Ferroelectric Liquid Crystalline Dendrimers: Synthesis, Thermal Behavior, and Electrooptical Characterization

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Received December 21, 1999; Revised Manuscript Received October 21, 2000

ABSTRACT: The preparation and characterization of a series of novel ferroelectric liquid crystalline dendrimers are presented. End-capping of 1-, 2-, and 3-generation dendrimers based on 2,2-bis-(hydroxymethyl)propionic acid with mesogens gave surface-functionalized liquid crystalline compounds with 6, 12, and 24 mesogen-containing units, respectively. 4″-((*R*)-1-Methylheptyloxy)phenyl 4-{4′-[10-(hydroxycarbonyl)decyloxy]phenyl}benzoate was synthesized and used as a mesogen-containing unit. The purity and structure of each compound were determined by ^{1}H NMR spectroscopy, size exclusion chromatography, and elemental analysis. Differential scanning calorimetry and optical microscopy were used to investigate the mesomorphic properties of the mesogen-functionalized dendrimers. The materials displayed a variety of mesophases, including the smectic C* phase. All the liquid crystalline dendrimers showed ferroelectricity, and tilt angle and spontaneous polarization measurements were performed. The obtained results show that the ferroelectric properties of the materials are independent of the generation number of the dendritic scaffold.

Introduction

Most thermotropic liquid crystalline polymers (LCPs) are structurally either main-chain, side-chain, or combined main/side-chain LCPs.[1] Recently, great scientific interest has been devoted to the preparation of dendritic liquid crystalline polymers (DLCPs). The preparation and applications of dendritic macromolecules, i.e., dendrimers and hyperbranched polymers, have been extensively reviewed.[2] Both hyperbranched polymers and dendrimers exhibiting thermotropic liquid crystalline properties have been synthesized according to two different approaches. In the first strategy, mesogen-containing branching units were used in the preparation of hyperbranched polymers[3] and dendrimers[4] displaying various mesomorphic properties. In the second approach, mesogen-containing units were coupled to functional end groups of dendritic scaffolds. Recently, Frey et al.[5] described the synthesis of mesogen-functionalized hyperbranched polyglycerols. Previously, Ramakrishnan et al. prepared both hyperbranched polyesters[6] and hyperbranched polyurethanes[7] functionalized with mesogen-containing units. However, these polymers did not exhibit thermotropic mesophases. More recently, attention has been focused on the preparation of dendrimers with terminal mesogen-containing units. Various types of mesogen-functionalized dendrimers, including organosiloxane,[8] carbosilane,[9] poly(propylene imine),[10] and poly(amidoamine)[11] dendrimers, have been synthesized. In almost all cases, smectic mesomorphisms were displayed by the DLCPs. Liquid crystalline dendrimers based on an octasilsesquioxane core[12] and ferrocene-containing liquid crystalline dendrimers[13] have also been reported.

In a previous paper,[14] we presented the synthesis and characterization of the first ferroelectric dendritic liquid crystalline polymer (FDLCP). A third generation dendritic aliphatic polyester, with 24 hydroxyl groups on its surface, was functionalized with ferroelectric mesogen-containing units. This material represents a novel class of ferroelectric liquid crystalline polymers (FLCPs) in addition to side-chain[15]and main-chain[16] FLCPs. Following the same idea, carbosilane dendrimers carrying chiral mesogen-containing units have recently been prepared in order to get a smectic C* mesophase. However, ferroelectric behavior was only observed when those chiral LC dendrimers were mixed with host materials.[9j]

We report, herein, the preparation, characterization, and ferroelectric properties of a series of novel LC dendrimers of generation 1−3 end-capped with 6, 12, and 24 mesogen-containing units, respectively. The synthesis of the chiral mesogen-containing unit is presented in detail. The influence of the generation number on the liquid crystalline and electrooptical properties is discussed.

Results and Discussion

Synthesis. The synthesis of the LC dendrimers can be divided into three main steps: (a) synthesis of the dendritic scaffolds, namely G#1-$(OH)_6$, G#2-$(OH)_{12}$, and G#3-$(OH)_{24}$ with 6, 12, and 24 terminal hydroxyl groups, respectively; (b) preparation of the mesogen-containing unit, 4″-((*R*)-1-methylheptyloxy)phenyl 4-{4′-[10-(hydroxycarbonyl)decyloxy]phenyl}benzoate (**8**), possessing a carboxylic acid terminal group; (c) coupling of **8** to the dendritic scaffolds via acid chloride reaction yielding **FerG#1**, **FerG#2**, and **FerG#3**.

(a) Synthesis of the Hydroxyl Functional Dendrimers. All hydroxyl functional dendritic polyesters, used as scaffolds in the preparation of the LC dendrimers, were synthesized according to previously described procedures.[17]

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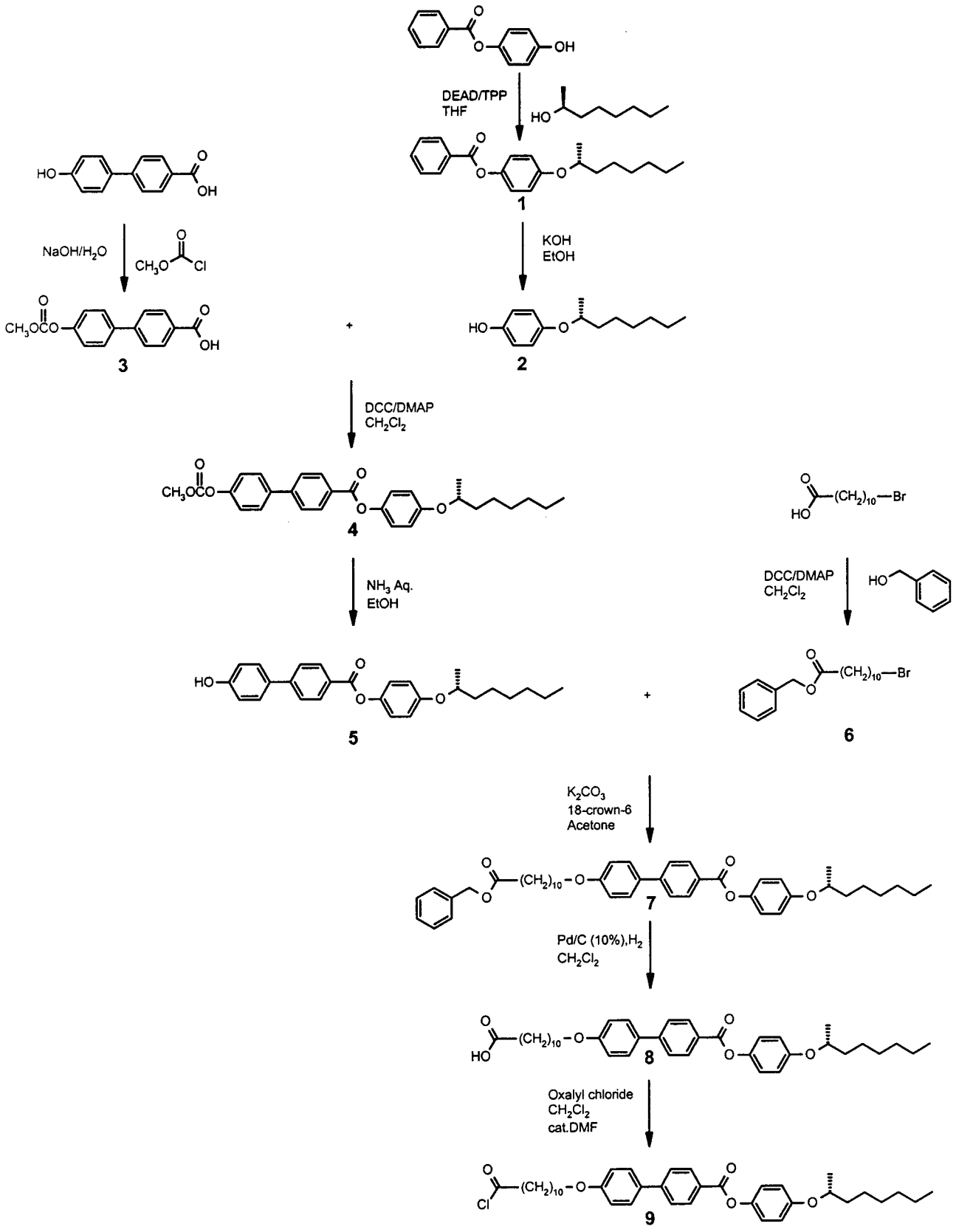
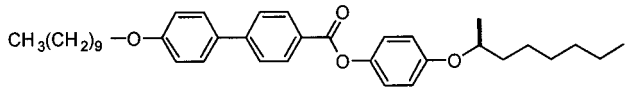
10.1021/ma992133e CCC: $20.00
Published on Web 01/24/2001

