**Liquid Crystals**
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

# Fluoroalkylated discotic liquid crystals

U. Dahn[a]; C. Erdelen[a]; H. Ringsdorf[a]; R. Festag[b]; J. H. Wendorff[b]; P. A. Heiney[c]; N. C. Maliszewskyj[c]
[a] Institut für Organische Chemie, Johannes Gutenberg-Universität Mainz, Mainz, Germany [b] Fachbereich Physikalische Chemie und wissenschaftliches Zentrum für Materialwissenschaft, Philipps-Universität Marburg, Marburg, Germany [c] Department of Physics, University of Pennsylvania, Philadelphia, Pennsylvania, U.S.A.

**To cite this Article** Dahn, U. , Erdelen, C. , Ringsdorf, H. , Festag, R. , Wendorff, J. H. , Heiney, P. A. and Maliszewskyj, N. C.(1995) 'Fluoroalkylated discotic liquid crystals', Liquid Crystals, 19: 6, 759 — 764

**To link to this Article: DOI:** 10.1080/02678299508031096

**URL:** http://dx.doi.org/10.1080/02678299508031096

LIQUID CRYSTALS, 1995, VOL. 19, NO. 6, 759–764

# Fluoroalkylated discotic liquid crystals

by U. DAHN*†, C. ERDELEN†, H. RINGSDORF†, R. FESTAG‡,
J. H. WENDORFF‡, P. A. HEINEY§ and N. C. MALISZEWSKYJ§

† Institut für Organische Chemie, Johannes Gutenberg-Universität Mainz,
J.-J.-Becher Weg 18-22, 55099 Mainz, Germany
‡ Fachbereich Physikalische Chemie und wissenschaftliches Zentrum für Materialwissenschaft,
Philipps-Universität Marburg, 35032 Marburg, Germany.
§ Department of Physics, University of Pennsylvania, Philadelphia, Pennsylvania 19104-6396, U.S.A.

(*Received 13 March 1995; accepted 26 May 1995*)

The concept of mesophase stabilization by partial fluorination of side chains has been extended to discotic systems. The mesophase structure is essentially unchanged, whereas the temperature range of the mesophase is strongly affected by the fluorinated side chains. Triphenylene substituted with only one partially fluorinated side chain exhibits a decrease of the clearing temperature, whereas for symmetrically substituted systems a broad range mesophase has been observed. This behaviour can be attributed to a segregation of the incompatible parts of the molecule giving rise to a stabilized columnar structure for the symmetrical substitution pattern.

## 1. Introduction

Compounds containing fluorocarbon chains in close proximity to hydrocarbon chains are of increasing interest in terms of their supramolecular properties. Due to the reduced affinities of fluorocarbons for aromatic and aliphatic species [1], they show 'amphiphilic' behaviour and tend to form highly organized structures. This gives rise to interesting surfactant effects [2] and mixing behaviour [3], to unusual solid state structures [4] and especially to liquid crystallinity.

It is known that diblock molecules such as $CF_3(CF_2)_n$–$(CH_2)_mCH_3$ exhibit liquid crystalline behaviour both as low molecular mass species [5] and as microblock polymers [6]. By attaching partially fluorinated alkyl chains to rod-like mesogens, 'hybrid tail' substituted calamitics are formed which consist of several segments incompatible on a molecular level [7]. Such systems tend towards microphase separation, and thus form mainly lamellar structures. The resulting smectic phases display enhanced stability, with clearing temperatures increasing monotonically with side chain length [8].

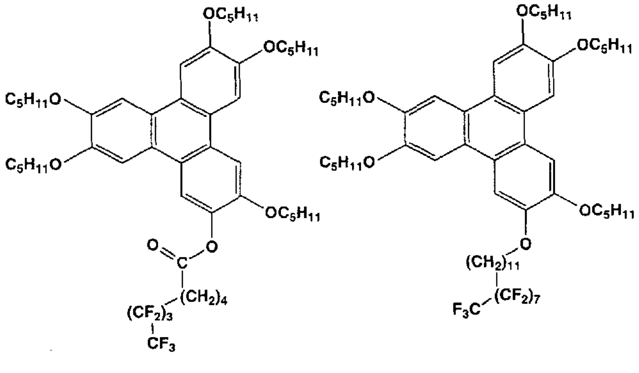
An intriguing issue therefore presents itself in the study of the influence of fluorocarbon–hydrocarbon chain interactions in systems of functional discotics [9], the second important class of mesogens. In order to establish a correspondence with other, non-fluorinated systems, we have chosen the well investigated triphenylene [10] as the discoid core.

