Effect of functionalization on glass formation by columnar mesophases of substituted triphenylene mesogens

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A new kind of discotic liquid crystal has been investigated where one out of the six ether side chains of a triphenylene core was replaced by an ester side chain. We have found greatly increased clearing temperatures and suppressed crystallization thus leading to glass forming discotics. Here we report the synthesis, X-ray and dielectric studies concerning the nature of the glass transition. Furthermore we give arguments as to why a 'mixed' substitution can lead to such drastic effects.

1. Introduction

During more than 10 years of research on liquid crystals a wide range of compounds have been found to exhibit discotic mesophases, and there exists general agreement on their classification into a discotic nematic and several columnar phases [1, 2]. The columns are formed by stacking of the centred cores as, for example triphenylene, to which flexible aliphatic side groups are attached. Despite their high viscosity columnar mesophases can be aligned macroscopically to form monodomains [3]. On cooling from the mesophase this macroscopic order most often is lost when the sample crystallizes which is not desirable for us if we want to study the molecular dynamics in the slow motion regime well suited for NMR measurements. One way to prevent crystallization is to incorporate discotics into polymers [4, 5]. Although such polymers can be ordered macroscopically [6, 7], the alignment that can be achieved in magnetic fields is always lower than that of low molar mass systems. It is therefore preferable to form low molar mass discotics which do not crystallize. Furthermore there exists an interest to increase the clearing temperature or better to stabilize the columnar structure. One way to accomplish this is to add electron acceptors thus forming charge-transfer complexes which have been shown not only to markedly enhance clearing temperatures, but also to induce columnar phases [8, 9]. Another possibility is the so called β-oxygen effect whereby the incorporation of oxygen atoms into the side chains preferably the β position leads to lower melting temperatures and the clearing temperatures are greatly increased [10, 11].

In a recent communication [12] we reported on a low molar mass discotic generated in an attempt to introduce molecular chirality into such systems. To this end only one out of the six ether side chains in hexakispentyloxytriphenylene was replaced by a chiral ester group (see figure 1), resulting in a glass-forming columnar phase. In this paper we show that a variety of glass forming triphenylene mesogens can be generated by introducing one hetero substituent and we discuss the conditions which the substituent R' must meet in order to prevent crystallization. The systems are collected

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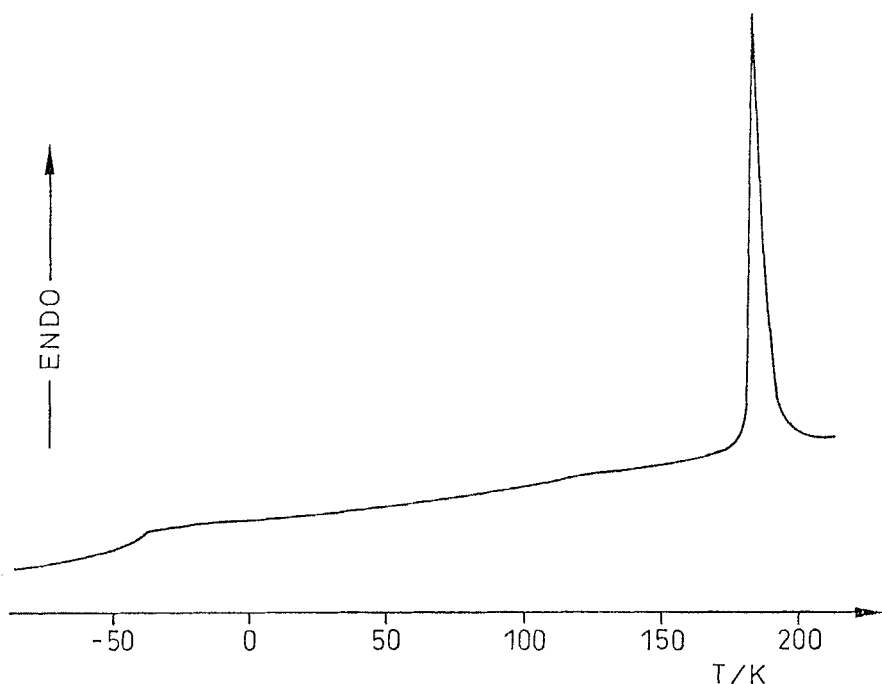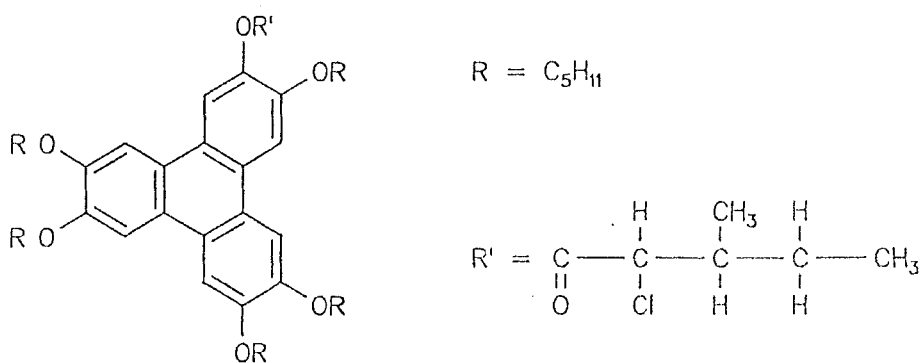
Figure 1.   Structure of the unsymmetrically substituted triphenylene mesogen, compound 1 and its DSC curve for the second heating run.

