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Dynamic properties of discotic liquid crystals with triphenylene and benzene cores, studied by broadband dielectric spectroscopy

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Dynamic properties of discotic liquid crystals with triphenylene and benzene cores, studied by broadband dielectric spectroscopy

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Broadband dielectric spectroscopy in the frequency range from 10^{-4} to 10^9 Hz was employed to study the molecular dynamics of various triphenylene and benzene derivatives in their isotropic and liquid crystalline phases. For all derivatives, two relaxation processes were detected in their columnar mesophases. The β-process shows an Arrhenius-like temperature dependence with activation energies between 37 and 40 kJ mol^{-1}. This process is assigned to a librational motion of the ester groups in the side chains. The α-process follows a Williams–Landel–Ferry temperature dependence and is correlated to the glass transition. This process is assigned to the hindered rotation of the molecular discs around the columnar axis. In the isotropic phase, the dielectric properties of the benzene derivatives are essentially different from the triphenylenes, most probably because of the difference in capability of conformational rearrangement.

1. Introduction

Columnar discotic phases are formed by molecules with a flat rigid core and flexible aliphatic side chains. In these columnar mesophases, the cores stack to form columns surrounded by the disordered aliphatic side chains [1]. Due to their high viscosity in the columnar phases, there are no applications for these materials in display devices so far. Nevertheless, they receive increasing attention in the field of one-dimensional conductors [2–4]. Of particular interest are the dynamical properties of these materials. In this paper, several discotic liquid crystal materials with benzene or triphenylene cores are investigated by broadband dielectric spectroscopy.

2. Experimental

2.1. *Broadband dielectric spectroscopy*

For the measurements, the samples were mounted between two gold plated brass electrodes, with the gap maintained by the glass fibres as spacers. In the frequency range from 10^{-4} to 10^7 Hz, the capacitor was 50 μm thick and 20 mm in diameter. The dielectric function $\varepsilon^*(\omega) = \varepsilon' - i\varepsilon''$ was measured using a frequency response analyser (Solartron Schlumberger 1260) combined with a buffer amplifier or using an impedance analyser (HP 4192 A). In the frequency range from 10^6 to 10^9 Hz, a coaxial reflectrometer (HP 4191 A) was employed with capacitors having a thickness of 20 ± 2 μm and a diameter of 5 mm. A complete description of the experimental set-up is given in [5].

2.2. *Materials*

The table shows the discotic liquid crystal materials investigated, their chemical structure and phase behaviour. The synthesis of these compounds is described elsewhere [6, 7]. The triphenylene derivative Tri11 is substituted with five ether groups and only one ester group; THA11 on the other hand is symmetrically substituted with six ester groups. The benzene derivatives are all symmetrically substituted with six ester groups. In the columnar and isotropic phases, the dielectric properties of the benzene derivatives are identical.

3. Results and discussion

The loss maxima of the measured dielectric function $\varepsilon^*(\omega)$ are usually broader than the ideal Debye relaxation and asymmetric in shape. Therefore the empirical

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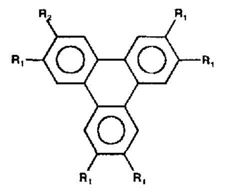
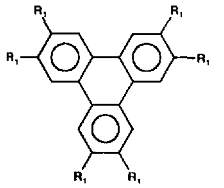
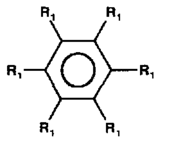
T_g: glass transition; D_{ho}: discotic columnar mesophase (hexagonal, ordered); D_{hd}: discotic columnar mesophase (hexagonal, disordered); D_t: discotic columnar mesophase (tilted); I: isotropic phase. Mesophase characterization and nomenclature according to Destrade *et al.* [12].