## 2. Synthesis

For the synthesis of the mono- and hexasubstituted triphenylene derivatives, various esterification, transesterification and etherification routes were applied.

Two monoperfluoroalkylated model compounds (**1** and **2**) as well as a homologous series of three hexasubstituted compounds (**5a–c**) were investigated. Compound **1** was prepared by esterification of monohydroxy-pentakispentyloxytriphenylene [11] with a partially fluorinated nonanoic acid [12] mediated by DCC (dicyclohexylcarbodiimide) and with *N,N*-dimethylaminopyridine as catalyst [13]. The ether **2** was obtained by a Mitsunobu reaction [14] of the same triphenylene species with a partially fluorinated nonadecanol [15].

The synthesis of the symmetrically hexasubstituted species **5a–c** is based on analogous experiments with

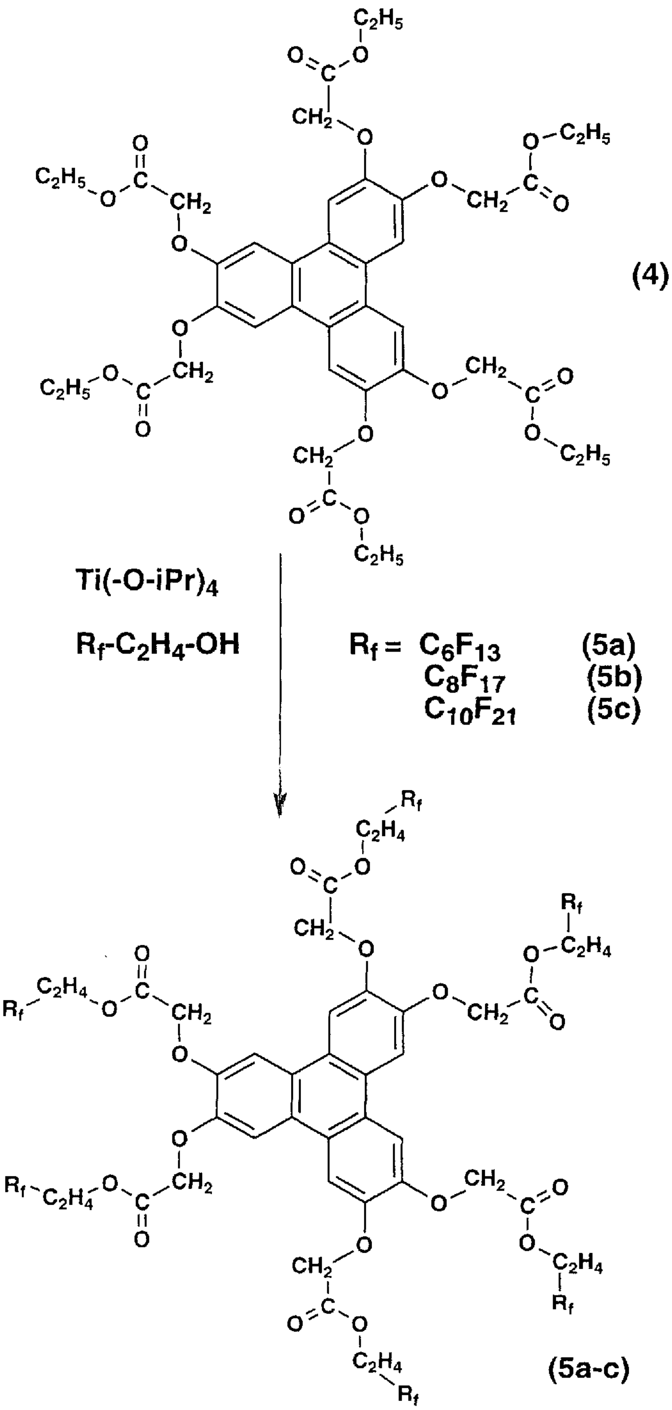


(1) (2)

Scheme 1.

---

* Author for correspondence.



Scheme 2.

non-fluorinated triphenylene derivatives [16]. They were prepared according to scheme 2: starting with the hexaethyl ester **4** (formed by deacylating etherification of hexa-acetoxytriphenylene [17]), a transesterification was achieved, catalysed by tetraisopropylorthotitanate [18] and using an excess of the fluorinated alcohol.

The synthetic details are given in the experimental section.

