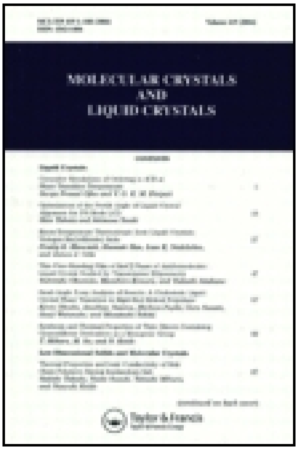

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New Carbosilane Ferroelectric Liquid Crystalline Dendrimers

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New Carbosilane Ferroelectric Liquid Crystalline Dendrimers

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For the first time a series of carbosilane ferroelectric liquid crystalline dendrimers of generations 1 – 3 with 8, 16 and 32 terminal ethyl-L-lactate-containing mesogenic groups, respectively, has been synthesised. Structures and purity of all new compounds were confirmed by ^{1}H NMR spectroscopy and GPC analysis. All LC dendrimers synthesised exhibit only a chiral smectic C mesophase in a broad temperature range. The highest spontaneous polarization is about 140 nC/cm^2 for the LC dendrimer of the first generation and is reduced with increase of generation number.

Keywords: liquid crystalline dendrimers; ferroelectric; mesophase

INTRODUCTION

Ferroelectric liquid crystalline polymers (FLCPs) have attracted great scientific and technological interests for many years, since 1984. Such polymers are considered as interesting materials for electrooptical applications [1]. Up to now a lot of main-chain and side-chain FLCPs have been synthesised and the correlation between the chemical structure and physical properties has been established.

However, in recent years a new class of liquid crystalline polymers, associated with three-dimensional superbranched systems, called LC dendrimers has appeared [2-12]. The most LC dendrimers known nowadays exhibit smectic phases. Lately the first information concerning a ferroelectric LC dendrimers of the third generation has been published by Busson et al. [13], but any values of spontaneous polarization (P_s) were absent there.

This paper presents a number of new carbosilane FLC dendrimers of the first, second and third generations, bearing terminal chiral mesogenic groups (Figure 1) and our preliminary data on their phase behaviour and ferroelectric properties. A choice of this series of dendrimers allows us to study the correlation between their properties (temperatures and enthalpies of phase transitions as well as spontaneous polarization) and molecular structural parameters (generation number)[*].

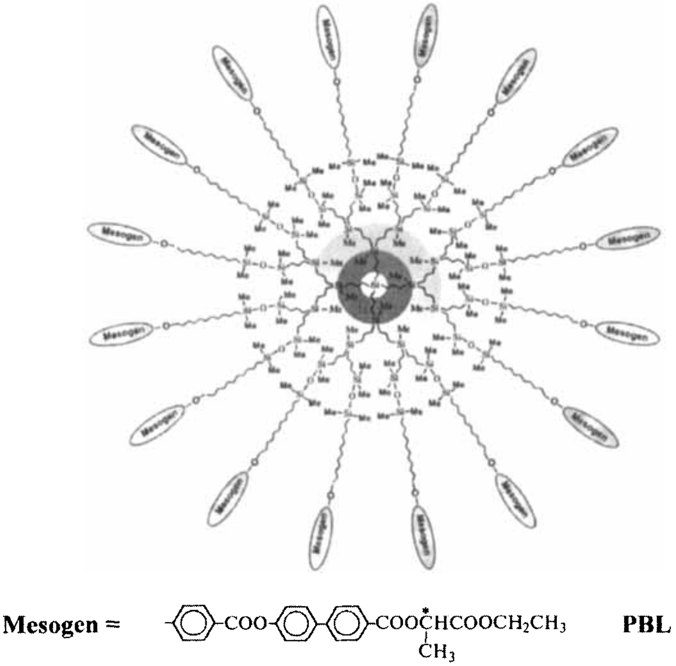

FIGURE 1 Chemical structure of LC dendrimer G-2(Und-PBL)$_{16}$[**].

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[*] Generation number can be defined as the number of branching layers in a spherically-symmetrical molecule of dendrimer [14].

[**] In the formula G-2 is the generation number, 16 is the number of terminal groups shown in the parentheses.