Scheme 1. Synthesis of the Mesogen-Containing Unit 8 and Its Acid Chloride Derivative 9



(b) Synthesis of the Mesogen-Containing Unit. (Scheme 1). 4″-((*R*)-1-Methylheptyloxy)phenyl 4-{4′-[10-(hydroxycarbonyl)decyloxy]phenyl}benzoate (**8**) was selected since its linear low molecular weight liquid crystal analogue **10** shows a broad SmC* phase and ferroelectric properties (Figure 1).[18]

(*S*)-2-Octanol was used to give the mesogen-containing unit its chiral character and coupled stereospecifically to 4-hydroxyphenyl benzoate in the presence of diethylazodicarboxylate (DEAD) and triphenylphosphine (TPP) to give **1**.[19] Compound **1** was subsequently deprotected by saponification with KOH to give **2**. 4′-



10

Cr 70 SmC* 125 SmA* 143 I

Figure 1. Structure and phase behavior of **10**, linear low molecular weight liquid crystal analogue of **8**.[18]

Hydroxy-4-biphenylcarboxylic acid was protected with methyl chloroformate at low temperature to yield **3**.[20] Compound **3** was then coupled to compound **2** in a low-temperature esterification procedure using *N,N′*-dicyclohexylcarbodiimide (DCC) as dehydrating agent and 4-(dimethylamino)pyridine (DMAP) as catalyst. The resulting carbonate ester **4** was stirred at room temperature in an ethanolic ammonia solution to yield the corresponding phenol ester **5**.[20] Compound **6** was prepared using the procedure described for **4**. 11-Bromoundecanoic acid and benzyl alcohol were used as starting materials. Compound **7** was obtained by alkylation of compound **5** with **6** in the presence of potassium carbonate and a catalytic amount of 18-crown-6. Finally, compound **8** was obtained by catalytic hydrogenolysis of the benzyl ester group of **7**. Methyl chloroformate and benzyl alcohol were used as protective groups in the stepwise preparation of **8** since they can be selectively removed without affecting the other functional groups present in the intermediate substances.

(c) Synthesis of the Mesogen-Functionalized Dendrimers (Scheme 2). In a previous work, a fourth-generation hydroxyl functional dendrimer based on bis-MPA was subjected to a variety of surface modifications by reaction with different acid chlorides.[17] All the LC dendrimers were prepared using a similar method. Coupling of the mesogen-containing units to the dendritic scaffolds was performed via acid chloride reaction in the presence of triethylamine (TEA) and DMAP. Compound **8** was reacted with oxalyl chloride in the presence of a catalytic amount of DMF to give the corresponding acid chloride **9**. For every terminal hydroxyl function, a 1.15 M excess amount of compound **9** was used to ensure full substitution of the dendritic scaffold. The products were highly soluble in dichloromethane, chloroform, and tetrahydrofuran but insoluble in methanol, ethanol, and water. Purification of each mesogen-functionalized dendrimer by column chromatography turned out to be unsuitable. In fact, the LC dendrimer and the remaining mesogen-containing unit could not be efficiently separated using silica gel. Therefore, the final purification was performed by precipitation of a solution of the dendrimer in dichloromethane into a large volume of methanol. This procedure was repeated until no starting mesogen-containing unit was detected by ^{1}H NMR spectroscopy. All the LC dendrimers were isolated as slightly yellow powders.

General Characterization. The chemical structures of the mesogen-functionalized dendrimers were confirmed by ^{1}H NMR, size exclusion chromatography (SEC), and elemental analysis.

^{1}H NMR spectroscopic data of compounds **1**−**9**, **FerG#1**, **FerG#2**, and **FerG#3** were in agreement with the structures proposed (see Experimental Section). ^{1}H NMR spectroscopy turned out to be a powerful tool in the determination of the purity of the dendritic structures. The disappearance of the signal around 3.5 ppm in the ^{1}H NMR spectra of the LC dendrimers (which corresponds to the methylene groups close to the hydroxyl functions in G#1-$(OH)_6$, G#2-$(OH)_{12}$, and G#3-$(OH)_{24}$) confirmed that all hydroxyl groups were functionalized. Moreover, in all cases, the lack of a signal at 2.35 ppm in the ^{1}H NMR spectra (which corresponds to the methylene group close to the carboxylic acid function in **8**) proved that no unreacted mesogen-containing unit was present in the final products.