## 3. Results and discussion

Compound **1**, which contains a single ester-bound $C_9$ chain with four fluorinated carbon atoms, displays LC behaviour similar to non-fluorinated triphenylenes. Within the ($D_h$) mesophase, the intercolumnar spacings are slightly enlarged (21·5 Å) compared to hexapentyloxytriphenylene [19]. In comparison to non-fluorinated analogues [20] the mesophase range is slightly depressed.

The length of the single $C_{19}$ chain in compound **2** exceeds a critical limit. This triphenylene derivative melts at 55°C, but no LC behaviour is detected by either polarized optical microscopy or by DSC measurements. Obviously, in this case the irregular geometry of the molecule and the tendency of the $-(CF_2)-$ segments towards crystallization are dominating factors.

The phase behaviour of the symmetrically substituted triphenylenes **5a–c**, as determined by DSC, is given in the table below. All these compounds exhibit broad mesophases compared to compound **4** (see the table). A clearing point cannot be observed for any of the homologous compounds because decomposition occurs at about 215°C. The melting points are rather low, compared to the starting hexaethyl ester **4**, and vary from 30 up to 115°C, increasing with the chain length. The DSC studies showed considerable supercooling of the recrystallization process and gave melting enthalpies between 20 and 51 $\mathrm{kJ\,mol^{-1}}$. Polarized optical microscopy observations on this series of compounds revealed birefringence, but no specific textures could be obtained since sample preparation is hindered by decomposition. In the liquid crystalline phase the samples are viscous and hardly deformable, indicating the presence of highly ordered structures.

The stabilization of the mesophase can be explained by the separation of the noncompatible fluorinated and non-fluorinated parts of the lateral chains, thus giving rise to columnar structures. The low clearing point of the mono-fluorinated compound (**1**) can accordingly be attributed to a disturbance of the columnar packing by the single fluorinated chain. All data as discussed for compounds **1**, **2** and **5a–c** are summarized in the table.

From X-ray powder diffraction we identify (see figure 1) the phase of both **5a** and **5b** as $D_{hd}$. The measured intercolumnar spacings are 30·3 and 32·5 Å (measured at 130 and 115°C), respectively. These values indicate that there must be some interdigitation of fluoroalkyl chain segments between columns. The structure of **5c** should follow the same trend, but in fact does not. Rather, the X-ray powder diffractogram in the nominal mesophase hints at a coexistence of two different structures of different correlation lengths.

Phase behaviour and intercolumnar distances for mono- and hexaperfluoroalkylated triphenylenes. Compound **3** (hexapentyloxytriphenylene) and **4** (see scheme 2) were used as reference systems.

| Compound | Phase behaviour/°C | $a_{\text{hex}}$/Å |
|---|---|---|
| **1** | Cr 38 $D_h$ 98I | 21·5 |
| **2** | Cr 55 I | — |
| **3** | Cr 69 $D_h$ 122 I | 20·19 |
| **4** | Cr 122 $D_h$ 172 I | 19·2 |
| **5a** | Cr 30 $D_h$ 210 decomp | 30·3 |
| **5b** | Cr 47 $D_h$ 217 decomp | 32·5 |
| **5c** | Cr 115 $D_?$ 215 decomp | — |

Transition temperatures in °C; Cr: crystalline, $D_h$: discotic hexagonal columnar, I: isotropic.

Common to all measured diffraction patterns is a halo of intensity comparable to, or larger than that of the Bragg reflections. The characteristic spacing is about 5·5 Å, about 1 Å larger than that measured for hydrocarbon chains. An intriguing feature of these diffractograms is the small intensity of the 100 reflection, which is commonly the strongest reflection in powder diffractograms of columnar mesophases. The enhanced intensity of the diffuse scattering relative to the 100 reflections can be explained in part by the increased electron density of the fluorocarbon tails relative to that of equivalent hydrocarbons.

Studies on the dielectric behaviour were performed over a broad temperature and frequency range to elucidate the molecular dynamics of both compounds **5b** and **5c** in the cystalline and discotic state. The molecular motions were expected to be strongly affected by the fluorination due to local phase separation tendencies and the increased rigidity of the fluorinated side chains. Three different relaxations were detected for both compounds. The dynamical behaviour will be discussed exemplarily for compound **5b** in the following text.

