenic group and a spacer group. The static and dynamic properties of the pretransitional effects were studied, using the electric birefringence technique (Kerr Effect). The data obtained will be discussed in relation to data available for low molecular weight mesogenic systems.

THEORY

The nematic-isotropic transition as well as pretransitional effects are usually treated in terms of the

Landau-de Gennes model, which is based on the simple phenomenological Landau theory of phase transitions⁵. It is generally accepted that this theory is an adequate qualitative description, while being quantitatively less reliable. According to this model, the free energy density $F(T)$ in the vicinity of the phase transition can be expressed as a function of the order parameter S as⁶:

$$F(T) = F_0(T)_{S=0} + \frac{1}{2} \cdot a(T)S^2 - \frac{1}{3} \cdot b(T)S^3 + \frac{1}{4} \cdot c(T)S^4 + \dots \quad (2)$$

In this model, the coefficient of the term quadratic is S , $a(T)$ is taken to be $a = a_0 \cdot (T - T^*)$, where T^* is a hypothetical second order phase transition temperature. The cubic term b has to be included in the case of the isotropic-nematic transition since the free energy for $S < 0$ is unequal to the free energy for $S > 0$. The inclusion of b has the consequence, that in a zero field a first order phase transition will take place at a temperature T_{NI} , at which the order parameter S will increase discontinuously from zero to a positive value. Below this transition, a second order phase transition at a temperature T^* is hidden.

As this temperature is approached the order parameter fluctuations in the isotropic state, increase very strongly. The expansion coefficients a , b , c are related to thermodynamic parameters, such as the discontinuous jump of the order parameter S_{NI} , the heat of fusion ΔH_{NI} and the first order transition temperature T_{NI} relative to the hypothetical second order phase transition:

$$S_{NI} = \frac{2 \cdot b}{3 \cdot c} \quad (3)$$

$$\Delta H_{NI} = \frac{2 \cdot a_0 \cdot b^2}{9 \cdot c^2} \cdot T_{NI} \quad (4)$$

$$T_{NI} = T^* + \frac{2 \cdot b^2}{9 \cdot a_0 \cdot c} \quad (5)$$

In the presence of an electric field, the average order parameter S will be $\neq 0$ in the isotropic phase. It will increase very strongly as the second order phase transition is approached. By taking into account the influence of the electric field E on the free energy density of the total system,

$$F(T) = F(T)_{E=0} - \frac{1}{6} \cdot \epsilon_0 \cdot E^2 \cdot [2 \cdot \Delta\epsilon^0 \cdot S + 3 \cdot \bar{\epsilon} - 3] + \dots \quad (6)$$

we obtain the result that the induced order parameter S_E in the Gauss approximation⁶ takes a value of

$$S_E = \frac{\Delta\epsilon^0 \cdot \epsilon_0 \cdot E^2}{3 \cdot a_0 \cdot (T - T^*)} \quad (7)$$

where ϵ_0 is the influence constant, and $\Delta\epsilon^0$ is the anisotropy of static dielectric constant of the ideally ordered nematic state ($S = 1$).

The macroscopically observed birefringence is given by

$$\Delta n_0 = \Delta n^0 \cdot S_E \quad (8)$$

where Δn^0 is the birefringence of the perfectly ordered molecules.

The Kerr constant B , is defined as

$$B = \frac{\Delta n_0}{\lambda \cdot E^2} \quad (9)$$

(λ is the wavelength of light)

and is thus given by

$$B = \frac{\Delta n^0 \cdot \Delta\epsilon^0 \cdot \epsilon_0}{3 \cdot \lambda \cdot a_0 \cdot (T - T^*)} \quad (10)$$

As T^* is approached B is predicted to diverge (the critical exponent being 1, according to the Landau theory).

