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Synthesis and comparative studies of carbosilane liquid crystalline dendrimers with chiral terminal mesogenic groups

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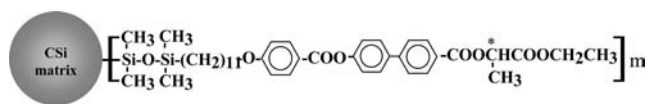
Abstract A new series of carbosilane liquid crystalline (LC) dendrimers from the first to the third generations with 8, 16 and 32 chiral terminal mesogenic groups, respectively, has been synthesized. The molecular structures and purity of all new compounds were confirmed by ^1H NMR spectroscopy and GPC analysis. Data of polarization microscopy and SAX analysis demonstrated that all LC dendrimers synthesized form a chiral smectic SmC^* phase at temperatures below 50 °C. It has been found that bistable electrooptical switching is observed for all dendrimers. The influence of chiral mesogenic fragment length on phase behavior and ferroelectric properties of carbosilane LC dendrimers is discussed.

Keywords Liquid crystalline dendrimers · Ferroelectric · Mesophase · Chiral mesogenic group

Introduction

The last 20 years have been characterized by growing interest in ferroelectric liquid crystalline polymers with quick response and ability to change the properties under electric field. This interest has been generated by their potential applications in display techniques [1]. Up to now, numerous side-chain and main-chain ferroelectric liquid crystalline polymers (FLCPs) have been synthesized and the correlation between their chemical structure and physical properties has been established [2–4]. However, recently interest in FLCPs was shifted to the new class of polymeric system-dendritic FLC. This interest is explained by unique superbranched architec-

ture, high density of peripheral functionalities, symmetrical shape and monodispersity, the absence of entanglements, the low solution and bulk viscosities of dendrimers (especially for large generations of dendrimers, when the shape of the their molecule can be approximated as spherical) [5]. The first information concerning a ferroelectric LC dendrimer of the third generation (G) has been published by Busson et al. [6], but it contained no values of spontaneous polarization (P_s). In our papers [7–9], for the first time, we have synthesized a series of carbosilane (CSi) ferroelectric dendrimers from first to third generations ($G = 1\text{--}3$) with terminal ethyl-L-lactate groups, revealing ferroelectric properties (Structure 1):

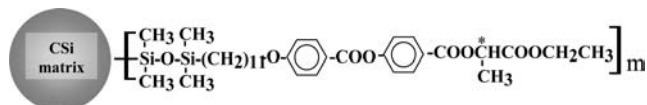


G-n(Und-PBL)m

Structure 1

It has been shown that spontaneous polarization (P_s) is reduced from 145 nC/cm^2 ($G=1$) to 45 nC/cm^2 ($G=3$) with increase of dendrimer generation number. Afterwards, in [10] a series of FLC dendrimers on the base of dendritic aliphatic polyesters have been synthesized and investigated. However, in contrast to carbosilane FLC dendrimers, these compounds have not revealed the dependence of spontaneous polarization from generation number and values of P_s were about 40 nC/cm^2 . Lately, ferroelectric carbosilane dendrimers of the zero generation with banana-shaped mesogenic units [11] and poly(propyleneimine) codendrimers of different generations [12] have been described. It should be noted that determination of spontaneous polarization practically for all synthesized FLC dendrimers was not possible in the full temperature range of SmC^* phase formation. The plausible reason is the high viscosity of functionalized dendrimers in certain temperature region, as most authors point out. Even for the carbosilane dendrimers, synthesized by us [7–9], which are characterized by the low glass transition temperatures ($T_g \sim -5^\circ\text{C}$) and very broad temperature region of chiral smectic mesophase formation (transition temperatures above 150°C), it was impossible to do any correct measurements of the P_s below 70°C . These limiting physical properties result in several problems in practical application. Moreover, at the present moment, we do not have enough information allowing us to establish the correlation between chemical structure and physical properties of FLC dendrimers, since all synthesized ferroelectric dendrimers are characterized by different chemical structures as dendritic matrix with terminal mesogenic groups.