in table 1, together with the parent compound with $R' = R$, compound 6. We also report our X-ray investigations and in more detail the results from dielectric relaxation measurements.

2.   Experimental

2.1.   *Synthetic part*

The various discotics were all synthesized from pentasubstituted triphenylene the synthesis of which is described elsewhere [13]. Pentakis(pentyloxy)triphenylene monoacetate (0·96 g, 1·37 × 10^{-3} mol) was dissolved in CH_2Cl_2 (30 ml) and ethylamine (20 ml) and stirred overnight to remove the acetate moiety. After evaporation of the solvents the mixture was purified by column chromatography (silica gel, CH_2Cl_2) and dried thoroughly in a dessicator under vacuum. The pentaalkylated triphenylene

(0·38 g, 5·7 × 10^{-4} mol) was dissolved in absolute CH_2Cl_2 (30 ml) and dicyclohex-ylcarbodiimide (0·17 g, 8·5 × 10^{-4} mol) and 4-dimethylaminopyridine (0·01 g) was added. Under ice cooling the acid (8·5 × 10^{-4} mol) was added and the solution left to warm to room temperature. After approximately 3 h the reaction was complete. Filtration of the urea and evaporation of the solvent yielded the crude product which was purified by column chromatography (CH_2Cl_2/cyclohexane, 2 : 1; silica gel). The 1-(1-methylpentyloxy)-2,5,6,9,10-pentakis(pentyloxy)triphenylene was synthesized by refluxing the monoacetate (0·20 g, 2·8 × 10^{-4} mol) together with 2-bromohexane (0·18 g, 0·16 ml) and K_2CO_3 (0·30 g) in isobutyl-methyl-ketone for four days. Filtration of the salts and evaporation of the solvents yielded the crude product which was purified by column chromatography (toluene, silica gel).

2.2. *Characterization*

All compounds were characterized by ^1H and ^{13}C NMR. The compounds were studied by polarization microscopy using a Zeiss Axiophot microstage equipped with a Linkam TMS 90 hot stage which allowed a precession of 0·1 K with the usual heating and cooling rates of 3 K min^{-1}. Calorimetric studies were performed with a Mettler DSC 30. Typical heating and cooling rates were 10 K min^{-1}. The data given are usually taken from the second heating run except when different phase transitions occur (i.e. see figure 1). Samples for X-ray analysis and dielectric measurements were aligned by slow rotation (0·1 Hz) around an axis perpendicular to the magnetic field (7·1 T) while slowly cooling from the isotropic liquid to the mesophase (0·1 K min^{-1}) [2, 6].

2.3. *X-ray diffraction*

The $\Theta - \Theta$ X-ray diffractograms were measured on a Siemens Kristalloflex diffractometer with collimator widths of 0·3 mm. The X-ray patterns of the aligned samples were recorded on a system consisting of a Rigaku 18 kW rotating anode source with pinhole collimation set-up combined with a rapid two dimensional detector (Siemens). Cu-K$_\alpha$ radiation was selected by a Ni-filter. The beryllium front window of the detector was concave with a radius of curvature of 240 mm. The sensitive area was roughly circular with a diameter of 115 mm and data was read in form of a 512 × 512 pixel array, each pixel occupying an area of 0·18 × 0·18 mm^2. Typical detector–sample distances were about 100–140 mm.

2.4. *Dielectric relaxation*

The dielectric measurements [14] covered the frequency range from 10^{-1} to 10^9 Hz using a frequency response analyser (Solartron-Schlumberger FRA 1254, frequency range 10^{-4}–6 × 10^4 Hz) with a high impedance preamplifier of variable gain, a Hewlett–Packard impedance analyser (HP 4192A, frequency range from 10 to 10^7 Hz) and a Hewlett–Packard impedance analyser based on the principle of a coaxial reflectometer (HP 4191A, frequency range from 10^6 to 10^9 Hz). A nitrogen gas heating system covered the temperature range from 100 K to 450 K, the stability of the temperature adjustment was ±0·02 K. The temperature gradient across the sample is estimated to be less than 0·04 K. For the measurements using the FRA 1254 and the HP 4192A the liquid-crystalline sample was kept between two gold plated brass electrodes (diameter 40 mm) and separated by a spacer (200 ± 10 μm). For the measurements using the HP 4191A the sample was mounted as part of the inner conductor (gold plated brass plmtes, diameter: 3 mm) of a coaxial short. A separation of 50 ± 2 μm was maintained by the use of two fused silica glass fibres, their contribution

to the volume in the sample capacitor was negligible. The sample temperature was measured with a platinum resistor (PT 100), which was inserted in the outer conductor of the coaxial cell.