Further investigation of the ^{1}H NMR spectra of the series showed small subtle changes in the chemical shifts of the signals with increasing the generation number. It is known that such changes with generation number are observable for the focal point group, terminal groups, and interior building blocks.[2f] Interestingly, in the case of **FerG#1**, **FerG#2**, and **FerG#3**, this tendency was observed for the mesogenic protons remote from the dendritic scaffold. The data reported in Figure 2 show that the doublets corresponding to the mesogenic aromatic protons shift upfield with increasing the generation number. Such changes could be attributed to differences in packing of the mesogens with increasing the generation number. Consequently, intramolecular and steric interactions are enhanced between the mesogens. Other series of LC dendrimers showed the same trend.[9d,h,10]

SEC analyses showed that only monodisperse LC dendrimers were obtained (Table 1). The molecular weights of the LC dendrimers determined by SEC were not in agreement with the theoretical molecular weights calculated from the molecular structures. In fact, this deviation is due to differences in the hydrodynamic volume of linear polystyrene standards and dendrimers. Dendrimers, because of their compact architecture, possess smaller hydrodynamic volume than their linear analogues.[2c] Similar observations have been stated for other types of LC dendrimers.[9d,11]

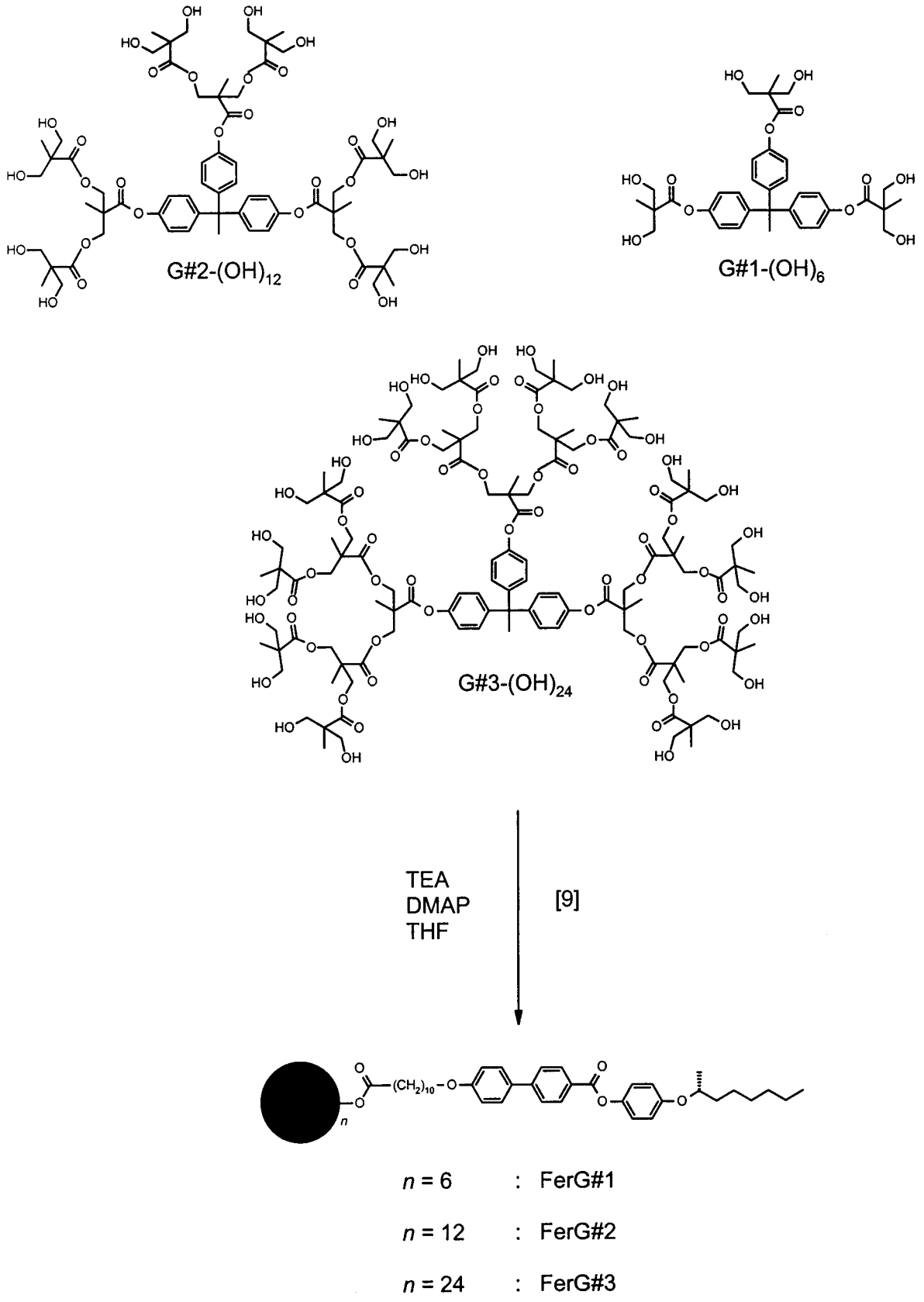
Finally, elemental analysis provided additional information on the high purity and individuality of each LC dendrimer (see Experimental Section).

Liquid Crystalline Properties. The mesomorphic and thermal properties of the mesogen-functionalized dendrimers were investigated by differential scanning calorimetry (DSC) and optical microscopy. The findings are summarized in Table 2.

The DSC scans of the three materials showed a second-order transition (glass transition) and a series of first-order phase transitions. The glass transition temperature (T_g) increased with the generation number, which is in agreement with previous theoretical and experimental studies related to dendritic structures.[21] All generations exhibit liquid crystalline behavior. In the case of **FerG#1**, only two first-order phase transitions, corresponding to the melting and clearing temperatures, were observed. Examination of the optical texture of a thin liquid crystalline film of **FerG#1** showed that both broken focal-conic fan and schlieren textures were formed when slowly cooling (0.5 °C/min) the sample from the isotropic state. These macroscopic textures suggest the formation of a smectic C* phase.[22]

The DSC thermograms of **FerG#2** and **FerG#3** show five first-order transitions, suggesting the presence of four different mesophases. Observation of the optical textures reveals that both LC dendrimers display comparable liquid crystalline behavior. Therefore, the following observations made in **FerG#3** are also valid for **FerG#2**.

Scheme 2. Synthesis of Mesogen-Functionalized Dendrimers[a]



[a] The circle represents the dendritic scaffold in FerG#1, FerG#2, and FerG#3. *n* corresponds to the number of mesogen-containing units in FerG#1, FerG#2, and FerG#3.

The LC dendrimer of the third generation exhibited a mixed focal-conic fan and homeotropic textures between 132 and 148 °C (Figure 3a). It is well-known that such textures are apparent in the chiral smectic A (SmA*) mesophase.[22] Between 80 and 105 °C, microscopic schlieren and broken focal-conic fan textures

Compd	chemical shifts δ(ppm) A (3"-*H* and 5"-*H*)	B (2'-*H* and 6'-*H*)	C (3-*H* and 5-*H*)	D (2-*H* and 6-*H*)
FerG#1	6.91	7.57	7.66	8.21
FerG#2	6.90	7.56	7.65	8.19
FerG#3	6.89	7.54	7.63	8.18

Note: Other aromatic mesogenic protons were not considered because of their overlap with the aromatic protons of the dendritic scaffolds.

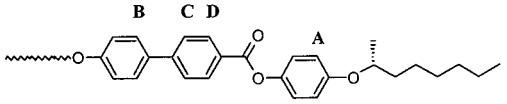


Figure 2. Chemical shifts of the signals corresponding to the mesogenic aromatic protons in the mesogen-functionalized dendrimers.

