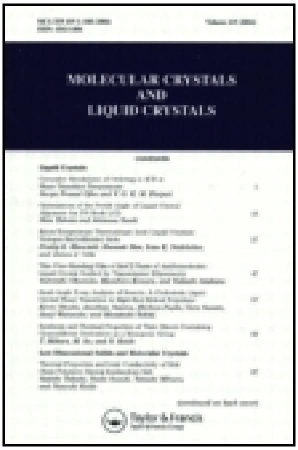

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Orientation Correlations in the Isotropic State of Low Molecular Weight and Polymeric Fluids

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Orientation Correlations in the Isotropic State of Low Molecular Weight and Polymeric Fluids

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The short range orientational order characteristic of molecular fluids is discussed as a function of the shape of the molecules and of intermolecular interactions. Low molecular weight and polymeric substances exhibiting only an isotropic melt or, in addition, liquid crystalline phases were taken into account. The discussion is based on experimental results obtained from dielectric relaxation, Kerr effect and X-ray studies. The characterization of the short range order is given in terms of correlation parameters, related to the general pair correlation function.

INTRODUCTION

Rigid, hard molecules having the shape of elongated cylinders or ellipsoids or having the shape of flat discs are intuitively expected to display some kind of orientational order in the condensed fluid state or in solution with spherical symmetric molecules. The requirement is that the density or the concentration of the elongated or flat molecules has to be large enough. Experiments as well as theoretical treatments have actually shown that a transition from an isotropic to an anisotropic state may happen at critical values of the density or the concentration.[1–4]

Intuition suggests, in addition, that the presence of attractive forces—anisotropic forces in particular—will facilitate the formation of an anisotropic fluid state. Again experimental results and calculations have shown this to be correct.[5–7] The relative importance of the shape of the molecules (governing the repulsive forces) and of the particular chemical structure (influencing the attractive forces) has been the subject of a large number of publications. More recent observations that the replacement of the stiff and easily polarizable phenyl-ring by the more flexible and less polarizable cyclohexane unit does not prevent the formation of anisotropic fluid phases, has stimulated new discussions about the nature of the forces, which induce anisotropic phases.[8,9]

The orientational order in the anisotropic fluid states is usually described in terms of an order parameter characterizing the long range orientational order.[10] It is known, however, that the orientational order is a very complex property and that the scalar long range order parameter S characterizes just one particular aspect of the total orientational order.[11-13]

This paper is concerned with the influence of the shape of the molecules as well as of intermolecular interactions on the short range orientational order. This short range order is known to influence macroscopical properties such as for instance dielectric properties. We will discuss in the paper experimental results, related to short range orientational order (obtained by us but also taken from the literature) for low and high molecular weight fluids which are either able to display just one isotropic fluid state or both an isotropic and an anisotropic fluid state. The following chapter will be concerned with a short introduction to the general statistical description of orientational order in fluids. Next we will discuss methods of analyzing this kind of orientational order. The main part of the paper will then be devoted to a discussion of the short range order observed for different kinds of model fluids.

STATISTICAL DESCRIPTION OF LONG AND SHORT RANGE ORDER

We will assume in the following, for the sake of simplicity, that the molecules are cylindrically symmetric and rigid. A particular configuration of N molecules can be represented, as shown in Figure 1, by a set of general coordinates $\bar{r}_i$, Ω_i where $\bar{r}_i$ points from the origin of the coordinate system to the center of molecule i and where Ω_i (Θ_i, φ_i) gives the orientation of the long axis of molecule i. Based on the general partition function

$$Q_N = Z_N / N! \qquad (1)$$

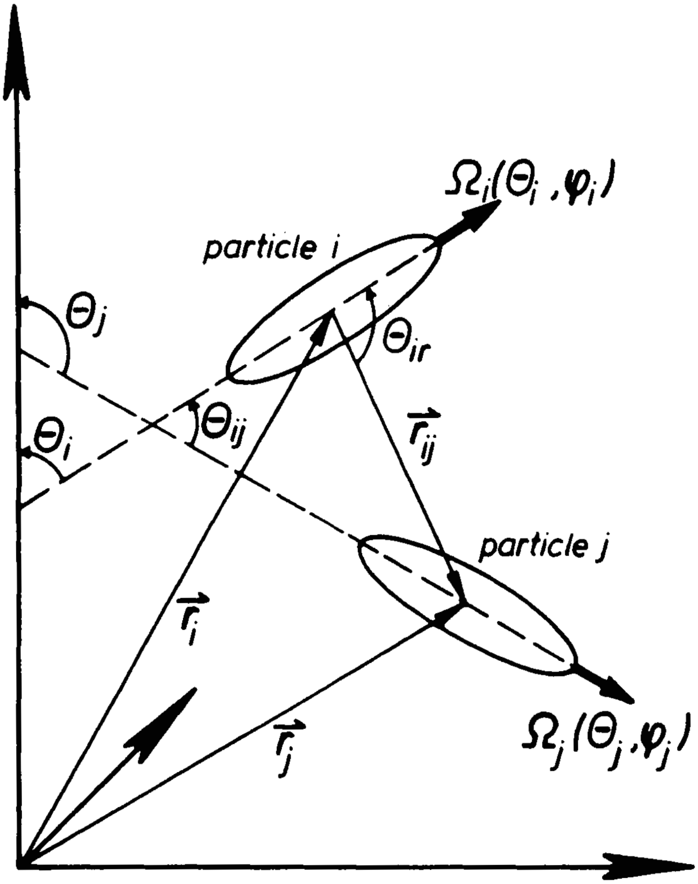


FIGURE 1 Configuration of two rigid, cylindrically symmetric, nonspherical particles *i,j* in a coordinate system.

$$Q_N = \int_r\int_\Omega \exp(-U(\vec{r}^N, \Omega^N)/kT) \cdot d\vec{r}^N \cdot d\Omega^N / N! \tag{2}$$

$$\vec{r}^N = (\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N) \tag{3}$$

$$\Omega^N = (\Omega_1, \Omega_2, \ldots, \Omega_N) \tag{4}$$

$$d\vec{r}^N = d\vec{r}_1 \cdot d\vec{r}_2 \cdot \ldots \cdot d\vec{r}_N \tag{5}$$

$$d\Omega^N = d\Omega_1 \cdot d\Omega_2 \cdot \ldots \cdot d\Omega_N \tag{6}$$

$$\int_{\Theta}\int_{\varphi} d\Omega = 4 \cdot \Pi \tag{7}$$

(k = Boltzmann constant)

singlet, pair, triplet and higher order distribution functions may be derived:[14,15]

$$P^{(1)}(\vec{r}_i, \Omega_i) = (N/Z_N) \cdot \int_r \int_\Omega \exp(-U(\vec{r}^N, \Omega^N)/kT) \cdot d\vec{r}_2^N \cdot d\Omega_2^N \tag{8}$$

$$P^{(2)}(\vec{r}_i, \Omega_i, \vec{r}_j, \Omega_j) = [N(N-1/Z_N] \cdot \int_r \int_\Omega \exp(-U(\vec{r}^N, \Omega^N)/kT) d\vec{r}_3^N d\Omega_3^N \tag{9}$$

The triplet and the higher order distribution functions are not readily accessible experimentally whereas this is the case for the singlet and also for the pair distribution function, at least to a certain extent. Thus these functions can be used to characterize the orientational order in fluids. The two distribution functions represent two different kinds of order, namely the short range and the longe range order introduced above.