3. Results and discussion

3.1. *Phase behaviour*

The side chain R' in 1 differs from the five other side chains, R, in several respects:

(i) it is linked to the triphenylene core via an ester rather than an ether group;
(ii) it contains a polar chlorine group;
(iii) it is chiral.

To find out which of these factors is important for promoting glass formation several other R' groups were considered including a racemate of compound 1 (2), an unbranched side chain of 1 (3), the chlorine was removed (4) and finally the ester linkage was replaced by an ether linkage (5), see table 1. All of the compounds exhibit discotic mesophases; the thermal data are collected in table 1. They appear to show that neither chirality (iii) nor the polar group (ii) are dominant effects which induce glass formation. It is the ester linkage which is crucial to this behaviour. Optical textures of the mesophases of all compounds are all alike and closely resemble that of the parent compound, 6. If the side chain R' apart from the different linkage to the triphenylene core is very similar to those of R, compound 4, crystallization is possible, but can easily be circumvented by rapid cooling (approximately $10 \, \text{K min}^{-1}$) from the mesophase.

Table 1. Table showing the different side chains which replace one side chain of the symmetrical 'parent compound' together with the thermal data. The data presented are the glass transition (T_g), the melting point (T_m), the temperature of isotropization (T_i) and the enthalpy of isotropisation (ΔH_i).

R'	T_g/K	T_m/K	T_i/K	$\Delta H_i/\text{kJ mol}^{-1}$	Phase
1 $\underset{*}{\overset{\overset{\text{O}}{\|}}{\text{O} \cdot \text{C}}}-\underset{*}{\overset{\overset{\text{Cl}}{\|}}{\text{CH}}}-\overset{\overset{\text{CH}_3}{\|}}{\text{CH}}-\text{C}_2\text{H}_5$	227	—	455	19·3	D_{ho}
2 2S, 3S $\underset{*}{\overset{\overset{\text{O}}{\|}}{\text{O} \cdot \text{C}}}-\underset{*}{\overset{\overset{\text{Cl}}{\|}}{\text{CH}}}-\overset{\overset{\text{CH}_3}{\|}}{\text{CH}}-\text{C}_3\text{H}_5$	232	—	455	21·6	D_{ho}
3 racemic $\overset{\overset{\text{O}}{\|}}{\text{O} \cdot \text{C}}-\overset{\overset{\text{Cl}}{\|}}{\text{CH}}-\text{C}_3\text{H}_7$	225	—	464	19·6	D_{ho}
4 $\overset{\overset{\text{O}}{\|}}{\text{O} \cdot \text{C}}-\text{C}_4\text{H}_9$	215	317‡	450	16·8	D_{ho}
5 $\overset{\overset{\text{CH}_3}{\|}}{\text{O} \cdot \text{CH}}-\text{C}_4\text{H}_9$	—	340†	324†	4·84	D_{ho}
6 $\text{O} \cdot \text{C}_5\text{H}_{11}$	—	342	395	8·18	D_{ho}

† The substance has a monotropic columnar phase when cooling from the isotropic melt. At a cooling rate of $10 \, \text{K min}^{-1}$ it crystallizes at $300 \, \text{K}$.

‡ The sample crystallizes only from solution.

The question then arises what causes this dominant effect of glass formation by a single ester substituent. In order to see whether this is due to steric hindrance of the protruding carbonyl-oxygen atom, a 1-methyl-pentyl side chain was attached (5). This new substance shows only a monotropic mesophase when cooling from the isotropic melt, demonstrating again that minor changes in the molecular structure may have large effects on the phase behaviour. In this context it is also interesting to note, that triphenylene derivatives carrying methyl substituents in the 1 or 2 position in all of the side chains are not mesomorphic. If on the other hand two ester side chains are added the clearing temperature can be raised even higher, up to 489 K, regardless of which isomer except for the ortho diester [15].