Label	Structure	Phase transition
Tri11	 $R_1 = \text{–OC}_5\text{H}_{11}$ $R_2 = \text{–OOC(CH}_2)_9\text{CH}_3$	T_g: 214 K D_{ho} 388 K I
THA11	 $R_1 = \text{–OOC(CH}_2)_9\text{CH}_3$	C 340 K D_t 391 K D_{hd} 393 K I
HAB-C8(4-Me)	 $R_1 = \text{–OOC(CH}_2)_2\text{(CHCH}_3\text{)(CH}_2)_3\text{CH}_3$	T_g: 193 K D_{hd} 369 K I

Havriliak–Negami function [8] was used to fit the data.

$$\varepsilon^*(\omega) = \varepsilon_\infty + \frac{\varepsilon_S - \varepsilon_\infty}{[1 + (i\omega\tau_{HN})^\alpha]^\beta}, \qquad (1)$$

where τ_{HN} is the characteristic relaxation time, ε_S and ε_∞ are low and high frequency values, respectively, of the real part of the dielectric function for the process under investigation. The parameters α and β describe the symmetrical and asymmetrical broadening of the distribution of relaxation times. Combining two relaxation functions according to equation (1) allows one to describe the data within the experimental accuracy.

The non-symmetric compound Tri11 has a glass transition at 214 K; hence the relaxation properties of the columnar phase can be investigated for this derivative over a broad temperature range. Figure 1 displays the dielectric loss, ε'', of Tri11 at different temperatures in the mesophase. The dielectric properties can be well described by two relaxation processes. The low-frequency process, connected to the glass transition (in the following text called the α-process) is stronger and has a narrower relaxation time distribution than the high frequency process. The lines in figure 1 represent the Havriliak–Negami fits of the α-process. The corresponding fit-parameters are included for three different temperatures. The high frequency process (in the following text called the β-process) broadens continuously with decreasing temperature. In agreement with earlier investigations on a non-symmetric triphenylene compound [9], the β-process shows an Arrhenius-like temperature dependence. The activation energy is 40 kJ mol^{-1}. This process is ascribed to a local librational motion of the side chains involving the carbonyl group of the ester linkage. The α-process follows in its temperature dependence the Williams–Landel–Ferry (WLF) equation [10]

$$\log \frac{\tau(T)}{\tau_0} = -\frac{c_1(T - T_g)}{c_2 + (T - T_g)}. \qquad (2)$$

In former dielectric and 2D-NMR investigations on another non-symmetric triphenylene derivative, this process was assigned to a hindered rotation of the whole molecule around the columnar axis [7].

The benzene derivative HAB-C8(4-Me) also has two relaxation processes in the columnar phase. In contrast to the WLF behaviour of the low-frequency α-process, the

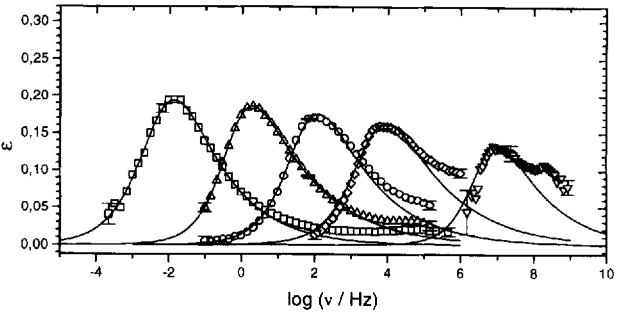


Figure 1. Compound Tri11. Dielectric loss versus frequency for different temperatures: (□) 213 K, (△) 221 K, (○) 233 K, (◇) 259 K and (▽) 347 K. The solid lines represent the fitted Havriliak–Negami functions for the low frequency process. The deviation of the data at high frequencies is caused by the β-process. For three temperatures the relevant Havriliak–Negami fit-parameters are: 213 K: $\Delta\varepsilon = 0{\cdot}845$; $\alpha = 0{\cdot}694$; $\beta = 0{\cdot}52$; $\tau = 26{\cdot}15$ s. 233 K: $\Delta\varepsilon = 0{\cdot}76$: $\alpha = 0{\cdot}783$; $\beta = 0{\cdot}4$; $\tau = 3{\cdot}50 \times 10^{-3}$ s. 347 K: $\Delta\varepsilon = 0{\cdot}5$; $\alpha = 0{\cdot}9$; $\beta = 0{\cdot}4$; $\tau = 3{\cdot}75 \times 10^{-8}$ s.