The long range order is reflected in the singlet distribution function, which can be expressed for a uniaxial, homogeneous and macroscopically isotropic fluid by

$$P^{(1)}(\vec{r}_i, \Omega_i) = (N/V) \cdot f(\Omega_i) = (N/V) \cdot [f(\Theta_i)/2 \cdot \Pi] \tag{10}$$

where N/V is the particle number density and $f(\Theta_i)$ the orientation distribution of the long axes of the molecules. Rather than using the total distribution function it is often sufficient to consider order parameters derived from the total distribution function. These are the expansion coefficients a_n for an expansion of $f(\Theta_i)$ in a series of spherical harmonics $P(\cos\Theta_i)$

$$f(\Theta_i) = \sum_{n=0}^{\infty} a_n \cdot P_n(\cos\Theta_i) \tag{11}$$

$$a_n = [(2n + 1)/2] \cdot \langle P_n(\cos\Theta_i)\rangle, \tag{12}$$

where $\langle \ldots \rangle$ denotes the ensemble average.

Usually one just considers the order parameter S:

$$S = \langle P_2(\cos\Theta_i)\rangle = (1/2) \cdot \langle 3\cos^2\Theta_i - 1\rangle \tag{13}$$

It is zero in the isotropic phase and 1 if all molecules are parallel to a given reference direction. It jumps discontinuously from zero to a positive value smaller than 1 at the isotropic to liquid crystal transition. The singlet distribution function and the order parameters derived from it are insensitive to the presence of a local order such as the parallel arrangement of neighbouring molecules.

This kind of order is, however, reflected in the pair distribution function. Assuming a homogeneous, macroscopically isotropic fluid, we may express this function as follows:

$$\begin{aligned} P^{(2)}(\vec{r}_i, \Omega_i, \vec{r}_j, \Omega_j) &= P^{(2)}(\vec{r}_{ij}, \Omega_i, \Omega_j) \\ &= P^{(1)}(\vec{r}_i, \Omega_i) \cdot P^{(1)}(\vec{r}_j, \Omega_j) \cdot g(\vec{r}_{ij}, \Omega_i, \Omega_j) \qquad (14) \\ &= [(N/V) \cdot f(\Omega_i)]^2 \cdot g(\vec{r}_{ij}, \Omega_i, \Omega_j) \end{aligned}$$

$\vec{r}_{ij}$ is the vector pointing from the center of molecule i to that of molecule j. $g(\vec{r}_{ij}, \Omega_i, \Omega_j)$ is the pair correlation function, which now contains information on the local orientational order and the correlation of the centers of gravity of the molecules. This general function is, unfortunately, experimentally unaccessible. The pair correlation function depends only on $\vec{r}_{ij}$, Θ_i and Θ_j, if locally a uniaxial orientational order is assumed to exist. One first step toward an evaluation of the short range order consists in expanding this function in terms of a complete series of spherical harmonics:

$$g(\vec{r}_{ij}, \Theta_i, \Theta_j) = \sum_{l_1 l_2 l_{12}} g^{l_1 l_2 l_{12}}(r) \cdot \phi^{l_1 l_2 l_{12}}(\Theta_i, \Theta_j, \Theta\vec{r}_{ij}) \tag{15}$$

with $r = |\vec{r}_{ij}|$, $\vec{r}_{ij}$ being the orientation of $\vec{r}_{ij}$. The indices m,n depend on the symmetry of the constituent molecules. They are zero for the assumptions made previously and therefore neglected in the following. Now the expansion coefficients $g^{l_1 l_2 l_{12}}(r)$ are correlation functions rather than scalar order parameters. Each of these functions describes the fluctuations and the spatial correlations of particular positional and orientational configurations. It has been demonstrated, for instance, that $g^{000}(r)$ depends just on the short range positional order of the centers of the molecules, irrespective of their mutual orientation. In addition, it has been shown that the first expansion functions represent:

$$G^{110}(r) = g^{110}(r)/g^{000}(r) \sim \langle \cos\Theta_{ij}(r) \rangle \tag{16}$$

$$G^{101}(r) = g^{101}(r)/g^{000}(r) \sim \langle \cos\Theta_{ir}(r) \rangle \tag{17}$$

$$G^{220}(r) = g^{220}(r)/g^{000}(r) \sim \langle 3 \cdot \cos^2\Theta_{ij}(r) - 1 \rangle \tag{18}$$

$$G^{202}(r) = g^{202}(r)/g^{000}(r) \sim \langle 3 \cdot \cos^2\Theta_{ir}(r) - 1 \rangle \tag{19}$$

Θ_{ij} is the angle between the molecular axes and Θ_{ir} is the angle between one molecular axis and the vector connecting the centers of the pairs of molecules considered (see Figure 1). There exist some experimental means by which it is possible to obtain information on some of these correlation functions. These are for instance Neutron scattering using the isotropic substitution technique,[16] depolarized light scattering[17,18] and absolute small angle X-ray scattering.[19] These methods are, however, restricted to a limited range of scattering vectors and thus to a limited range of intermolecular distances. These and a large number of other methods, including electric or magnetic birefringence[20,21,22] or dielectric relaxation[23,24] are, however, able to yield information on orientational order parameters (so called pair correlation parameters), derived from correlation functions. They are defined by:

$$g_1 = 1 + \sum_{i,i \neq j}^{N} \langle \cos\Theta_{ij}(r) \rangle \approx \int_0^\infty G^{110}(r) \cdot r^2 \cdot dr \tag{20}$$

$$g_2 = 1 + (1/2) \cdot \sum_{i,i \neq j}^{N} \langle 3\cos^2\Theta_{ij}(r) - 1 \rangle \approx \int_0^\infty G^{220}(r) r^2 dr \tag{21}$$

They represent the spatial average of the correlation functions. They are small—of the order of 1—, if no short range order exists and they increase strongly as the correlation function becomes long ranged. We will use experimental results on some of these order parameters in order to gain insight into the orientational order.

