

Chiral Codendrimers Derived from Poly(propyleneimine) Dendrimers (DAB)

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A number of codendrimers derived from chiral and achiral Schiff bases and poly(propyleneimines) (DAB) have been synthesized. The molecular structure and purity of these novel compounds has been verified by NMR spectroscopy, elemental analysis, and GPC. The phase behavior was studied by polarizing optical microscopy, differential scanning calorimetry, and X-ray diffraction techniques. It was found that all of these materials display a chiral smectic C mesophase over a wide temperature range. Although switching was observed for small concentrations of chiral compound when an electric field was applied, spontaneous polarization could not be measured in any of the codendrimers.

Introduction

In recent years researchers in the field of liquid crystal (LC) polymers have paid a great deal of attention to a special class of LC polymer: liquid crystal dendrimers.^{1–12} These molecules are unique in that they lack entanglements, a characteristic that leads to good solubility in almost all organic solvents and, in principle, offers a lower intrinsic viscosity. Most of the LC dendrimers described to date were prepared using a dendrimeric core that is functionalized at the surface. This approach has led to a variety of different dendrimers

such as the polycarbosilanes described by Shibaev et al. and Frey et al.,² the poly(propyleneimines)³ reported by Lattermann et al. and Meijer et al., polyamidoamines reported by Ueda et al.,⁴ carboxylazane reported by Mehl et al.,⁵ silsesquioxanes from Goodby et al.,⁶ and even metallomesogenic dendrimers by Deschenaux et al.⁷ The majority of LC dendrimers exhibit achiral

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Table 1. Codendrimers Synthesized (%L* = percentage of monomer L chiral, theor = theoretical value, exp = experimental value) and Optical^a and Thermal Properties

generation	%L* _{theor}	%L* _{exp}			optical and thermal properties				
G = 1(heating)	25	19	C	108.3					I
G = 1(cooling)			C	23.7	SmC*	64.3			I
G = 2	25	22	g	-2.5	SmC*	49.9	SmA	69.5	I
G = 3	25	22	g	8.0	SmC*	65.6	SmA	74.5	I
G = 4	25	22			SmC*	80.0	SmA	90.5	I
G = 5	25	32			SmC*	97	SmA	110	I
G = 2	0	0	C	65.2	SmC	91.9	SmA	100.8	I
G = 2	10	9			SmC*	78.6	SmA	92.5	I
G = 2	25	22	g	-2.5	SmC*	49.9	SmA	69.5	I
G = 2	50	48	g	-12.3	SmC*	31.3	SmA	33.2	I
G = 2	75	75	g	-7.2					I
G = 2	100	100	g	-10.8					I
G = 4	0	0	g	43.3	SmC	68.9	SmA	102.8	I
G = 4	10	7			SmC*	98.6	SmA	105.4	I
G = 4	25	22			SmC*	80.0	SmA	90.5	I
G = 4	50	49			SmC*	43.8			I
G = 4	75	68	g	6.8	SmC*	35			I
G = 4	100	100	g	38					I

^a C = crystal; g = glass; SmC = smectic C mesophase; SmA = smectic A mesophase; I = isotropic liquid.

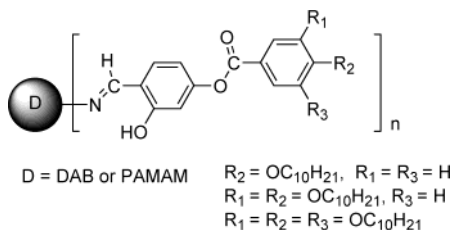
smectic mesophases. In 1998 the synthesis of the first ferroelectric third-generation LC dendrimer, based on 2,2-bis(hydroxymethyl)propionic acid, was reported by Hult et al.⁸ Ferroelectric⁹ and NLO¹⁰ properties have also been described in three derivatives prepared by the same group.

Shibaev et al. have described chiral LC dendrimers based on polycarbosilanes and these materials show ferroelectric properties.¹¹ This work demonstrated that as the generation number increases, the spontaneous polarization diminishes; the maximum value for the first-generation dendrimer is about 140 nC/cm²^{11a}.

Other examples of chiral LC dendrimers (silsesquioxane derivatives) have been described by Goodby et al.⁶ In this case the compounds exhibited a cholesteric mesophase.