We conclude, therefore, that the specific conformation and/or possibly the dipole interaction of the carbonyl group are dominant. For comparison we consider a typical all-ester substituted triphenylene mesogen, THA8 [1,2], with its phase sequence

$$C \ 337 \ K \ D_{rd} \ 403 \ K \ I.$$

Two important features typical for the all-ester substituted triphenylene are noticed. First, the tendency to form disordered columns and second, the formation of mostly rectangular two dimensional arrays of columns which is a direct result of a strong molecular tilt inside the columns. In a similar comparative study, recently published, the effect of either alkoxy, alkyl or alkoxymethyl substitution of the metal-free phthalocyanine core on the molecular packing was investigated. Here too, alkoxy substitution leads to an ordered hexagonal phase whereas substitution by other side chains leads to a molecular tilt inside the columns and thus to a rectangular packing of the columns [16]. ^2H NMR data [17–19] provide strong evidence that the dominant conformation for carbonyl side chains is out-of-plane whereas the alkoxy side chains tend to remain more strongly aligned in the aromatic plane. This leads to a picture where five pentoxy chains spread out smoothly in the aromatic plane whereas one alkanoyl chain sticks out of this plane thus interfering strongly with the side chains of the adjacent molecules (see figure 2). It is easy to conceive that this strong interaction between tightly packed adjacent molecules in a column not only stabilizes the columnar structure, but also prevents crystallization leading to a glass forming mesophase. Note also that the clearing enthalpy is more than doubled in the unsymmetrically ester substituted compounds as compared to the parent compound. Since no significant differences in the packing (neither degree of orientation nor symmetry) was observed, this, too, points to an additional positive enthalpic interaction.

3.2. *X-ray analysis*

In order to check the molecular packing of the mesophases wide angle diffract-ograms in transmission geometry were taken from magnetically aligned samples (see §2.2), i.e. *the columns are uniaxially ordered with the incident beam perpendicular to the column director.* A typical X-ray diffraction pattern of compound 1 is shown in figure 3. In our assignment we follow the proposal of Levelut [1]. Three main features are visible in the X-ray diffractogram:

(i) a wide angle arc which is attributed to the stacking distance (*D*) inside a column of the meridian axis. The maximum of the reflection shifts somewhat to smaller q values with increasing temperature. At 303 K it corresponds to a periodicity of 3·45 Å and it increases linearly to 3·65 Å at 453 K. From vertical cross sections a coherence length of about 60 Å is deduced which stays
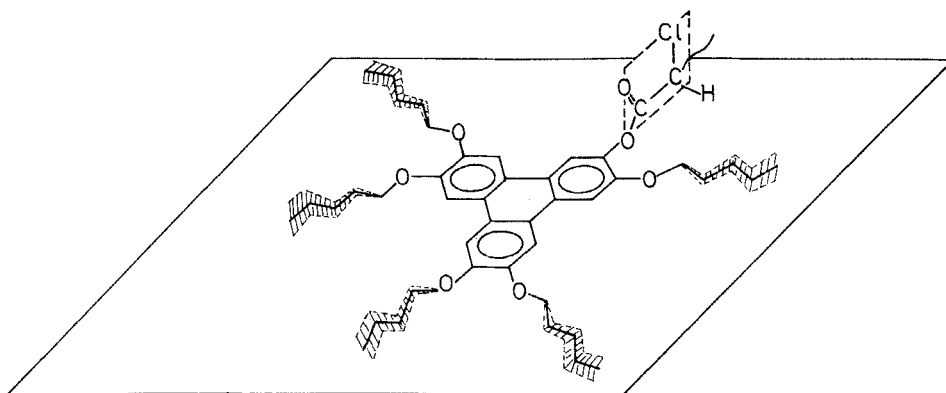
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Figure 2.   Schematic drawing of the mesogen in its most probable conformational state inside
the column [18].

constant up to 440 K and then drops to 55 Å at 450 K close to T_i. This value is
much lower than the value of 300 Å reported by Levelut [1], but corresponds
well to the 70 Å of the helix pitch. Heiney *et al.* [20] on the other hand, report
for the thioanalogues a correlation length of 30 Å which at elevated
temperatures drops to 16 Å. The intensity distribution along the arcs points
towards a rather high degree of orientational order as expected from ordered
hexagonal columnar structures, but no attempt of quantification was made;

(ii)   a rather diffuse arc exhibiting much less orientational order. It has basically
the same breadth and peak position as the halo for amorphous alkanes with
typical distances of 4·30–4·50 Å and it is attributed to the amorphous packing
of the side chains;

(iii)   a rather sharp reflection with strong intensity which is assigned to the (1, 0, 0)
Bragg reflection of the hexagonal packing of the columns. Note some smaller
satellite spots of very low intensity originating from small unoriented domains.
From this Bragg reflection the intercolumnar distance (K) can easily be
calculated.

Additionally we observed Bragg spots of higher order on the horizontal axis with the
ratios $1 : 1/\sqrt{3} : 1/2 : 1|\sqrt{7}$ in varying intensities depending on the compound which are
in agreement with a hexagonal packing of the columns being indicated as (1, 0, 0),
(1, 1, 0), (2, 0, 0) and (2, 1, 0) reflections, respectively. In figure 3 the (2, 1, 0) reflection can
be seen as it is unusually strong in compound **1**. We conclude therefore that all of the
compounds under investigation form columnar discotic mesophases with a hexagonal
packing of the columns and an ordered stacking of the molecules within the columns.