For this reason, we made it our task in this work to synthesize and investigate carbosilane dendrimers of the generation one to three with terminal ethyl-L-lactate group and two benzyl rings in mesogenic fragment (Structure 2) in contrast dendrimers synthesized earlier [7, 8] with three benzene rings in mesogenic fragment (Structure 1):



Structure 2

$$\begin{aligned} m &= 8 : & G - 1(\text{Und} - \text{ELB})_8 \\ m &= 16 : & G - 2(\text{Und} - \text{ELB})_{16} \\ m &= 32 : & G - 3(\text{Und} - \text{ELB})_{32} \end{aligned}$$

Moreover, the selection of this series of dendrimers allows us to study the influence of chiral mesogen fragment length on phase behavior and ferroelectric properties of carbosilane LC dendrimers.

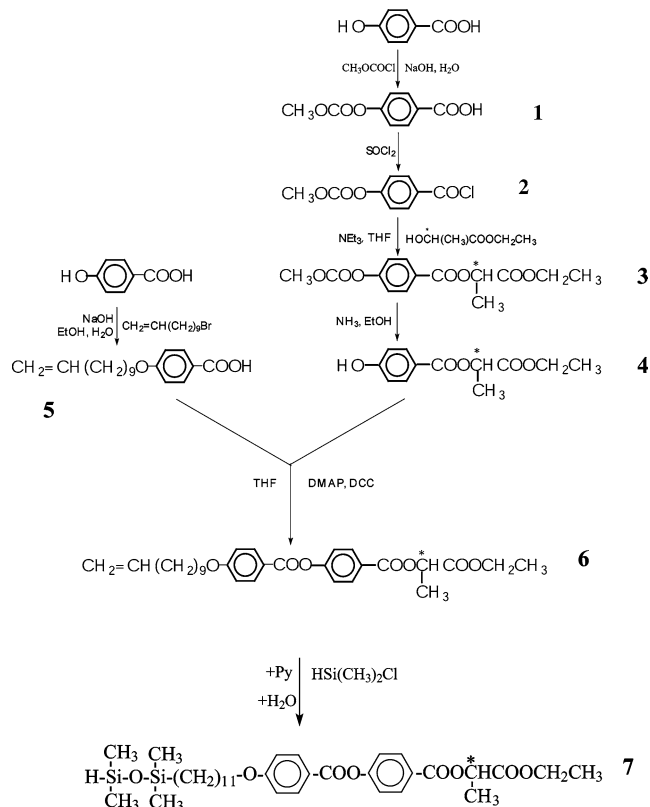
Experimental

Materials

4'-Hydroxy-4-benzoic acid, ethyl-(S)-lactate, 11-bromo-1-undecen, were purchased from Lancaster. *N,N*-dicyclohexylcarbodiimide (DCC) and 4-(dimethylamino)pyridine (DMAP) were purchased from Aldrich Chemical Co. All substances were used without further purification.