Recently, Tschierske has described a carbosilane-based dendrimer with banana-shaped mesogenic units which exhibit ferroelectric switching.¹²

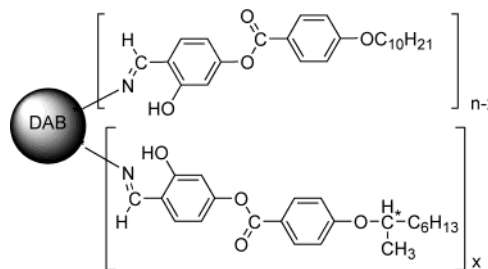
In our previous work we described a number of LC dendrimers derived from PAMAM and DAB cores.^{3g,4b,4c,13}



The functionalization of the dendrimers was performed by incorporating mesogenic units linked at the terminal position and using an imine bond, which was stabilized by the formation of an intramolecular hydrogen bond. Whereas PAMAM dendrimers bearing one terminal chain exhibit only a SmA mesophase, dendrimers derived from DAB bearing only one terminal chain exhibit calamitic SmA and SmC mesophases.

The work described here concerns the synthesis of a series of chiral codendrimers bearing chiral and achiral terminal chains (Table 1) in an effort to mimic the

situation occurring in mixtures using chiral dopants to obtain ferroelectric LC mesophases. On the other hand, codendrimers have the advantage that the mesogenic groups are in a fixed position and therefore segregation does not take place.



Results and Discussion

Synthesis. The codendrimers were synthesized by the condensation of 4-(4'-decyloxybenzoyloxy)salicylaldehyde and 4-[4'-(2-methylheptyloxybenzoyloxy)]salicylaldehyde in different proportions (Table 1) with the terminal amino group of the corresponding generation of DAB (Scheme 1).

All the compounds were isolated as air-stable yellow glasses that are soluble in solvents such as dichloromethane, chloroform, and THF, but are insoluble in ethanol.

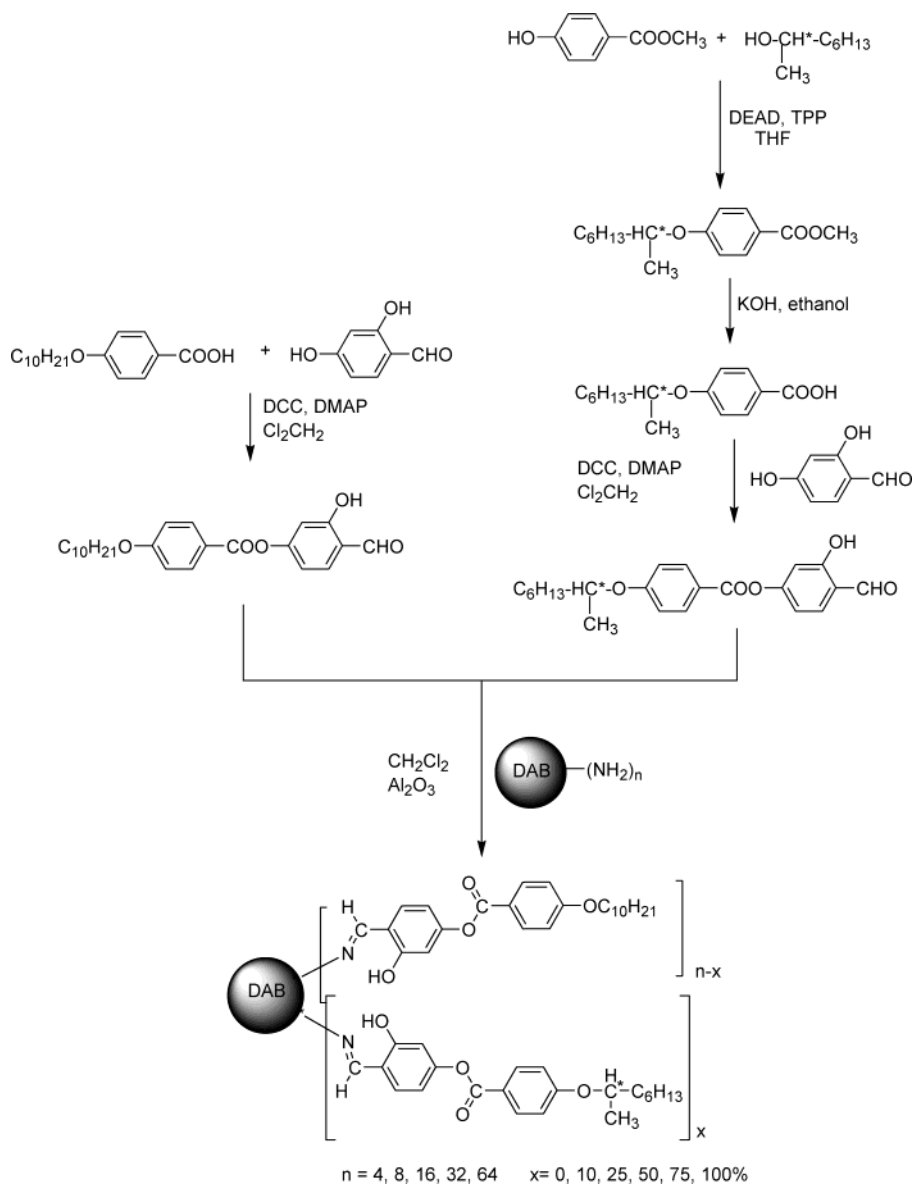
Characterization. The chemical structures of these compounds were established on the basis of ¹H, ¹³C NMR, and IR spectroscopy, and also by elemental analysis. All these techniques gave satisfactory results. GPC measurements (mobile phase, THF; calibration standard, polystyrene) confirmed the presence of practically monodisperse polymers in all cases. However, as is often the case with dendrimers, a marked deviation from the calculated molecular weight was found in the experimental data.¹⁴

