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Liquid Crystals

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Molecular dynamics and the glass transition in a columnar liquid crystal formed by a chiral discotic mesogen

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A new type of chiral discotic liquid crystal is described. It is based on a triphenylene core but carries only one asymmetric side chain per mesogen. This system displays a columnar liquid-crystalline mesophase with a helical superstructure and a pitch of 3·0 nm over a temperature range of 227 K. Upon cooling it forms a glassy state. By broadband dielectric and ^2H NMR spectroscopy two motional processes are detected. The axial rotation of the discs around the column axis exhibits non-Arrhenius behaviour and is directly related to the glass transition. The second process is ascribed to localized side chain motions involving the ester linkages.

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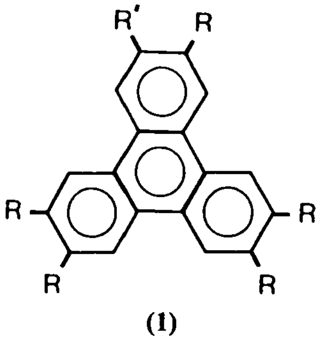
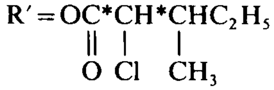
Several attempts to introduce molecular chirality into liquid crystals composed of discotic molecules with a triphenylene core, where the asymmetric centre was placed in all of the six flexible side chains have been reported [1–3]. This is, however, a rather strong chiral perturbation and it is somewhat difficult to imagine how this could generate a spiral column with a pitch extending over several discs within the column. The chiral perturbation per molecule is much smaller, if only one of the side chains carries the asymmetric centres as in (2*S*,3*S*)-2-chloro-3-methyl-penta-noyloxy-pentakis(pentyloxy)-triphenylene (**1**) considered here



$R = OC_5H_{11}$



$R' = O\underset{\overset{\|}{O}}{C}{}^*\underset{\overset{|}{Cl}}{C}H^*\underset{\overset{|}{CH_3}}{C}HC_2H_5$

(**1**)

This discotic molecule was synthesized starting from pentasubstituted triphenylene [5] and esterification with the chiral acid by the DCCI method. This monosubstituted asymmetric system has a clearing temperature as high as 455 K and the enthalphy of isotropization is 19·3 kJ mol^{-1}. Optical textures reveal highly ordered columnar phases and X-ray scattering on samples aligned in a magnetic field prove a hexagonal ordered phase and a helical superstructure with a pitch of 3·0 nm which corresponds

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to a stack of eight molecules [5]. Upon cooling, this system does not crystallize, but shows a glass transition at 228 K as revealed by differential scanning calorimetry. This also shows that **(1)** exhibits a columnar liquid-crystalline mesophase over an extremely broad temperature range. The occurrence of the glass transition is interesting in itself, because partially ordered glassy systems, in which discotic liquid-crystalline order is frozen in have, so far, only been reported for discotic dimers, oligomers, and polymers [4]. The interlinking of the discs in these systems strongly hinders the rotation of the discs around the column axis, even in the liquid-crystalline phase [6]. Therefore, it is not clear how this motion, characteristic of the dynamic behaviour in discotic liquid-crystalline phases, is related to the glass transition.

In this communication we report preliminary results from a study of the molecular dynamics of the chiral discotic **(1)** by broadband dielectric and ^{2}H NMR spectroscopy. As described elsewhere [7–9] our dielectric measurement systems allow us to follow dynamic processes over a wide range of relaxation rates (10^{-1} to 10^9 Hz). For the dielectric measurements at frequencies below 10^6 Hz the discotic liquid-crystalline sample **(1)** was kept between two gold plated brass electrodes (sample area: 314 mm^2), separated at 200 μm by a fused silica spacer ring. For the high frequency measurements above 10^6 Hz the sample was mounted as part of the inner conductor: gold plated brass plates, 3 mm in diameter, spaced at 50 μm [9].

The dielectric loss ε'' of the sample as a function of frequency and temperature is displayed in figure 1. The largest local dipole moments of the discotic are associated with the ester group and the adjacent chloro substituent in the chiral side chain. As discussed elsewhere [10, 11] dielectric relaxation will, therefore, be sensitive to both side chain motions and rotation of the discs around the column axis. Two pronounced relaxation processes are found, labelled α and β. The low temperature β relaxation has similar characteristics to the dielectric relaxation in related discotic liquid-crystalline polymers [11]. It corresponds to the motion of the side chains and is dominated by

