

This article was downloaded by:

On: 26 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Liquid Crystals

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713926090>

Supramolecular self organization via molecular aggregation. Non-discotic three chain diols displaying a hexagonal columnar phase

M. Ebert^a; R. Kleppinger^a; M. Soliman^a; M. Wolf^a; J. H. Wendorff^b; G. Lattermann^b; G. Stauer^b

^a Deutsches Kunststoff-Institut, Darmstadt, F. R. Germany ^b Makromolekulare Chemie I, Sonderforschungsbereich SFB 213, Universität Bayreuth, Bayreuth, F. R. Germany

To cite this Article Ebert, M. , Kleppinger, R. , Soliman, M. , Wolf, M. , Wendorff, J. H. , Lattermann, G. and Stauer, G.(1990) 'Supramolecular self organization via molecular aggregation. Non-discotic three chain diols displaying a hexagonal columnar phase', *Liquid Crystals*, 7: 4, 553 – 570

To link to this Article: DOI: 10.1080/02678299008033832

URL: <http://dx.doi.org/10.1080/02678299008033832>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Supramolecular self organization via molecular aggregation Non-discotic three chain diols displaying a hexagonal columnar phase

by M. EBERT, R. KLEPPINGER, M. SOLIMAN, M. WOLF, and
J. H. WENDORFF

Deutsches Kunststoff-Institut, D-6100 Darmstadt, F.R. Germany

G. LATTERMANN and G. STAUFER

Makromolekulare Chemie I, Sonderforschungsbereich SFB 213, Universität
Bayreuth, D-8580 Bayreuth, F.R. Germany

(Received 4 April 1989; accepted 2 November 1989)

A new class of mesogen formed by three chain diols is described. These compounds consist of a central part to which three aliphatic chains of various length ($n = 4-14$) are attached at one end and two hydroxy groups at the other. X-ray scattering, dilatometric measurements, dielectric and Kerr relaxation studies were carried out. Both X-ray investigations, dielectric and electro-optic studies revealed that the molecules are aggregated in the isotropic fluid state and that hydrogen bonding and dipole correlation contribute to this aggregation. Columnar assemblies of up to several hundred molecules are orientationally correlated in the isotropic fluid phase. Correlated reorientations occur in the presence of external electric fields. The X-ray data show that the aggregates pack in a hexagonal way at lower temperatures giving a structure which strongly resembles that of the hexagonal disordered columnar phase. This anisotropic phase can be quenched to a glassy liquid-crystalline state. It is evident that the mesogenic properties of this new class of compounds are a function of the disc-like shape of the aggregates rather than the shapes of the individual molecules.

1. Introduction

This paper describes the formation of a columnar mesophase by compounds which, as judged from the shape of the individual molecules, would not be expected to have mesogenic properties. This new type of mesogen carries three aliphatic chains at one end of a central core and two OH groups at the other [1, 2]. The aliphatic chains of the compounds contain between 4 and 14 carbon atoms. These compounds apparently form disc-like entities due to molecular aggregation and these disc-like entities in turn aggregate to form a columnar mesophase. This is a rather unusual mesogenic behaviour. The general observation is that mesogenic molecules are either rod-like (calamitics) or disc-like (discotics) [3-7]. However, other shapes such as pyramidal, board-like or biforked mesogens may give rise to the formation of other types of liquid-crystalline phases [8-10]. In most liquid-crystalline systems it is predominantly the molecular shape which determines which kind of liquid-crystalline phase is formed.

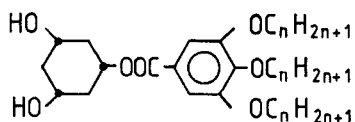
The formation of order in the fluid state may, however, also be controlled by intermolecular aggregation due either to microphase separation or due to the presence of specific interactions between the molecules. An example is the so-called phasmids [11-13] where a rod-like aromatic core is substituted at each end by three aliphatic

chains. Microphase separation is known to control, for instance, the formation of order in micellar systems or in block copolymers [14, 15]. The role of specific interactions between local sites along the molecules in the formation of liquid-crystalline structures has only been recognized more recently. Molecules carrying strong longitudinal dipoles, for instance, have been found to display several different smectic A phases characterized by the presence of single layers, bilayers, partial bilayers etc, to form in some cases antiphases resulting from the incommensurability of the single molecule and the pair length and to exhibit in other cases reentrant phases again due to the possibility of pair formation [16, 17]. Another example for intermolecular forces causing thermotropic liquid-crystalline phases are the ionic interactions in alkali [18] and thallium salts [19] of aliphatic carboxylic acids and in long chain ammonium salts [20]. Examples are further known where charge transfer interactions form dimeric rod-like mesogens [21, 22]. Hydrogen bonding is known to be responsible for the formation of rod-like dimers of benzoic acid derivatives [23], and in numerous cases for smectic A bilayer phases in carbohydrates [24], related compounds [25] and aliphatic diols [26].

The liquid-crystalline structure formation based on molecular aggregation described in this paper differs from the previous cases in that the individual molecules do not possess mesogenic shapes such as rod-like or disc-like shapes but rather approximately triangular shapes if the aliphatic chains are confined to a plane or approximately cone-like shapes if the chains are not confined to a plane. We will give evidence here which is in favour of a model according to which the planar triangularly shaped molecules form disc-like aggregates which in turn form a columnar hexagonal structure. These systems thus resemble the disc-like dimers of the diisobutylsilandiols [27] where the appearance of the individual molecules does not suggest mesogenic properties and where the hydrogen-bonded disc-like dimers stack to form a hexagonal columnar mesophase. X-ray scattering results, results obtained on the dielectric relaxation behaviour, on the electro-optical properties, on thermodynamic properties and finally on the density as a function of the length of the aliphatic chains will be analyzed with respect to the self organization process taking place in this new type of mesogen.

2. Experimental

The diols studied here have the general structure shown in figure 1 and the synthesis of these materials has been described earlier [1, 2]. Calorimetric analysis was performed by means of a Perkin Elmer DSC 4 and the volumetric analysis with a mercury filled glass dilatometer. The X-ray data were obtained by means of a Siemens wide angle diffractometer and a Kratky small angle compact camera, using a position sensitive detector. Both set-ups were equipped with a thermostated sample cell. Flat film cameras were used for oriented samples. The electro-optic results



$$n = 4 - 14$$

Figure 1. Molecular formula of the diols investigated.

(Kerr results) were obtained with the experimental arrangement described previously [28, 29]. An electric field was applied to the isotropic fluid and the induced optical birefringence was monitored as a function of the temperature and the magnitude of the applied field. The dielectric relaxation studies were performed with a Hewlett Packard automatic bridge (Impedance Analyzer HP 4192).

Additional information on the conformation of the individual diol molecules as well as on their aggregation was derived from molecular dynamics calculations. A conjugate gradient minimizing program was used to obtain the configurations [30]. These configurations were subsequently passed to a molecular dynamics program, performing the calculations at constant temperature. We had to introduce distance constraints in order to be able to analyse the aggregate structure. The hydroxy groups were forced towards each other by attaching a harmonic potential to the hydroxy groups one at a time. This gave rise to a fairly mobile aggregate without leading to problems arising from the use of periodic boundary conditions. These have the tendency to induce the formation of crystalline arrangements. The aliphatic chains were ignored to simplify most of the calculations, only one capping CH_3 remained as far as the aggregates are concerned. Single molecules were analysed for the case that the aliphatic chain consisted of 12 CH_2 -units.