IR and ¹H and ¹³C NMR spectroscopic techniques have proved very useful in confirming the structure and purity of these materials. In addition, the excellent solubility of these codendrimers in CDCl₃ allowed us to

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Scheme 1



confirm in all cases that the expected dendrimers were obtained. Evidence of the condensation reaction was provided by the lack of a signal at $\delta = 192$ in the ^{13}C NMR spectra (which corresponds to the carbonyl of the aldehyde) along with the total absence of the NH_2 signals from the starting compound in ^1H NMR and IR spectra

The relative proportions of the different mesogenic units were studied by means of ^1H NMR spectroscopy (Figure 1).

The relative ratios of the two different promesogenic units were determined by considering the integration of the signals of the $\text{O}-\text{CH}^*(\text{CH}_3)-$ and $-\text{O}-\text{CH}_2-$ groups. Therefore, by comparing the integration of the proton NMR signals of H_1^* and H_2 (Figure 1) to the ratio of promesogenic units L^* and L , it was possible to determine the average relative concentration of each promesogenic unit in a given codendrimer. Experimental values of L^* and L determined by this method are presented in Table 1.

Mesogenic Behavior. The liquid crystalline properties of these compounds were studied by polarizing

optical microscopy and differential scanning calorimetry, and confirmed by X-ray diffraction. The thermal data are summarized in Table 1.

It is important to note that the presence of small quantities of the chiral mesogenic unit favors the formation of the smectic C^* phase and that this mesophase disappears only when the ratio of chiral terminal groups is very high (75%).

The five generations of dendrimers with a proportion of 25% of chiral units are represented in Figure 2. As can be seen, all proportions exhibit SmC^* mesomorphism and this is monotropic in the generation-one dendrimer and enantiotropic for the next four generations. The stability of the SmC^* phase increases as the generation number of the dendrimer increases. These derivatives also exhibit a SmA phase at higher temperatures. In generations 3, 4, and 5, it was not possible to detect the glass transition by calorimetry methods, despite the significant increase in the viscosity observed when the temperature was decreased.

Figure 3 shows the thermal data corresponding to generation 2 with 0, 10, 25, 50, 75, and 100% propor-