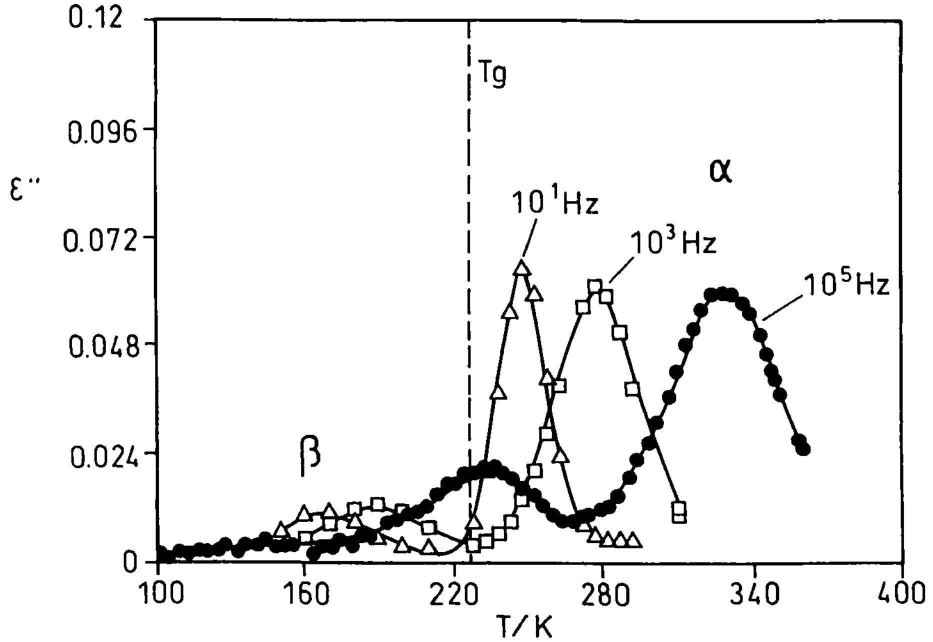

Figure 1. Isochronal representation of the dielectric loss ε'' versus temperature at the frequencies indicated.

the rotation of the ester group around the linkage to the discotic core. Its correlation time exhibits a substantial distribution with a half-width of 3·5 decades at 180 K (for details of the data analysis see [5, 9]). In addition a second pronounced low frequency relaxation is apparent in figure 1, which at a given frequency occurs at higher temperatures, and so we label it as an α relaxation. Contrary to the β relaxation this process is only observed above the glass transition, as indicated by the dashed line. Thus the α relaxation is directly related to the glass transition. Since a corresponding relaxation is not observed in discotic liquid-crystalline polymers [10], where the rotation of the discs around the column axis is hindered, we wonder whether the α process detected here may be ascribed to this axial motion.

In order to test this conjecture, system (**1**) was selectively deuteriated at the aromatic core by recrystallization of the pentasubstituted precursor in deuterotrifluoroacetic acid. Temperature dependent ^{2}H NMR spectra of isotropic samples were recorded as described elsewhere [6]. In figure 2 such spectra are shown for three temperatures. At 200 K, well below T_g the spectrum is characteristic of a powder spectrum for rigid triphenylene rings [12], displaying a slight asymmetry of the electric field gradient. As discussed in [12], the larger quadrupole splitting in the region of the singularities is

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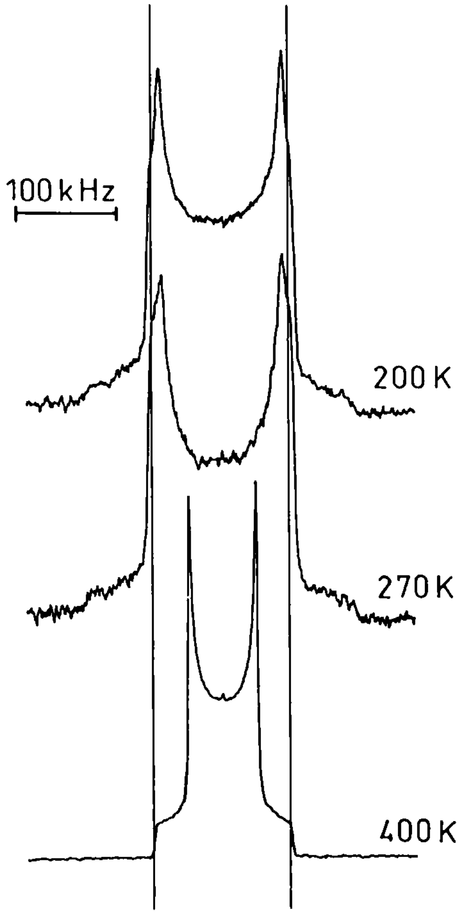

Figure 2. Solid state ^{2}H NMR spectra at the temperatures indicated. Additional vertical lines at the singularities of the low temperature spectra and the outer edges of the high temperature spectrum are drawn to guide the eye.