The calculation of the unknown quantity $\Delta\epsilon^0$ is based on the Onsager model⁷

$$\Delta\epsilon^0 = 4 \cdot \pi \cdot N \cdot \left[\Delta\alpha + F' \cdot \mu^2 \cdot \frac{(3 \cos^2 \beta - 1)}{2kT} \right] \cdot h \cdot F' \quad (11)$$

where N is the number of molecules per cm^3 ; $\Delta\alpha$ is the anisotropy of molecular polarization; μ is the permanent dipole moment; β is the average angle between molecular long axis and permanent dipole;

$$h = \frac{3 \cdot \bar{\epsilon}}{2 \cdot \bar{\epsilon} + 1}; \quad \bar{\epsilon} = \frac{2 \cdot \epsilon_{\perp} + \epsilon_{\parallel}}{3}$$

$$F' = \frac{1}{1 - \bar{\alpha} \cdot f} \quad (\text{reaction field})$$

$\bar{\alpha}$ is the average molecular polarizability

$$f = \frac{8 \cdot \pi \cdot N \cdot (\bar{\epsilon} - 1)}{3 \cdot (2 \cdot \bar{\epsilon} + 1)}$$

Thus B may be expressed as:

$$B = \frac{4 \cdot \pi \cdot N \cdot \Delta n^0 \cdot \epsilon_0 \cdot h \cdot F'}{3 \cdot \lambda \cdot a_0 \cdot (T - T^*)} \cdot \left[\Delta\alpha + \frac{F' \cdot \mu^2 \cdot (3 \cos^2 \beta - 1)}{2 \cdot k \cdot T} \right] \quad (12)$$

Up to now, only the static response has been considered. The dynamical properties will now be considered. It is known that fluctuations in the neighbourhood of a critical point show a critical slowing down of the characteristic relaxation time. This is primarily due to a strong increase in the size of the fluctuations correlation length. According to the de Gennes treatment, the relaxation time of the electric birefringence is governed by the dynamic properties of the order parameter S^8 . In this hydrodynamical theory the dynamic properties of the order parameter fluctuations are related to spatial fluctuations of the velocity field. Based on the assumption that the time response of the order parameter is much faster than that of the velocity field, the time dependence of S may be expressed as⁹

$$\eta \cdot \frac{\partial S}{\partial t} = \frac{2 \cdot \epsilon_0 \cdot \Delta\epsilon^0 \cdot E^2}{9} - \frac{2}{3} \cdot a \cdot S \quad (13)$$

neglecting the expansion terms of third and fourth order in S ($\eta = \text{viscosity}$).

The result for the rise and decay are as follows:

$$S_R(t) = A \cdot (1 - e^{-t/\tau}) \quad (14)$$

$$S_D(t) = A \cdot e^{-t/\tau} \quad (15)$$

or

$$\Delta n_R(t) = \Delta n_0 \cdot (1 - e^{-t/\tau}) \quad (16)$$

$$\Delta n_D(t) = \Delta n_0 \cdot e^{-t/\tau} \quad (17)$$

with

$$A = \frac{2 \cdot \Delta \epsilon^0 \cdot \epsilon_0 \cdot E^2 \cdot \tau}{9 \cdot \eta} = \frac{\Delta \epsilon^0 \cdot \epsilon_0 \cdot E^2}{3 \cdot a} \quad (18)$$

The relaxation time τ is given by

$$\tau = \frac{3 \cdot \eta(T)}{2 \cdot a_0 \cdot (T - T^*)} \quad (19)$$

Thus the relaxation time diverges as T^* is approached; the critical exponent being 1. $\eta(T)$ represents the temperature dependence of the viscosity of the polymer, which in turn influences the temperature dependence of the reorientational relaxation time of the molecular groups.

EXPERIMENTAL

Kerr effect studies

The sample cell consisted of two polished aluminium electrodes, to which two microscope slides were glued. The length of the cell in the direction of the passing light was 3.27 mm, and the distance between the electrodes was 1.2 mm. In order to remove the air bubbles, the cell containing the polymer sample was annealed at elevated temperatures in a vacuum oven. The cell was thermostatically controlled using a large aluminium chamber, the temperature of which could be controlled to within 0.1 K. The temperature was measured directly in the ground electrode, using a Ni-CrNi thermocouple.

The laser light used for the experiments was the green line ($\lambda = 514.5$ nm) of an argon ion laser. The stability of the light intensity was very good, due to the light control

mode used. The experimental set-up is shown in Figure 1. The voltage used in the static experiments varied up to 2 kV. In the case of dynamic experiments, a pulse generator with a pulse amplifier, was employed, resulting in a rectangular voltage pulse with an amplitude of 1.3 kV and a duration of 3 ms. The rise and decay times were less than 10 μ s.