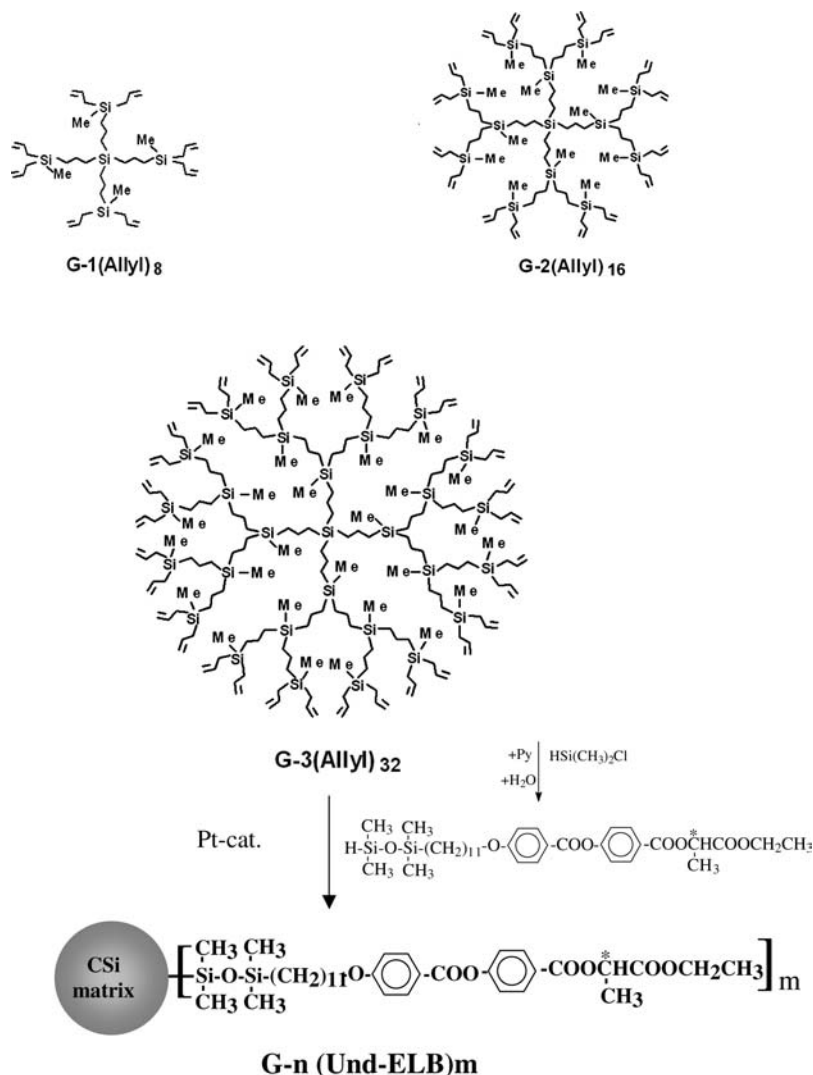
Synthesis of dendrimers

Synthesis of the chiral carbosilane dendrimers was carried out as shown in Schemes 1 and 2.



Scheme 1

Scheme 2



n-Methoxycarbonyloxybenzoic acid (1) 4'-Hydroxy-4-benzoic acid (72 mmol) was placed in a 500-ml three-neck flask equipped with a stirrer, a dropping funnel and a thermometer, and a solution of NaOH (212.5 mmol) in 200 ml of water was added. The flask was cooled in an ice bath to 1–3 °C and methyl chloroformate (117.5 mmol) was slowly added dropwise for 3 h. The mixture was stirred for a further 2 h and hydrochloric acid was added until pH 5 was achieved. The precipitate formed was filtered and washed with water. After drying in vacuum over P₂O₅, the product was recrystallized from ethanol and a white crystalline compound was obtained with a yield of 9.1 g (69%). mp. = 169–171 °C. IR (cm⁻¹): 3100–2600 (OH), 1760 (CO in MeOCOOAr), 1690 (CO in ArCOOH), 1600 (C-C in Ar) and 1260 (COC).

n-Methoxycarbonyloxybenzoyl chloride (2) *n*-Methoxycarbonyloxybenzoic acid (15.3 mmol), thionyl chloride

(5 ml) and a drop of DMF were added successively to a 200-ml round-bottom flask equipped with a reflux condenser with a calcium chloride tube. The excess thionyl chloride was removed with a rotor evaporator and the residue was recrystallized from a toluene-heptane mixture (1:5). The acid chlorides obtained were colorless needleshaped crystals. Yield-94%, mp. = 82 °C.

(*S*)-(+) -4'-[1-(ethoxycarbonyl)-ethyl]-4-methoxycarbonyloxybenzoate (3) A solution of *n*-Compound 2 (46.6 mmol) in dry THF was added dropwise to a solution of ethyl-(*S*)-lactate (61.5 mmol) and triethylamine (9 ml) in 100 ml TGF, cooled in an ice bath. The mixture was stirred for 3 days. Then 500 ml of diethyl ether was added and the solution was washed successively with water (three times with 500 ml). An ether extract was dried over anhydrous Na₂SO₄. After the solvent was distilled in vacuum, the product was purified by column chromatography (eluent: ethylacetate-tolu-

ene 1:10). Yield 56%, colorless oil. IR (cm^{-1}): 1770 (CO in MeOCOAr), 1760 (CO in ArCOO), 1720 (CO in RCOOEt), 1600 (C–C in Ar), 1260 (C–O–C). $[\text{M}]_{\text{D}}^{25} = +55.4^\circ$ (CHCl_3).