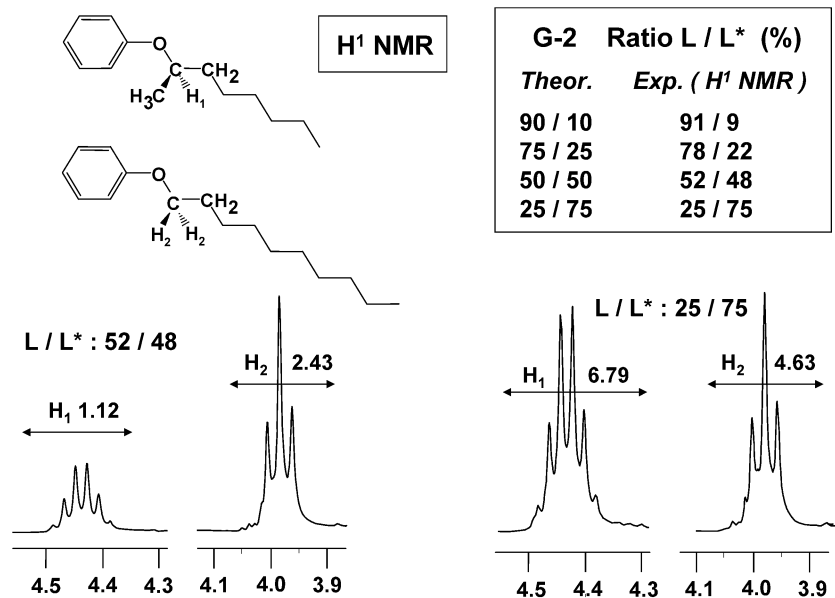


Figure 1. Relative proportions of different mesogenic units studied by ^1H NMR for codendrimers $G = 2\%L^*_{\text{theor}}50\%$ and $G = 2\%L^*_{\text{theor}}75\%$.

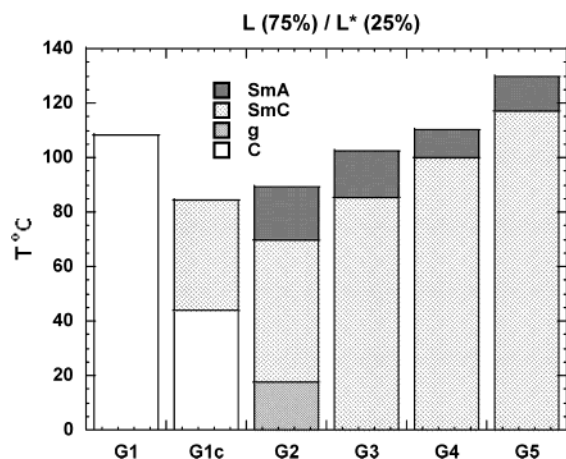


Figure 2. Mesogenic behavior of codendrimers $G = 1$ to $G = 5\%L^*_{\text{theor}}25\%$.

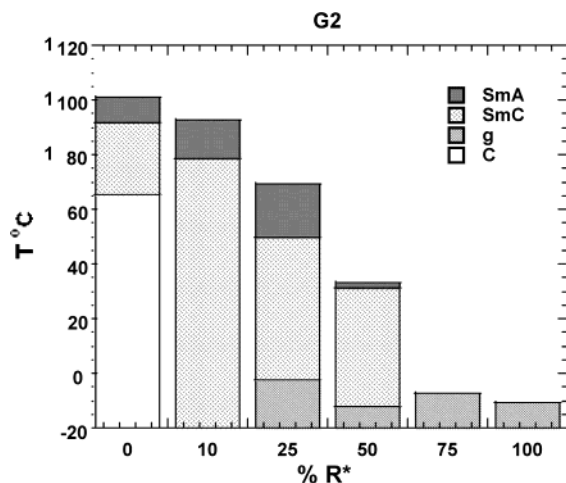


Figure 3. Mesogenic behavior of codendrimers $G = 2$.

tions of chiral units. In the generation 2 compounds an increase in the number of chiral units produced a significant decrease in the clearing point and in the SmC^*-SmA transition temperature.

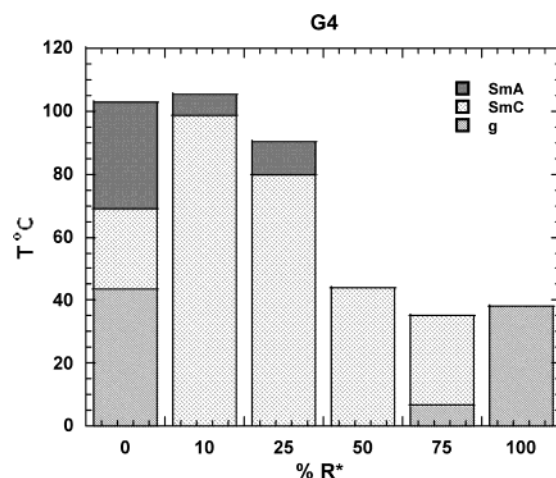


Figure 4. Mesogenic behavior of codendrimers $G = 4$.

Indeed, when the number of chiral groups is very high, i.e., 75 or 100%, the compounds do not exhibit liquid crystalline behavior and are isotropic liquids at room temperature. On the other hand, it is important to note that the presence of small quantities of the chiral mesogenic units favors the SmC^* mesophase and only when the ratio of chiral terminal groups is very high (75%) does this mesophase disappear.