high frequency β-process is activated Arrhenius-like. Figure 2 shows the dielectric loss at different temperatures. The increase of ε'' at low frequencies is caused by a charge migration process. The contribution to the dielectric loss can be described by the relation

$$\varepsilon''(\omega) = \frac{\sigma(0)}{\varepsilon_0 i\omega^s}, \tag{3}$$

where $\sigma(0)$ is the extrapolated conductivity at $\omega = 0$ [11]. The exponent s has a value around 0·8 typical for charge transport in disordered systems. That conductivity contribution is most probably due to a small amount of ionic impurities in the sample. The strong influence of the conductivity on the dielectric loss at low frequencies prevents analysis of the α-process of HAB-C8(4-Me) below 10^{-1} Hz. The β-process is very weak in its dielectric strength. Besides, the loss maximum broadens strongly at lower temperatures. For that reason, it is not possible to make a clear analysis of the β-process at low temperatures. Only at higher temperatures can the two processes be separated (see figure 3).

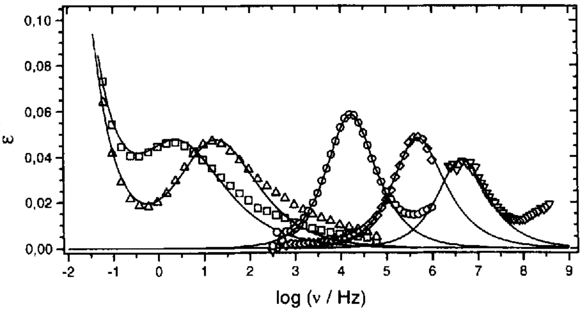


Figure 2. Compound HAB-C8(4-Me). Dielectric loss versus frequency for 5 different temperatures: (□)190·1 k, (△) 196·5 k, (○) 254·3 K, (◇) 309·5 k and (▽) 359·3 k. The solid lines represent the fitted Havriliak–Negami functions for the low frequency process. The weak high frequency process is broadens strongly at lower temperatures. The exponential increase of ε'' on the low-frequency side is caused by a charge migration process. The Havriliak–Negami fit parameters are: 190·1 K: $\Delta\varepsilon = 0{\cdot}171$; $\alpha = 0{\cdot}647$; $\beta = 0{\cdot}85$; $\tau = 6{\cdot}8 \times 10^{-2}$ s; $\sigma = 2{\cdot}5 \times 10^{-13}$ s m^{-1}; $s = 0{\cdot}8$. 254·3 K: $\Delta\varepsilon = 0{\cdot}130$; $\alpha = 0{\cdot}961$; $\beta = 0{\cdot}896$; $\tau = 1{\cdot}04 \times 10^{-5}$ s. 359·3 K: $\Delta\varepsilon = 0{\cdot}088$; $\alpha = 0{\cdot}96$; $\beta = 0{\cdot}86$; $\tau = 4{\cdot}04 \times 10^{-8}$ s.