(*S*)-(+) -4'-[1-(ethoxycarbonyl)-ethyl]-4-hydroxybenzoate (4) Compound 3 (4.5 mmol) was dissolved in 50 ml of ethanol, cooled in an ice bath and a 25% aqueous solution of ammonia (25 ml) was added. The reaction was monitored by thin-layer chromatography (eluent-ethylacetate-toluene 1:2). In 2 h the reaction was usually complete. Then the solution was acidified with acetic acid until a weak alkaline reaction was achieved, diluted with water and extracted several times with diethyl ether (total volume of the extract was about 500 ml). The solution was dried over anhydrous Na_2SO_4 and the solvent was removed on a rotary evaporator. The yield of colorless oil was 89%. IR (cm^{-1}): 3460 (OH), 1740 (CO in ArCOOR), 1720 (CO in RCOOEt), 1600 (C–C in Ar), 1260 (C–O–C). $[\text{M}]_{\text{D}}^{25} = +64.5^\circ$ (CHCl_3).

4-(10-undecen-1-yloxy) benzoic acid (5) A mixture of 4-hydroxybenzoic acid (37.7 mmol), KI (0.1 g) and NaOH (95.1 mmol) in 60 ml of mixture of water/ethanol (3:1) was heated under reflux with stirring for 1 h while 11-bromo-1-undecene (45.2 mmol) was added dropwise. The mixture was refluxed for 12 h. After cooling the 300 ml of water was added to the reaction mixture. The solution was then acidified with HCl until pH 3–4 was achieved. The precipitated formed was filtered. After drying in vacuum the product was recrystallized from ethanol. A white crystalline compound was obtained with a yield of 68%. Phase transitions: K 77 °C–SmC 117 °C–N 130 °C–I. IR (cm^{-1}): 3420 (OH in COOH), 2940, 2860 (CH_2), 1680 (CO in COOH), 1640 (C=C), 1600 (C–C in Ar), 1260 (C–O–C).

(*S*)-(+) -4-[1-(ethoxycarbonyl)-ethoxycarbonyl]-4'-phenyl-(10-undecen-1-yloxy) benzoate (6) 4-(10-undecen-1-yloxy) benzoic acid (3.74 mmol), phenol 4 (3.74 mmol) and *N,N*-dimethylaminopyridine (3.74 mmol) were dissolved in 3 ml of TGF. Dicyclohexylcarbodiimide (DCC) (4.49 mmol) was added and the resulting mixture stirred for 36 h. The reaction was monitored by TLC using a toluene-ethyl acetate 10:1 mixture as eluent. The precipitate was filtered off, washed with TGF and then diethyl ether (300 ml) was added to the filtrate. The solution was washed successively with water, a 5% solution of acetic acid and finally with water, to pH 7. The ether extract was dried over anhydrous Na_2SO_4 . After the solvent was distilled in vacuum, the product was purified by column chromatography using chloroform as eluent. Yield-75%. ^1H NMR (CDCl_3 , 250 MHz) δ (in ppm): 1.2–1.4 (m, 15H in $(\text{CH}_2)_n$), 1.6 (d, 1H in $\text{COOCH}(\text{CH}_3)\text{COO}$), 1.8 (m, 2H, in $\text{CH}_2\text{CH}_2\text{CH}_2\text{O}$), 2.0 (t, 2H, in $\text{CH}_2=\text{CHCH}_2$), 4.0 (t,

2H, in $\text{CH}_2\text{CH}_2\text{O}$), 4.2 (t, 3H, in COOCHCH_3), 5.0 (m, 2H, in $\text{CH}_2=\text{CHCH}_2$), 5.3 (t, 1H, in $\text{COOCH}(\text{CH}_3)\text{COO}$), 5.8 (m, 1H, in $\text{CH}_2=\text{CHCH}_2$), 7.0 (d, 2H, in Ar-H), 7.3 (d, 2H, in Ar-H), 8.15 (d, 2H, in Ar-H), 8.25 (d, 2H, in Ar-H).