EXPERIMENTAL

^{1}H NMR spectra of the samples were recorded using Bruker WP-250 spectrometers in $CDCl_3$ solution. GPC analysis was performed in THF on Knauer set up equipped with Ultrastyragel 8×300 mm column (Waters) having pore size 10^3 Å, detector – UV spectrometer Knauer. Waters 19×300 mm column fulfilled with Ultrastyragel 10^3 Å was used for preparative GPC. Phase transitions were studied by differential scanning calorimetry (DSC) with a Mettler TA-4000 thermosystem at a scanning rate of 10 K/min. The polarising microscopic investigations were performed using a Mettler FP-800 central processor equipped with a hot stage Mettler FP-82 and control unit in conjunction with a Lomo R-112 polarising microscope. The hysteresis loops were obtained by integration of cell current. A sine-wave voltage (up to 120 V peak to peak at 80Hz) was applied across a 10 μm thick sample. The ohmic leakage was roughly compensated by an active resistance and fine compensation was achieved by on-line loop calculation by IBM PC equipped with an analog-to-digital converter.

Synthesis

The FLC dendrimers were synthesised according to the technique described previously [4]. The synthesis includes three steps.

1. Synthesis of mesomorphous chiral monomer with terminal carbon-carbon double bond according to Figure 2.

Etherification reaction of 11-bromo-1-undecene with 4-hydroxybenzoic acid gave 4-(11-undecenoyloxy)-benzoic acid. Chiral biphenolic ester **2** was synthesised by coupling ethyl-L-lactate with 4-methoxycarbonyloxy-biphenyl-4-carboxylic acid under standard conditions and subsequent deprotection with ammonia in ethanol. The mesogenic α-olefin **3** was prepared by etherification of **1** with compound **2** and purified by silica gel column chromatography. The chemical structure of compound **3** (L)-(+)-4-[1-(ethoxycarbonyl)-(ethoxycarbonyl)]biphenyl-4'-(10-undecenyl-oxy)phenyl-4'-carboxylate has been confirmed by ^{1}HNMR spectroscopy ($CDCl_3$, 250MHz): δ = 1.200-1.560 (m, 15H), 1.646 (d, 3H), 1.821 (m, 2H), 2.043 (m, 2H), 4.044 (t, 2H), 4.242 (q, 2H), 4.956 (m, 2H), 5.333 (q, 1H), 5.814 (m, 1H), 6.976 (d, 2H), 7.305 (d, 2H), 7.668 (d, 4H), 8.158 (d, 4H). $[M]_D^{22}$ = = +133.2° ($CHCl_3$).

Phase behaviour of the monomer synthesised (compound **3**) is given below: Cr_1 52°C Cr_2 66°C SmC* 80°C SmA 134°C I.

2. Synthesis of mesogen-containing fragment with a Si-H terminal group summarised in Figure 3.

The synthetic route has been described in detail elsewhere [4]. The completeness of the reactions was checked by infrared (IR) and ^{1}H NMR spectroscopy.

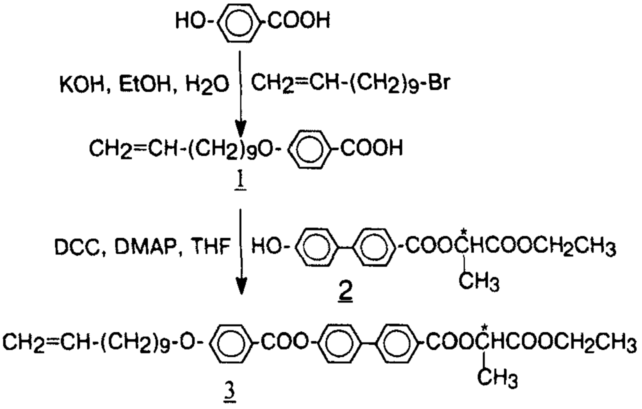
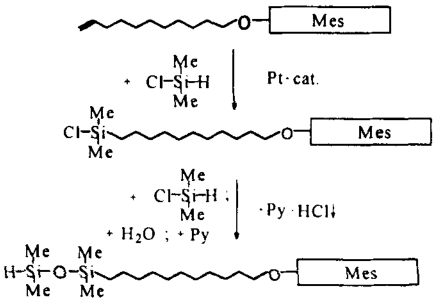


FIGURE 2 Scheme of synthesis of the chiral vinyl monomer.



4

Where Pt-cat = Platinum-divinyltetramethyl-disilaxane complex PC072

FIGURE 3 Scheme of synthesis of the mesogen-containing fragments with reactive terminal Si-H groups.

^{1}H NMR data of compound **4** ($CDCl_3$, 250MHz): δ = 0.053 (s, 6H), 0.156 (d, 6H), 0.523 (t, 2H), 1.200-1.520 (m, 19H), 1.643 (d, 3H), 1.821 (m, 2H), 4.043 (t, 2H), 4.240 (q, 2H), 4.670 (m, 1H), 5.331 (q, 1H), 6.975 (d, 2H), 7.301 (d, 2H), 7.666 (d, 4H), 8.155 (d, 4H).