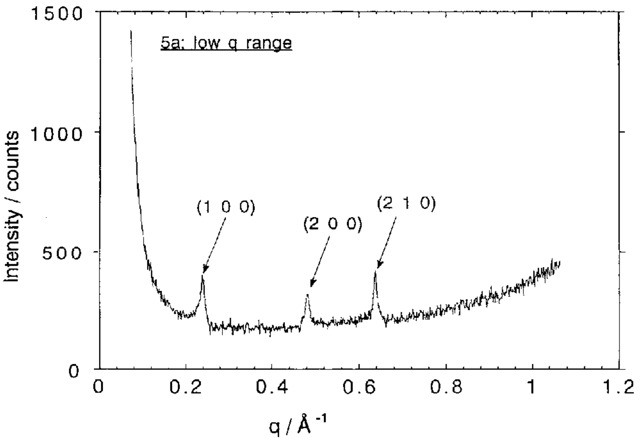


Figure 1. Low angle range of the X-ray powder diffractogram of compound **5a** at 130°C, showing the low angle side of the amorphous halo and the Bragg peaks of the hexagonal lattice.

As shown in figure 2, one secondary ($\gamma$)-relaxation occurred in a temperature domain between 140 and 210 K. This relaxation is thermally activated (Arrhenius behaviour) with an activation energy of 32 kJ mol$^{-1}$ (see figure 3). This process can be attributed to the motion of the ether linkage of the side chains: secondary relaxations in that temperature region and with activation energies of nearly 30 kJ mol$^{-1}$ are well known from triphenylene derivatives symmetrically substituted with alkoxy chains [21] in the crystalline state.

The second secondary ($\beta_1$)-relaxation process between 290 and 330 K has an unusually high activation energy of 160 kJ mol$^{-1}$ (see figure 3) which has not been observed for triphenylene derivatives so far. We propose a locally hindered motion of the (ester-)linkage group to the perfluoro chain. The relaxation strength turned out to be as expected for such ester groups, but due to the perfluoroalkylation, an unusually high activation energy is obviously characteristic for this kind of motion. The fluorination seems to lead to a higher stiffness of the side chain and therefore to a stronger coupling to the neighbourhood.

In addition to these processes a third relaxation ($\beta_2$) was detected at high temperatures, in the liquid crystalline phase. A secondary relaxation process has previously been reported for the discotic columnar glassy state [22]; it was attributed to motions of ester or ether groups in the corresponding glassy state. The process discussed in [22] happened, however, at a much lower temperature, corresponding to the one characteristic of the $\gamma$-process described above. The $\beta_2$-relaxation process is disturbed by the phase transition in the accessible frequency region and therefore the evaluation of the data must be performed with great care. This relaxation process is also thermally activated (see figure 3) with an activation energy of 60 kJ mol$^{-1}$, and it is thus not a cooperative process.

To get more detailed information we investigated the distribution of relaxation times using the approach of Havrilak and Negami [23] (see figure 4), which revealed the different behaviour of the relaxations in the crystalline and liquid crystalline state.

In the crystalline state the distribution is relatively broad ($\alpha = 0{\cdot}64$) and more or less symmetric ($\beta = 0{\cdot}5$), whereas in the liquid crystalline state the relaxation is narrow ($\alpha = 0{\cdot}09$) and relatively symmetric ($\beta = 0{\cdot}6$).

The relaxation behaviour of discotic mesogens with fluorocarbon–hydrocarbon chains differs strongly from those not containing fluorocarbon side chains. A typical feature seems to be the high activation energy of one secondary relaxation. Of particular interest is the secondary relaxation in the discotic state. Due to the occurrence of the phase transition the strength of this third relaxation