Table 2 lists the important parameters of the molecular packing of the compounds
under investigation. Note that no significant changes in either the intercolumnar
distance or the interdisc spacing occur. It appears rather that the unsymmetrically ester
substituted discs pack even more closely inside the column than in the symmetrical
parent compound, **6**. In our preliminary communication we also reported the
occurrence of a helical superstructure. This structure has not been fully proven yet. At
small angles we observe an additional peak the intensity and the position of which is
strongly temperature dependent. More studies are needed to elucidate fully this
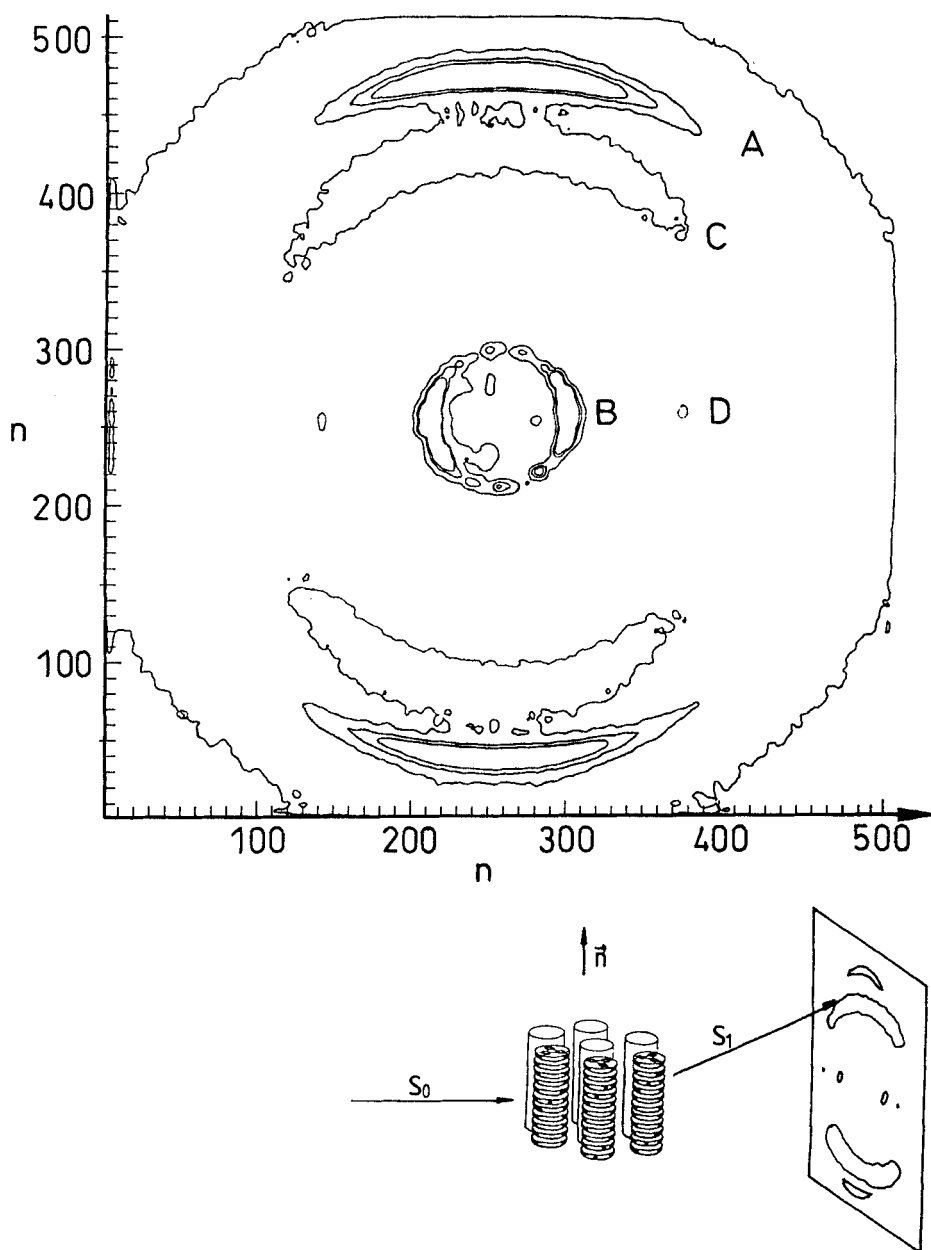question.

Figure 3.   Typical X-ray diffraction pattern of a magnetically aligned sample (compound 1). The columns have been uniaxially aligned and the X-ray beam is perpendicular to the column director. The main features have been assigned A, B, C, D and are discussed in the text.

3.3. *Dielectric relaxation*

As concluded from a combination of broadband dielectric and ^{2}H NMR spectroscopy [12] one of the particularly interesting aspects of the glass forming discotics studied here is the fact that the glass transition can be related to a single dynamic process, namely the freezing of the axial motion of the discs around the

Table 2. Summary of the main results of the X-ray measurements: temperature of the measurement from which data are taken (T), core–core distance inside the column (D), main reflection of the hexagonal grid $(1, 0, 0)$ and the lattice parameter of the hexagonal grid (intercolumnar spacing, K).