3. Synthesis of LC dendrimers.

The carbosilane dendrimers of the first, second and third generations with 8,16 and 32 allyl terminal groups [15], correspondingly, were used as the dendritic matrix. The chiral ethyl-L-lactate containing mesogenic groups were linked to them through -O-$(CH_2)_{11}$-$Si(CH_3)_2OSi(CH_3)_2$- spacers by a hydrosilylation reaction (Figure 4) in the presence of Pt-catalyst according to the technique [4]. The purity and the chemical structures of the new FLC dendrimers synthesised were proved by ^{1}H NMR spectroscopy and GPC methods (Table).

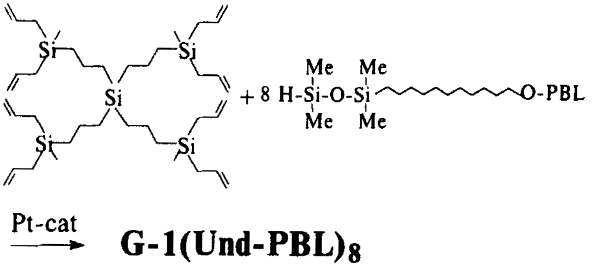


FIGURE 4 Scheme of coupling of the mesogen-containing fragments to carbosilane dendritic matrix of the first generation.

^{1}H NMR data of the LC dendrimers synthesised are shown below: ($CDCl_3$, 250 MHz):**G-1(Und-PBL)$_8$**: δ = -0.072 (s, 12H), 0.031 (s, 96H), 0.543 (m, 64H), 1.187-1.529 (m, 176H), 1.640 (d, 24H), 1.813 (m, 16H), 4.022 (t, 16H), 4.236 (q, 16H), 5.323 (q, 8H), 6.958 (d, 16H), 7.290 (d, 16H), 7.654 (d, 32H), 8.147 (d, 32H). **G-2(Und-PBL)$_{16}$**: δ = -0.073 (s, 36H), 0.029 (s, 192H), 0.551 (m, 112H), 1.200-1.521 (m, 360H), 1.636 (d, 48H), 1.800 (m, 32H), 4.015 (t, 32H), 4.233 (q, 32H), 5.321 (q, 16H), 6.956 (d, 32H), 7.287 (d, 32H), 7.652 (d, 64H), 8.142 (d, 64H). **G-3(Und-PBL)$_{32}$**: δ = -0.072 (s, 84H), 0.029 (s, 384H), 0.559 (m, 240H), 1.200-1.527 (m, 728H), 1.633 (d, 96H), 1.801 (m, 64H), 4.010 (t, 64H), 4.230 (q, 64H), 5.320 (q, 32H), 6.954 (d, 64H), 7.285 (d, 64H), 7.650 (d, 128H), 8.140 (d, 128H).

RESULTS AND DISCUSSION

Phase behaviour

Differential scanning calorimetry and polarising optical microscopy studies of the mesogen-containing dendrimers reveal only a chiral SmC* phase. The samples of all three dendrimers form a broken fan-shaped texture over the entire temperature until the clearing point. This texture is characteristic of the tilted smectic C phase. Only one endothermic peak which corresponds to transition SmC* → I is observed on the DSC thermograms of the FLC dendrimers. Let us emphasis that clearing temperatures and enthalpy phase transitions of FLC dendrimers are reduced with increase of the generation number. On the contrary to that their glass transition temperatures don't depend on the generation number. Note that FLC dendrimers synthesised are characteristic of low glass transition temperatures (T_g ~ -5°C). Temperatures and enthalpy of the phase transitions, polydispersity and maximum P_s values for the dendrimers are summarised in Table.

TABLE Phase behaviour, enthalpies of phase transitions, polydispersity and maximum P_s values of the FLC dendrimers.

Compound	Phase transitions, °C (in the parenthesis -- transition enthalpy, J/g)	M_w/M_n(GPC)	P_s max, nC/cm^2
G-1(Und-PBL)$_8$	g -5 SmC* 175 (10.1) I	1.02	145
G-2(Und-PBL)$_{16}$	g -4 SmC* 167 (8.5) I	1.02	57
G-3(Und-PBL)$_{32}$	g -4 SmC* 158 (6.3) I	1.02	24

Ferroelectric properties

Electrooptical investigations have shown that all FLC dendrimers synthesised exhibit a clear bistable electro-optical switching in the SmC* phase. The switching between two stable states having opposite P_s directions results in hysteresis phenomena, as illustrated in Figure 5 for polarization.