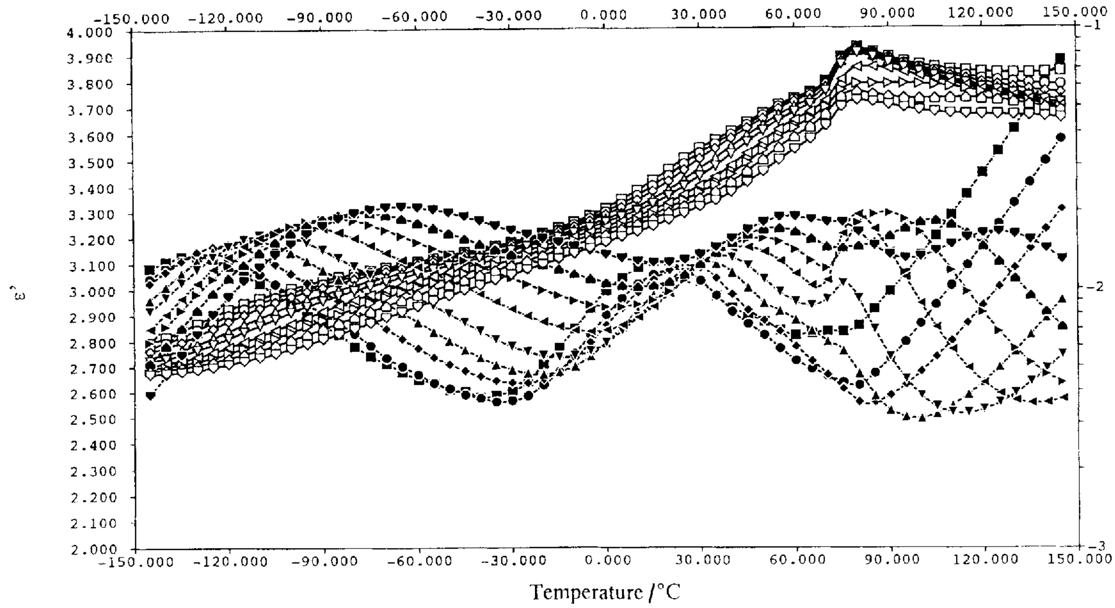


Figure 2. Temperature dependent measurements of the dielectric constant $\varepsilon'$ and the loss factor $\tan \delta$ of compound **5b**. ■ $f = 139$ Hz; ● $f = 373$ Hz; ◆ $f = 1$ kHz; ▲ $f = 3{\cdot}75$ kHz; ▼ $f = 10$ kHz; ◀ $f = 37{\cdot}5$ kHz; ▶ $f = 100$ kHz; ⬆ $f = 250$ kHz; ⬇ $f = 667$ kHz.

cannot be determined. Therefore we can only speculate about the molecular reason for this unusual relaxation process; perhaps it relates to an additional molecular motion which is only possible in the liquid crystalline state.

The compound **5c** shows a similar relaxation behaviour with slight differences in activation energies due to the different chain length: $\gamma$-relaxation $\Delta H = 26{\cdot}5\,\mathrm{kJ\,mol^{-1}}$, $\beta_1$-relaxation $178\,\mathrm{kJ\,mol^{-1}}$, $\beta_2$-relaxation $43\,\mathrm{kJ\,mol^{-1}}$.

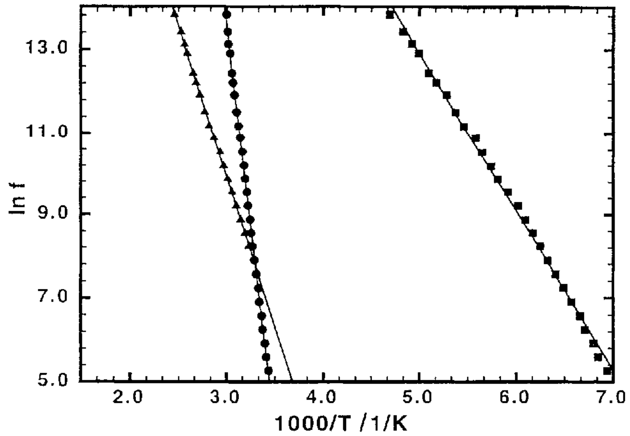


Figure 3. Activation energies of the secondary relaxations of compound **5b**. ■ $\Delta H = 31{\cdot}7\,\mathrm{kJ\,mol^{-1}}$; ● $\Delta H = 160\,\mathrm{kJ\,mol^{-1}}$; ▲ $\Delta H = 60\,\mathrm{kJ\,mol^{-1}}$.

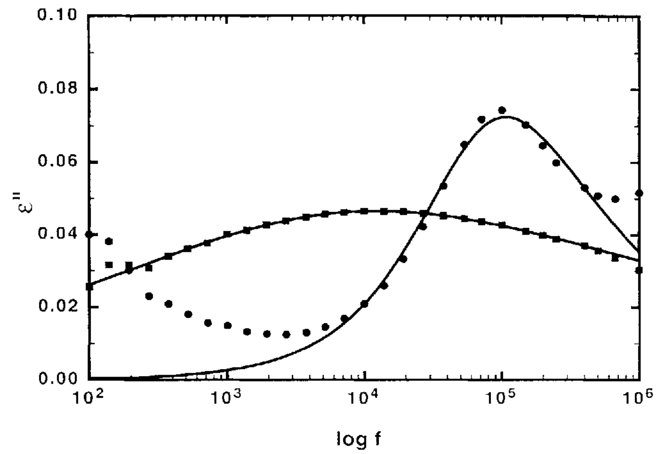


Figure 4. Distribution of the relaxation times in the crystalline state (low temperature relaxation ■ $T = 163$ K) and the liquid crystalline state (● $T = 363$ K); compound **5b**.