(*S*)-(+) -4-[1-(ethoxycarbonyl)-ethoxycarbonyl]-4'-phenyl-(11-tetramethyl-disiloxyundecen-1-yloxy) benzoate (7) A solution (10 μL) of platinum-divinyltetramethylsiloxane complex in xylene (PC072) was added to the solution of compound 6 (3.12×10^{-3} mol) and dimethylchlorosilane (0.0156 mmol) in absolute toluene (3 ml). The resulting solution was stirred under argon at room temperature for 48 h. The completion of the reaction was checked by IR and ^1H NMR spectroscopy. In the IR spectrum of the reaction products, the disappearance of the band for the stretching vibrations of the terminal carbon-carbon double bonds in the region $1,640\text{ cm}^{-1}$ was observed. Simultaneously, the appearance of the absorption band in the region $1,260\text{ cm}^{-1}$ corresponding to the stretching vibration of the Si- CH_3 bond was detected. ^1H NMR spectrum of the reaction products exhibits no signals due to protons of the terminal carbon-carbon double bond (4.95 and 5.8 ppm). These results proved the fact that hydrosilylation was complete. After that, dimethylchlorosilane (0.112 mol) and 15 ml of THF was added to the reaction mixture. To the resulting solution cooled by water/ice a mixture of water (1.1 ml), pyridine (8.32×10^{-2} mol) and THF (10 ml) was added slowly with vigorous stirring. The reaction mixture was stirred for 2 h at 20 °C. Then 300 ml ether was added to the reaction mixture. The ether layer was separated and then washed with water three times and dried over sodium sulphate. Then the solution was evaporated to dryness in vacuum. The residue was purified by column chromatography over silica-gel using toluene/ethylacetate (20:1) as the eluent. Yield = 60%. $T_m = 32^\circ\text{C}$ ^1H NMR (250 MHz, CDCl_3) δ (in ppm): 0.05 (s, 6H, $\text{OSi}(\text{C}_2\text{H}_5)_2$), 0.15 (d, 6H, $\text{HSi}(\text{C}_2\text{H}_5)_2$), 0.5 (t, 2H, SiC_2H_5), 1.2–1.4 (15H, $\text{SiCH}_2(\text{C}_2\text{H}_5)_7$), 1.6 (d, 1H, $\text{COOCH}(\text{C}_2\text{H}_5)\text{COO}$), 1.8 (m, 2H, $\text{CH}_2\text{C}_2\text{H}_5\text{O}$), 4.0 (t, 2H, $\text{CH}_2\text{C}_2\text{H}_5\text{O}$), 4.2 (3H, $\text{COOCH}_2\text{C}_2\text{H}_5$), 4.7 (m, 1H, $\text{HSi}(\text{CH}_3)_2$), 5.3 (1H, $\text{COOCH}(\text{CH}_3)\text{COO}$), 7.0 (d, 2H, Ar-H), 7.3 (d, 2H, Ar-H), 8.15 (d, 2H, Ar-H), 8.25 (d, 2H, Ar-H).

G-1(Und-ELB)₈ To the solution of compound 7 (0.396 g, 0.615 mmol) and G-1(All)₈ (0.0357 g, 0.051 mmol) in 3 ml absolute toluene, 10 μL PC072 was added. The resulting solution was stirred under argon for 7 days at 33 °C. The completeness of the reactions was checked by ^1H NMR spectroscopy and GPC analysis. After the reaction was complete, the Pt-catalyst was removed by column chromatography over silica-gel using toluene as the eluent. After that the target product should be purified by GPC. Yield = 68%. ^1H NMR (250 MHz, CDCl_3) δ (in ppm): -0.075 (s, 12H), -0.047 –

0.153 (m), 0.557 (m, 64H), 1.180–1.540 (m, 176H), 1.626 (d, 24H, $J=7.2$ Hz), 1.808 (m, 16H), 4.024 (t, 16H, $J=6.4$ Hz), 4.231 (q, 16H, $J=7.1$ Hz), 5.308 (q, 8H, $J=7.0$ Hz), 6.958 (d, 16H, $J=8.8$ Hz), 7.291 (d, 16H, $J=8.8$ Hz), 8.138 (dd, 16H, $J=7.0$ Hz).

G-2(Und-ELB)₁₆ was synthesized from carbosilane dendritic matrix G-2 (All)₁₆ (0.043 g, 0.025 mmol) and compound **7** (0.515 g, 0.8 mmol) according to the procedure for G-1 (Und-ELB)₈. Yield = 65%. ¹H NMR (250 MHz, CDCl₃) δ (in ppm): -0.079 (s, 36H), -0.040–0.150 (m), 0.552 (m, 144H), 1.150–1.500 (m, 360H), 1.616 (d, 48H, $J=7.2$ Hz), 1.797 (m, 32H), 4.011 (t, 32H, $J=6.4$ Hz), 4.222 (q, 32H, $J=7.1$ Hz), 5.300 (q, 16H, $J=7.0$ Hz), 6.946 (d, 32H, $J=8.8$ Hz), 7.281 (d, 32H, $J=8.8$ Hz), 8.127 (dd, 64H, $J=7.0$ Hz).