METHODS OF ANALYSIS

The method which was primarily used to study short range orientational order in fluids was electric birefringence, yielding g_2. The apparatus consisted of an argon-ion-laser ($\lambda = 514.5$ nm) as the light source working in the "light control modus." The Kerr cell could be heated electrically up to 500 K. The temperature was controlled within 0.1 K. The optical path length of the Kerr cells used for studying liquid crystals was 3 to 6 mm; the distance between the brass electrodes was 1.6 mm. Linear detection including a quarter wave device was used for determining the induced birefringence. The polarizer was oriented at 45° with respect to the electric field; the analyzer was rotated precisely by a known fixed angle α relative to the direction of extinction. Using a photodiode in connection with a lock-in-amplifier we were able to detect a minimum birefringence of $\Delta n_0 = 10^{-10}$ in the case of static experiments. The applied electric fields were less than $2 \cdot 10^6$ V/m. Details of the experimental set-up were described previously.[25]

The birefringence induced by the electric field E_0 is proportional to the square of the electric field, provided that the electric field is not too strong ($E_0 \leqslant 10$ MV/m).

The Kerr constant B can—to a first approximation—be related to order parameters representing the short range order and to molecular data:[20,26]

$$B = [\Delta n_s/15\lambda kT][(\epsilon+2)^2/9] \cdot \{\Delta\alpha^E g_2 + (f \cdot \mu^2/kT) \cdot [2(g_1-1)+g_2]\} \quad (22)$$

g_1 and g_2 are the order parameters introduced above, λ is the wavelength of the light, ϵ the average static dielectric constant, μ the permanent electric dipole moment, $\Delta\alpha^E$ the anisotropy of the electric polarizability and f a factor describing the orientation of the permanent electric dipole relative to the long molecular axis. Δn_s is the saturation value of the birefringence for perfect orientation.

Information on g_1 (Kirkwood factor) is available from dielectric relaxation studies:[23,27]

$$g_1 = [9 \cdot (\epsilon - \epsilon^\infty) \cdot (2\epsilon + \epsilon^\infty) kT\epsilon_0] / [\epsilon \cdot \mu^2 \cdot (\epsilon^\infty + 2)^2 \cdot (N/V)] \quad (23)$$

$\epsilon^{\infty} \approx \bar{n}^2$ = mean dielectric constant in the high frequency limit

$\bar{n}$ = mean refractive index

ϵ_0 = influence constant

The mean static permittivity ϵ were measured at low frequencies (40...120 Hz) by using a "General Radio" bridge, as a function of the temperature in the vicinity of the phase transition to the isotropic phase. The mean refractive indices $\bar{n}$ were determined in a glass-wedge with known angle of aperture δ.

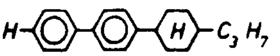
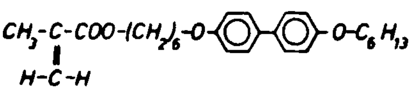
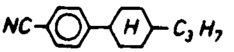
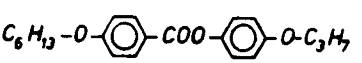
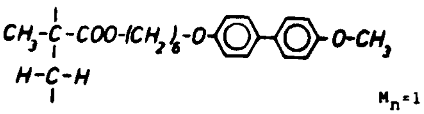
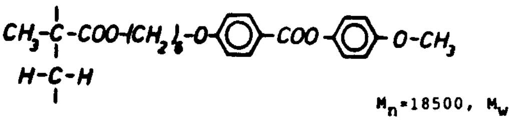
Molecular data ($\mu, \Delta\alpha^E \approx 1.1 \cdot \Delta\alpha^0$,[28] where $\Delta\alpha^0$ = anisotropy of optical polarizability) were obtained from the chemical structure of the molecules or the segments and based on results from the literature, as far as possible. In the case of polymeric liquid crystals, some birefringence studies on macroscopically well oriented samples were performed with a polarization microscope. From the results, conclusions on the anisotropy of the optical polarizability were drawn by using the well known Lorentz-Lorenz equation.[29] In the case of polymeric liquid crystals, we tried to orient the samples in the mesophase in a homogeneous magnetic field (B_m = 10 kG) to get an information on the anisotropy of permittivity $\Delta\epsilon$. Absolute small angle X-ray studies were performed to get additional informations on the positional and orientational short range order represented by $g^{101}(r)$ and $g^{202}(r)$. The method and the information accessible from it have been described in the literature.[19] The enthalpy change ΔH at the phase transition to the isotropic state was determined by calorimetry (DSC); a Perkin Elmer DSC 4 was used.

SAMPLES

We performed studies on low molecular weight as well as high molecular weight fluids, exhibiting either just an isotropic fluid state or exhibiting also an anisotropic fluid state. The samples studied as well as their transition temperatures are given in Table I. Some of the samples were commercially available (samples 1,3); other samples were provided by Prof. H. Ringsdorf, University of Mainz (sample 5) and Prof. H. Finkelmann, University of Freiburg (samples 2,4,6). We are grateful to Prof. H. Ringsdorf and Prof. H. Finkelmann for providing these samples to us. Results on other samples were taken from the literature or from our earlier results.[25,35]

TABLE I

Low and high molecular weight liquid crystalline samples studied (including transition temperatures)
(a)Ref.,[30,31] b)Ref.,[31,32] c)Ref.,[33] d)Ref.,[34] *) own GPC measurements)

	sample	temperatures in K
1.	BCH 30 	k 342.6 s 364.9 i a)
2.	BMA 66 (Monomer) 	k 352.4 s 355.4 i
3.	S 1103 PCH 	k 315.0 n 319.0 i b)
4.	PB 36 	k 345.0 n 353.6 i
5.	Polymer 1 (P1)  T_g = 358 c)	sc 390.2 lc, n 406.8 i M_n=11700, M_w=34000, U=1.85 *)
6.	Polymer 2 (P2)  T_g = 323 d)	n 386.4 i M_n=18500, M_w=85600, U=3.63 *)

(sc=semicrystalline, k=crystalline, s=smectic, n=nematic, lc=liquid crystalline, i=isotropic, T_g=glas transition temperature)