Linear detection was used for determining the induced birefringence. A quarter wave device, oriented at 45° relative to the electric field direction was used. The analyser was rotated by 5° relative to the direction of extinction. The sign of the rotation was chosen in such a way that a negative Kerr effect resulted in an increase of the light intensity. The intensity of the laser light and the birefringence were monitored simultaneously using two photodiodes. The signal was monitored on a 'lock-in amplifier' in the case of static measurements; and a storage oscilloscope in the case of dynamic experiments. The total response time of detection was less than 5 μ s.

Optical studies

Birefringence studies were performed in the nematic phase in order to determine the unknown quantity Δn^0 . For this purpose the sample was placed between two glass slides, having a separation of about 14 μ m. The glass slides were covered with a thin polyimide/SnO₂ layer and subsequently rubbed in a given direction. This procedure is known to orient the nematic director along this axis throughout macroscopic areas within the sample film. The orientation was induced by annealing the sample extensively at a temperature, about 4 K below the nematic-isotropic transition temperature T_{NI} . The birefringence in the oriented regions was determined using a quartz compensator.

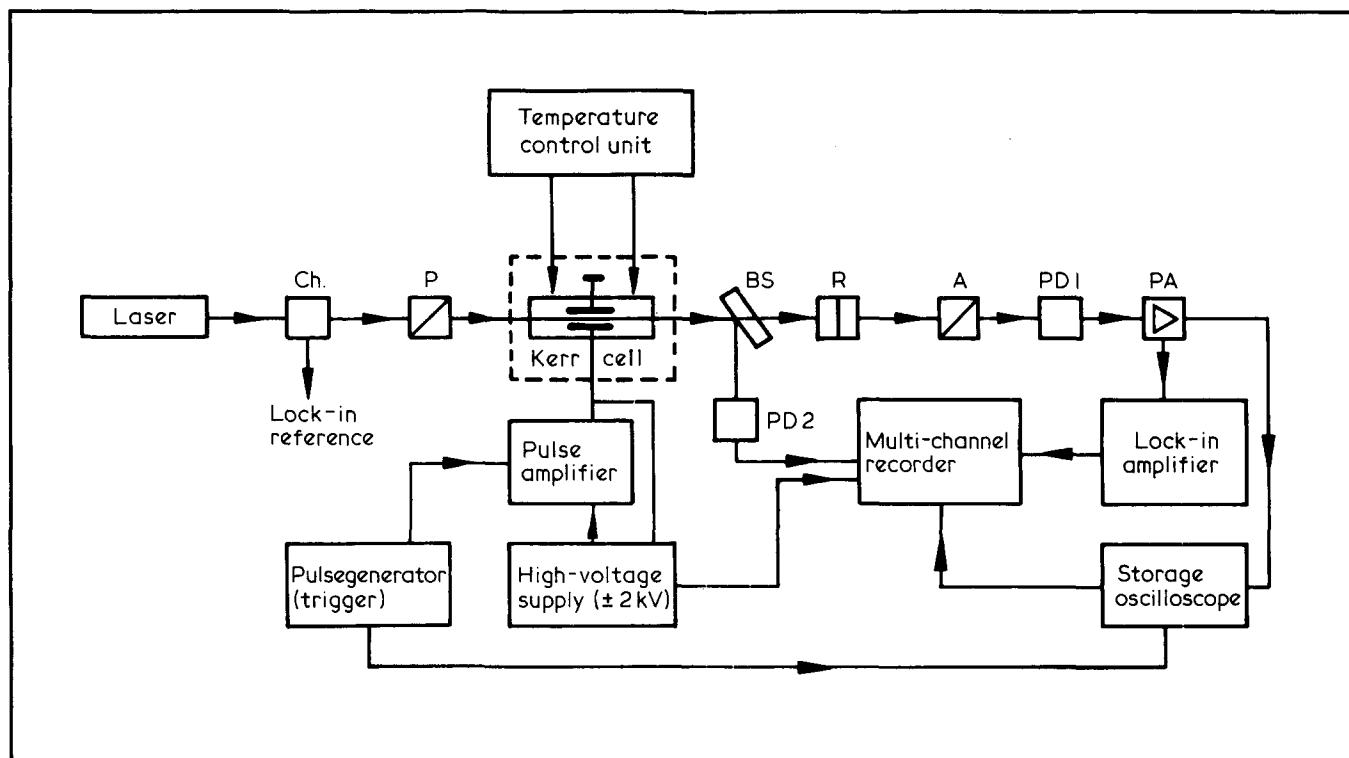


Figure 1 Schematic diagram of electro-optical measuring arrangement. Chopper (CH), polarizer (P), beam-splitter (BS), $\lambda/4$ - retarder (R), analyser (A), preamplifier, +40 dB (PA), photodiode (birefringence) (PD 1), photodiode (intensity) (PD 2)