3. Results and discussions

3.1. Thermodynamic properties

Water plays an important thermodynamic and structural role in the systems described here. This paper will only be concerned with the behaviour of dry samples. A detailed analysis of the thermal behaviour, including the influence of water, will be described elsewhere [31].

Figure 2 shows as an example the DSC heating curve of the diol with $n = 8$. A glass transition as well as a first order phase transition from the liquid-crystalline to the isotropic fluid state are apparent. Similar behaviour was found for all compounds except for the diols with a chain length larger than 10 for which no glass transition could be detected. The dependence of the glass transition temperature, the melting point, and the clearing temperature on the alkyl chain length is shown in figure 3. It is apparent that the glass transition temperature is more or less independent of the chain length n . The crystal melting temperature is relatively high for the $n = 4$ compound (85°C) and assumes an approximately constant value of the order of 40°C for larger values of n . The clearing temperature displays the strongest dependence on the chain length. It varies by as much as 50 K. The liquid-crystalline-isotropic transition temperature increases with increasing chain length, the transition becomes enantiotropic for $n > 6$ and the transition temperature decreases again slightly with increasing $n > 9$.

The transition temperature, enthalpies and entropies are listed in table 1. The enthalpies of the liquid-crystalline-isotropic transition vary approximately between 0.1 kJ/mole and 2 kJ/mole. They are comparable with values found for calamitic or discotic thermotropic systems [32]. The transition enthalpies and entropies increase rather strongly with increasing chain length for smaller values and stay nearly constant for larger values of the chain length. This result taken with the rather low absolute value of the latent heats and entropies strongly suggests that the transition to the isotropic phase is not predominantly controlled by an appreciable disordering of the aliphatic chains beyond that which has already taken place at the crystalline-liquid-crystalline transition.

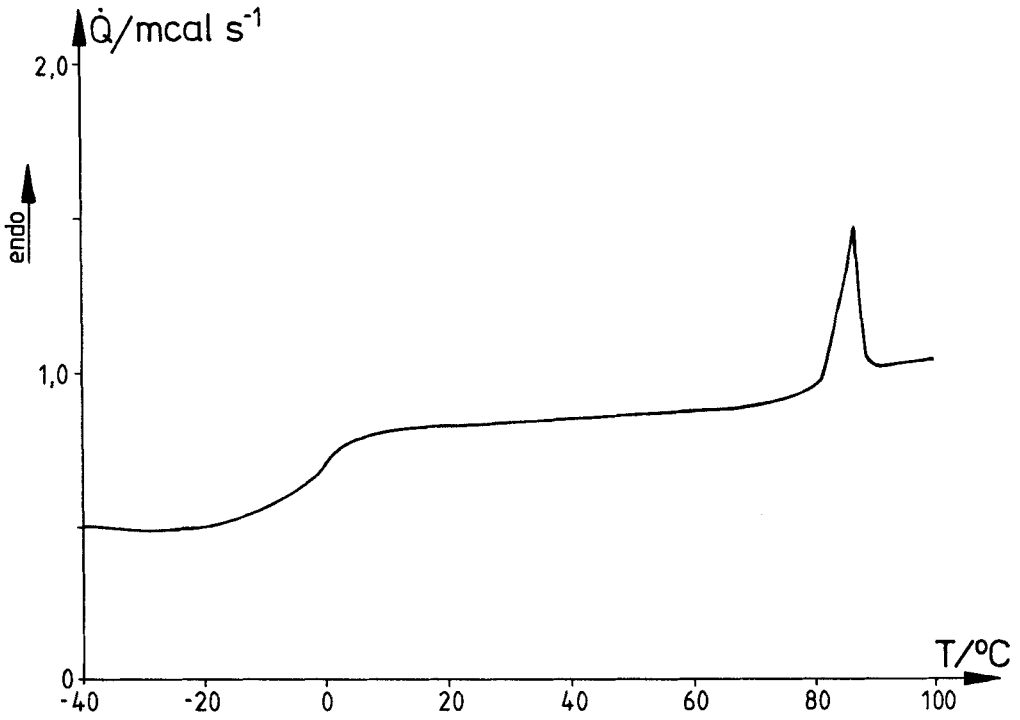


Figure 2. DSC heating curve (20 K/min) for the $n = 8$ diol.

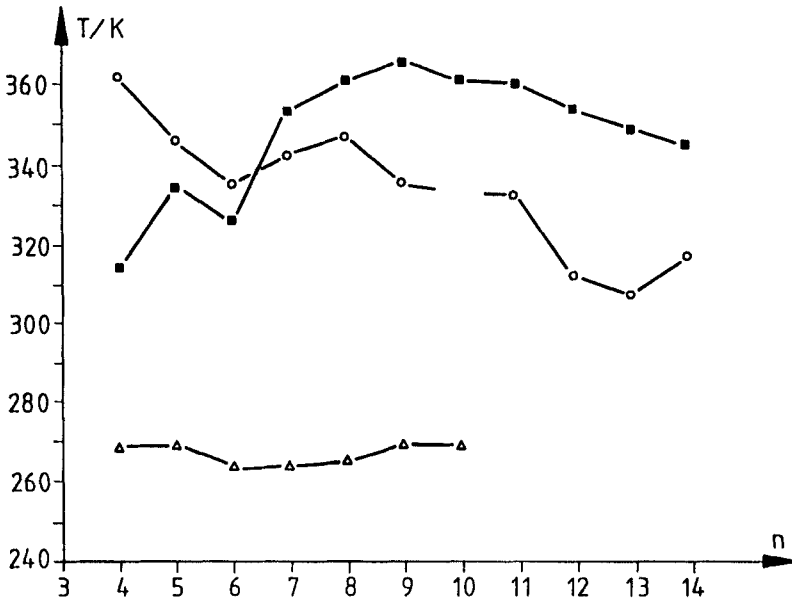


Figure 3. Dependence of the transition temperatures on the chain length n (Δ : glass transition temperature, \circ : crystal melting temperature, \blacksquare : clearing temperature).

Table 1. Dependence of the transition temperatures, enthalpies and entropies on the chain length n of the diols ($n = 4-14$); T_g : glass transition temperature, ΔC_p : increase of the molar heat capacity at the glass transition, T_{lei} : clearing temperature, ΔH_{lei} : enthalpy of the liquid-crystalline-isotropic transition, ΔS_{lei} : entropy of the liquid-crystalline-isotropic transition.

n	T_g/K	$\Delta C_p/JK^{-1} \text{ mol}^{-1}$	T_{lei}/K	$\Delta H_{lei}/kJ \text{ mol}^{-1}$	$\Delta S_{lei}/JK^{-1} \text{ mol}^{-1}$
4	270	208	315	0.1	0.4
5	271	103	335	0.8	2.5
6	265	67	326	0.6	1.9
7	266	253	353	1.4	4.0
8	267	261	360	1.6	4.4
9	271	260	365	1.5	4.2
10	271		360	1.6	4.4
11			359	1.4	3.8
12			353	1.2	3.4
13			348	1.6	4.7
14			344	2.0	5.7

Table 1 also shows the stepwise increase of the specific heat at the glass transition. Variations of the order of four are apparent. The absolute value is similar to that reported for low molar mass and polymeric liquid crystals [32]. In addition to the calorimetric properties the specific volumes of the compounds were investigated from room temperature up to the isotropic fluid state. A typical example is shown in figure 4 for the diol with n of 8. The specific volume displays an increase at the melting transition indicative of a first order phase transition. A second very weak increase which is hardly noticeable in figure 4 takes place at the clearing point. The specific volume at room temperature is of the order of $1 \text{ cm}^3/\text{g}$ and the increase at the transition into the liquid-crystalline state is of the order of 4 per cent, as apparent from figure 4. This is a typical value for the crystal melting transition. The specific