RESULTS ON LOW MOLECULAR WEIGHT FLUIDS

Data taken from the literature as well as results from our own studies were used to calculate the correlation parameters g_1 and g_2 as well as contributions of g^{101}, g^{202} to the total orientational order. The parameters are shown in Table II, which also contains information on the shape of the molecules as well as their dipolar properties. The

TABLE II

Molecular data and orientation correlation parameters g_2, g_2 for several isotropic fluids at room temperature ([a])Ref.,[36] [b])Ref.,[37] [c])Ref.,[38] [d])Ref.,[39,40] [e])Ref.,[17,41] [*])calculated from own results)

molecule	carbon-tetrachloride CCl_4	benzene C_6H_6	heptane C_7H_{16}	dodecane $C_{12}H_{26}$	carbon-disulfide CS_2	chloroform $CHCl_3$	nitro-benzene $C_6H_5NO_2$
shape	nearly spherical	disk-like	flexible short chain	flexible short chain	rigid rod		cylindrically
dimension	diameter D ≈ 6...7 Å	D ≈ 6...7 Å	length L≈8Å D ≈ 2 Å L/D ≈ 4	L ≈ 14 Å D ≈ 2 Å L/D ≈ 7	L ≈ 3 Å D≈1.5 Å L/D ≈ 2	D ≈ 6...8 Å	L ≈ 7..8 Å D ≈ 4 Å L/D ≈ 2
polarity	weakly polar	weakly polar	weakly polar	weakly polar	nonpolar	polar $\mu \approx 1$ D a)	strongly polar $\mu \approx 4.2$ D a)
remark						$\mu \perp$ axis of greatest α	$\mu \parallel$ axis of great. α
Kerr constant							
$B \cdot 10^{15} m/V^2$ (λ =514.5 nm)	+0.95 b)	+6.7 c)	+0.86	+1.47	+35.7 c)	- 36	+3400
g_1						1.55 *)	0.95 *)
g_2		0.8..1.0 d)	2.2 *)	1.6 *)	2.05 d)	1.63 *) 2 e)	1.9 *) 2.3 e)

α = polarizability

shape of the molecules considered here varies from nearly spherical symmetric (CCl_4) to elongated (CS_2) and disk-like (benzene). The rigidity was varied from non-rigid, flexible (n-alkanes) to very rigid (benzene) and the dipolar properties were varied from strongly dipolar (nitrobenzene) to very weakly dipolar (CCl_4) for different directions of the molecular dipole. The general result is that the short range orientational order, as expressed in g_1, g_2 and also g^{101}, g^{202} is very weak or even absent. Both g_1 and g_2 are of the order of 1 – 2.5 and g^{101}, g^{202} are zero. Dense packing can apparently be achieved even for nonspherical molecules without the formation of an extended orientational short range order. Long range order, as represented by S, is of course also absent.

RESULTS ON POLYMER MELTS

Data on the short range orientational order in the melt of flexible chain molecules are sparse. Results obtained for the correlation parameters g_1 and g_2 as well as for g^{101}, g^{202} are given in Table III. It is obvious, again, that the short range order is very weak. g_1 is about 1 or even below 1, indicative of a slight anticorrelation of the dipoles in the side chain (PMMA). g_2 is of the order of 2 to 7 and contributions of g^{101} and g^{202} to the total orientational order were found to be absent.[42] The observed values of g_2 have sucessfully been attributed to intramolecular correlations, resulting from restrictions of the angles between covalent bonds and of the rotation angles. Thus the conclusion was that the melt of flexible chain molecules is characterized by a weak short range intramolecular correlation and practically no intermolecular orientational order. The intramolecular correlations are known to increase strongly as the chains become more rigid.[45]

RESULTS ON LOW MOLECULAR WEIGHT LIQUID CRYSTALS

Smectogenic substances

First of all we will discuss results obtained for two substances which are able to exhibit a smectic phase and an isotropic phase. The two substances differ in molecular rigidity, dipolar structure and the nature of the mesogenic core (i.e. phenyl- versus cyclohexane-ring). The electrically induced birefringence for the two samples obeys the Kerr law, i.e. it is linear in E_0^2 in the isotropic melt.[43] The obtained

TABLE III

Pair correlation parameters g_1, g_2 for some flexible polymer chains ($^{a)}$Ref.,[42] $^{b)}$Ref.[43,44])

substance	g_1	g_2	measuring method
polystyrene (PS)	---	2 $^{a)}$ (300-430 K)	depol. light scattering
polycarbonate (PC)	---	7 $^{a)}$	depol. light scattering
poly(methylmethacrylate) (PMMA)$^{b)}$	0.3...0.9 (T = 300-410 K)	2.3...1.7	electrically induced birefringence

Kerr constants B are displayed in Figure 2. The sign of B of the two substances is different, due to their dipolar structure. The dipole is parallel to the long axis of the molecule in the case of BCH 30 and about perpendicular to the long axes of the molecule for BMA 66. Based on these results and results obtained for the number density, the refractive index and the dielectric constant, displayed in Table IV, we were able to calculate the correlation parameters g_1 and g_2. These values are also displayed in Table IV for different temperatures in the vicinity of the phase transition. It is obvious that the dipolar correlation, represented by g_1 is rather weak, BCH 30 actually shows some degree of anticorrelation. The values of g_2 are surprisingly large, particular for the molecule of BCH 30. In addition a rather strong temperature dependence of g_2 is obvious. One is tempted to represent these results in terms of a Landau theory, characteristic of the nematic-isotropic transition, which will be discussed below.

According to this treatment, B^{-1} should be a linear function of the temperature T; i.e. B should vary according to $(T - T^*)^{-1}$, where T^* is a hypothetical transition temperature of a second order phase transition.[10] Therefore a critical increase of the orientation correlation parameter g_2 must be observable as the temperature is lowered. As can be seen from Figure 2, this behaviour does not hold in the case of these samples and the temperature region studied. A significant curvature is detectable in our experimental results.