Samples

The samples used for the experiments were obtained by radical polymerization. The monomer unit is displayed in Figure 2. The data for the transition temperatures are shown¹⁰. The tacticity was reported to be:

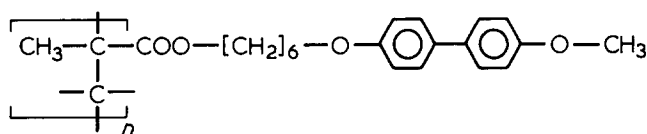
isotactic	2% sequences
syndiotactic	63% sequence
heterotactic	35% sequence

RESULTS AND DISCUSSION

Static Kerr investigations

The electrically induced birefringence was found to be a linear function of the square of the applied electric field. Figure 3 shows the effect of temperature on this behaviour.

Within the voltage range, we applied ($E \leq 1.5$ MV/m),



semicrystalline 390.2K nematic 406.8K* isotropic
 $T_g = 358$ K

*transition temperature measured with polarization microscope

Figure 2 Monomer unit of the liquid crystal polymer (with transition data)

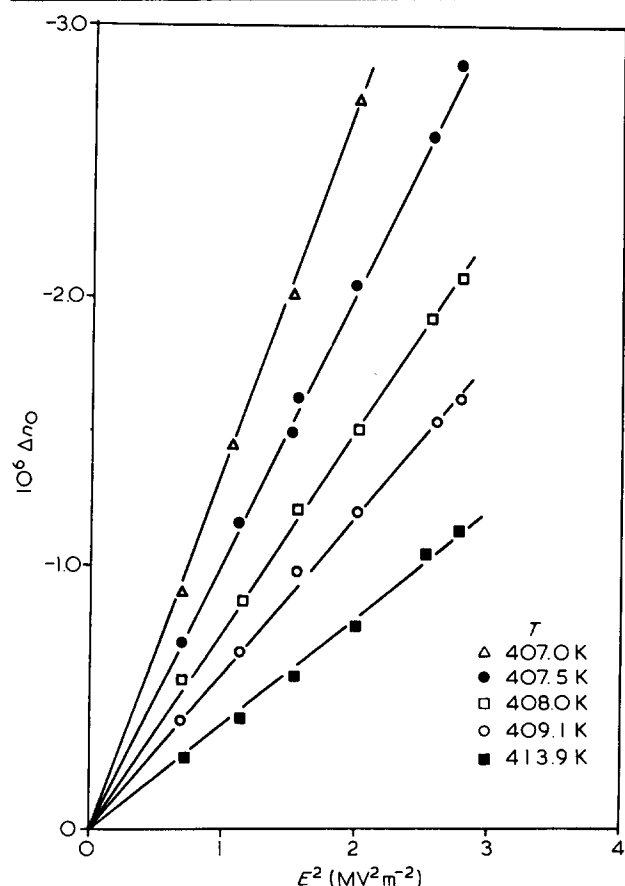


Figure 3 Kerr plot of poly(*p*-biphenylmethacrylate) at various temperatures: 407.0 (Δ), 407.5 (●), 408.0 (□), 409.1 (○), 413.9 K (■), ($\lambda = 514.5$ nm)

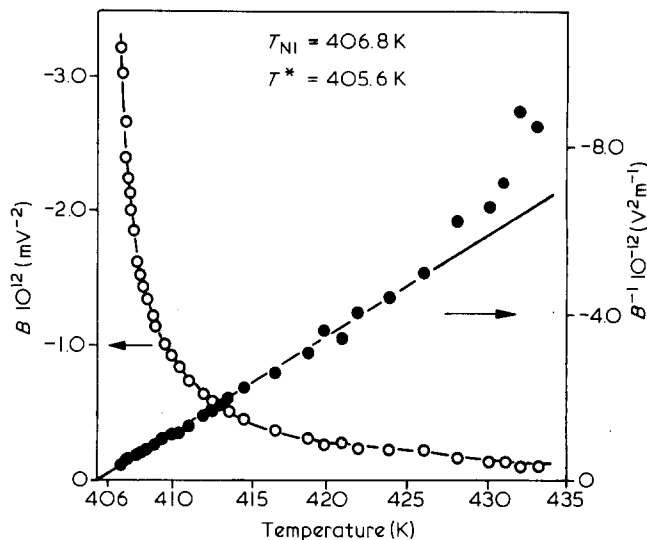


Figure 4 Kerr constant B and B^{-1} versus temperature ($\lambda = 514.5$ nm)