Similar behavior is observed in the generation 4 materials, which contain 32 mesogenic units (Figure 4): an increase in the number of chiral units produced a significant decrease in the clearing point. However SmC mesophase is exhibited for 0, 10, 25, 50, and 75% proportions, and only when the number of chiral groups is 100% is liquid crystalline behavior not exhibited.

X-ray Diffraction Study. Five compounds were studied by X-ray diffraction over a range of temperatures. Two compounds were chosen as representative examples of generation 2 (the first containing $\%L^*_{\text{Exp}}22\%$, and the second $\%L^*_{\text{Exp}}48\%$). Another two compounds were studied as representative examples of generation 4 ($\%L^*_{\text{Exp}}7\%$ and 22%). Finally, compound 5 (generation 5, containing $\%L^*_{\text{Exp}}32\%$) was also inves-

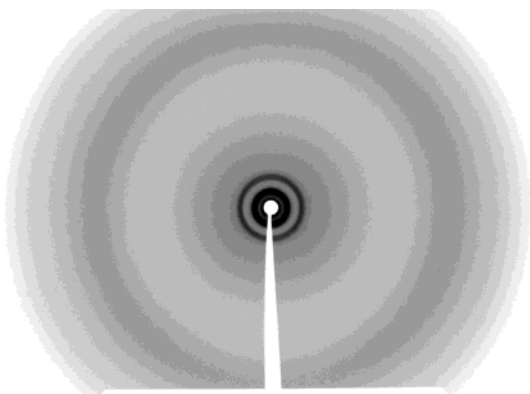


Figure 5. X-ray pattern of compound $G = 2$, $\%L^*_{\text{Exp}}22\%$ taken at room temperature in the SmC^* phase. The two small-angle rings are, respectively, the first- and the second-order reflections on the smectic planes. The wide-angle halo is characteristic of the liquidlike order of the aliphatic groups (hydrocarbon chains and DAB dendrimer).

Table 2. Structural Data of the Mesophases Measured by X-ray Diffraction; Each Column Lists, Respectively, the Generation, the Composition, the Temperature of the Experiment, the Mesophase Type, and the Interlayer Spacing (Layer Thickness, d)

compound	$\%L^*_{\text{theor}}$	$\%L^*_{\text{Exp}}$	temp. ($^{\circ}\text{C}$)	mesophase	d (\AA)
$G = 2$	25	22	room	SmC^*	47
			53	SmA	50
			63	SmA	47
$G = 2$	50	48	room	SmC^*	47
$G = 4$	10	7	room	SmC^*	52
			92	SmC^*	48
			98	SmA	48
$G = 4$	25	22	room	SmC^*	52
$G = 5$	25	32	room	SmC^*	58
			room ^a	SmC^*	53

^a Sample submitted to a thermal treatment that consists of heating to the isotropic liquid and then cooling to room temperature.

tigated. All of these dendrimers exhibit SmC^* and SmA mesophases.

The X-ray patterns taken at room temperature in all five cases confirmed them to be mesomorphic in the virgin state. The diffraction photographs are consistent with a SmC^* phase, and they contain two small-angle maxima with a reciprocal spacing ratio of 1:2 (Figure 5). This ratio is typical of layered systems and confirms the smectic order. The interlayer spacing can be calculated by applying Bragg's law to these maxima (Table 2). In addition to the aforementioned maxima, the patterns show a broad, diffuse halo in the wide-angle region, which is characteristic of the terminal hydrocarbon chains and of the central dendrimer in a conformationally disordered state. Application of Bragg's law gives a mean distance of 4.5–4.6 \AA from this halo. No other diffraction peak is observed in the wide-angle region even in long-exposure-time patterns.