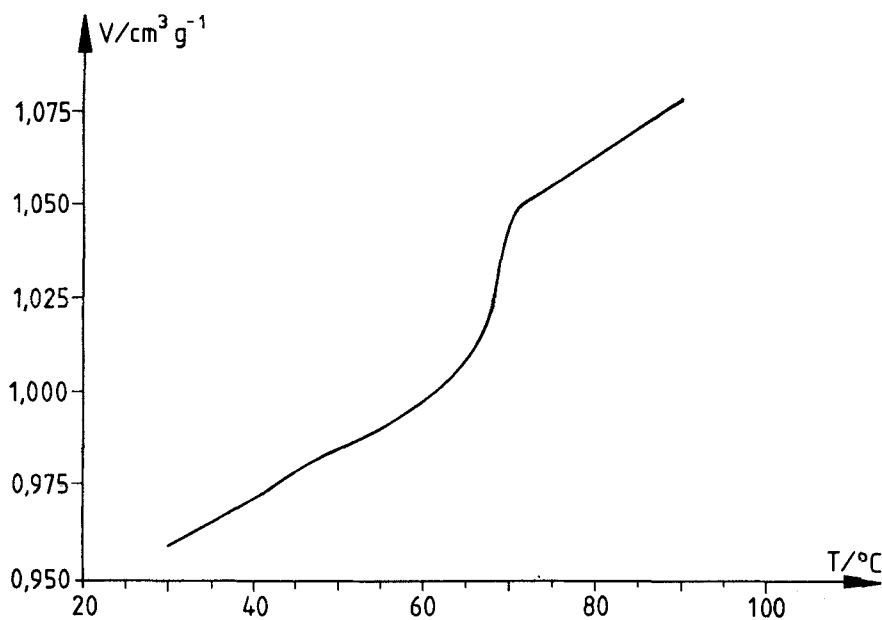


Figure 4. Variation of the specific volume of the $n = 8$ diol with temperature.

volume increase accompanying the anisotropic to isotropic fluid transition, about 0.1 per cent, is lower, by more than an order of magnitude, again in agreement with similar values found for calamitic and discotic systems [4]. Similar results were obtained for all of the compounds.

3.2. X-ray studies

The X-ray patterns were obtained both in the small angle and in the wide angle region on macroscopically isotropic samples. In addition, studies were performed on macroscopically oriented samples in glass capillaries. The orientation was induced by surface interaction and improved by annealing. To start with the results obtained for oriented samples within the liquid-crystalline phase will be discussed. The samples display a two dimensional hexagonal structure as is apparent from figure 5. It appears that the scattering pattern results from a single mono-domain displaying a sixfold symmetry. The hexagonal lattice spacing is definitely larger (by a factor of approximately 1.5) than the length of the individual molecules. This must indicate some type of molecular aggregation. IR spectroscopic results which indicate the occurrence of hydrogen bonding [1] agree with this interpretation. The hexagonal structure rules out simple pairing of molecules as in the case of rod-like mesogens carrying strong longitudinal dipoles. It is indicative rather of the formation of aggregates having, for instance, a cylindrical symmetry. These aggregates are the basic units forming a hexagonal lattice. The hexagonal packing is evident also from X-ray results obtained on macroscopically isotropic samples. We find an amorphous halo in the wide angle scattering region, a very prominent sharp reflection with two additional weak reflections in the small angle region as far as the compounds with a chain length larger than four are concerned. The diol with n of 4 has only one small angle reflection. A typical small angle X-ray diagram is shown in figure 6. The assignment of the small angle reflections to a two dimensional hexagonal lattice is in agreement with results on macroscopically aligned samples described here.

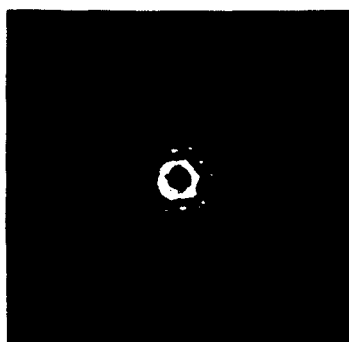


Figure 5. X-ray diffraction photograph of a sample of the $n = 10$ diol which had oriented spontaneously in a glass capillary ($T = 295$ K).

The X-ray data show that the position of the small angle reflections depends on the length of the aliphatic chains. This is apparent from figure 7 where the hexagonal lattice spacing is plotted as a function of the chain length. No temperature dependence of the spacings was observed. The spacing obtained for the compound with n of 4 is well within the range derived by the extrapolation to this value of n . The extrapolation

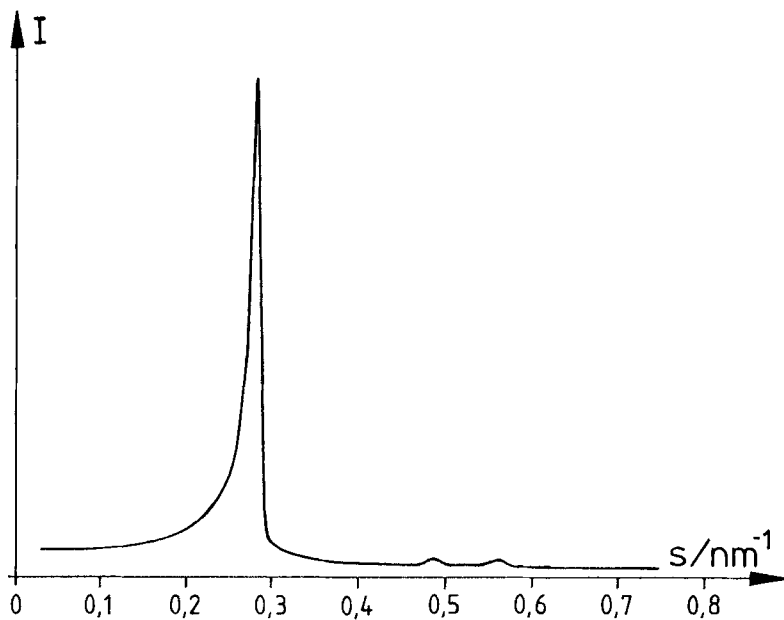


Figure 6. Profiles of the small angle X-ray peaks of the $n = 10$ diol in the liquid-crystalline state ($T = 295 \text{ K}$)