R'	$T/°C$	$D/\text{Å}$	$(1,0,0)/\text{Å}$	$K/\text{Å}$
1 O·C–CH–CH–C$_2$H$_5$ (O Cl CH$_3$) 2S, 3S	30	3·45	17·53	20·24
2 O·C–CH–CH–C$_2$H$_5$ (O Cl CH$_3$) racemic	30	3·45	17·53	20·24
3 O·C–CH–C$_3$H$_7$ (O Cl)	30	3·47	18·09	20·89
4 O·C–C$_4$H$_9$ (O)	30	3·46	17·59	20·31
5 O·C–C$_4$H$_9$ (CH$_3$)	49	3·55	17·50	20·20
6 O·C$_5$H$_{11}$	80	3·60	17·20	19·86

K, intercolumnar spacing; D, interdisc spacing.

column axis. Moreover we stated that this motion appears to be a collective process. Only mean values for the correlation times of this motion, however, were reported in our previous communication. A characteristic feature of dynamic processes freezing in at the glass transition is non-exponential relaxation corresponding to a distribution of correlation times [21]. This can be determined from a comprehensive analysis of the frequency dependent real (ε') and imaginary (ε'') part of the complex dielectric function. As discussed in [12] the largest local dipole moments of the discotic, **1**, are associated with the ester group and the adjacent chloro-substituent in the chiral side chain. Dielectric relaxation will, therefore, be sensitive to both, axial rotation of the discs and side chain motions. They have been labelled α and β, respectively (see figure 4). The studies were performed on aligned and unaligned samples giving qualitatively the same results except that the relaxation strengths for all of the processes of the aligned samples were enhanced by approximately a factor of three. However, no attempt of quantification was made as the degree of order in the cells could never be determined. Measurements were done on several compounds; however we discuss only compound **1** as it is representative for all of the others.

The loss curves for the α-process are broad and asymmetric (see figure 5) and so the Havriliak–Negami function is used to fit the experimental data

$$\varepsilon^*(\omega) = \varepsilon_\infty + \frac{\varepsilon_{st} - \varepsilon_\infty}{(1 + (i\omega\tau)^{\alpha_{HN}})^{\gamma_{HN}}}. \tag{1}$$

This empirical function has proved to give a good description of dielectric data in glass forming systems [22]. Here ε_∞ is the limiting low frequency value of the complex
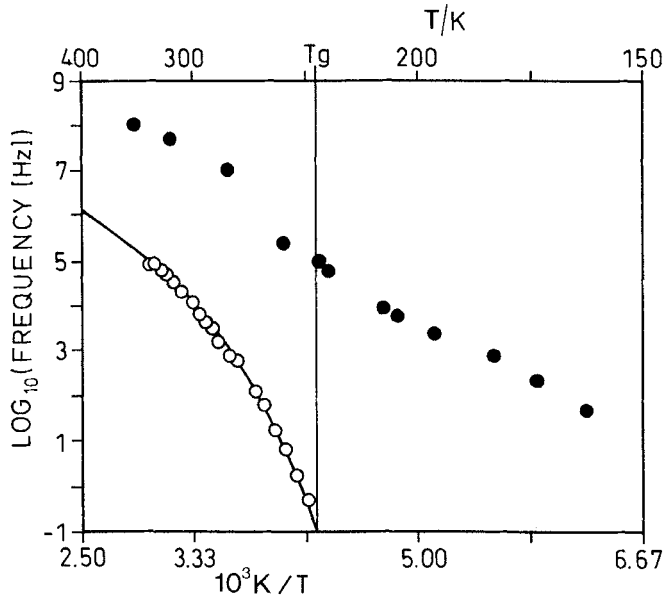
Figure 4. Mean relaxation rate v versus inverse temperature showing the α and β process. The dashed line represents the glass transition temperature as determined by DSC. The curved solid line indicates the fit according to the WLF equation.

dielectric function, $\varepsilon_{st} - \varepsilon_\infty$ denotes the relaxation strength, α_{HN} is a parameter characterizing a symmetrical broadening of distribution of relaxation times, and β_{HN} characterizes an asymmetrical broadening ($0 < \alpha_{HN}, \beta_{HN} \leqslant 1$). The steep rise of ε'' at low frequencies is caused by frequency-dependent electrical conductivity according to

$$\varepsilon''(\omega) = \frac{\delta_0}{\varepsilon_0 (2\pi v)^s}, \tag{2}$$

with δ_0 and s being fitting parameters (see dotted line in figure 5) [23]. The value of $s = 0.8$ points towards a hopping mechanism of conduction. In order to ease comparison with other experimental techniques the dipole–dipole correlation function $\phi(t)$ is evaluated for the identical temperature shown in figure 6. This is extracted from the imaginary part $\varepsilon''(\omega)$ by a half-sided cosine transformation, since $\varepsilon'(\omega)$ and $\varepsilon''(\omega)$ are related via the Kramers–Kronig relation

$$\phi(t) = \frac{2}{\pi} \int_0^\infty \frac{\varepsilon''(\omega)}{\varepsilon_{st} - \varepsilon_\infty} \frac{\cos \omega t}{\omega} \, d\omega. \tag{3}$$