The conclusion is that BCH 30 exhibits an extended short range order, characterized by a parallel arrangement of the long axes with an antiparallel correlation of the dipolar axes. BMA 66 shows a

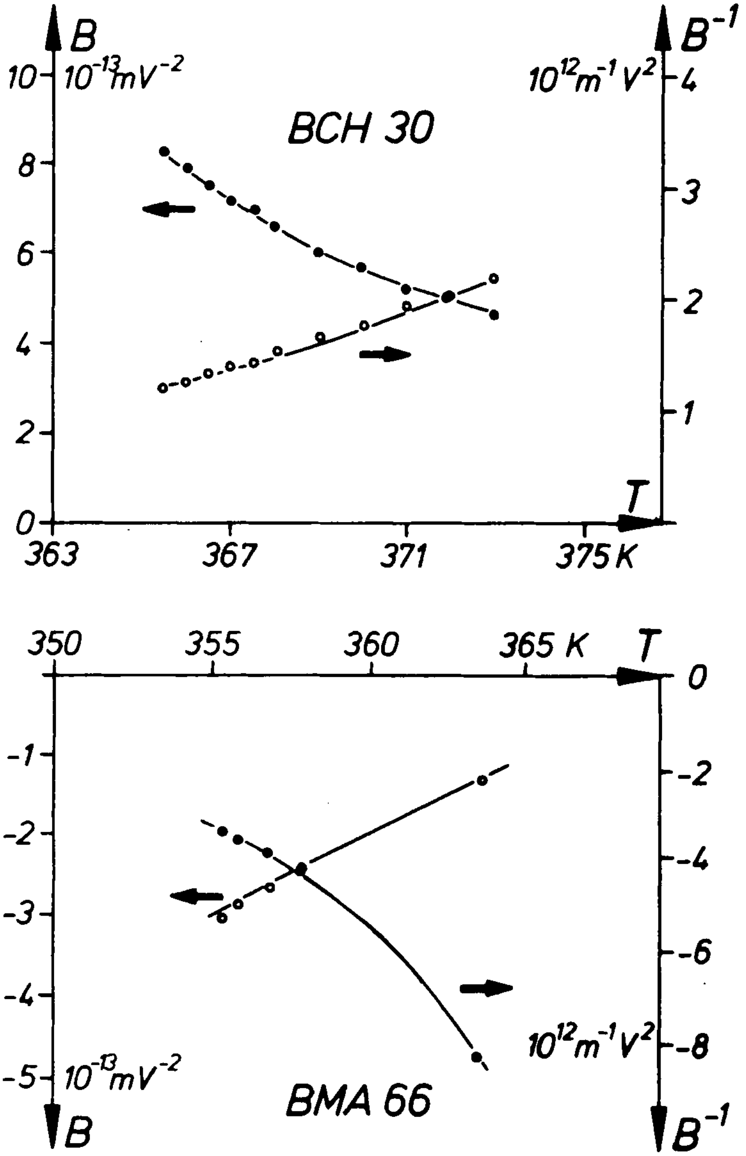


FIGURE 2 Kerr constants B and B^{-1} for BCH 30 and BMA 66 versus temperature T (λ = 514.5 nm).

TABLE IV

Molecular data and orientational correlation parameters g_1, g_2 for two low molecular weight samples showing an isotropic-smectic phase transition (${}^{a)}$Ref.,[30] ${}^{b)}$Ref.,[46] ${}^{*)}$ values assumed to be identical with those of the monomer unit of *P*1 (see Tables I,VI))

sample	BCH 30 (T=366 K)	BMA 66 (T=360 K)
N/V (m^{-3})	$2.17 \cdot 10^{27}$	$1.51 \cdot 10^{27}$
$\bar{n}$	1.55	1.56
ε	2.62 (40 Hz)	4.32 (40Hz)
μ (D)	1.05 ${}^{a)}$	2.4 ${}^{b)}$
$\Delta\alpha^{E} \cdot 10^{39}$ (Fm^2)	2.5	2.31 ${}^{*)}$
Δn_s	0.18	0.20 ${}^{*)}$
g_1	0.50 (T=366K)	1.45 (T=360K)
g_2	15 (T=365.5K)	6 (T=355.6K)
	14 (T=366.0K)	5 (T=356.5K)
	12 (T=367.0K)	4 (T=358.5K)
	10 (T=370.0K)	3 (T=362.5K)
	8 (T=375.0K)	2 (T=365.5K)

weaker correlation of the molecular long axes but a weak correlation of the dipoles, which are oriented perpendicular to the long axes. We have found, in general, that smectic phases are characterized by correlation functions g^{101}, g^{202} which have nonzero values, indicative of a correlation between the orientation of the intermolecular center-center-vector and the molecular long axis.[47]

Nematogenic substances

Next we will discuss some of our own results on low molecular weight liquid crystals, showing an isotropic-nematic transition. The measurements were performed, as described earlier. As expected, the induced birefringence was found to depend quadratically on the applied electric field E_0 in the whole temperature range studied $(T_{NI} + 32\ K) \geq T \geq T_{NI}$. The temperature dependence of the Kerr constants *B* for *S* 1103 PCH and PB 36 is shown in Figure 3. The

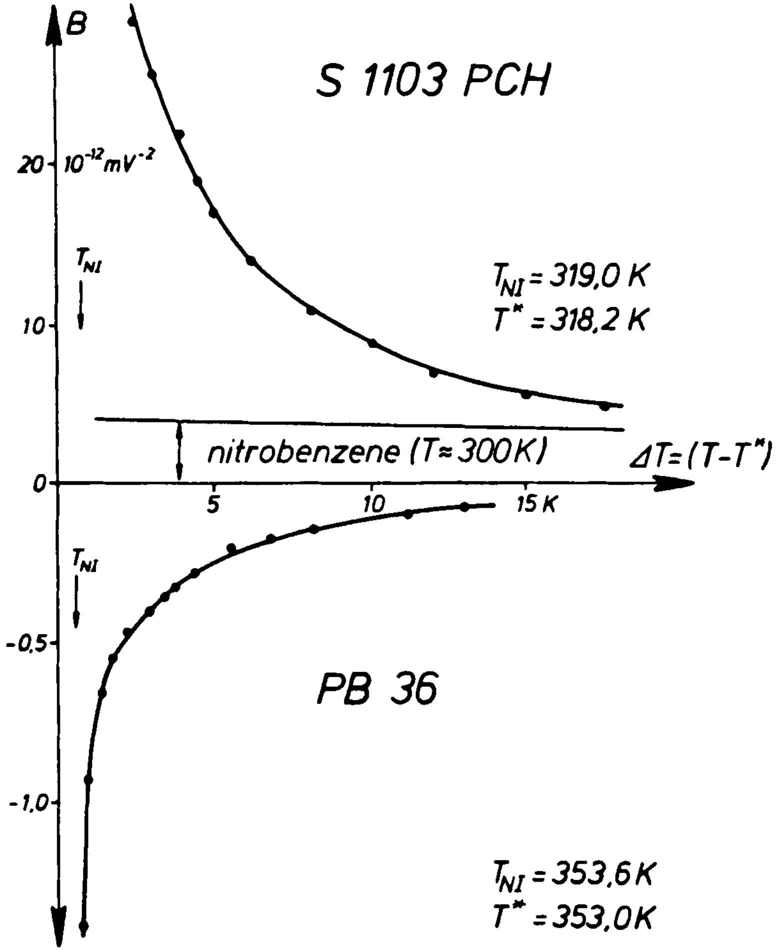


FIGURE 3 Kerr constants B for S 1103 PCH and PB 36 versus the temperature distance ΔT from the extrapolated fictive second order phase transition temperature T^* (λ = 514.5 nm).