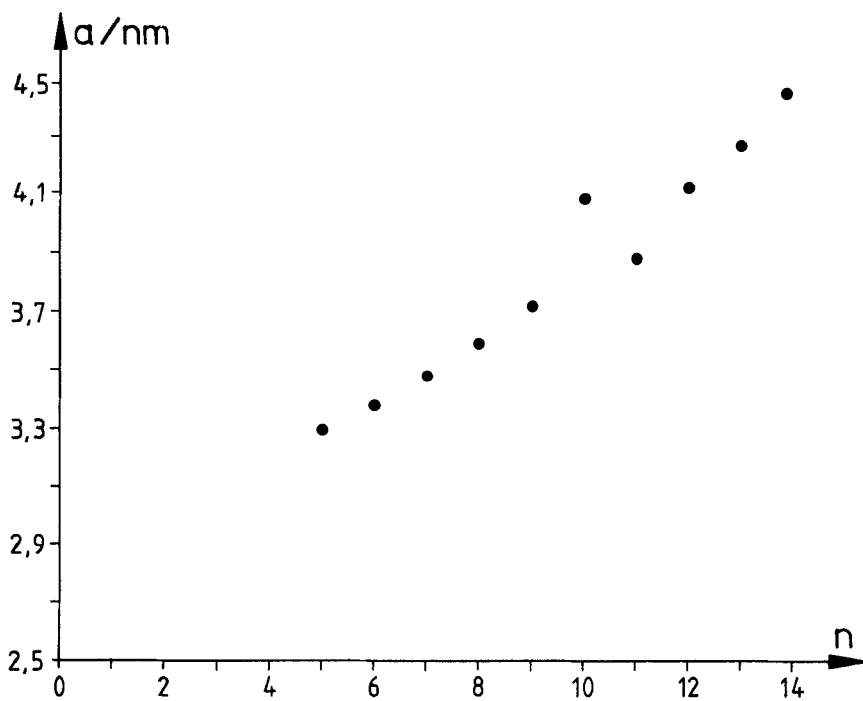
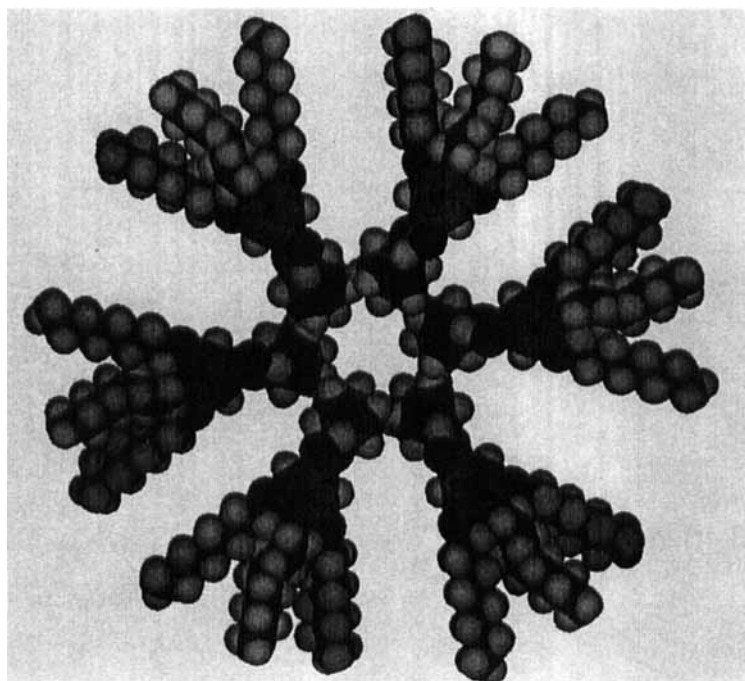
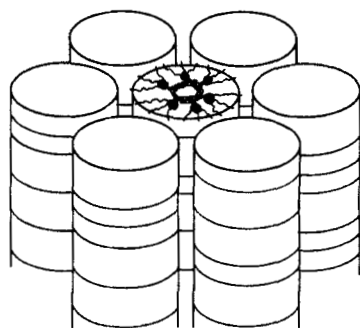


Figure 7. Dependence of the hexagonal lattice constant a on the chain length n of the diols obtained for the liquid-crystalline state.

to $n = 0$ leads to a distance of about 2.7 nm, which should represent the packing of the central part. This distance does not correspond to the length of a single molecule but more closely to the length of a pair with 2.8 nm, taking an antiparallel arrangement of the dipoles into account. The increment of the spacing per CH_2 -unit in the chain and thus per two CH_2 -units for a disc-like aggregate is about 0.11 nm. This is definitely much less than expected for a fully extended aliphatic chain. The additional observation is that the location of the wide angle halo is independent of the chain length. The average distance which is characteristic of the short range order and which



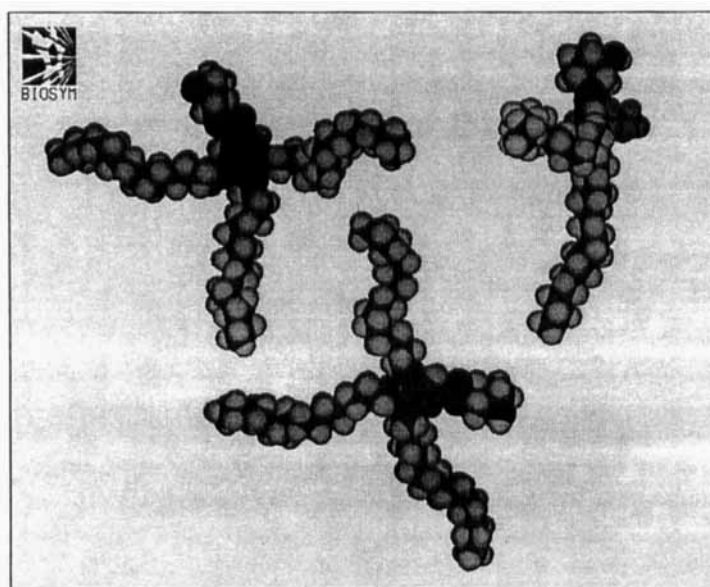
(i)



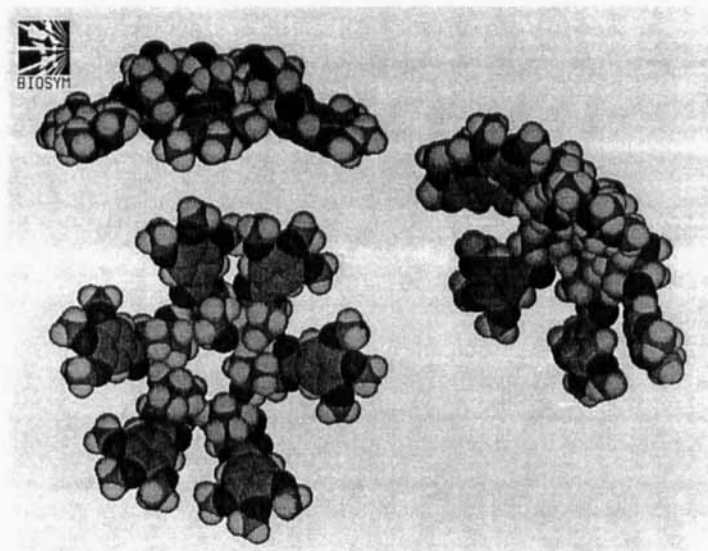
(ii)

(a)

Figure 8. Structural model for the anisotropic fluid state (a) (i) top view on a single disc (Structural model designed with the program INSIGHT/DISCOVER on a SILICON GRAPHICS IRIS 4D workstation.) and (ii) disordered columnar structure; (b) result of molecular dynamics calculations: (i) Configuration of a single diol molecule (chain length $n = 12$) and (ii) configuration of an aggregate of six diol molecules as obtained from molecular dynamics calculations.



(i)



(ii)

(b)

Figure 8 (continued).

can be derived from the location of the halo is about 0.50 nm. The modified Bragg equation, $2d \sin \theta = 1.117\lambda$, was used in this case [33].