In order to calculate $\phi(t)$ from this equation by numerical integration, the functional form of the Havriliak–Negami description is used to evaluate $\varepsilon''(\omega)$ over the whole frequency range. In figure 6 the correlation function $\phi(t)$ versus time is shown. It can be fitted by the Kohlrausch–Williams–Watt (KWW) function [24, 25]

$$\phi(t) = \exp\left[-\left(\frac{t}{\tau_{KWW}} \right)^{\beta_{KWW}} \right] \tag{4}$$

The parameter β_{KWW} describes the stretched exponential decay of the correlation function, and τ_{KWW} is the mean correlation time. As shown in figure 5 the data can be adequately fitted to this function, except from a small systematic deviation at long
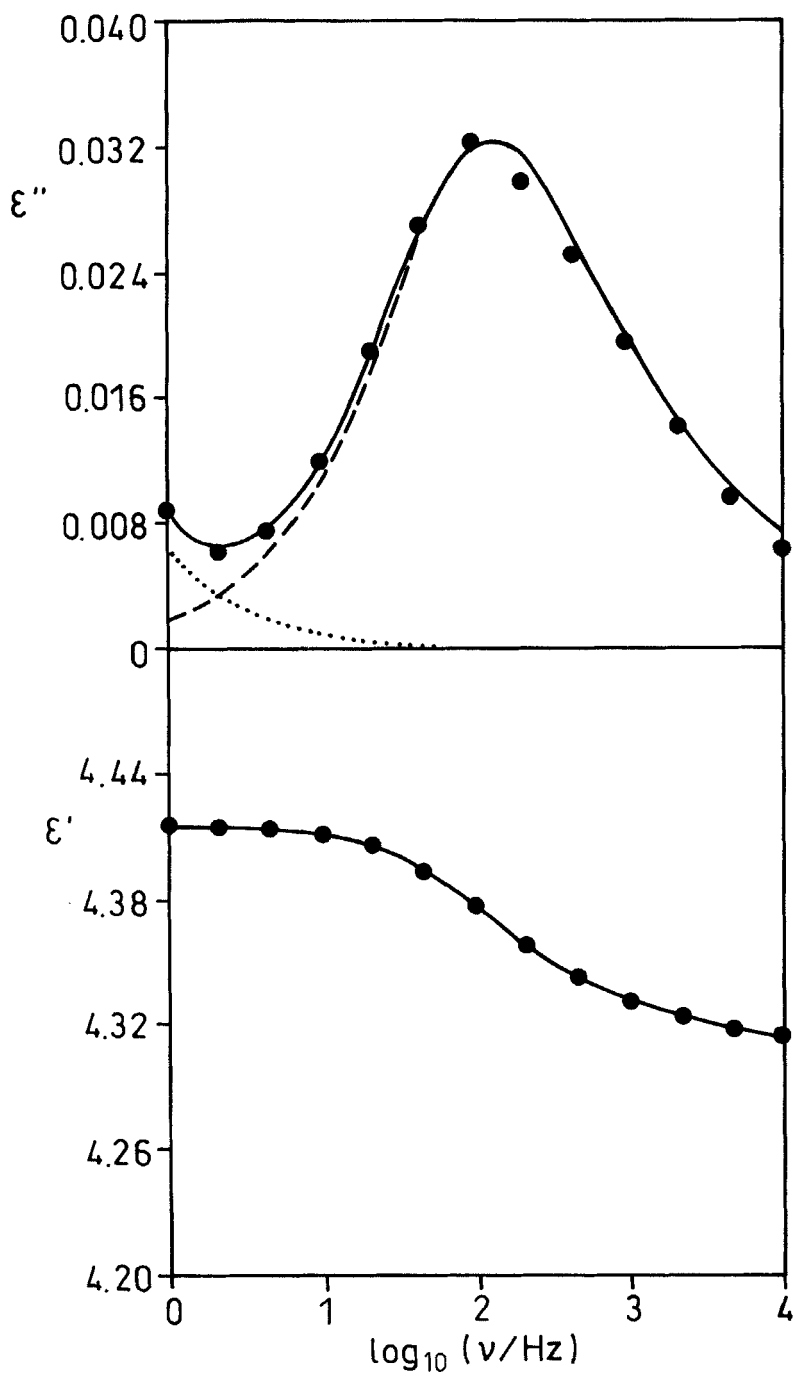
Figure 5.   Real (ε') and imaginary (ε'') part of the complex dielectric response function versus frequency at 263·3 K for the α process. The solid lines represent the fit of the data using the empirical Havriliak–Negami function. For the loss function an additional conductivity contribution has to be considered (dotted line). Addition of the conductivity contribution and the HN-function (dashed line) results in the presented fit (solid line).
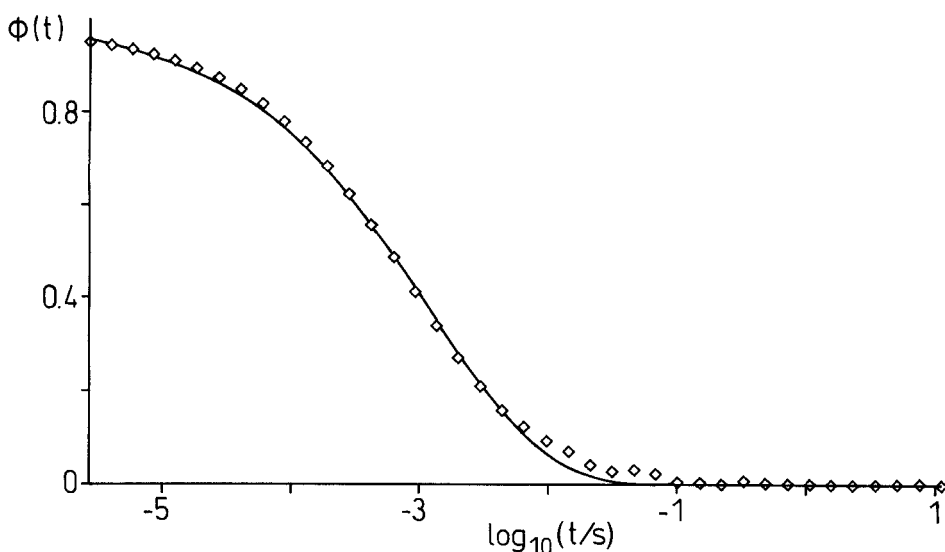
$\phi(t)$