Table 1. SEC Data of the LC Dendrimers

LC dendrimer	*M*(calcd) (g/mol)	$\bar{M}_w$(SEC) (g/mol)	$\bar{M}_n$(SEC) (g/mol)	$\bar{M}_w/\bar{M}_n$
FerG#1	4 158	5 700	5 400	1.06
FerG#2	8 358	10 700	10 000	1.07
FerG#3	16 758	14 800	14 000	1.05

Table 2. Phase Transition Temperatures of the LC Dendrimers

LC dendrimer	T_g (°C)	transition temperatures (°C)
FerG#1	57	Cr 68 SmC* 119 I
FerG#2	60	Cr 82 SmC* 89 Sx1 115 Sx2 126 SmA* 147 I
FerG#3	64	Cr 80 SmC* 105 Sx1 125 Sx2 132 SmA* 148 I

[a] T_g = glass transition temperature, Cr = crystal state, SmA* = chiral smectic A phase, SmC* = chiral smectic C phase, Sx1 = unknown tilted smectic phase, Sx2 = unknown tilted smectic phase, I = isotropic liquid.

characteristic of the SmC* mesophase were displayed (Figure 3d).[22] Two intermediate phases, Sx1 and Sx2, were observed by DSC between the aforementioned phases. Breakage of the focal-conic fan texture and replacement of the homeotropic texture by a sanded texture were displayed at the transition SmA*−Sx2. These textures coexisted through the whole temperature range of the Sx2 phase (Figure 3b). In the Sx1 mesophase, the texture of the broken focal-conic fans appeared less blurred, whereas the sanded texture turned to a pseudo-homeotropic texture (Figure 3c). Finally, the aforementioned textures of the SmC* mesophase were observed below the transition Sx1−SmC*.

Structural investigations of the Sx1 and Sx2 mesophases need to be carried out. Currently, X-ray diffraction measurements are performed to obtain more details about the liquid crystalline organization of the molecules, especially in the Sx1 and Sx2 mesophases.

To conclude, it appears that the formation of the different liquid crystalline phases in the mesogen-functionalized dendrimers depends on the generation number. As can be seen in Figure 1, the low molecular weight analogue **10** possesses SmA* and SmC* phases. In the case of **FerG#1**, only a SmC* phase is observed, and no conformational changes seem to take place within this mesophase. Increasing the number of mesogen-containing units at the periphery of the dendritic scaffold leads to the formation of SmA*, Sx2, and Sx1 phases. Therefore, **FerG#2** and **FerG#3** have liquid crystalline properties comparable to **10**. To get additional information on the properties of the SmC*, Sx1, and Sx2 mesophases, the LC dendrimers were subjected to electrooptical studies.

Ferroelectric Properties. The electrooptical properties of the mesogen-functionalized dendrimers were studied according to a previously reported method.[23] Commercial 4 μm glass cells (EHC, Japan) were used in the determination of the tilt angle (θ) and the spontaneous polarization (*Ps*). Each compound was heated to the isotropic state and filled into the cell by capillary forces. **FerG#2** and **FerG#3** gave films of reasonable optical quality. However, **FerG#1** gave films of poor optical quality, and subsequently shear cells of a conventional sandwich type[23] were used in the determination of the electrooptical properties.

All LC dendrimers showed ferroelectric switching in the temperature range of the SmC* phase. Moreover, a ferroelectric response was observed in the Sx1 and Sx2 mesophases of **FerG#2** and **FerG#3**. The ferroelectric switching of **FerG#2** in the Sx1 mesophase is shown in Figure 4. On the basis of these results, the two phases between the SmA* and SmC* mesophases must be tilted smectics.

Determination of the electrooptical properties of the materials was not possible in the full temperature range of the tilted phases. Although each LC dendrimer exhibited typical ferroelectric switching almost down to the crystallization temperature, the high viscosity made the response time too long for the switching to be fully developed when approaching this temperature. Therefore, the polarization current was no longer visible as a distinct peak in the current response, and measurements of *Ps* became impossible. Moreover, the high viscosity, in combination with ionic effects, affected the determination of θ since the helix of the ferroelectric phase could not be fully unwound on switching. These restrictions are typical of ferroelectric polymeric systems.

To study the influence of the generation number on the electrooptical properties, the measurements are presented at the same reduced temperature T_r given by

$$T_r = T - T_{tr} \quad (1)$$

where T_{tr} corresponds to the I−SmC* transition temperature in **FerG#1** and to the SmA*−Sx2 transition temperature in **FerG#2** and **FerG#3**. T is the temperature at which the spontaneous polarization and tilt angle measurements are performed. The obtained results are reported in Figure 5 and Figure 6, respectively.

FerG#1, **FerG#2**, and **FerG#3** showed comparable values for both measurements. At the same reduced temperature $T_r \approx -25$ °C, the three LC dendrimers had a spontaneous polarization $Ps \approx 35$ nC/cm^2 and a tilt angle $\theta \approx 25°$. The weight ratio between the dendritic scaffold and the mesogen-containing units is approximately the same for all three dendrimers, and it is quite likely that this relation holds for the volume ratio. Therefore, the results indicate that the electrooptical properties of the materials were not influenced by the size of the dendritic scaffold. The obtained data are in the same range as those determined for **10** at the same reduced temperature.[24] Consequently, as long as the viscosity of the LC dendrimers is sufficiently low, these materials show electrooptical properties similar to those obtained for the low molecular weight molecule **10**.

Conclusions

A series of novel dendritic liquid crystalline polymers have been successfully prepared. The 1-, 2-, and 3-gen-