The temperature dependence of the spontaneous polarization for the FLC dendrimers is shown in Figure 6. The highest P_s, which are shown in Table, were carried out at 85°C, 100°C and 115°C for the FLC dendrimers of the first, second and third generations, respectively. It was impossible to do any correct measurements of the P_s below these temperatures. The error of measurements becomes unambiguous when viscosity of the sample increases. As is seen from the Table, the spontaneous polarization decreases with increase of the generation number. This may be explained by reduction of the tilt angle of mesogenic groups in the smectic layers when generation number of FLC dendrimers increases. In order to confirm this suggestion X-ray measurements are in progress.

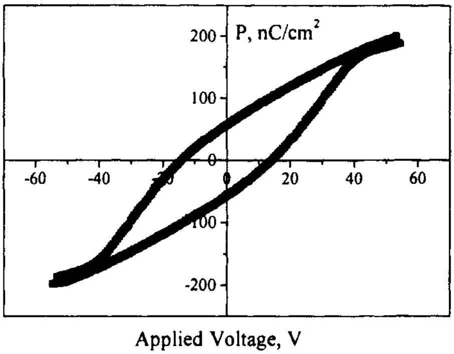


FIGURE 5 Hysteresis of the polarization in the SmC* phase of G-2(Und-PBL), T = 100°C.

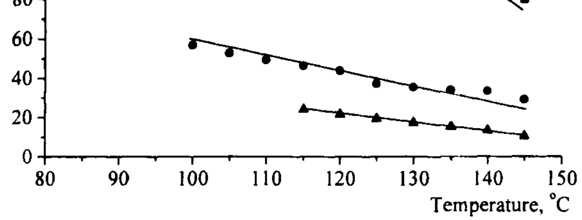


FIGURE 6 The temperature dependence of P_s for the FLC dendrimers.

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References

[1] M.V. Kozlovsky, W. Haase, *Electrical and Optical Polymer Systems,* Edited by D.L. Wise et al, 1141, Marcel Dekker, Inc. (1998).
[2] S.A. Ponomarenko, E.A. Rebrov, N.I. Boiko, N.G. Vasilenko, A.M. Muzafarov, Ya.S. Freidzon, and V.P. Shibaev, *Polym. Sci., Ser.A.* **36,** 896 (1994).
[3] V.Percec, P.Chu, G.Ungar, J.Zhou, *J. Am. Chem. Soc,* **117,** 11441 (1995).
[4] S.A. Ponomarenko, E.A. Rebrov, A.Yu. Bobrovsky, N.I. Boiko, A.M. Muzafarov, V.P. Shibaev, *Liquid Crystals,* **21,** 1 (1996).
[5] H. Frey, K. Lorenz, R. Mülhaupt, *Macromol. Symp.,* **102,** 19 (1996).
[6] K. Lorenz, D. Hölter, B. Stühn, R. Mülhaupt, H. Frey, *Adv. Mater.,* **8,** 414 (1996).
[7] V. Percec, G. Johansson, G. Ungar, J. Zhou, *J. Am. Chem. Soc.,* **118,** 9855 (1996).
[8] V.S.K. Balagurusami, G. Ungar, V. Percec, G. Johansson, *J. Am. Chem. Soc.,* **119,** 1539 (1997).
[9] J.Cameron, A.Facher, G.Lattermann, S.Diele, *Adv. Mater.,* **9,** 398 (1997).
[10] R.M. Richardson, S.A. Ponomarenko, N.I. Boiko and V.P. Shibaev, *Liquid Crystals,* **26,** 101 (1999).
[11] R.M. Richardson, I.J. Whitehouse, S.A. Ponomarenko, N.I. Boiko, V.P. Shibaev, *Mol. Cryst. Liq. Cryst.,* **330,** 1411 (1999).
[12] S.A. Ponomarenko, N.I. Boiko, E.A. Rebrov, A.M. Muzafarov, R.M. Richardson, I.J. Whitehouse, V.P. Shibaev, *Mol. Cryst. Liq. Cryst.,* **332,** 2553 (1999).
[13] P. Busson, H. Ihre, A. Hult, *J. Am. Chem. Soc.,* **120,** 9070 (1998).
[14] D.A. Tomalia, H.D. Durst, *Top. curr. Chem.,* **165,** 193 (1993).
[15] S.A. Ponomarenko, E.A. Rebrov, N.I. Boiko, N.G. Muzafarov, V.P. Shibaev, *Polym. Sci., Ser. A,* **40,** 763 (1998).