Kerr constants of both materials were found to increase strongly with decreasing temperature. A plot of B^{-1} versus T yielded a straight line, which could be used to extrapolate a fictive temperature T^* at which B becomes infinite. This behaviour is well documented in the literature.[10,20,48] The explanation is that the phase transition at the temperature T_{NI} is only weakly first order and shows some features which are characteristic of a second order phase transition happening at T^*. We found T^* to be about 1 K below T_{NI} in this case. Based on a Landau-de Gennes treatment of this phase transition the electrically induced long range order is predicted to be

$$S_E = (\Delta\epsilon_s \cdot \epsilon_0 \cdot E_0^2) / [3 \cdot a_0 \cdot (T - T^*)] \tag{24}$$

and the induced birefringence is predicted to be

$$\begin{aligned}\Delta n_0 &= [g_2 \cdot \Delta n_s \cdot \Delta\epsilon_s \cdot \epsilon_0 \cdot (\bar{n}^2+2)^2 \cdot E_0^2] / [135(N/V)kT] \\ &= (\Delta n_s \cdot \Delta\epsilon_s \cdot \epsilon_0 \cdot E_0^2) / [3a_0(T - T^*)] \end{aligned} \tag{25}$$

where a_0 is an expansion coefficient of the free energy of the system with respect to the order parameter S:

$$F(T) = F_0 + (1/2)a_0 \cdot (T - T^*)^{\gamma} \cdot S^2 - (b/3) \cdot S^3 + (c/4) \cdot S^4 + \ldots \tag{26}$$

a_0, b, c being the Landau coefficients

γ = critical exponent, which takes a value of 1 in any mean field treatment

F_0 = free energy of the system in the isotropic phase ($S=0$)

The prediction of this theory is that the orientation fluctuations represented by $g^{220}(r)$ become long ranged and that g_2 consequently diverges as[20]

$$g_2 = [45 \cdot (N/V) \cdot kT] / [a_0 \cdot (T - T^*) \cdot (\bar{n}^2 + 2)^2] \tag{27}$$

as the temperature T^* is approached. The results obtained for g_2 are shown in Figure 4. As can be seen, g_2 actually increases strongly with decreasing temperature and approaches values above 100 close to the temperature T_{NI}. Based on the values for the refractive index, the dielectric constant etc. shown in Table V we were able to calculate also g_1 and the Landau coefficients. It is obvious that g_2 diverges whereas g_1 remains small as the temperature is lowered. Thus the conclusion is that the long axes of the molecules becomes more or less parallel within rather large correlation volumes whereas the dipolar correlation stays weak and short ranged. Again an anticorrelation is observed for molecules for which the dipole points in the direction of the long axis and a weak correlation for molecules for which the dipole is located about perpendicular to the long axis. Table V contains additional data taken from the literature which agree with the results discussed here. Thus the influence of molecular structure

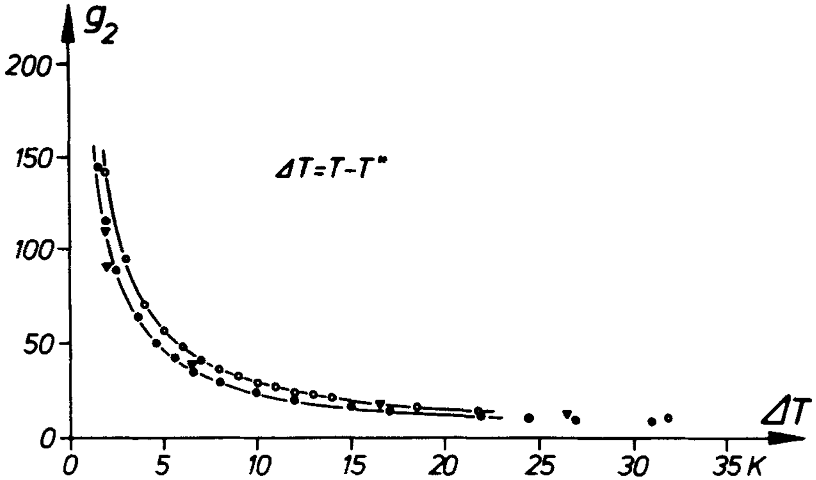


FIGURE 4 Pair correlation parameter g_2 versus $\Delta T = (T - T^*)$ for low molecular weight liquid crystals (○ S 1103 PCH, ● PB 36, ▼ MBBA,[20,49,50] ▽ 5-cyanobiphenyl[51,52]).

and rigidity on g_2 seems to be small whereas the dipolar structure seems to influence g_1 to a certain degree. We showed in previous studies that g^{101} and g^{202} contribute heavily to the orientational order of those substances in the isotropic phase which are able to exhibit nematic phases.[19]

We concluded that a correlation exists for the angle Θ_{ir} between the vector connecting the centers of pairs of molecules and the direction of the reference molecular long axis. This correlation increases with decreasing temperature but stays continuous at the temperature T^*. No information was available on the particular interactions responsible for this type of short range orientational order.

RESULTS ON POLYMERIC LIQUID CRYSTALS

In the following we want to present results on polymeric side chain liquid crystals. After a careful preparation, the electrically induced birefringence Δn_0 could be measured in a wide temperature range within the isotropic melt. The Kerr law was found to be valid as in the case of low molecular weight samples.[43] Figure 5 shows a plot of the Kerr constants B and the inverse Kerr constants as a function of the temperature T. The sign of B is negative for both samples, as expected, because of their dipolar structure (see Table I). A linear