## 4. Experimental

### 4.1. *2-(5-Perfluorobutyl)pentanoyloxy-3,6,7,10,11-pentakispentyloxytriphenylene* 1

Monohydroxy-pentakispentyloxytriphenylene (75 mg, 0·11 mmol), 5-perfluorobutylpentanoic acid (33 mg, 0·09 mmol), dicyclohexylcarbodiimide (22 mg, 0·11 mmol) and a catalytic amount of *N*,*N*-dimethylaminopyridine were stirred in 15 ml of dichloromethane under exclusion of moisture for 4 d. After filtering the precipitated dicyclohexylurea, the solution was washed with water, 5 per cent acetic acid and again water. Drying with $Na_2SO_4$ and removing the solvent afforded the crude product which was purified first by flash chromatography (petroleum ether/acetone: 6/1) jand then by preparative TLC (toluene/acetone: 70/1). Yield: 64 mg (73 per cent); $R_f$ (toluene/acetone: 6/1) = 0·6: colourless solid; m.p. 38°C (DSC 10°C min$^{-1}$); calculated for $C_{52}H_{69}F_9O_7$ (976·5 g mol$^{-1}$): C 63·9; H 7·1; Found: C 60·7; H 7·2; $^1$H NMR ($CDCl_3$, 200 MHz) $\delta$[ppm] = 0·98 (t, $C\mathbf{H}_3-(CH_2)_4-$, 15 H), 1·91 (m, aliphatic, 14 H), 2·17 (m, $C_4F_9-C\mathbf{H}_2-$, 2 H), 2·73 (t, $-C\mathbf{H}_2-COO-$, Ar 2 H), 4·22 (m, $-O-C\mathbf{H}_2-$, 10 H), 8·06–7·99 m (aromatic, 6 H); FD-MS, *m/Z* (per cent): 976·5 (100); $[M]^{\bullet +}$.

### 4.2. *2-(11-Perfluorobutyl)undecyloxy-3,6,7,10,11-pentakispentyloxytriphenylene* **2**

Monohydroxy-pentakispentyloxytriphenylene (80 mg, 0·12 mmol) and 11-perfluorooctylundecanol (77 mg, 0·13 mmol) were dissolved in 8 ml THF and 36 mg (0·14 mmol) of triphenylphosphine, dissolved in 2 ml THF were added. Diethyl azodicarboxylate (31 mg, 0·18 mmol) in 1 ml THF was injected at 0°C during 20 min. After warming to room temperature, the mixture was stirred for another 20 h with exclusion of moisture and oxygen. Most of the solvent was evaporated, the oily residue was washed with a mixture of hexane and ethyl acetate and filtered. The filtrate was evaporated and the residue purified first by column chromatography (petroleum ether/$CH_2Cl_2$: 3/2) and then by preparative TLC ($CH_2Cl_2$/MeOH: 100/1). Yield: 62 mg (42 per cent); $R_f$ ($CH_2Cl_2$/petroleum ether: 1/1) = 0·55; colourless solid; m.p. 55°C (Pol. mic. 2°C min$^{-1}$); Analysis calculated for $C_{62}H_{83}F_{17}Q_6$ (1246·6 g mol$^{-1}$): C 59·7, H 7·7; Found: C 59·7, H 7·2, $^1$H NMR ($CDCl_3$, 200 MHz) $\delta$[ppm] = 0·94 (t, $-C\mathbf{H}_3-CH_2$, 15 H), 1·25–1·62 (m, aliphatic, 36 H), 1·93 (m, aliphatic, 14 H), 4·21 t, $O-C\mathbf{H}_2-$, 12 H), 7·83 (s, aromatic, 6 H); FD-MS, *m/z* (per cent): 1246·7 (100); $[M]^{\bullet +}$.

### 4.3. *2,3,6,7,10,11-Hexakis(1H,1H,2H,2H-perfluoro-octyloxycarbonylmethylenoxy)triphenylene* **5a**, *2,3,6,7,10,11-Hexakis(1H,1H,2H,2H-perfluoro-decyloxycarbonylmethylenoxy)triphenylene* **5b** *and* *2,3,6,7,10,11-Hexakis(1H,1H,2H,2H-perfluoro-dodecyloxycarbonylmethylenoxy)triphenylene* **5c**