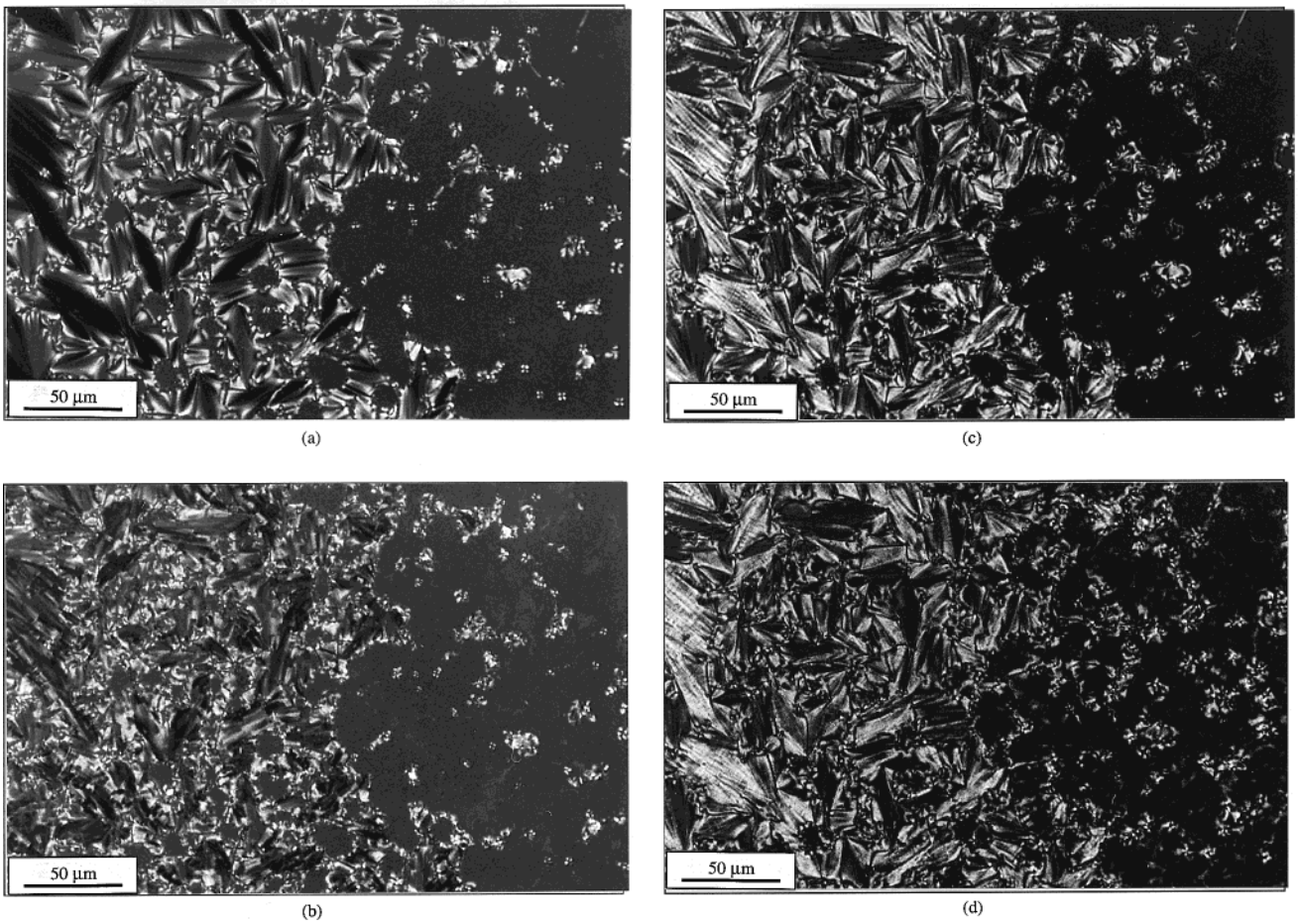


Figure 3. Polarized photomicrographs of **FerG#3** obtained during cooling: (a) SmA*, $T = 135$ °C; (b) Sx2, $T = 130$ °C; (c) Sx1, $T = 115$ °C; (d) SmC*, $T = 90$ °C.

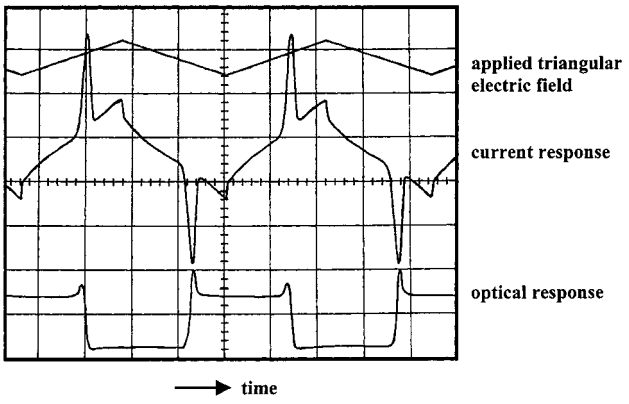


Figure 4. Typical optical and current responses (bottom and middle, respectively) to an applied triangular electric field (top) in **FerG#2** at 94.6 °C (Sx1 mesophase).

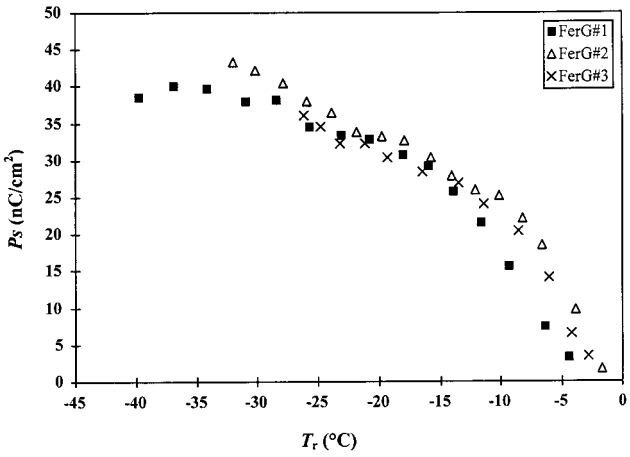


Figure 5. Spontaneous polarization (*Ps*) of the mesogen-functionalized dendrimers as a function of the reduced temperature T_r.

eration of DLCPs with 6, 12, and 24 peripheral mesogen-containing units showed SmC* mesomorphism. The first-generation dendrimer, **FerG#1**, showed only this mesomorphism. Higher generations (**FerG#2** and **FerG#3**) displayed SmA* and SmC* phases. Two tilted mesophases, Sx2 and Sx1, were observed between the aforementioned phases, and electrooptical studies indicated that these phases are tilted smectic phases. The three mesogen-functionalized dendrimers exhibited clear ferroelectric response in their tilted phases. Moreover, the electrooptical measurements revealed that no major differences in *Ps* and θ values were obtained with increasing generation number. These results open the way for the preparation of a novel class of FLCPs, namely ferroelectric dendritic liquid crystalline polymers (FDLCPs). Besides, due to the extensive availability of dendritic structures and mesogenic compounds, the liquid crystalline and electrooptical properties of the FDLCPs can easily be tailored for specific applications. For example, incorporation of a polar chromophore within the mesogen-containing unit should make those materials valuable for nonlinear optical purposes.

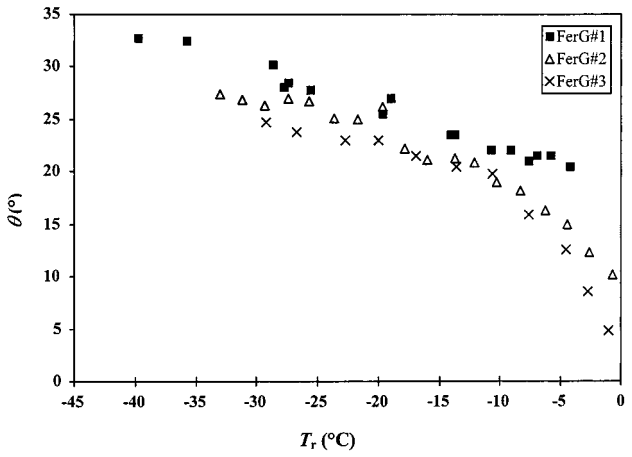


Figure 6. Tilt angle (θ) of the mesogen-functionalized dendrimers as a function of the reduced temperature T_r.