Next we consider briefly the scattering data obtained for the isotropic melt. The result is that all compounds display two halos, one in the small and one in the wide angle region. The small angle halo shifts linearly to smaller scattering angles with increasing chain length. This linear dependence allows the extrapolation of the characteristic distance within the isotropic phase for the pure central part, e.g. $n = 0$. The distance derived in this way is about 2.6 nm. The increment per two CH_2 -units

within the aggregate (one CH₂-unit per single molecule) turns out to be about 0.12 nm. This result shows, as for the anisotropic fluid state, that strong deviations of the chain conformation from a fully extended chain have to exist since an extended chain would give rise to an increment of 0.13 nm per CH₂ group. It seems, however, that the configurations are somewhat different for the case of the isotropic and anisotropic fluids states.

The X-ray results revealing the existence of a hexagonal structure in the liquid-crystalline state resemble those obtained for columnar discotic systems, composed of disc-like molecules. It seems therefore that the individual molecules aggregate to disc-like units apparently due to hydrogen bonding; this is shown schematically in figure 8 (a). Such aggregations seem to occur already in the isotropic melt, as is evident from the X-ray results. The anisotropic phase differs from the isotropic phase in that such disc-like aggregates self organize in the liquid-crystalline state to form a two dimensional hexagonal lattice, as shown schematically in figure 8 (a). Accepting this model, the absence of a sharp reflection in the wide angle region and the presence of a wide angle halo have to be taken as an indication that the structure corresponds to a columnar hexagonal disordered structure.

Additional information on aggregate formation is available from molecular dynamics calculations. The results of the calculations are shown in figure 8 (b). The finding for the case of individual diol molecules is that the aliphatic chains are able to move freely and even to fold back on themselves. They remain, however, predominantly in the plane defined by the plane of the benzene ring. So, in principle, the average shape of a single molecule corresponds to that of a triangle. The configuration of the aggregate which emerges from the molecular dynamics calculations evidently does not correspond to a flat disc-like entity but seems rather to be dome shaped, as shown in figure 8 (b). The particular shape is the result of the low energy arrangement of the hydrogen bonds within the aggregate. The mean diameter of the aggregate corresponds closely to the value observed by X-ray scattering. It is apparent that the simulations give indications for a structure which resembles, in certain aspects, pyramidal phases [8].

No definite information on the internal structure of the columns as well as on the average intercolumnar distance can be derived directly by X-ray investigations on columnar disorder phases. The experimentally observed halo is probably predominantly the result of the short range order characteristic of the aliphatic chains, as in the case of discotic systems. It does not therefore lend itself beyond any doubt to a reliable determination of the intracolumnar distance. But an additional indirect piece of information on the structure of the columns is available from a comparison of the data obtained on the densities of the compounds and the X-ray data. The values amount, for the particular case that the length n of the flexible chains is zero, to about 0.46 nm if six molecules form the disc-like aggregate and to about 0.38 nm if five molecules form this aggregate. The first distance seems more reasonable in view of the X-ray data obtained on low molecular weight disordered discotics [34] and main chain polymers with similar chemical composition of the core, as far as disordered stackings are concerned [9, 35]. Also, the sixfold symmetry of the aggregates conforms better to the hexagonal symmetry of the lattice.

3.3. Results of dielectric relaxation studies

Figure 9 shows the dielectric results for the diol with $n = 8$. The real part of the dielectric constant is shown as a function of temperature for various test frequencies.

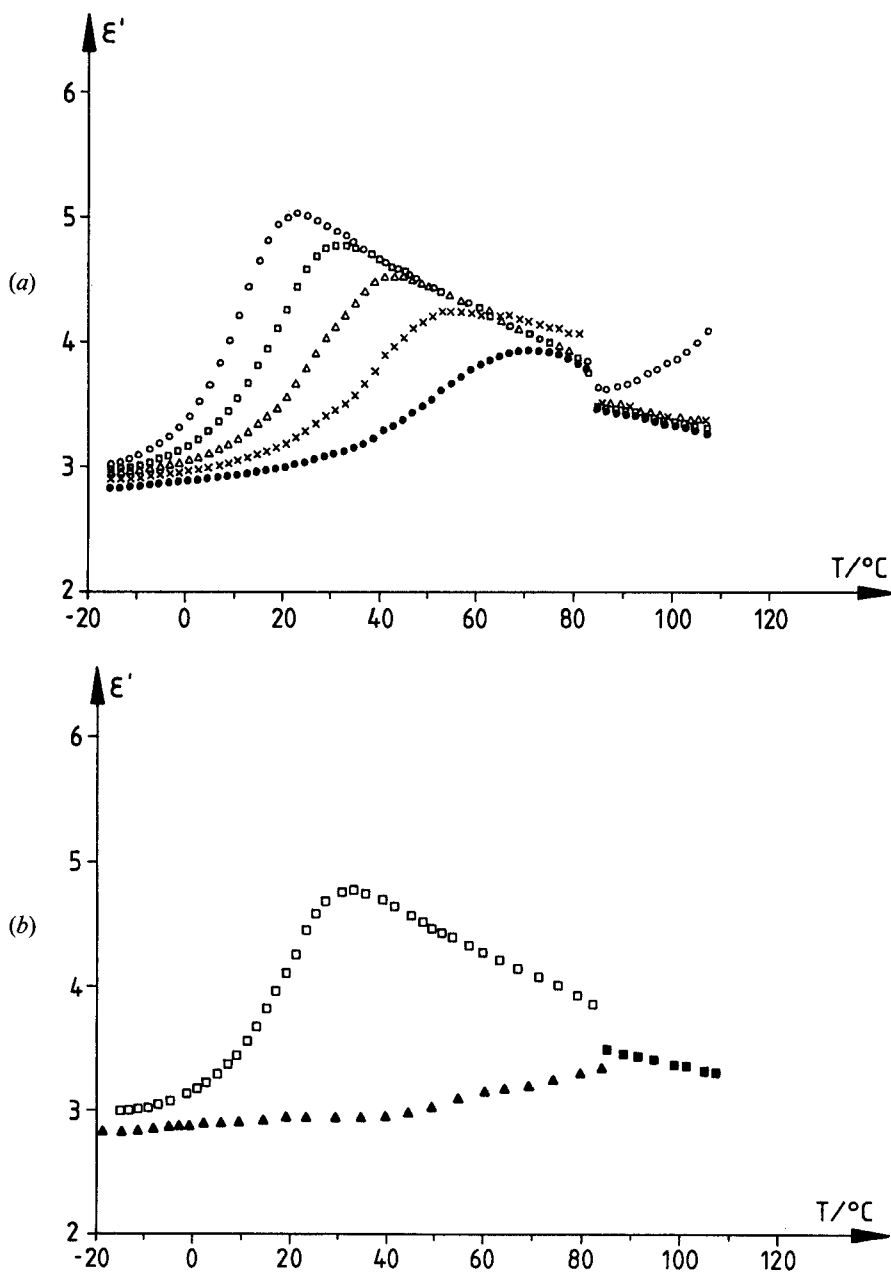


Figure 9. (a) Variation of the real part of the dielectric constant with temperature at various frequencies (\circ) 100 Hz; (\square) 1 kHz; (\triangle) 10 kHz; (\times) 100 kHz (\bullet) 1 MHz obtained for the $n = 8$ diol. (b) Resolution of the parallel and perpendicular components, (\square) ϵ'_\parallel (\blacktriangle) ϵ'_\perp ; (\blacksquare) ϵ'_{iso} .