no saturation effects were detected. In all cases the Kerr law $\Delta n_0 \sim E^2$ was observed. The results show that the Kerr constant is negative in all cases:

$$(n_{\parallel} - n_{\perp}) = \Delta n_0 < 0 \quad (20)$$

where the direction given refers to the direction defined by the electrical field. From Figure 3 it is already apparent that the Kerr constant depends very strongly on temperature. The Kerr constant increases with decreasing temperature as the nematic transition temperature is approached. The temperature dependence of the Kerr constant in the temperature range $T_{NI} \leq T \leq (T_{NI} + 25$ K) is shown in Figure 4.

The Kerr constant B tends to infinity as the hypothetical temperature T^* is approached. This temperature may be obtained from a plot of B^{-1} versus T . This plot is shown in Figure 4. The hypothetical temperature T^* was found to be 405.6 K for the samples studied here. It is thus about 1.2 K below the actual isotropic–nematic transition temperature. Thus the Kerr constant behaves (as a function of the temperature)

$$B \sim (T - T^*)^{-\gamma} \quad (21)$$

with $\gamma \approx 1$.

Dynamic Kerr investigations

In the case of the dynamic experiments the rise and decay time of the electrically induced birefringence was determined as a function of the temperature. A typical experimental result is shown in Figure 5, which was obtained at a temperature of 406.9 K. The saturation value of Δn_0 was attained within 2 ms (the same holds for the decay behaviour).

Figure 6 shows the normalized rise and decay behaviour for various temperatures.

It is clear that the rise and decay responses are very similar. Furthermore, it is observed that the characteristic time scale of the response diverges as the temperature is decreased. The characteristic relaxation time was calculated from

$$\langle \tau_{\text{Rise}} \rangle = \int_0^{2.1 \text{ ms}} \left(1 - \frac{\Delta n_R(t)}{\Delta n_0} \right) dt \quad (22)$$

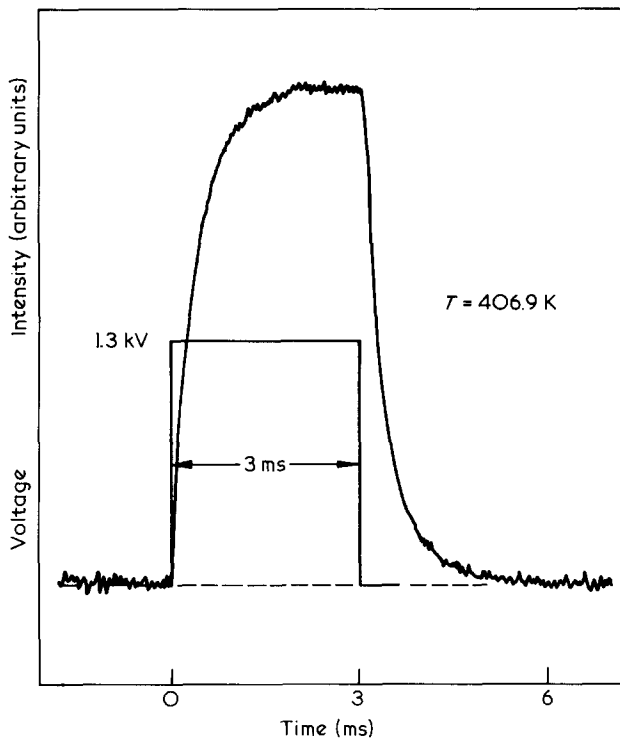


Figure 5 Applied voltage pulse and birefringence transients at $T=406.9\text{ K}$ ($\lambda=514.5\text{ nm}$, $E=1.08\text{ (MV/m)}$)

$$\langle \tau_{\text{Decay}} \rangle = \int_0^{2.1\text{ ms}} \frac{\Delta n_D(t)}{\Delta n_0} \cdot dt \quad (23)$$

since the rise and decay do not follow a simple exponential law. Using a William-Watts function

$$\Delta n_D(t) \sim \exp\left(-\left(\frac{t}{\tau}\right)^{\beta_D}\right) \quad (24)$$

with a characteristic value of $\beta_R \approx \beta_D \approx 0.7$, we were able to represent the time dependent response.