TABLE V

Molecular data, pair correlation parameters g_1, g_2 and Landau coefficients for some low molecular weight liquid crystals showing an isotropic-nematic phase transition (MBBA = p-methoxybenzylidene-p-butylaniline, n-CB = C_nH_{2n+1}-cyanobiphenyl homologues a)Ref.,[32] b)Ref.,[31] c)Ref.,[36] d)Ref.,[46] e)Ref.,[23,24] f)Ref.,[20,24] g)Ref.,[24] h)Ref.,[20,49,50] i)Ref.,[51,52] j)Ref.[22] values in Jcm^{-3}K^{-1}, Jcm,$^{-3}$ k)Ref.[51] values in Jcm^{-3}K^{-1}, Jcm^{-3}, l)Ref.,[51] *)values assumed to be identical with the monomer unit of *P*2, see tables I, VI)

sample	S1103 PCH	PB 36	MBBA	5-CB	7-CB
N/V (m^{-3})	$2.76 \cdot 10^{27}$ (T=323K) a)	$2.1 \cdot 10^{27}$ (T=356 K)			
$\bar{n}$	1.498	1.512			
ε	9.83 b)	4.56 *)			
μ (D)	4.2 c)	2 d)			
$\Delta\alpha^E \cdot 10^{39}$ Fm^2	0.69	1.72			
Δn_s	0.13 b)	0.25 *)			
g_1	0.62 (T=323K)	1.35 (T=363K)	0.74 e) (T=T_{NI})	0.45..0.57 (T=T_{NI}) f)	0.43..0.54 (T=T_{NI}) g)
g_2	see fig.4	see fig.4	110 h) (T=T_{NI})	90 i) (T=T_{NI})	
a_o (J/grK)	0.103	0.139	0.062 j)	0.13 k)	0.21 k)
b (J/gr)	0.562	0.36	0.47 j)	1.6 k)	3.3 k)
c (J/gr)	0.851	0.545	0.79 j)	3.9 k)	8.1 k)
ΔH_{NI} (J/gr)	3.18	3.01	1.6 j)	1.41 l)	2.41 l)

variation of B^{-1} with the temperature T is observed similar to the case of low molecular weight nematic systems. The deviations of B^{-1} versus T from the straight line behaviour at higher temperatures are probably due to experimental errors, because of the relatively small values of the Kerr constants in this temperature region. This plot allowed to determine the fictive temperature T^*. It was found to be about 1 K below the actual transition temperature T_{NI}. Based on our experimental results on molecular parameters such as refractive in-

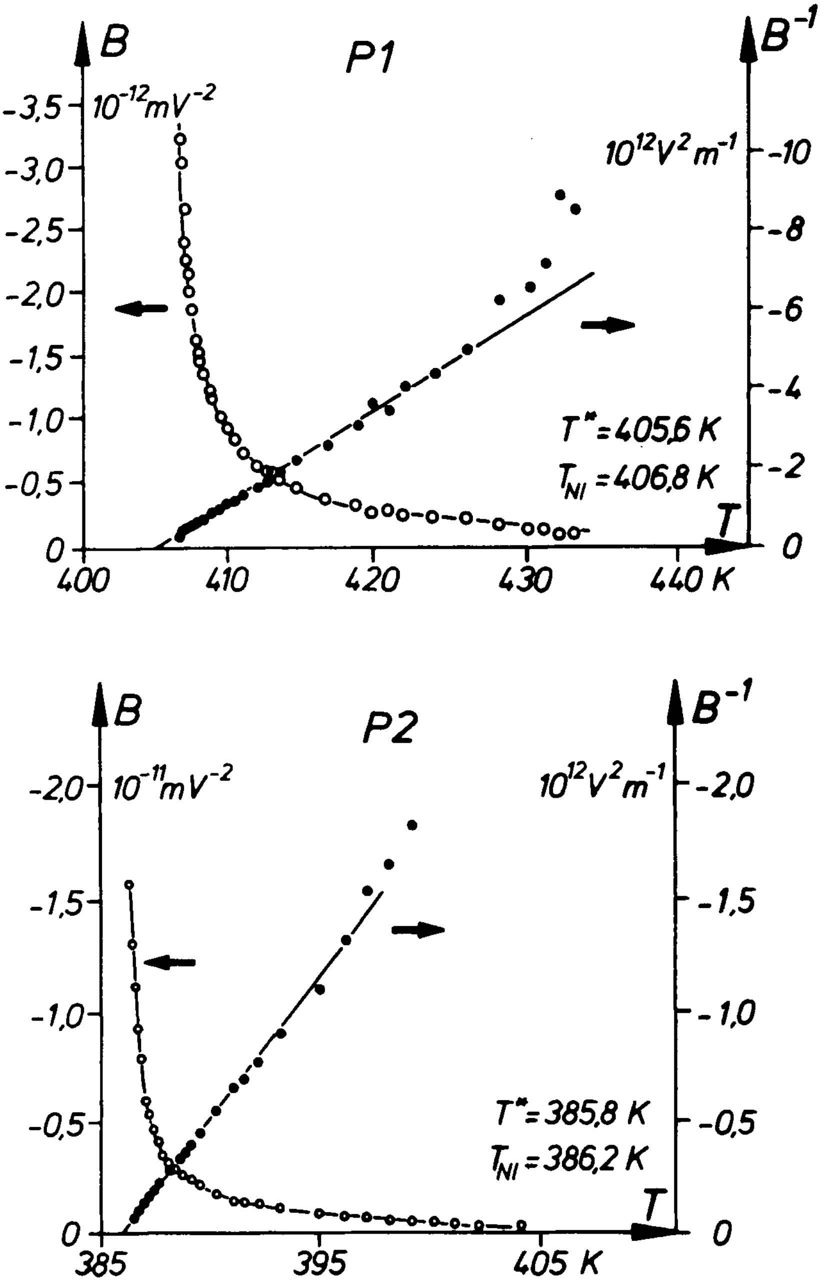


FIGURE 5 Kerr constants B and inverse Kerr constants B^{-1} versus temperature T for the two liquid crystalline side chain polymers $P1$, $P2$ (λ = 514.5 nm).

dex, dielectric constant etc. (see Table VI), data for g_1 and the Landau coefficients on *P*1 and *P*2 could be obtained. They are also displayed in Table VI.