It is interesting to note that the layer spacing measured at room temperature is practically constant within each generation (compare compounds $G = 2\%L^*_{\text{Exp}}22\%$ to compound $G = 2\%L^*_{\text{Exp}}48\%$, and compound $G = 4\%L^*_{\text{Exp}}7\%$ to compound $G = 4\%L^*_{\text{Exp}}22\%$ in Table 2). This situation is not unexpected for dendrimers with a very similar chemical composition. Moreover, the measured spacing increases as the gen-

eration number increases. However, this increase on passing from the 2nd to the 4th generation and from the 4th to the 5th generation is not as large as one would expect if the central dendrimer were in a fully extended conformation in the direction of the main molecular axis. This discrepancy is due to the fact that the dendrimer branches tend to curl so they can efficiently fill the central slab between the two sublayers that contain the mesogenic units.^{4b}

The variable-temperature study of compound $G = 2\%L^*_{\text{Exp}}22\%$ indicates that the layer spacing slightly increases upon heating from the SmC^* phase up to the SmA phase as usual in classical liquid crystal (see Table 2). In compound $G = 4\%L^*_{\text{Exp}}7\%$, within the SmC^* phase, the layer thickness is smaller at higher temperatures. Moreover, in this compound the parameters measured in the SmC^* phase at 92 $^{\circ}\text{C}$ and in the SmA phase at 98 $^{\circ}\text{C}$ are identical, although in the SmA phase the molecules are parallel to the layer normal whereas those in the SmC^* phase are tilted. The same effect has been observed in other dendrimers¹³ and can be accounted for by the higher conformational freedom of the aliphatic parts of the molecules (central dendrimer and peripheral chains), which gives rise to a decrease in the effective molecular length. It is concluded that the increase in layer thickness expected for the SmA phase is canceled out by the decrease due to the higher conformational freedom. Finally, it is interesting to note that for compound $G = 5\%L^*_{\text{Exp}}32\%$ the measured layer thickness is smaller in a sample that has been heated to the isotropic liquid stage and cooled to room temperature than it is for a virgin sample. This phenomenon, which is not observed to such a large extent in the lower generations of the series, might well be connected to the conformational disorder of this high-generation dendrimer. Such disorder would lead to a significant reduction in the molecular length at high temperatures and this reduction is maintained when the sample is cooled to room temperature.

In all cases, the measured layer thickness is much smaller than the theoretical molecular length estimated from Dreiding stereomodels for a fully extended conformation of both the dendrimer branches, the mesogenic units, and the terminal chains. For instance, for $G = 2$ the theoretical length would be 80–81 \AA for the completely nonchiral dendrimer and 73–74 \AA for the completely chiral dendrimer. This is accounted for not only by the high conformational freedom of the dendrimer and the hydrocarbon chains, but also by the statistical fluctuations of the direction of the main axes of the mesogenic units.

Ferroelectric Properties. Despite favoring SmC^* mesomorphism, these codendrimers exhibit poor ferroelectric properties. Unfortunately, switching was detected only in the small dendrimers ($G=1$ and $G=2$) and in codendrimers bearing a small number of chiral mesogenic units. Even in these cases very high voltages were required to produce this switching and even then switching only occurred at temperatures close to the SmC^*-SmA transition. For this reason, spontaneous polarization could not be measured in any case. This problem clearly prevents the use of these compounds for practical applications. The use of DAB derivatives appears to produce dendrimers with very high viscosi-

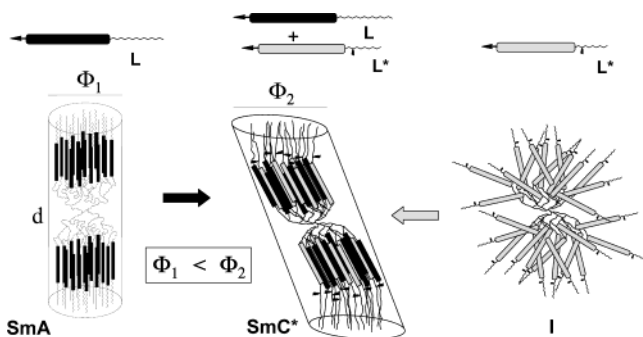


Figure 6. Schematic representation of liquid crystal codendrimers in SmA, SmC*, and I phases.

ties and hence molecular movement in these systems is extremely difficult.

Conclusions

The introduction of a large number of chiral groups increases the cross-sectional area of the hydrocarbon chain. Thus, the volume occupied by the flexible external part of the dendrimer increases to such an extent that it precludes the order necessary for the formation of the desired mesophase (Figure 6).

The introduction of a limited number of chiral terminal chains causes stabilization of the SmC mesophase because the tilt of the mesogenic units increases the area at the base in the cylinder model, which allows the mesogenic units to order themselves in a parallel fashion (Figure 6).

Despite favoring SmC* mesomorphism, these chiral codendrimers exhibit poor ferroelectric properties due to very high viscosity of the SmC mesophase. Switching was detected only in codendrimers bearing a small number of chiral mesogenic units, and spontaneous polarization could not be measured in any case.