The experimentally observed relaxation times have to be corrected for the temperature dependence of the viscosity of the polymer according to equation (19)¹¹. We did this by using the WLF equation for calculating the temperature shift factor. The justification for the use of the WLF equation is, that the temperature range in which we performed the experiments was close to the glass transition temperature of about 358 K¹². The magnitude of the viscosity will be discussed below. After these corrections the characteristic relaxation time of the correlated motions was found to diverge according to

$$\tau \sim (T - T^*)^{-\gamma} \quad (25)$$

as the characteristic temperature T^* is approached (in agreement with theory). The exponent was thus found to be close to $\gamma \approx 1$. The characteristic temperature was $T^* = 405.6\text{ K}$ (as in the case of the static experiments). In order to obtain the approximate magnitude of the relaxation times for the rise and decay, we calculated the time, after which the normalized response attained the value $1/e$ and $(1 - 1/e)$ (for the decay and rise respectively). The viscosity was then calculated on the basis of equation (19). The results are displayed in Table 1.

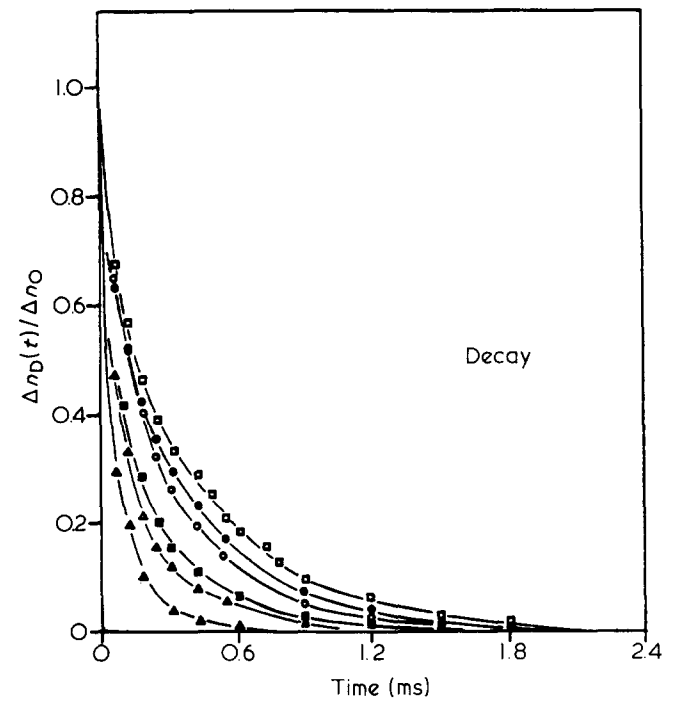
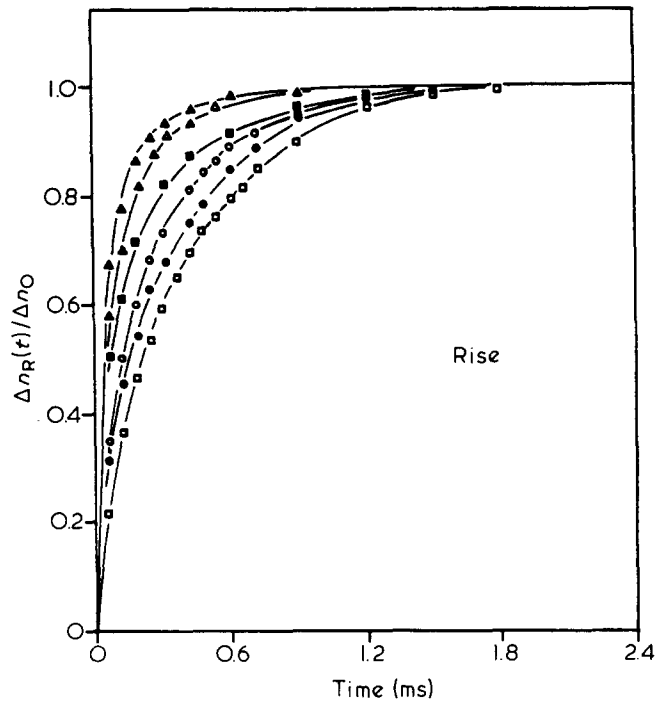