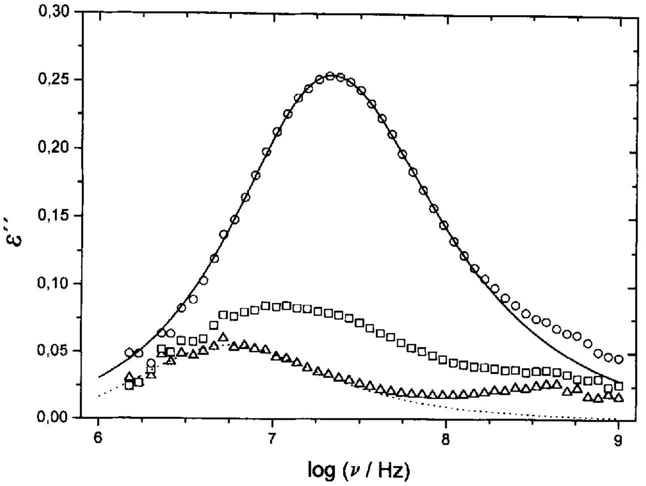


Figure 3. Compound HAB-C8(4-Me). Dielectric loss versus frequency in the discotic columnar mesophase ($T = 365{\cdot}4$ K) (△) and in the isotropic phase ($T = 372{\cdot}1$ K) (○). The dielectric strength of the α-process increases strongly and the relaxation maximum shifts to higher frequencies. The dashed and the solid line represent the fitting function for the α-process in the columnar and in the isotropic phase, respectively. The Havriliak–Negami fit parameters are: 365·4 K: $\Delta\varepsilon = 0{\cdot}127$; $\alpha = 0{\cdot}954$; $\beta = 0{\cdot}89$; $\tau = 3{\cdot}23; \times 10^{-8}$ s. 372·1 K: $\Delta\varepsilon = 0{\cdot}618$; $\alpha = 0{\cdot}955$; $\beta = 0{\cdot}756$; $\tau = 9{\cdot}32 \times 10^{-9}$ s. [(□) 368·9 K].

At the phase transition from the discotic columnar to the isotropic phase, a new loss process appears. Its dielectric strength is about ten times higher than that of the α-process in the columnar phase and its mean correlation time lies between the α- and β-processes of the mesophase (see figure 3). The intramolecular sterical hindrance of the ester groups leads to a strong mean square dipole moment of the whole molecule, and hence the higher mobility of the benzene core in the isotropic phase compared to that in the columnar phase leads to a strong increase of the dielectric strength at the phase transition.

The triphenylene derivative with six ester groups (THA11) is crystalline below 340 K. In that crystalline phase, no relaxation process can be detected. In the columnar mesophase, the dielectric data are similar to Tri11. Also two relaxation processes can be detected with comparable relaxation times, but the dielectric strength of the β-process is higher for THA11 than for Tri11.

Figure 4 displays the dielectric loss data for Tri11 and

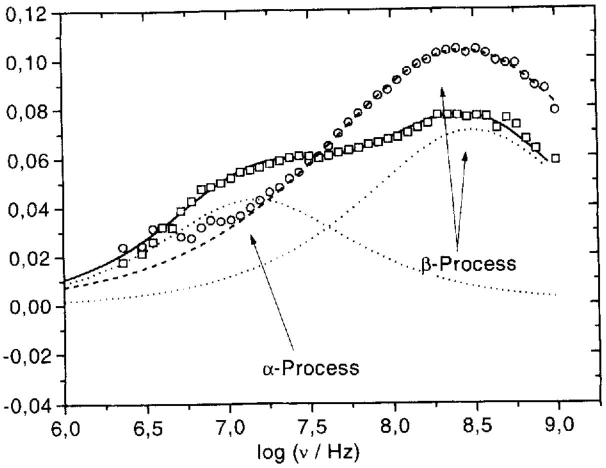


Figure 4. Dielectric loss versus frequency at 393 K for Tri11 (□) and THA11 (○) in the isotropic phase. The dotted lines represent the fitting data for the single α- and β-process of Tri11, respectively; the solid line is the sum of both processes. The dashed line represents the fitting data for the single β process of THA11. The Havriliak–Negami fit parameters are: THA11 (β-process): $\Delta\varepsilon = 0{\cdot}36$; $\alpha = 0{\cdot}66$; $\beta = 0{\cdot}98$; $\tau = 5{\cdot}9 \times 10^{-10}$ s. Tri11 (α-process): $\Delta\varepsilon = 0{\cdot}11$; $\alpha = 0{\cdot}87$; $\beta = 1$; $\tau = 1{\cdot}4 \times 10^{-8}$ s. Tri11 (β-process): $\Delta\varepsilon = 0{\cdot}19$; $\alpha = 0{\cdot}80$; $\beta = 1$; $\tau = 4{\cdot}8 \times 10^{-10}$ s.