Experimental Section

Materials. 4′-Hydroxy-4-biphenylcarboxylic acid, 4-hydroxyphenyl benzoate, and 18-crown-6 were purchased from Lancaster. (*S*)-2-Octanol, triphenylphosphine (TPP) *N*,*N*′-dicyclohexylcarbodiimide (DCC), 4-(dimethylamino)pyridine (DMAP), oxalyl chloride, and 11-bromoundecanoic acid were purchased from Acros Organics. Diethylazodicarboxylate (DEAD) was purchased from Aldrich. All substances were used without further purification.

Techniques. ^{1}H NMR spectra were recorded on a Bruker AM 400 at 400 MHz using $CDCl_3$ and DMSO-d_6 as solvents. The solvent signals were used as internal standards. All purifications were performed by medium-pressure liquid chromatography as described by Baeckström et al.,[25] unless specified otherwise. Size-exclusion chromatography (SEC) measurements were performed on a Waters GPC system using a solvent delivery system (M510), automatic injector (WISP 710B), and a differential refractometer (Waters 410) as a detector. All measurements were made at 25 °C with a 10 μm mixed B column from Polymer Labs. THF was used as eluent at a flow rate of 1.0 mL/min. The molecular weights were computed using a calibration curve constructed by linear polystyrene standards with narrow molecular weight distribution. Elemental analysis was performed at the Analytische Laboratorien GmbH, Lindlar, Germany. Transition temperatures were determined by differential scanning calorimetry on a Mettler Toledo DSC 820 under a nitrogen atmosphere (80 mL/min). In all cases, heating and cooling rates were 10 °C/min. Optical texture studies were made using a Leitz Ortholux POL BK II polarized optical microscope equipped with a Mettler Hot Stage FP 82 and an FP 80 central processor. Equipment and techniques used to determine the electrooptical properties have been previously described.[23]

Synthesis. 4′-((*R*)-1-Methylheptyloxy)phenylbenzoate (1). TPP (5.24 g, 20 mmol) was added all at once to a stirred solution of DEAD (3.48 g, 20 mmol), 4-hydroxyphenyl benzoate (4.28 g, 20 mmol), and (*S*)-2-octanol (2.6 g, 20 mmol) in dry THF (40 mL). The reaction mixture was stirred for 12 h, and the solvent was evaporated under vacuum. The remaining product was purified by column chromatography (silica gel, hexane/EtOAc as eluent) to give a colorless oil. Yield: 5.67 g (87%). ^{1}H NMR ($CDCl_3$): δ = 0.89 (t, 3H, $-(CH_2)_5CH_3$), 1.27−1.50 (m, 11H, $-OCH(CH_3)CH_2(CH_2)_4CH_3$), 1.55−1.75 (m, 2H, $-OCH(CH_3)CH_2-$), 4.32 (m, 1H, $-OCH(CH_3)CH_2-$), 6.92 (d, 2H, 3′-*H* and 5′-*H*), 7.11 (d, 2H, 2′-*H* and 6′-*H*), 7.49 (t, 2H, 3-*H* and 5-*H*), 7.63 (t, 1H, 4-*H*), 8.18 (d, 2H, 2-*H* and 6-*H*).

4-((*R*)-1-Methylheptyloxy)phenol (2). Compound **1** (4.89 g, 15 mmol) and KOH (85%) (1.98 g, 30 mmol) were stirred in ethanol (95%) (80 mL) under reflux for 5 h. The solution was allowed to cool and acidified by HCl (2 M). The mixture was subsequently extracted with CH_2Cl_2. The organic phase was washed three times with $NaHCO_3$ (10%) and then with water, dried over $MgSO_4$, and filtered. The solvent was evaporated to give a colorless oil. Yield: 3.2 g (96%). ^{1}H NMR ($CDCl_3$): δ = 0.89 (t, 3H, $-(CH_2)_5CH_3$), 1.27−1.50 (m, 11H, $-OCH(CH_3)CH_2(CH_2)_4CH_3$), 1.52−1.73 (m, 2H, $-OCH(CH_3)CH_2-$), 4.19 (m, 1H, $-OCH(CH_3)CH_2-$), 4.56 (s, 1H, −O*H*), 6.76 (q, 4H, 2-*H*, 3-*H*, 5-*H*, and 6-*H*).

4-[4′-(Methoxycarbonyloxy)phenyl]benzoic Acid (3). NaOH (2.4 g, 60 mmol) was dissolved in water (40 mL), and the solution was stirred at −10 °C for 5 min. 4′-Hydroxy-4-biphenylcarboxylic acid (4.28 g, 20 mmol) was then added, and the mixture was vigorously stirred for 10 min at −10 °C. Methyl chloroformate (2.83 g, 30 mmol) was added dropwise to the suspension, and stirring was continued at −5 °C for 3 h. The mixture was then brought to pH = 5 by addition of HCl (2 M). The voluminous white precipitate was filtered off, washed with water, and dried under vacuum. Yield: 5.33 g (98%). ^{1}H NMR (DMSO-d_6): δ = 3.85 (s, 3H, CH_3O-), 7.36 (d, 2H, 3′-*H and* 5′-*H*), 7.79 (d, 2H, 2′-*H* and 6′-*H*), 7.81 (d, 2H, 3-*H* and 5-*H*), 8.02 (d, 2H, 2-*H* and 6-*H*), 13.00 (bd, 1H, −COO*H*).

4″-((*R*)-1-Methylheptyloxy)phenyl 4-[4′-(Methoxycarbonyloxy)phenyl]benzoate (4). 3 (2.72 g, 10 mmol), **2** (2.22 g, 10 mmol), DCC (2.48 g, 12 mmol), and DMAP (0.30 g, 2.5 mmol) were dissolved in CH_2Cl_2 (40 mL) and stirred for 24 h at room temperature. The reaction was then cooled in a freezer, and the white precipitate of 1,3-dicyclohexylurea was filtered off from the solution. The solvent was evaporated, and the resulting product was purified by column chromatography (silica gel, hexane/ EtOAc as eluent) to give a white powder. Yield: 4.09 g (86%). ^{1}H NMR ($CDCl_3$): δ = 0.89 (t, 3H, $-(CH_2)_5CH_3$), 1.29−1.47 (m, 11H, $-OCH(CH_3)CH_2(CH_2)_4CH_3$), 1.51−1.73 (m, 2H, $-OCH(CH_3)CH_2-$), 3.94 (s, 3H, CH_3O-), 4.33 (m, 1H, $-OCH(CH_3)CH_2-$), 6.92 (d, 2H, 3″-*H* and 5″-*H*), 7.12 (d, 2H, 2″-*H* and 6″-*H*), 7.30 (d, 2H, 3′-*H* and 5′-*H*), 7.66 (d, 2H, 2′-*H* and 6′-*H*), 7.69 (d, 2H, 3-*H* and 5-*H*), 8.25 (d, 2H, 2-*H* and 6-*H*).