Figure 6 Rise and decay of normalized birefringence at various temperatures: 406.8 (□), 407.0 (●), 407.2 (○), 407.4 (■), 407.7 (△), 408.5 K (▲), ($\lambda=514.5\text{ nm}$, $E=1.08\text{ (MV/m)}$)

Table 1 Temperature dependence of measured and corrected relaxation times and viscosity

T (K)	τ_D (36.8%)		$\tau_{\text{corr.}}$ (μs)	η (Poise)
	τ_R (63.2%)	(μs)		
406.8	405		405	873
407.0	320		339	853
407.2	240		264	760
407.4	175		199	645
407.7	125		151	571
408.5	90		128	668

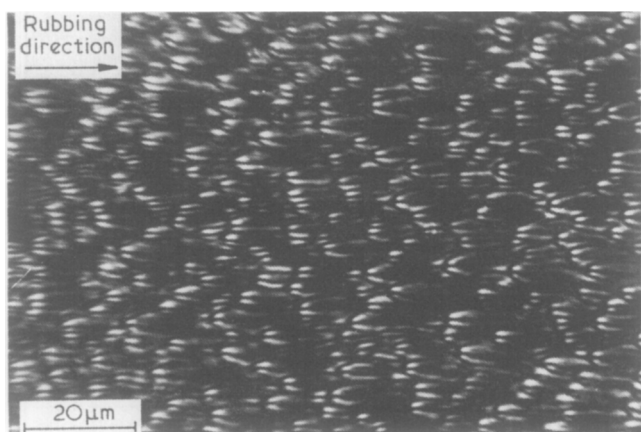


Figure 7 Micrograph from polarizing microscope showing orientation of the sample

Optical studies

These investigations revealed, that in certain areas of the polymer film (located between the glass slides), a macroscopically preferred orientation could be induced along the direction defined by rubbing (Figure 7). The birefringence studies of a single domain yielded a value of $\Delta n = +0.079$. If we take a characteristic value of the order parameter for side chain polymers of $S \approx 0.40$ ¹³ at a reduced temperature $T_r = (T_{\text{meas.}}/T_{\text{NI}}) \approx 0.99$, we obtain the birefringence of the perfectly ordered molecules $\Delta n^0 = (n_{\parallel} - n_{\perp}) \approx +0.20$ with respect to the direction of rubbing ($T_{\text{meas.}}$ = measured temperature). By assuming that the long axes of the mesogenic side chains of the polymer are oriented parallel to the rubbing direction, one can expect that the optical polarizability is much larger in this direction than perpendicular to it. This is in agreement with experimental results on low molecular weight liquid crystals as well as with the results obtained in our studies.

Now, since the anisotropy of the optical polarizability was found to be positive and the Kerr constant to be negative, we have to conclude from equation (12), that the permanent dipoles, which also contribute to the Kerr constant¹⁴ were oriented with an angle $\beta \geq 54.7^\circ$ relative to the direction of the long axes of the mesogenic groups. The consequence is, that we expect the anisotropy of the dielectric constant in the nematic phase to be negative:

$$\Delta \epsilon^0 < 0 \quad (26)$$

This has to be checked by dielectric relaxation studies, which are currently being performed. Experimental studies on several low molecular weight liquid crystals have given similar results^{15,16}. The consequence is that the molecular long axes orient preferentially perpendicular to the applied electric field.