It has to be pointed out that the sample *P*1 could not be oriented at temperatures just below T_{NI} in a magnetic field of 10 kG; therefore no experimental result on $\Delta\epsilon$ was available. From the $B(T)$ curve, a value of $\Delta\epsilon_s = -0.8$ ($T = 402$ K) was calculated assuming a nematic order parameter of $S = 0.4$ at this temperature. ΔS_{NI} in both polymeric samples is taken to be 0.35.[54] The best fit of the Kerr effect data yields a permanent dipole moment of $\mu = 2.7$ D for the monomer unit of the sample *P*2. The anisotropy of the permittivity $\Delta\epsilon$ could

TABLE VI

Molecular data, pair correlation parameter g_1 and Landau coefficients for two polymeric side chain liquid crystals ([a]Ref.,[53] [b]Ref.,[34] [c]Ref.[46])

sample	Polymer 1 (P1) (T=410 K)	Polymer 2 (P2) (T=387 K)
N/V (m^{-3})	$1.8 \cdot 10^{27}$ a)	$1.68 \cdot 10^{27}$ b)
$\bar{n}$	1.56	1.53
ϵ	4.6	4.56
μ (D)	2.4 c)	2.7 c)
$\Delta\alpha^E \cdot 10^{39}$ (Fm^2)	2.31	3.08
Δn_s	0.2 (S=0.4)	0.25 (S=0.4)
g_1	1.05 (T=408 K)	0.93 (T= 388 K)
ΔH_{NI} (J/gr)	3.7	2.8
$\Delta\epsilon_s$	-0.8 (calculated)	-1.1 (T=384 K)
a_0 (J/grK)	0.15	0.113
b (J/gr)	1.52	0.7
c (J/gr)	2.91	1.39

be measured in this case. It was found to be negative in accordance with the Kerr effect data.[43] The correlation parameters g_2 for these polymeric samples were determined according to equation 27; the results are shown in Figure 6. The values are somewhat smaller than the values obtained for low molecular weight liquid crystals.

It seems probable that the overall correlation is weaker than in the case of low molecular weight liquid crystals since the rigid core and the flexible spacer groups of the side chains exhibit different correlations. It was shown, for instance, that the order parameter of the core is much larger than that of the spacer groups in the nematic phase for similar side chain liquid crystals.[55] This may lead to the decrease of g_2 observed here. It seems furthermore highly probable that the orientation correlations are disturbed by the coupling of side chains to the main chain, which has the shape of a random coil and that the disturbance is expressed more strongly in the spacer group. The intramolecular correlation observed for the pure main chain (PMMA) apparently does not contribute to the total short range order in the sense that it increases g_2 over the value due to independent side chains. This is also indicative from the correlation parameter g_1 which show an absence of correlation ($g_1 \approx 1$) as indicated in Table VI.

It should be emphasized that in the case of polymer 1 other authors propose only one mesophase (a smectic) for this polymeric liquid

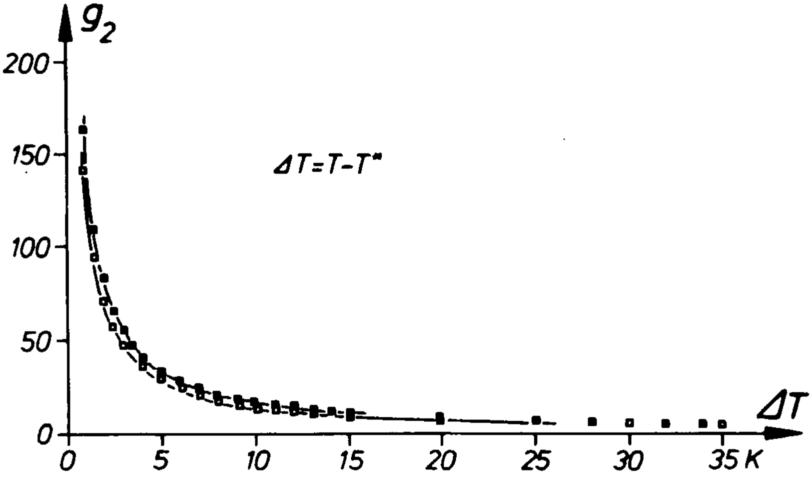


FIGURE 6 Pair correlation parameter g_2 versus $\Delta T = (T - T^*)$ for two liquid crystalline side chain polymers (□ $P1$, ■ $P2$).

crystal.[56] If one analyzes, however, the transition liquid crystal-isotropic in a DSC calorimeter very carefully, one is able to detect at least three or four transitions within a temperature range of about 5 K. Furthermore, one observes under the polarization microscope several changes of the texture in this temperature range. The Kerr effect studies show, without any doubt, that the high temperature mesophase is a nematic one. We therefore decomposed the total phase transition peak into different components and used only the upper temperature peak for calculating the change of enthalpy ΔH_{NI}.

The results presented above and additional results obtained from calorimetric studies and NMR studies[55] allow us to obtain the coefficients of the Landau expansion (equ. 26). Table V and VI compare the coefficients obtained for the liquid crystalline polymers with those of low molecular weight liquid crystals. It is obvious that the values are similar. The thermodynamic potential is thus not influenced to a considerable degree by attaching the mesogenic groups to a flexible main chain.

A peculiar behaviour was observed for the liquid crystalline polymer *P*2. The Kerr constant was found to increase by a factor of about 6 if the sample was kept at elevated temperatures in the isotropic fluid state. In addition we found that the Kerr constant did not longer diverge as the temperature was lowered towards the isotropic-nematic phase transition. A peculiar behaviour became also apparent in the dynamic properties, since the Kerr relaxation times increased with annealing time at constant temperature.[43] Furthermore, the transients for rise and decay of the induced birefringence became asymmetric. These findings seem to indicate changes in orientational correlations as well as in reorientation dynamics. The changes in the dynamical properties can be rationalized in terms of a rotational diffusion, characteristic of strongly dielectric positive substances.[29] The Kerr effect is governed, in this case, by the dipolar structure. Results on the ratio of the areas enclosed by the rise and decay curves as well as results obtained for sign reversal of the applied electric field agree with this interpretation. We currently attribute this behaviour to some kind of aggregation developing in the melt. This aggregation has already been described in the literature and a structural model has been proposed.[57] Our results are consistent with a model, proposing that the total aggregate has an effective dipole moment which orients parallel to the applied electric field and that the aggregate has its major axis of polarizability perpendicular to the direction of the effective dipole.

The observation that the Kerr constant does not diverge, approaching the calorimetrically obtained phase transition temperature

T_{NI}, is surprising. One possible interpretation is that the critical exponent γ is much less than 1. Critical exponents of $\gamma \approx (0.5 \ldots 0.7)$ have been reported for systems with strong dipole-dipole interactions[58] and strong positive dielectric anisotropy.[59]

CONCLUSIONS

1. The short range orientational order was found to be weak in low molecular weight isotropic fluids and the melts of flexible chain molecules, provided that no low temperature liquid crystal phase was present. The short range order did not depend strongly on molecular shape and dipolar interactions.

2. The short range order was found to become strong and spatially extended within the isotropic melt if a nematic phase was approached and to a much lesser degree if a smectic phase was approached. Low molecular weight and polymeric substances were found to display a similar orientational order.

3. A particular polymeric liquid crystal was observed to change its orientational order in the melt as a function of the annealing time. This behaviour was attributed to aggregation effects.

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