It was found that a dispersion takes place at about the glass temperature. This can be attributed to the onset of the glass relaxation process as apparent from calorimetric studies. This causes an increase of the dielectric constant with increasing temperature at a constant frequency, as is apparent from figure 9. The low temperature and high temperature limits of the dielectric response will be considered first. The total increase

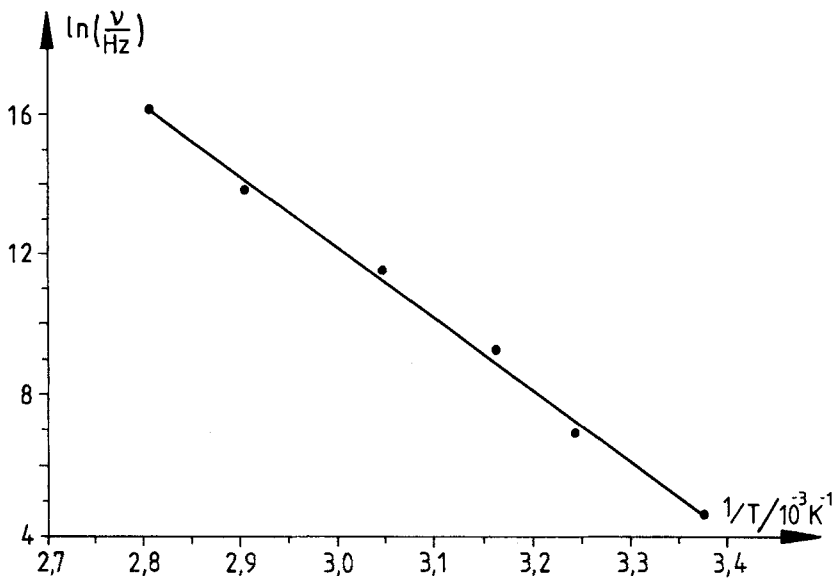


Figure 10. Activation diagram characteristic of the dielectric relaxation of the $n = 8$ diol.

of the dielectric constant due to this process amounts to about 0.8 leading from a low temperature value of 2.8 to a high temperature value of 3.6 for the isotropic fluid. The temperature at which the dispersion is detected is shifted to larger values with increasing frequency. This effect can be analyzed to yield the temperature-frequency superposition; the activation diagram is plotted in figure 10. The apparent activation energy is of the order of 170 kJ/mole which is of about the magnitude expected for a glass relaxation process. However, in general, a curved rather than a straight line is expected for the glass relaxation process. The frequency range is obviously too small to show this curvature.

The expectation based on results characteristic of rod-like mesogens is that two relaxation processes control the dielectric response, provided that individual molecules contribute to the relaxation properties. One should be related to the glass relaxation and contain, for instance motions, of the mesogen about its long axis. The other should be related to the much slower δ process which is associated with the reorientational motion of the mesogen about a short axis. However, we observe just a single relaxation process, which seems to be related to the glass relaxation process as judged from the characteristic frequency range and the shape of the Cole-Cole plot. This does not give rise to a semicircle, indicative of a single relaxation time, but rather to a shape indicative of a very broad relaxation time distribution. The expected δ process which is controlled by the reorientational relaxation of the parallel component of the molecular dipoles is apparently missing. This can be taken as an indication for the occurrence of aggregates for example disc-like ones (see figure 8) which results in a strong restriction of the rotational mobility of the molecules about their short axes.

So far the very peculiar variation of the dielectric constant in the temperature range in which the anisotropic fluid state exists has not been considered. The dielectric constant is found to increase above the glass transition temperature due to the onset of the glass relaxation, to decrease again in a continuous fashion with increasing temperature and finally to decrease discontinuously at the liquid crystalline-isotropic

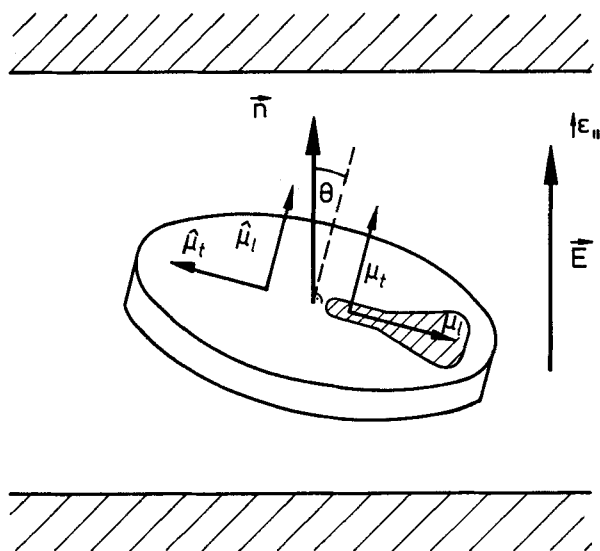


Figure 11. Configuration in which the dielectric relaxation studies were performed, definition of the symbols used.

transitions (see figure 9). This finding indicates, in agreement with similar results obtained from X-ray studies that the sample orients spontaneously in the cell and that this orientation is destroyed at the transition into the isotropic phase.

The data for the mean dielectric constant $\bar{\epsilon}$ and the dielectric constant ϵ_{\parallel} obtained for an electric field applied parallel to the plane defined by the substrate and the electrodes allow us to calculate the dielectric constant perpendicular to the electric field from

$$\bar{\epsilon} = 1/3(\epsilon_{\parallel} + 2\epsilon_{\perp}),$$

assuming uniaxial symmetry; the result is shown in figure 9 (b). Structural models have then to be used to relate these data to molecular data. In the following we shall use the symbol “^” to distinguish molecular properties related to the disc-like aggregate from these related to the individual diol molecules, as shown schematically in figure 11 in order to minimize the confusion. Based on the fact that the anisotropy of the dielectric constant is enhanced by the onset of the glass relaxation we conclude that it is the perpendicular component of the dipole moment of the individual molecules μ_t (see figure 11) which controls this relaxation, i.e. the discs tend to orient with their normals parallel to the substrate normal. Redefining the local axis with respect to the disc-like aggregate as for disc-like molecules we conclude that it is the longitudinal dipole component of the disc $\hat{\mu}_l$ (parallel to the disc normal, see figure 11) which controls this relaxation process. We can then estimate the anisotropy of the dielectric constant $\Delta\epsilon = \epsilon_{\parallel} - \epsilon_{\perp}$ where ϵ_{\parallel} is parallel to the director, defined by the disc normals. The values turn out to be for instance $\epsilon_{\parallel} = 4.8$ and $\epsilon_{\perp} = 3.0$ as determined for a temperature of 30° C and a frequency of 1 kHz. These data can then be used to obtain information on the order parameter S characteristic of the macroscopic sample and on the effective dipole moment per disc. The dielectric properties of the isotropic phase are available from

$$\epsilon_{\text{iso}} = \epsilon_{\text{iso}}^{\infty} + (\hat{N}hF^2/(3\epsilon_0 kT))\hat{\mu}^2,$$

where h and F are internal field corrections, \hat{N} is the number density of the discs, ϵ_0 is the dielectric constant of free space and $\epsilon_{\text{iso}}^\infty$ is the dielectric constant of the isotropic phase at infinite frequencies, as derived from the refractive index n . The analysis of this expression leads to an effective dipole moment per disc $\hat{\mu}$ of 7.0×10^{-30} C m. This is an extremely small value in view of the large number of molecular groups per disc carrying dipole moments. Next we consider the stepwise increase of the dielectric constant $\delta\epsilon$ within the anisotropic phase. The treatment of the dielectric relaxation behaviour of liquid-crystalline phases, in particular of the nematic phase by Maier and Meier [37, 38] leads to

$$\delta\epsilon_{\parallel} = (\hat{N}hF^2/\epsilon_0)(\hat{\mu}_i^2/3kT)(1 + 2S).$$

This expression allows the determination of the term $\hat{\mu}_i^2(1 + 2S)$ which can be evaluated to yield the lower limit for the order parameter S by assuming that the longitudinal dipole moment $\hat{\mu}_c$ to correspond to the total dipole moment; this gives S_{min} of 0.57 at 303 K. Any other choice of the dipole moment leads to larger values of the order parameter. This choice also allows the determination of the lower limit of the order parameter jump at the clearing temperature T_{cl} . It turns out to be 0.24.