*Generalized procedure*: In a 10 ml-polymerization vial, the triphenylenehexaethyl ester **4** (77 mg, 0·09 mmol) and the respective fluorinated alcohol, for example, 1H,1H,2H,2H-perfluoro-octanol (3 g, 8·2 mmol) were heated up to 80°C without any contact with moisture and air until the solution or melt was homogeneous. Then, into the stirred mixture, the catalyst, $Ti(O-iPr)_4$ (40 mg 0·15 mmol), was injected and after a few minutes the pressure was reduced continuously to 170 mbar. Bubbles formed in the mixture indicated the beginning of the transesterification. Stirring was continued under the same conditions for 7 h, and overnight under normal pressure. The reaction can be followed by NMR spectroscopy where the characteristic ethoxy-multiplets of the starting product **4** eventually completely vanish. 5 ml of *i*-propanol was added and the mixture left at 4°C for 5 h. The precipitated solid was filtered off and washed thoroughly with chloroform and methanol. The crude product was purified by repeated reprecipitation from trifluoroacetic acid of hexafluoroisopropanol.

**5a**: yield: 146 mg (60 per cent); colourless solid; m.p. 30°C (DSC 10°C min$^{-1}$); analysis calculated for $C_{78}H_{42}F_{78}O_{18}$ (2748·3 g mol$^{-1}$): C 34·1; H 1·5; Found: C 34·3; H 1·73. $^1$H NMR ($CF_3CO_2D$, 200 MHz) $\delta$[ppm] = 2·5 (m, $-OCH_2-C\mathbf{H}_2-R_f$, 12 H), 4·59 (t, ($-OC\mathbf{H}_2-CH_2-R_f$ 12 H), 5·0 (s, $-O-C\mathbf{H}_2-$, 12 H) 7·92 (s, aromatic, 6 H); FD-MS, *m/z* (per cent): 2749·0 (100); $[M]^{\bullet +}$.

**5b**: yield: 148 mg (49 per cent); colourless solid; m.p. 47°C (DSC 10°C min$^{-1}$); analysis calculated for $C_{90}H_{42}F_{102}O_{18}$ (3348·2 g mol$^{-1}$): C 32·3; H 1·3; found: C 32·9; H 1·7 $^1$H NMR ($CF_3CO_2D$, 200 MHz) $\delta$[ppm] = 2·53 (t, $-OCH_2-C\mathbf{H}_2-R_f$, 12 H), 4·64 (s, $-OC\mathbf{H}_2-CH_2-R_f$, 12 H), 5·0 (s, $-O-C\mathbf{H}_2-CO_2-$, 12 H), 7·89 (aromatic, 6 H); FD-MS; *m/z* (per cent): 3352·3 (100); $[M]^{\bullet +}$.

**5c**: yield: 160 mg (45 per cent); colourless solid; m.p. 115°C (DSC 10°C min$^{-1}$); analysis calculated for $C_{102}H_{42}F_{126}O_{18}$ (3948·2 g mol$^{-1}$): C 31·1; H 1·1; Found: C 31·9; H 1·62, $^1$H NMR ($CF_3CO_2D$, 200 MHz) $\delta$[ppm] = 2·48 (m, $-OCH_2-C\mathbf{H}_2-R_f$, 12 H), 4·6 (t, $-OC\mathbf{H}_2-CH_2-R_f$, 12 H), 4·98 ($-O-C\mathbf{H}_2-CO_2-$, 12 H), 7·95 (s, aromatic, 6 H); FD-MS; *m/z* (per cent): 3951·6 (100); $[M]^{\bullet +}$.

### 4.4. *Materials and methods*

The partially fluorinated alchohols were purchased from Riedel-de-Haen and the perfluoroalkyl iodide (for the synthesis of the nonanoic acid) from Aldrich. The monoacetoxy-pentakispentyloxytriphenylene, the starting product to obtain compound **1**, was a gift from BASF AG, Ludwigshafen. NMR spectra were recorded on a Bruker AC-200 spectrometer (200 MHz) with fourier transform data analysis. Chemical shifts are reported in ppm downfield in relation to tetramethylsilane. The DSC measurements were performed on a Perkin–Elmer DSC7 microcalorimeter at a scan rate of 10 K min$^{-1}$ and computed by a TADS data analysis system for the second heating scan. X-ray powder diffractograms were measured using $CuK_{\alpha_1}$ radiation produced by an Elliot GX13 rotating anode X-ray generator (operating at 2·7 kW) and collimated using a singly bent focusing LiF monochromator. Diffracted radiation was analysed using a flat LiF (2 0 0) crystal and collected using a scintillation counter. The resulting instrumental resolution was $\Delta q = 0{\cdot}0045$ Å$^{-1}$, full width at half minimum (FWHM). The dielectric relaxation was measured using a Hewlett–Packard 4284A impedance analyser system (20 Hz to 1 MHz) and a nitrogen heating system with a deviation in temperature of 0·1 K. The samples were unoriented and the condenser plates were assembled at 100°C with the material between them, using 50 µm glass fibres as spacers and by exerting pressure mechanically.