G-3(Und-ELB)₃₂ was synthesized from carbosilane dendritic matrix G-3 (All)₃₂ (0.050 g, 0.013 mmol) and compound **7** (0.552 g, 0.86 mmol) according to the procedure for G-1 (Und-ELB)₈. Yield = 67%. ¹H NMR (250 MHz, CDCl₃) δ (in ppm): -0.073 (s, 84H), -0.035–0.150 (m), 0.558 (m, 304H), 1.175–1.505 (m, 728H), 1.613 (d, 96H, $J=7.2$ Hz), 1.793 (m, 64H), 4.007 (t, 64H, $J=6.4$ Hz), 4.221 (q, 64H, $J=7.1$ Hz), 5.304 (q, 32H, $J=7.0$ Hz), 6.940 (d, 64H, $J=8.8$ Hz), 7.279 (d, 64H, $J=8.8$ Hz), 8.121 (dd, 128H, $J=7.0$ Hz).

Techniques

¹H NMR spectra of all samples were recorded using Bruker WP-250 spectrometer in CDCl₃ solution. GPC analysis was performed in THF on a Knauer set up equipped with Ultrastaygel 8×300 mm column (Waters) having pore size 1,000 Å, detector—UV spectrometer Knauer. Waters 19×300 mm column fulfilled with Ultrastaygel 1,000 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 optical investigation of all textures was performed by polarization microscopy using Lomo R-112 polarizing microscope with a hot stage Mettler FP-800. X-ray diffraction measurements were made using CuK α radiation ($\lambda=1.542$ Å) from a 1.2 kW sealed tube. Monochromatisation was done with a graphite crystal. Electric measurements of dendrimers were performed using a repolarisation method [9]. A sine-wave voltage (up to 120 V peak to peak, frequency range 10–100 Hz) was applied across a 4- μ m thick sample.

Results and discussion

Synthesis

The LC dendrimers were synthesized according to the technique offered previously [5]. The synthesis includes

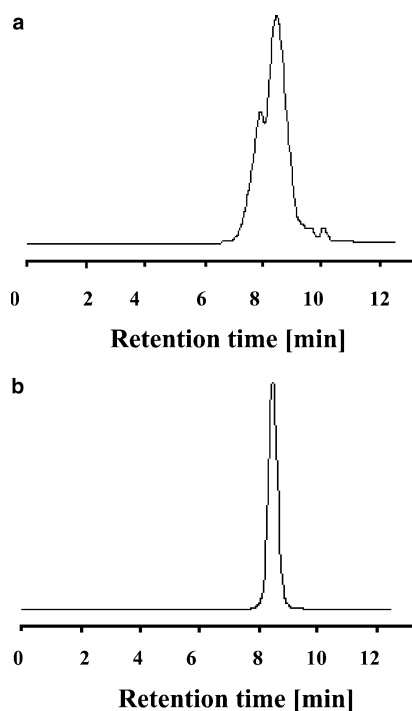
four steps: (a) synthesis of carbosilane dendrimers of different generations with allyl terminal group; (b) synthesis of mesomorphous chiral fragments with terminal double C=C bond (c) synthesis of mesogen-containing fragments with Si-H terminal group, (d) coupling of modified mesogenic groups to the dendritic matrixes (Schemes 1, 2).