Experimental Section

Chemicals. 4-Decyloxybenzoic acid was purchased from Frinton Laboratories. Methyl 4-hydroxybenzoate, (*S*)-2-octanol, diethyl azodicarboxylate (DEAD), triphenylphosphine (TPP), dicyclohexylcarbodiimide (DCC), 4-(dimethylamino)pyridine (DMAP), and poly(propyleneimine) dendrimers ($G = 1, 2, 3, 4, 5$) were purchased from The Aldrich Chemical Co. All substances were used without further purification.

Synthesis. Synthesis of the codendrimers was carried out as shown in Scheme 1. Salicylaldehydes were synthesized by classical methods described in the literature.^{15,16}

The general procedure for the condensation of chiral and achiral salicylaldehydes with DAB dendrimers was as follows. To a stirred solution of the two salicylaldehydes in the appropriate proportions (x mole of chiral and $n - x$ mole of achiral) in CH_2Cl_2 (15 mL) was added neutral activated grade Y alumina (0.5 g) followed by the corresponding poly(propyleneimine) (DAB). The mixture was heated under reflux under nitrogen until the aldehydes had completely reacted (usually overnight). The alumina was filtered off and the solvent from the filtrate was evaporated under vacuum. The resulting solid was purified by column chromatography using hexane/ CH_2Cl_2 (2:1) as eluent. Yield 70–85%.

Characterization. The purity of each compound (intermediates and codendrimers) was confirmed by elemental analysis, ^1H NMR, IR spectroscopy, and GPC analysis. The data are in full agreement with the structures proposed.

Because of the similarity of the NMR spectra of these materials, only the NMR data for codendrimer 1 are given as a representative example.

Codendrimer $G = 1\%L^*\text{exp}19\%$. ^1H NMR (300 MHz, CDCl_3): δ 0.87 (t, $J = 6.22$ Hz, 12H); 1.16–1.49 (m, 56H); 1.71–1.84 (m, 18H); 2.34–2.58 (m, 11H); 3.59 (t, $J = 6.05$ Hz, 8H); 4.00 (t, $J = 6.59$ Hz, 6H); 4.42–4.50 (m, 1H); 6.67 (dd, $J = 2.01$ Hz, $J = 8.42$ Hz, 4H); 6.75 (s, 4H); 6.93 (d, $J = 8.78$ Hz, 8H); 7.21 (d, $J = 8.42$ Hz, 4H); 8.09 (d, $J = 8.79$ Hz, 8H); 8.28 (s, 4H); 14.03 (s, 4H). ^{13}C NMR (300 MHz, CDCl_3): δ 164.46, 164.37, 164.27, 163.61, 163.60, 154.27, 142.69, 132.28, 132.06, 121.40, 116.46, 115.23, 114.29, 112.13, 110.58, 68.30, 31.83, 29.48, 29.30, 29.23, 29.15, 29.13, 29.06, 25.92, 22.59, 22.50, 14.02, 13.97. IR (Nujol, cm^{-1}) 1603.5, 1724, 1738.5. Anal. Calcd: 73.0 C; 8.2 H; 4.6 N. Found: 72.1 C; 8.5 H; 4.2 N.

Codendrimer $G = 2\%L^*\text{exp}0\%$. IR: (Nujol, cm^{-1}) 1631.5, 1731.8. Anal. Calcd: 73.0 C; 8.4 H; 5.1 N. Found: 72.0 C; 8.6 H; 5.1 N.

Codendrimer $G = 2\%L^*\text{exp}9\%$. IR: (Nujol, cm^{-1}) 1605.4, 1631.5, 1732.73. Anal. Calcd: 73.0 C; 8.4 H; 5.2 N. Found: 71.9 C; 8.0 H; 4.9 N.

Codendrimer $G = 2\%L^*\text{exp}22\%$. IR: (Nujol, cm^{-1}) 1604.5, 1728.9. Anal. Calcd: 72.8 C; 8.3 H; 5.2 N. Found: 71.8 C; 8.3 H; 5.3 N.

Codendrimer $G = 2\%L^*\text{exp}48\%$. IR: (Nujol, cm^{-1}) 1604.5, 1732.7. Anal. Calcd: 72.6 C; 8.2 H; 5.3 N. Found: 71.4 C; 7.8 H; 5.2 N.