## 5. Conclusions

The introduction of semi-fluorinated alkyl chains into discotic systems affects thermodynamic, structural and dynamic properties strongly and is a versatile way to broaden the mesophase. The structures do not significantly differ from the normal ones, but show larger intercolumnar dimensions corresponding to the length of the lateral chains. The dielectric relaxation studies reveal the presence of three secondary relaxations in such systems with rather unusually high activation energies or small relaxation time distributions. The observed effects should be applicable to mesogens other than the triphenylene core and furthermore lateral ($-CF_2-$) chains could even lead to an induction of LC behaviour in planar, but not discotic molecules by enforcing the columnar structure.

P. A. Heiney and N. Maliszewskyj were supported by National Science Foundation Grants DMR MRL 92-20668 and DMR 93-15341.

## References

[1] Hildebrand, J. H., Fischer, B. B., and Benesi, H. A., 1950, *J. Am. chem. Soc.*, **72,** 4348.
[2] Bennett, M. K., and Zisman, W. A., 1963, *J. phys. Chem*, **67,** 1534.
[3] Rabolt, R. P., Twieg, R. J., Russel, T. P., and Siemens, R. L., 1985, *Macromolecules*, **18,** 1361.
[4] Rabolt, R. P., Twieg, R. J., Russel, T. P., and Siemens, R. L., 1986, *Macromolecules*, **19,** 1135.
[5] Mahler, W., Guillon, D., and Skoulios, A., 1985, *Liq. Crystals*, **2,** 111.
[6] Wilson, L. M., and Griffin, A. C., 1993, *Polym. Prep.*, **34,** 407.
[7] Nguyen, H. T., Sigaud, G., Achard, M. F., Hardouin, F., Tweig, R. J., and Betterton, K., 1991, *Liq. Crystals*, **10,** 389.
[8] Chiang, Y. H., Ames, A. E., Guandiana, R. A., and Adams, T. G., 1991, *Molec. Crystals liq. Crystals*, **208,** 85.
[9] Destrade, C., Nguyen, T. H., Gasparoux, H., Levelut, A. M., and Malthête, J., 1987, *Molec. Crystals liq. Crystals*, **71,** 111.
[10] Destrade, C., Modon, M. C., and Malthête, J., 1979, *J. Phys.*, **40,** C13–17.
[11] Closs, F., Häußling, L., Henderson, P., Ringsdorf, H., and Schuhmacher, P. J., *J. chem. Soc.*, *Perkin Trans, 1*, (accepted).
[12] Brace, N. O., 1973, *J. org. Chem.*, **38,** 3167.
[13] Pielartzik, H., Irmisch-Pielartzik, B., and Eicher, T., 1985, *Houben-Weyl, Methoden der Organischen Chemie*, vol. E4, edited by G. Thieme and H. Müller, 674.
[14] Mitsunobu, O., 1981, *Synthesis*, 1.
[15] Höpken, J., and Möller, M., 1991, *New Pol. Mat.*, **2,** 339.
[16] Plesnivy, T., Ringsdorf, H., Schuhmacher, P., Diele, S. and Nütz, U., 1995, *Liq. Crystals*, **18,** 185.
[17] Kreuder, W., and Ringsdorf, H., 1983, *Makromolek. chem. rap. Commun.*, **4,** 807.
[18] Seebach, D., Hungerbühler, E., Naeff, R., Schnurrenberger, P., Weidmann, B., and Zäger, M., 1982, *Synthesis*, 138.
[19] Bengs, H., Closs, F., Frey, P., Funhoff, D., Ringsdorf, H., and Siemensmeyer, K., 1993, *Liq. Crystals*, **15,** 565.
[20] Werth, M., and Spiess, H. W., 1993, *Makromolek. chem. rap. Commun.*, **14,** 329.
[21] Möller, M., Wendorff, J. H., Werth, M., Spiess, H. W., Bengs, H., and Ringsdorf, H., *Liq. Crystals* (accepted).
[22] Valerien, S. U., Werth, M., Kremer, F., and Spiess, H. W., 1990, *Liq, Crystals*, **8,** 889.
[23] Havrilak, S., and Negami, S., 1966, *J.Polym. Sci.*, **14,** 99.