Finally we consider the general expression for the dielectric constant parallel and perpendicular to the preferred orientation as derived by Maier and Meier

$$\epsilon_{\parallel} = \epsilon_{\parallel}^\infty + \hat{N}hF^2/3\epsilon_0kT(\hat{\mu}_i^2(1 + 2S) + \hat{\mu}_r^2(2 - 2S)),$$

$$\epsilon_{\perp} = \epsilon_{\perp}^\infty + \hat{N}hF^2/3\epsilon_0kT(\hat{\mu}_i^2(1 - S) + \hat{\mu}_r^2(2 + S)).$$

Hence we can account for the observed values of ϵ_{\parallel} and ϵ_{\perp} solely on the basis of the longitudinal component $\hat{\mu}_c$ of 7.0×10^{-30} C m. One conclusion we can draw is that this value is very small indeed, in view of the significant number of molecules within a disc, carrying components of the dipole moments perpendicular to the molecular long axis, i.e. parallel to the disc normal. This has to be taken as a strong indication of anticorrelations taking place between these components. Assuming that the dipole components considered here are able to rotate independently of each other, we expect for the contribution along the disc normal

$$\langle \hat{\mu}_i^2 \rangle = \langle \hat{\mu}_r^2 \rangle = \sum_i \mu_{r,i}^2,$$

which would amount to about 18×10^{-30} C m. The Kirkwood correlation parameter g thus amounts to 0.18 which is extremely small.

A second conclusion is either that no significant effective transverse component $\hat{\mu}_t$ along the plane of the discs exists due again to anticorrelations (in agreement with the model proposed in figure 8) or that the transverse components do not contribute to the dielectric properties in the temperature and frequency range considered here for kinetic reasons. Dynamic Kerr relaxation studies were therefore performed which can be extended in a much lower frequency range.

3.4. Results of electro-optic studies

The electro-optic (Kerr effect) studies consisted of applying an electric field to the isotropic phase. The optically and dielectrically anisotropic molecules align in the external field, causing a birefringence, which increases linearly as the square of the applied field,

$$\Delta n = \lambda BE^2,$$

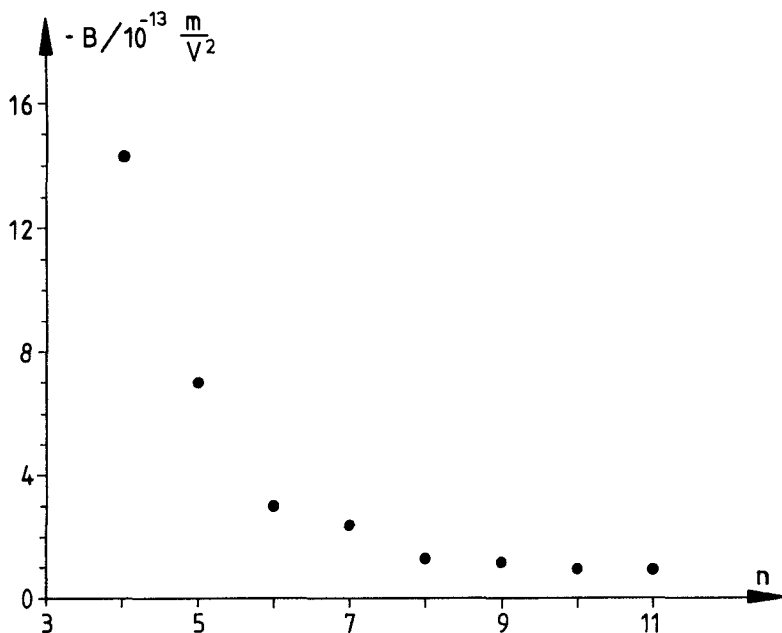


Figure 12. Variation of the Kerr constant B as a function of the chain length, n for a reference temperature 15 K above the transition into the isotropic fluid state.

where B is the Kerr constant and λ is the wavelength of the light. The variation of the absolute value of the Kerr constant with the chain length n is shown in figure 12 (at a reference temperature, taken to be 15 K above the transition into the anisotropic fluid state). The Kerr constant remains negative and its absolute value increases with decreasing chain length in a non-linear fashion. The negative value of the Kerr constant found for the systems considered here indicates, in terms of the structural model shown in figures 8 and 11, that the dipolar structure has to be such that the transverse dipolar component of the disc-like aggregate is much smaller than that which is parallel to the disc normal. The reason is that the latter axis is the one along which the optical polarizability is the largest. This result is in agreement with the conclusion drawn earlier that a strong compensation of the transverse intradisc dipole moment exists due to anticorrelations.

The absolute values of the Kerr constants are surprisingly larger in view of the rather low intrinsic optical anisotropy and dipole moment of these molecules. The reason for the observed effects has to be an increased magnitude of the orientational correlations present in the isotropic melt. Additional support for the assumption of orientational correlation comes from the observed temperature dependence of the Kerr constants. It increases quite strongly with decreasing temperature; this is a characteristic feature of nematic-isotropic phase transitions for both calamitic and discotic systems. It is related to the fact that this transition is only weakly first order and so displays pretransitional effects characteristic of a second order phase transition [6]. No such fluctuations are expected for isotropic phases neighbouring columnar phases. Actually we find that a plot of the inverse of the Kerr constant versus temperature is not a straight line,—as it is for a nematic-isotropic transition, but is curved. So it is apparent that the strong variation of the Kerr constant with temperature has to have a different origin. We tentatively attribute this variation to the presence of aggregates in the isotropic fluid state and their partial destruction with

Table 2. Dependence of the correlation parameter g_2 on the chain length n (at a reference temperature 15 K above the clearing temperature) as derived from the absolute value of the Kerr constant B .

n	Temperature/K	$-B/10^{-13} \text{ m V}^{-2}$	g_2
4	330	14.2	402
5	350	7.0	282
6	341	3.5	186
7	368	2.4	238
8	375	1.3	213
9	380	1.3	220
10	375	1.0	167
11	374	1.0	98

increasing temperature. The absolute values of the Kerr constant can, in principle, be used to obtain an estimate of the degree of aggregation in the isotropic state as well as on the variation of this number with temperature. Based on the dielectric relaxation data, on the optical anisotropy data as well as on the density the absolute value of the Kerr constant can be evaluated to give information on the orientational correlation factor g_2 (20, 21) defined as

$$g_2 = 1 + \sum_{ij} 1/2 (3 \cos^2 \phi_{ij} - 1),$$

where ϕ_{ij} is the angle between the symmetry axes of molecules i and j . The correlation parameter g_2 is extremely large. Its absolute value and its dependence on the chain length is displayed in table 2 for a reference temperature which is 15 K above the liquid-crystalline-isotropic transition temperature. It amounts to several hundreds and seems to increase with decreasing length of the flexible chains. For a given chain length n it decays only slowly with increasing temperature. The aggregates are still quite stable in the isotropic fluid state, obviously due to the existence of strong hydrogen bondings. This result also agrees with the results of transient Kerr effect investigations which will be considered briefly. The investigations reveal that no low frequency process takes place other than the glass relaxation. The assignment of the Kerr relaxation process to the glass relaxation is based first on the fact that the activation energy correspond to that obtained by dielectric relaxation studies and secondly on the fact that the time scales also agree roughly. This is evident if we take account of the relation between the dielectric and Kerr relaxation times [38, 39]:

$$\tau_{\text{Kerr}} = \tau_{\text{DK}} g_2.$$

The absence of a second relaxation process is a further indication that there are severe restrictions imposed on reorientational motion, resulting from the aggregation effects.