Based on the experimental results on T^* and T_{NI} as well as on the heat of transition $\Delta H_{\text{NI}} = 8.14 \text{ J cm}^{-3}$ and assuming that at T_{NI} the order parameter changes discontinuously from zero to approximately $S_{\text{NI}} \approx 0.35$ ¹³ we are able to calculate the characteristic constants of the phenomenological Landau-de Gennes theory. The values are:

$$a_0 = 0.33 \text{ J cm}^{-3} \text{ K}^{-1}; \quad b = 3.36 \text{ J cm}^{-3}; \quad c = 6.41 \text{ J cm}^{-3};$$

$$\Delta \epsilon_{\text{cal}}^0 \approx -0.8; \quad \rho_{\text{isotr.}} = 1.1 \text{ g cm}^{-3} \text{ }^{10}$$

In the case of an electric field of 1 MV/m and a temperature of $T = 408.6 \text{ K}$ (corresponding to $\Delta T = 3 \text{ K}$), we calculated an induced order parameter in the isotropic melt of about

$$|S_{\text{E}}| \approx 5 \times 10^{-6}$$

The values given above correspond closely to the values known for low molecular weight liquid crystals, for instance for n-heptylcyanobiphenyl^{17,18}. This indicates that the thermodynamic properties of low molecular weight mesogenic materials and polymeric mesogenic materials are similar. In the case of the dynamical studies we found, however, that the time scale of the characteristic relaxation is quite different from the corresponding time scale of low molecular weight liquid crystals^{19,20}. This may be attributed to the very large values of the viscosity of the polymer melt, displayed in Table 1. It is larger by a factor 10^3 – 10^4 , as compared with the corresponding values of low molecular weight liquid crystals such as MBBA²¹. The viscosity is of the same order of magnitude as observed for main chain mesogenic polymers such as copolymers of PETB and PHB, which are able to display nematic melts²².

ACKNOWLEDGEMENTS

This work was supported by the Deutsche Forschungsgemeinschaft (SFB 41 Mainz/Darmstadt). We wish to thank Dr H. Finkelmann (University of Clausthal) for stimulating discussions.

REFERENCES

- 1 Kelker, H. and Hatz, H. in 'Handbook of Liquid Crystals', Verlag Chemie, Weinheim 1980
- 2 Dettenmaier, M. *Prog. Colloid Polym. Sci.* 1979, **66**, 169
- 3 de Gennes, P. G. *Phys. Lett.* 1969, **A30**, 454
- 4 Blumstein, A. in 'Liquid Crystalline Order In Polymers', Academic Press, New York, San Francisco, London 1978
- 5 Landau, L. and Lifshiz, E. in 'Statistical Physics', Pergamon Press Ltd., Headington Hill Hall, Oxford, 1958
- 6 Senbetu, I. and Woo, C. *Mol. Cryst. Liq. Cryst.* 1982, **84**, 101
- 7 Maier, W. and Meier, G. Z. *Naturforsch.* 1961, **16a**, 262
- 8 de Gennes, P. G. in 'Physics of Liquid Crystals', Oxford Univ. Press, London, 1974
- 9 Krause, S. in 'Molecular Electro-Optics', Plenum Press, New York, London, 1981, 435
- 10 Hahn, B., Wendorff, J. H., Portugall, M. and Ringsdorf, H. *Colloid Polym. Sci.* 1981, **259**, 875
- 11 Stinson III, T. W. and Litster, J. D. *Phys. Rev. Lett.* 1970, **25**, 503
- 12 Hahn, B. *Diplom-Arbeit*, TH Darmstadt, 1980
- 13 Finkelmann, H., Benthack, H. and Rehage, G. *Journal de Physique Chimie*, in press
- 14 Beevers, M. S., Crossley, J., Garrington, D. and Williams, G. J. *Chem. Soc., Farad. Trans. 2* 1976, **72**, 1482
- 15 Bischofberger, T., Yu, R. and Shen, Y. R. *Mol. Cryst. Liq. Cryst.* 1977, **43**, 287
- 16 Tsvetkov, V. and Ryumtsev, E. *Sov. Phys. Cryst.* 1968, **13**, 225
- 17 Dunmur, D. A. and Tomes, A. E. *Mol. Cryst. Liq. Cryst.* 1981, **76**, 231
- 18 Poggi, Y., Filippini, J. and Aleonard, R. *Phys. Lett.* 1976, **57A**, 53
- 19 Coles, H. J. *Mol. Cryst. Liq. Cryst. Lett.* 1978, **49**, 67
- 20 Yamamoto, R., Ishihara, S., Hayakawa, S. and Morimoto, K. *Phys. Lett.* 1978, **69A**, (4), 276
- 21 Stinson, T. W. and Litster, J. D. *Journal de Physique* 1972, **C1**, 69
- 22 Jerman, R. E. and Baird, D. G. *J. Rheol.* 1981, **25** (2), 275