Figure 6.   Dipole–dipole correlation function $\phi(t)$ versus time evaluated at 263·3 K from the dielectric response function in figure 5. The solid line indicates the fit according to the KWW function.

times, $\tau_{KWW} > 0.01$ s. The shape parameters $\alpha_{HN} = 0.80$ and $\gamma_{HN} = 0.60$ of the Havriliak–Negami function (1) do not change significantly over the whole measured frequency range. The alternative description by the KWW function (4) shows constant values for β_{KWW} of 0·49. This analysis shows that the axial rotation of the discs not only exhibits a non-Arrhenius temperature dependence characteristic of a glass transition, but also the non-exponential relaxation has the same characteristics as known for other glass forming isotropic liquids and polymers [26,27]. This emphasizes again, that the discotics considered here despite their molecular complexity may serve as model systems for the glass transition, since the molecular dynamics are so well defined. Currently 2D exchange ^{2}H NMR experiments are being performed to check the symmetry of the molecular reorientation.

The second dynamic process is assigned to local ester group rotations which do not seem to be influenced by the glass transition. Due to the lower dielectric strength of this process, the experimental data can be well fitted only in the range of the frequency response analyser (FRA 1254, resolution $\tan \delta = 10^{-5}$), for example, for a temperature of 180·1 K rather low values of $\alpha_{HN} = 0.50$ and $\gamma_{HN} = 0.40$ are found. This indicates that the β process likewise is not uniform, but corresponds to a considerable distribution of correlation times as found previously for discotic polymers [18,19].

The interesting question of the influence of the glass transition upon the β process [28] cannot be solved at the moment, since at these temperatures the mean relaxation frequencies are in the range of the frequency gap (2–10 MHz) between the plate condenser geometry and the coaxial line technique. However, we hope to overcome this experimental problem of dielectric spectroscopy by the use of solid-state ^{2}H NMR on side chain deuteriated substances.

4.   Conclusions

This comparative study of six triphenylene based discotic mesogens where only one side chain is systematically varied reveals the molecular origin of the glass transition

found in unsymmetrically substituted systems. At this point we would like to state that we found this effect of a hetero ester chain for a large number of new triphenylene based low molecular weight and polymeric compounds which form columnar mesophases and we feel it is a more general feature. Steric effects due to the preferred out-of-plane conformation and possibly the dipole moment of the ester substituent has a strongly stabilizing influence upon the intramolecular interactions thus leading to significantly higher clearing temperatures. It also leads to a suppression of crystallization giving rise to a glass transition at substantially lower temperatures. The dynamic glass transition is revealed by dielectric measurements and ^{2}H NMR and is clearly assigned to the rotations of the discs inside the columns. A second dynamic process is attributed to rotations of the ester dipole moments around local axes.

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