4. Conclusions

From the X-ray data, the dielectric relaxation and Kerr relaxation studies, thermal analysis and dilatometry we conclude that the molecules aggregate to form columnar type structures. These aggregates are already present within the isotropic phase and in the mesophase they pack in a hexagonal array giving a phase with a structure similar to that of a columnar discotic phase.

The microphase separation of aliphatic nonpolar and aromatic polar units gives a driving force toward aggregation of the assemblies, held together by specific interaction, i.e. by hydrogen bonding which is apparent from infrared studies. Dielectric relaxation and the Kerr relaxation studies have revealed that strong dipolar correlations exist within the aggregates and that external electrical fields cause just one type of reorientational motion of the aggregates within the fluid state, the time scale of which is controlled by the glass relaxation.

We wish to acknowledge gratefully the support of the Fonds der Chemischen Industrie and of the BMFT (Bundesministerium für Forschung und Technologie) which provided us generously with a graphic work station and with the software for molecular modelling. In addition we would like to thank the staff of Biosym Technologies in San Diego for helpful discussions and for their help in setting up the model calculations.

References

- [1] LATTERMANN, G., and STAUFER, G., 1989, *Liq. Crystals*, **4**, 347.
- [2] LATTERMANN, G., STAUFER, G., and RENNER, G., 1988, *12th International Liquid Crystal Conference*, Freiburg.
- [3] DE GENNES, P. G., 1974, *The Physics of Liquid Crystals* (Clarendon Press).
- [4] KELKER, H., and HATZ, R., 1980, *Handbook of Liquid Crystals* (Verlag Chemie).
- [5] FLORY, P. J., 1984, *Adv. Polym. Sci.*, **59**, 1.
- [6] CHANDRASEKHAR, S., 1981, *Molec. Crystals liq. Crystals*, **63**, 171.
- [7] DESTRADE, C., FOUCHER, P., GASPAREUX, H., NGUYEN HUU TINH, LEVELUT, A. M., and MALTHETE, J., 1984, *Molec. Crystals liq. Crystals*, **106**, 121.
- [8] ZIMMERMANN, H., POUPKO, R., LUZ, Z., and BILLARD, J., 1985, *Z. Naturf. (a)*, **40**, 149.
- [9] HERRMANN-SCHÖNHERR, O., WENDORFF, J. H., RINGSDORF, H., and TSCHIRNER, P., 1986, *Makromolek. Chem. rap. Commun.*, **7**, 791.
- [10] DESTRADE, C., and NGUYEN HUU TINH, 1988, *Molec. Crystals liq. Crystals*, **159**, 163.
- [11] MALTHETE, J., LEVELUT, A. M., and NGUYEN HUU TINH, 1985, *J. Phys. Lett., Paris*, **46**, 875.
- [12] NGUYEN HUU TINH, DESTRADE, C., LEVELUT, A. M., and MALTHETE, J., 1986, *J. Phys. Paris*, **47**, 553.
- [13] LEVELUT, A. M., MALTHETE, J., DESTRADE, C., and NGUYEN HUU TINH, 1987, *Liq. Crystals*, **2**, 877.
- [14] RINGSDORF, H., SCHLARP, B., and VENZMER, J., 1988, *Angew Chem Int. Ed. Engl.*, **27**, 113.
- [15] LYNGBAEE-JORGENSEN, J., 1985, *Processing, Structure and Properties of Block Copolymers*, edited by M. J. Folkes (Elsevier).
- [16] PROST, J., 1984, *Adv. Phys.*, **33**, 1.
- [17] DEMUS, D., DIELE, S., GRANDE, S., and SACKMANN, H., 1984, *Adv. liq. Crystals* **6**, 1.
- [18] SANESI, M., FERLONI, P., and FRANZOSINI, P., 1977, *Z. Naturf. (a)*, **32**, 1173.
- [19] LINDAU, J., KÖNIG, H. J., and DÖRFLER, H.-D., 1983, *Colloid Polym. Sci.*, **261**, 236.
- [20] BUSICO, V., CERNICCHIARO, P., CORRADINI, P., and VACATELLO, M., 1983, *J. phys. Chem.*, **87**, 1631.
- [21] SHARMA, N. K., PELZL, G., DEMUS, D., and WEISSFLOG, W., 1980, *Z. phys. Chem.*, **261**, 579.
- [22] KOLBE, A., PELZL, G., and WEISSFLOG, W., 1984, *Adv. Molec. Relax. Interact. Proc.*
- [23] GRAY, G. W., 1974, *Liquid Crystals and Plastic Crystals.*, Vol. 1, edited by G. W. Gray and P. A. Winsor (Ellis Harwood), p. 109.
- [24] JEFFREY, G. A., 1984, *Molec. Crystals liq. Crystals*, **110**, 221.
- [25] JEFFREY, G. A., 1986, *Accts chem. Rev.*, **19**, 168.
- [26] DIELE, S., GEISSLER, E., VORBRODT, H. M., and ZASCHKE, H., 1984, *Molec. Crystals liq. Crystals Lett.*, **102**, 181.
- [27] BUNNING, J. D., LYDON, J. E., EABORN, C., JACKSON, P. M., GOODBY, J. W., and GRAY, G. W., 1982, *J. chem. Soc. Faraday Trans.*, **78**, 713.
- [28] ULLRICH, K. H., 1984, Ph.D. thesis, TH Darmstadt.

- [29] EICH, M., ULLRICH, K. H., and WENDORFF, J. H., 1984, *Polymer*, **25**, 1271.
- [30] MACKAY, D. H., CROSS, A. J., and HAGLER, A. T. (to be published).
- [31] LATTERMANN, G., and STAUFER, G. (to be published).
- [32] WUNDERLICH, B., and GREBOWICZ, J., 1984, *Adv. Polym. Sci.*, **60/61**, 1.
- [33] GUINIER, A., 1983, *X-ray Diffraction* (W. H. Freeman).
- [34] CHANDRASEKHAR, S., SADASHIVA, B. K., and SURESK, K. A., 1977, *Pramana*, **9**, 471.
- [35] HERRMANN-SCHÖNHERR, O., 1987, Ph.D. thesis, TH Darmstadt.
- [36] MAIER, W., and MEIER, G., 1961, *Z. Naturf. (a)*, **16**, 262.
- [37] KRESSE, H., 1984, *Adv. liq. Crystals.*, **6**, 109.
- [38] KRAUSE, S., 1981, *Molecular Electro-Optics* (Plenum Press).
- [39] DUNMUR, D. A., 1981, *Molecular Electro-Optics*, edited by S. Krause (Plenum Press).