observed if the magnetic field B_0 is perpendicular to the aromatic ring, i.e. the column axis. The spectrum remains unchanged up to 270 K, thus excluding ring motions at rates higher than approximately 10 kHz. In the temperature range between 280 K and 380 K the lineshape changes due to the onset of ring motion with rates between 10 kHz and 10 MHz [13–15]. In the fast exchange limit (see figure 2 (400 K)), this motion leads to a Pake type spectrum, reduced in width by about a factor of two, characteristic of the axial motion of the discs around their column axis [6]. Note that the outer edges of the motionally narrowed Pake spectrum correspond to the larger quadrupole splitting in the region of the singularities in the low temperature spectra, which makes this assignment unique [12]. Comparison of this behaviour with the dielectric relaxation curves in figure 1 shows that the ring motion detected in the ^{2}H NMR spectra indeed corresponds to the α process of the dielectric relaxation.

The mean correlation times for both processes extracted from the dielectric data in figure 1, as described in [5, 9], are plotted in figure 3. The β process shows an Arrhenius behaviour with an activation energy of 37 ± 3 kJ/mol and is essentially unaffected by the glass transition at T_g, indicated by the dotted line. This further supports our assignment of this process to localized side chain motions involving the ester linkages. The mean correlation time τ_α, however, describing the time scale of the axial motion of the discotic mesogens, exhibits strong deviations from Arrhenius behaviour when approaching T_g. In fact the temperature variation of τ_α follows the Williams–Landel–Ferry (WLF) equation [16], deduced from the temperature dependence of the mechanical relaxation of glass-forming organic materials in the vicinity of T_g, namely

$$\log\frac{\tau(T)}{\tau_0} = -\frac{C_1(T - T_g)}{C_2 + (T - T_g)}.$$

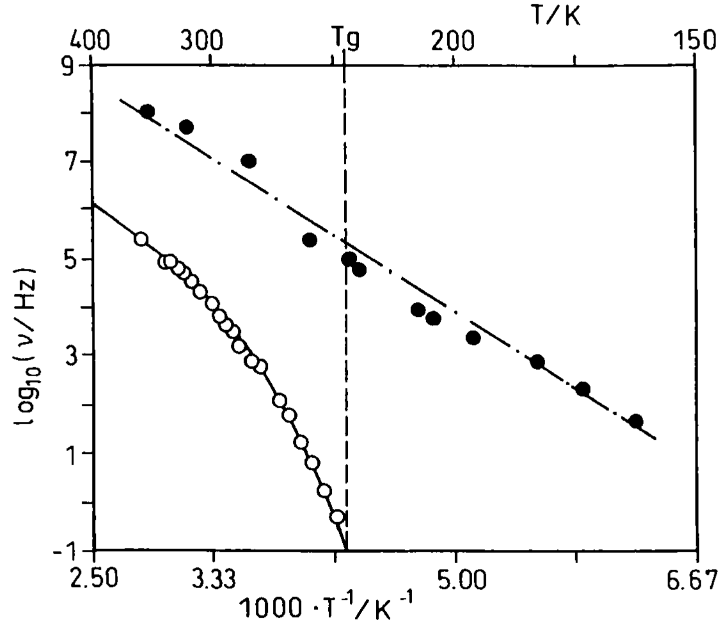

Figure 3. Mean relaxation rate ν_τ versus inverse temperature. The dashed line represents the glass transition temperature as determined by DSC. The curved solid line indicates the fit to the WLF equation.

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Here C_1 and C_2 are constants and τ_0 corresponds to the correlation time at T_g. The fitted WLF curve in figure 3 yields $C_1 = 9{\cdot}7$, $C_2 = 61\,\mathrm{K}$ and $\tau_0 = 10\,\mathrm{s}$. These parameters are very similar to those observed for other organic glasses, where the glass transition is generally ascribed to the onset of cooperative motions [16]. Our observation that the rather well-defined axial motion of the discs around the column axis can be related directly to the glass transition in such a discotic system is somewhat difficult to rationalize if the discs are assumed to rotate independently of each other. Apparently this is not the case. As noted earlier [17], in a discotic liquid-crystalline polymer not only is the rotation of the mesogens interlinked by the polymer chain hindered but also that of discotic monomers dissolved in the polymer. This indicates that the axial motion in the closely packed columns is a cooperative process involving several discs within the column, which makes the close relation of this process to the glass transition much easier to reconcile. More detailed information about the geometry of this slow motion in the vicinity of the glass transition can be provided by the 2D-exchange NMR [18] experiments curently underway.

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