THA11, both in the isotropic phase. In contrast to the columnar phase of THA11, where two relaxation processes exist, only the β-process is still present. For Tri11, both the α- and β-processes are still present in the isotropic phase. Because of its non-symmetric structure, Tri11 has a mean square dipole moment in the plane of the molecule and therefore a rotational motion causes a dielectric loss process. THA11 has not necessarily a net molecular dipole moment in the plane of the molecule. Nevertheless the α-process can be detected in the columnar phase. Hence, the conformation of the carbonyl groups in the columnar mesophase must be disordered, leading to a mean square dipole moment in the plane of the molecule. The conformational rearrangement of the carbonyl groups is hindered in the columnar phase, where relatively strong intermolecular dipole and sterical interactions of the ester groups exist between neighbouring discs. The observed β-process is only a liberational relaxation at small angles. In the isotropic phase, fast conformational rearrangement of the ester groups is possible. These fluctuations occur on the same time scale as the β-process. Hence, the slower α-process is no longer correlated with the mean square dipole moment and no longer contributes to the dielectric function. Figure 5 summarizes the observed relaxation processes for the three compounds in an activation plot.

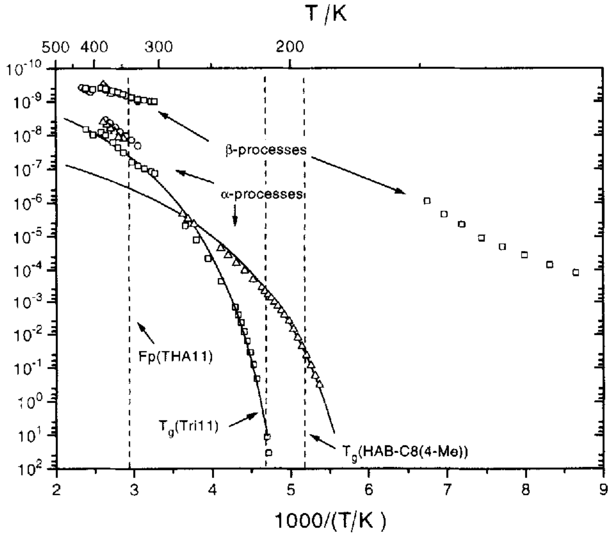


Figure 5. Activation plot for the three discotic liquid crystals investigated. The dashed lines represent the mesophase–crystalline transition temperature of THA11 and the glass transition temperatures of Tri11 and HAB-C8(4-Me). The solid lines represent fits of the WLF-equation.

4. Conclusions

All the discotic compounds investigated have two dielectric loss processes in their columnar mesophases. The high frequency process is assigned to a local librational motion of the ester groups. The activation energies are in all cases between 37 and 40 kJ mol^{-1}. The low frequency process is assigned to a hindered rotational motion of the molecular discs around their columnar axis. The mean relaxation time has no Arrhenius-like temperature dependence, and for the samples with a glass transition it can be described by the Williams–Landel–Ferry (WLF) equation. In the columnar phase of the symmetrically substituted compounds, the conformation of the ester groups is disordered. In the isotropic phase, the compounds differ in their dielectric properties. The non-symmetrically substituted triphenylene derivative Tri11 still has two relaxation processes, whereas the symmetrically substituted triphenylene derivative THA11 shows only the β-process in the isotropic phase. Due to fast conformational rearrangement, the mean square dipole moment is no longer correlated with the α-proces, only with the fast local fluctuations of the ester groups. The ester groups of HAB-C8(4-Me), in contrast, are sterically hindered in their conformational rearrangement, even in the isotropic phase, and therefore the slow α-process is still correlated with the molecular mean square dipole moment. The weak β-process is covered by the α-process.

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