- Synthesis of carbosilane dendrimers of different generations with allyl terminal groups. All carbosilane dendrimers, namely G-1(All)₈, G-2(All)₁₆ and G-3(All)₃₂, used as dendritic matrix in preparation of LC dendrimers, were synthesized according to previously described procedures [13].
- Synthesis of mesomorphous chiral fragments with terminal double C=C bond (Scheme 1, compound **6**). Compound **6** was obtained by the reaction of esterification between compounds **4** and **5**. For synthesis of compound **4** we have used the technique “protection” hydroxy-4-benzoic acid by methyl chloroformate (compound **1**) whereupon ethyl-(S)-lactate chiral group was coupled to compound **1** to give **3**. Compound **3** was subsequently deprotected by ammonia to give the resulting carbonate ester **4**. Compound **5** was prepared by alkylation of 4-hydroxybenzoic acid with 11-bromo-1-undecene.
- Synthesis of mesogen-containing fragments with Si-H terminal group (Scheme 1, compound **7**) The obtained compound **6** underwent hydrosilylation with fivefold excess dimethylchlorosilane in the presence of a platinum catalyst. The completion of the reaction was checked by the disappearance of the signals due to protons of the terminal carbon–carbon double bond ($\delta_1=4.95$ (m, 2H), $\delta_2=5.80$ (m, 1H)) in the ¹H NMR spectra. By the cohydrolysis of obtained silanechloride in 40-fold excess of DMCS and in the presence of equal quantities of water and pyridine, compound **7** was synthesized. Compound **7** was purified by the method column chromatography on silica gel using toluene/ethyl acetate mixture as eluent. Individuality of the obtained substance was proved by the method of TLC, and of structure—by the method of ¹H NMR spectroscopy.
- Coupling of modified mesogenic groups to the dendritic matrixes (scheme 2). Compound **7** was used in the fourth step of synthesis—the coupling of the mesogenic groups to the dendrimers with terminal allyl groups. Coupling was carried out by the reaction of hydrosilylation in the presence of Pt-catalyst. For all generations of dendrimers 1.5-fold excess of the compound **7** was used for providing the completeness of coupling of mesogenic groups to all allyl groups of dendritic matrixes. The bands and proton signals corresponding to the allylic double bonds of the initial dendritic matrix are absent in IR and ¹H NMR spectra of chiral dendrimers. The

Table 1 Phase behavior, enthalpies of phase transitions and polydispersity of the synthesized dendrimers

Dendrimer	Layer spacing (30 °C, Å)	Phase transitions ^a (°C)	M_w/M_n (GPC)
G-1(Und-ELB) ₈	41.0 ± 0.5	g-17 SmC* 47 (7.3) I	1.02
G-2(Und-ELB) ₁₆	42.7 ± 0.5	g-17 SmC* 46 (5.1) I	1.02
G-3(Und-ELB) ₃₂	44.7 ± 0.5	g-17 SmC* 44 (4.1) I	1.02

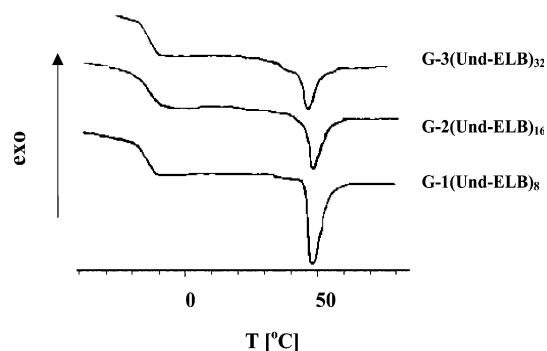
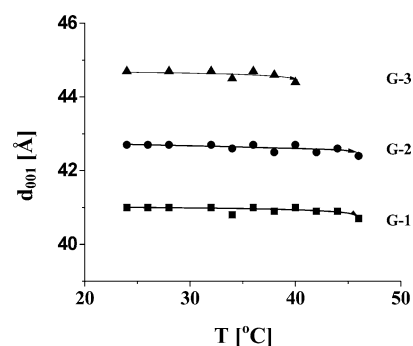
^a Enthalpies of SmC*-I transitions are shown in *parentheses*, J/g

**Fig. 1** GPC trace of G-1(Und-ELB)₈ before (a) and after (b) purification

purity of the final dendrimers obtained was established by GPC. The GPC trace of the synthesized dendrimers had a symmetric peak after final purification (Fig. 1). The molecular mass distribution (M_w/M_n) of the LC dendrimers was 1.02, confirming the monodispersity of compounds synthesized (see Table 1).

Phase behavior and structure

All synthesized dendrimers exhibit liquid crystalline behavior. According to the data obtained by polarizing optical microscopy, the LC dendrimers are characterized by a broken fan-shaped texture, typical of the SmC* phase, both on heating and cooling. The DSC scans (Fig. 2) of the obtained dendrimers showed a second-order transition (glass transition) and only one first-order

**Fig. 2** DSC data of synthesized dendrimers**Fig. 3** Temperature dependences of interlayer spacing for dendrimers G-*n*(Und-ELB)

der phase transition, which corresponds to the transition from smectic phase to isotropic melt (clearing temperature, I). As seen from Fig. 2 and Table 1, clearing temperature decreases very slightly with increasing generation numbers, but enthalpy of this phase transition decreases nearly monotonically with the generation number growth. The glass transition temperature (T_g) is constant for all dendrimers, which is in agreement with previous experimental studies related to carbosilane LC dendrimers [9, 14].