4″-((*R*)-1-Methylheptyloxy)phenyl 4-(4′-Hydroxyphenyl)benzoate (5). Compound **4** (3.57 g, 7.5 mmol) was stirred in a mixture of ethanol (90 mL) and aqueous ammonia (25%) (50 mL) for 6 h. The extent of the reaction was monitored by thin-layer chromatography. Once the starting material was no longer detected, the solution was poured into water and extracted three times with dichloromethane. The organic phases were combined, washed repeatedly with water, dried over $MgSO_4$, and filtered. The solvent was evaporated to give a white solid. Yield: 2.82 g (90%). ^{1}H NMR ($CDCl_3$): δ = 0.89 (t, 3H, $-(CH_2)_5CH_3$), 1.29−1.49 (m, 11H, $-OCH(CH_3)CH_2(CH_2)_4CH_3$), 1.55−1.74 (m, 2H, $-OCH(CH_3)CH_2-$), 4.33 (m, 1H, $-OCH(CH_3)CH_2-$), 5.13 (s, 1H, −O*H*), 6.92 (d, 2H, 3″-*H* and 5″-*H*), 6.94 (d, 2H, 3′-*H* and 5′-*H*), 7.12 (d, 2H, 2″-*H* and 6″-*H*), 7.55 (d, 2H, 2′-*H* and 6′-*H*), 7.67 (d, 2H, 3-*H* and 5-*H*), 8.23 (d, 2H, 2-*H* and 6-*H*).

11-Bromoundecanoic Benzyl Ester (6). 11-Bromoundecanoic acid (5.3 g, 20 mmol), benzyl alcohol (2.37 g, 22 mmol), DCC (4.95 g, 24 mmol), and DMAP (0.61 g, 5 mmol) were dissolved in CH_2Cl_2 (40 mL) and stirred for 5 h at room temperature. The reaction was then cooled in a freezer, and the white precipitate of 1,3-dicyclohexylurea was filtered from the solution. The solvent was evaporated, and the resulting product was purified by column chromatography (silica gel, hexane/EtOAc as eluent) to give a viscous oil. Yield: 6.09 g (86%). ^{1}H NMR ($CDCl_3$): δ = 1.27−1.42 (m, 12H, $-CH_2(CH_2)_6CH_2-$), 1.64 (m, 2H, $-OOCCH_2CH_2-$), 1.84 (m, 2H, $BrCH_2CH_2-$), 2.35 (t, 2H, $-OOCCH_2-$), 3.40 (t, 2H, $BrCH_2-$), 5.11 (s, 2H, $-OCH_2Ar$), 7.35 (m, 5H, $-OCH_2ArH$).

4″-((*R*)-1-Methylheptyloxy)phenyl 4-{4′-[10-(Benzyloxycarbonyl)decyloxy]phenyl}benzoate (7). A mixture of compound **5** (2.09 g, 5 mmol), anhydrous K_2CO_3 (0.72 g, 5.25 mmol), and 18-crown-6 (catalytic amount) in acetone (50 mL) was stirred at 60 °C for 1 h. To the resulting solution was added a solution of compound **6** (1.95 g, 5.5 mmol) in acetone (5 mL), and stirring was continued at 60 °C for 36 h. The mixture was cooled to room temperature, and the solvent was evaporated. The residue was dissolved in CH_2Cl_2 and extracted three times with brine. The organic phase was dried over $MgSO_4$ and filtered, and the solvent was evaporated. The

resulting product was purified by column chromatography (silica gel, hexane/ EtOAc as eluent) and recrystallized from EtOH to give a white powder. Yield: 2.59 g (75%). ^{1}H NMR ($CDCl_3$): δ = 0.89 (t, 3H, $-(CH_2)_5CH_3$), 1.27−1.49 (m, 23H, $-OCH(CH_3)CH_2(CH_2)_4CH_3$ and $-CH_2(CH_2)_6CH_2-$), 1.52−1.73 (m, 4H, $-OCH(CH_3)CH_2-$ and $-OOCCH_2CH_2-$), 1.81 (m, 2H, $-ArArOCH_2CH_2-$), 2.36 (t, 2H, $-OOCCH_2-$), 4.01 (t, 2H, $-ArArOCH_2-$), 4.33 (m, 1H, $-OCH(CH_3)CH_2-$), 5.12 (s, 2H, $-OCH_2Ar$), 6.92 (d, 2H, 3″-*H* and 5″-*H*), 7.01 (d, 2H, 3′-*H* and 5′-*H*), 7.12 (d, 2H, 2″-*H* and 6″-*H*), 7.35 (m, 5H, $-OCH_2ArH$), 7.59 (d, 2H, 2′-*H* and 6′-*H*), 7.68 (d, 2H, 3-*H* and 5-*H*), 8.22 (d, 2H, 2-*H* and 6-*H*).

4″-((*R*)-1-Methylheptyloxy)phenyl 4-{4′-[10-(Hydroxycarbonyl)decyloxy]phenyl}benzoate (8). A 0.21 g sample of Pd/C (10%) was added to a solution of compound **7** (2.08 g, 3 mmol) in CH_2Cl_2 (20 mL). The round-bottom flask was evacuated from air and filled with H_2. The mixture was stirred overnight at room temperature. The Pd/C was filtered off and carefully washed with $CHCl_3$. The filtrate was evaporated to give a white solid. Yield: 1.71 g (95%). ^{1}H NMR ($CDCl_3$): δ = 0.89 (t, 3H, $-(CH_2)_5CH_3$), 1.27−1.49 (m, 23H, $-OCH(CH_3)CH_2(CH_2)_4CH_3$ and $-CH_2(CH_2)_6CH_2-$), 1.52−1.73 (m, 4H, $-OCH(CH_3)CH_2-$ and $-OOCCH_2CH_2-$), 1.81 (m, 2H, $-ArArOCH_2CH_2-$), 2.35 (t, 2H, $HOOCCH_2-$), 4.01 (t, 2H, $-ArArOCH_2-$), 4.33 (m, 1H, $-OCH(CH_3)CH_2-$), 6.92 (d, 2H, 3″-*H* and 5″-*H*), 7.01 (d, 2H, 3′-*H* and 5′-*H*), 7.12 (d, 2H, 2″-*H* and 6″-*H*), 7.59 (d, 2H, 2′-*H* and 6′-*H*), 7.68 (d, 2H, 3-*H* and 5-*H*), 8.22 (d, 2H, 2-*H* and 6-*H*).

4″-((*R*)-1-Methylheptyloxy)phenyl 4-{4′-[10-(Chlorocarbonyl)decyloxy]phenyl}benzoate (9). Oxalyl chloride (0.508 g, 4 mmol) was added drop by drop to a solution of **8** (1.204 g, 2 mmol) and 3 drops of DMF in CH_2Cl_2 (20 mL). The reaction was allowed to reach completion for 3 h at room temperature. The excess of oxalyl chloride was removed on the rotary evaporator to give a white solid that was used without any further purification. Yield: 1.24 g (quantitative). ^{1}H NMR ($CDCl_3$): δ = 0.89 (t, 3H, $-(CH_2)_5CH_3$), 1.27−1.49 (m, 23H, $-OCH(CH_3)CH_2(CH_2)_4CH_3$ and $-CH_2(CH_2)_6CH_2-$), 1.52−1.73 (m, 4H, $-OCH(CH_3)CH_2-$ and $ClOCCH_2CH_2-$), 1.81 (m, 2H, $-ArArOCH_2CH_2-$), 2.88 (t, 2H, $ClOCCH_2-$), 4.01 (t, 2H, $-ArArOCH_2-$), 4.33 (m, 1H, $-OCH(CH_3)CH_2-$), 6.92 (d, 2H, 3″-*H* and 5″-*H*), 7.01 (d, 2H, 3′-*H* and 5′-*H*), 7.12 (d, 2H, 2″-*H* and 6″-*H*), 7.59 (d, 2H, 2′-*H* and 6′-*H*), 7.68 (d, 2H, 3-*H* and 5-*H*), 8.22 (d, 2H, 2-*H* and 6-*H*).