Data of X-rays measurements confirms the forming of only one smectic mesophase by the dendrimers of 1–3 generations with an interlayer spacing d_{001} that remains approximately constant with temperature. However, the

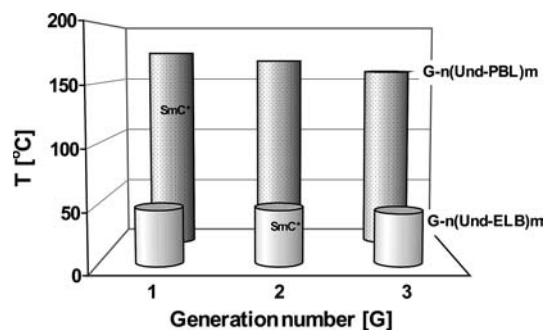


Fig. 4 Phase behaviour of chiral carbosilane LC dendrimers

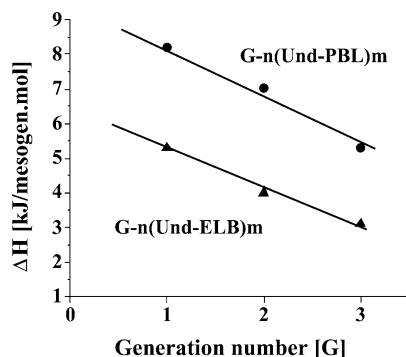


Fig. 5 Dependences of enthalpy transition SmC*—isotropic melt as a function of the generation number

measured spacing increases as the generation number increases (Fig. 3). It should be noted that the X-ray measurements did not allow determination of the tilt angle of mesogenic groups in smectic layers because we did not succeed in orienting the samples even using a high magnetic field (9.4 T). Nevertheless, a clear bistable electrooptical switching observed in thin electrooptical cells of these dendrimers at temperatures near clearing temperature, proved the formation of the tilted SmC* phase.

As mentioned above, the molecular structure of dendrimers of series G-*n*(Und-PBL)m, synthesized in [7, 9] differed from dendrimers synthesized in this work only by the presence of the additional benzene rings in mesogenic groups. As seen from the Figs. 4 and 5, the decrease of mesogenic fragment length results in a dramatic decrease of clearing temperature (more than 100 °C) and the transition enthalpy is twice lower for carbosilane dendrimers with two ring terminal ethyl-L-lactate groups. Meanwhile, all dendrimers are characterized by a common tendency to a decrease of transition enthalpy from smectic phase SmC* to isotropic melt

with an increase of the generation number, and the values of enthalpy lost by each following generations is about 1 kJ/mol mesogenic group.

It is known that increasing the generation number gives rise to an increase of the number of terminal groups in dendritic molecule by a geometrical progression law (see structure of a dendritic molecule). At the same time, the size of the dendritic molecule and, therefore, the “surface” accessible for allocation of terminal groups is increased in quadratic dependence for the each generation [15]. This leads to decrease of the free volume accounted for in one mesogenic group with the increasing generation that produces the sterical hindrances for anisotropic ordering of mesogenic groups. As a result the whole anisotropy of the system is decreased and the transition enthalpy of LC phase-isotropic melt reduces. The decrease of the length of the rigid mesogenic fragment in the terminal group of dendrimer leads to the same effect because the lateral interactions among mesogenic groups responsible for LC ordering fall off.

Conclusions

In summary, the decrease of mesogenic fragment length from three ring to two ring terminal ethyl-L-lactate groups result in dramatic decrease of clearing temperature (more than 100 °C) and the transition enthalpy in chiral LC dendrimers because of the decrease of lateral interactions among mesogenic groups responsible for the formation of LC order.

In spite of the fact that switching was detected for all dendrimers with two ring terminal ethyl-L-lactate groups at temperatures nearly the SmC*—isotropic melt transition (40–46 °C), the spontaneous polarization could not be measured. It is probably explained by the high viscosity of the dendritic matrix at temperatures of SmC* phase existence. In other words the response time is too long for the switching that can lead to errors of measurement. That assumption is based on the fact that it was impossible to do any correct measurements of the Ps below 55 °C for carbosilane dendrimers G-*n*(Und-PBL)m series with three benzyl rings in mesogenic fragment and the same chiral group [9].

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