FerG#1. Compound **9** (1.241 g, 2 mmol), diluted in a small amount of THF, was added dropwise to a solution of G#1-$(OH)_6$ (0.189 g, 0.29 mmol), DMAP (0.106 g, 0.87 mmol), and TEA (0.264 g, 2.609 mmol) in THF (5 mL) at 0 °C. After stirring at 0 °C for 1 h, the mixture was allowed to reach ambient temperature and stirred for a further 24 h. The solvent was then evaporated under vacuum, and the yellow residue was dissolved in CH_2Cl_2. The solution was first extracted three times with saturated $NaHCO_3$, then three times with HCl (2 M), and finally with brine. The organic phase was dried over $MgSO_4$ and filtered, and the solvent was evaporated. Finally, a solution of the crude product, in a minimum amount of CH_2Cl_2, was precipitated into a large volume of methanol (volume/volume ratio ≈ 1:10). The precipitated powder was filtered off and dried under vacuum. This procedure was repeated until no starting mesogen-containing units were detected by ^{1}H NMR spectroscopy. A pure pale yellow powder was obtained. Yield: 0.86 g (71%). ^{1}H NMR ($CDCl_3$): δ = 0.89 (t, 18H, $-(CH_2)_5CH_3$), 1.27−1.49 (m, 147H, $-OCH(CH_3)CH_2(CH_2)_4CH_3$, $-CH_2(CH_2)_6CH_2-$, and $-CH_3$), 1.52−1.75 (m, 24H, $-OCH(CH_3)CH_2-$ and $-OOCCH_2CH_2-$), 1.81 (m, 12H, $-ArArOCH_2CH_2-$), 2.14 (s, 3H, $-CH_3$), 2.33 (t, 12H, $-OOCCH_2-$), 3.99 (t, 12H, $-ArArOCH_2-$), 4.34 (m, 18H, $-OCH(CH_3)CH_2-$ and $-CH_2CH_2-$), 6.91 (d, 12H, 3″-*H* and 5″-*H*), 6.97 (m, 18H, Ar*H*, 3′-*H*, and 5′-*H*), 7.10 (m, 18H, Ar*H*, 2″-*H*, and 6″-*H*), 7.57 (d, 12H, 2′-*H* and 6′-*H*), 7.66 (d, 12H, 3-*H* and 5-*H*), 8.21 (d, 12H, 2-*H* and 6-*H*). Anal. Calcd for $C_{263}H_{330}O_{42}$: C, 75.87; H, 7.99. Found: C, 75.70; H, 7.88.

FerG#2. This compound was prepared from the dendritic matrix G#2-$(OH)_{12}$ (0.195 g, 0.145 mmol), compound **9** (1.241 g, 2 mmol), DMAP (0.106 g, 0.87 mmol), and TEA (0.264 g, 2.609 mmol) according to the method described for **FerG#1**. Yield: 0.81 g (67%). ^{1}H NMR ($CDCl_3$): δ = 0.89 (t, 36H, $-(CH_2)_5CH_3$), 1.24−1.49 (m, 303H, $-OCH(CH_3)CH_2(CH_2)_4CH_3$, $-CH_2(CH_2)_6CH_2-$, and $-CH_3$), 1.52−1.65 (m, 48H, $-OCH(CH_3)CH_2-$ and $-OOCCH_2CH_2-$), 1.79 (m, 24H, $-ArArOCH_2CH_2-$), 2.14 (s, 3H, $-CH_3$), 2.28 (t, 24H, $-OOCCH_2-$), 3.98 (t, 24H, $-ArArOCH_2-$), 4.21 (q, 24H, $-CH_2CH_2-$), 4.32 (m, 12H, $-OCH(CH_3)CH_2-$), 4.40 (s, 12H, $-CH_2CH_2-$), 6.90 (d, 24H, 3″-*H* and 5″-*H*), 6.97 (m, 30H, Ar*H*, 3′-*H*, and 5′-*H*), 7.10 (m, 30H, Ar*H*, 2″-*H*, and 6″-*H*), 7.56 (d, 24H, 2′-*H* and 6′-*H*), 7.65 (d, 24H, 3-*H* and 5-*H*), 8.19 (d, 24H, 2-*H* and 6-*H*). Anal. Calcd for $C_{521}H_{666}O_{90}$: C, 74.77; H, 8.02. Found: C, 74.65; H, 8.12.

FerG#3. This compound was prepared from the dendritic matrix G#3-$(OH)_{24}$ (0.198 g, 0.072 mmol), compound **9** (1.241 g, 2 mmol), DMAP (0.106 g, 0.87 mmol), and TEA (0.264 g, 2.609 mmol) according to the method described for **FerG#1**. Yield: 0.84 g (69%). ^{1}H NMR ($CDCl_3$): δ = 0.89 (t, 72H, $-(CH_2)_5CH_3$), 1.15−1.49 (m, 615H, $-OCH(CH_3)CH_2(CH_2)_4CH_3$, $-CH_2(CH_2)_6CH_2-$, and $-CH_3$), 1.52−1.65 (m, 96H, $-OCH(CH_3)CH_2-$ and $-OOCCH_2CH_2-$), 1.78 (m, 48H, $-ArArOCH_2CH_2-$), 2.14 (s, 3H, $-CH_3$), 2.28 (t, 48H, $-OOCCH_2-$), 3.98 (t, 48H, $-ArArOCH_2-$), 4.15−4.41 (m, 108H, $-CH_2C-$ and $-OCH(CH_3)CH_2-$), 6.89 (d, 48H, 3″-*H* and 5″-*H*), 6.94 (m, 54H, Ar*H*, 3′-*H*, and 5′-*H*), 7.09 (m, 54H, Ar*H*, 2″-*H*, and 6″-*H*), 7.54 (d, 48H, 2′-*H* and 6′-*H*), 7.63 (d, 48H, 3-*H* and 5-*H*), 8.18 (d, 48H, 2-*H* and 6-*H*). Anal. Calcd for $C_{1037}H_{1338}O_{186}$: C, 74.23; H, 8.04. Found: C, 74.04; H, 8.00.

Acknowledgment. This work was supported by the Swedish Research Council for Engineering Sciences (TFR, Grant 95-807), the Swedish Natural Science Research Council (NFR, Grant K-AA/KU01910-312), and the Defense Material Administration (FMV, Grant 64065-LB108704).

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MA992133E