Codendrimer $G = 2\%L^*\text{exp}75\%$. IR: (Nujol, cm^{-1}) 1602.8 cm^{-1} , 1729.8 cm^{-1} . Anal. Calcd: 72.4 C; 8.2 H; 5.4 N. Found: 71.6 C; 8.2 H; 5.4 N.

Codendrimer $G = 2\%L^*\text{exp}100\%$. IR: (Nujol, cm^{-1}) 1602.5 cm^{-1} , 1729.8 cm^{-1} . Anal. Calcd: 72.2 C; 8.0 H; 5.5 N. Found: 71.5 C; 8.4 H; 5.5 N.

Codendrimer $G = 3\%L^*\text{exp}22\%$. IR: (Nujol, cm^{-1}) 1605.6 cm^{-1} , 1735.4 cm^{-1} . Anal. Calcd: 73.0 C; 8.4 H; 5.5 N. Found: 72.0 C; 8.6 H; 5.3 N.

Codendrimer $G = 4\%L^*\text{exp}0\%$. IR: (Nujol, cm^{-1}) 1604.5 cm^{-1} , 1726.9 cm^{-1} . Anal. Calcd: 72.9 C; 8.5 H; 5.5 N. Found: 71.9 C; 8.7 H; 5.3 N.

Codendrimer $G = 4\%L^*\text{exp}7\%$. IR: (Nujol, cm^{-1}) 1605.4 cm^{-1} , 1633.4 cm^{-1} , 1730.8 cm^{-1} . Anal. Calcd: 72.8 C; 8.4 H; 5.6 N. Found: 71.3 C; 8.8 H; 5.7 N.

Codendrimer $G = 4\%L^*\text{exp}22\%$. IR: (Nujol, cm^{-1}) 1604.5 cm^{-1} , 1726.9 cm^{-1} . Anal. Calcd: 72.7 C; 8.4 H; 5.6 N. Found: 71.9 C; 8.2 H; 5.4 N.

Codendrimer $G = 4\%L^*\text{exp}49\%$. IR: (Nujol, cm^{-1}) 1604.4 cm^{-1} , 1630.5 cm^{-1} , 1728.8 cm^{-1} . Anal. Calcd: 72.5 C; 8.3 H; 5.7 N. Found: 71.6 C; 8.3 H; 5.5 N.

Codendrimer $G = 4\%L^*\text{exp}68\%$. IR: (Nujol, cm^{-1}) 1603.5 cm^{-1} , 1730.8 cm^{-1} . Anal. Calcd: 72.3 C; 8.2 H; 5.8 N. Found: 72.0 C; 8.0 H; 5.5 N.

Codendrimer $G = 4\%L^*\text{exp}100\%$. IR: (Nujol, cm^{-1}) 1605.3 cm^{-1} , 1730.0 cm^{-1} . Anal. Calcd: 72.1 C; 8.1 H; 5.9 N. Found: 71.8 C; 8.2 H; 5.4 N.

Codendrimer $G = 5\%L^*\text{exp}32\%$. IR: (Nujol, cm^{-1}) 1604.4 cm^{-1} , 1725.9 cm^{-1} . Anal. Calcd: 72.7 C; 8.4 H; 5.7 N. Found: 71.5 C; 8.1 H; 6.2 N.

Techniques. Microanalyses were performed with a Perkin-Elmer 240B microanalyzer. Infrared spectra were obtained with a Perkin-Elmer 1600 (FTIR) spectrophotometer in the range $\nu = 400\text{--}4000$ cm^{-1} . ^1H and ^{13}C NMR spectra were recorded on a Varian Unity 300 MHz spectrometer in CDCl_3 solutions. Gel permeation chromatography (GPC) was carried out in a Waters liquid chromatography system equipped with a 600E multisolvent delivery system and 996 photodiode array detector. Two Ultrastayreeage columns (Waters; pore size 500 and 10^4 Å) were connected in series. THF was used as the mobile phase with a flow rate of 0.8 mL min^{-1} . Calibration was performed with polystyrene standards. The optical textures of the mesophases were studied with a Nikon polarizing microscope equipped with a Mettler FP8 hot-stage and an FP80 central processor. The transition temperatures and enthalpies were measured by differential scanning calorimetry with a Perkin-Elmer DSC-7 instrument operated at a scanning

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rate of 10 °C min⁻¹ on heating. The apparatus was calibrated with indium (156.6 °C; 28.4 J g⁻¹) as the standard. XRD patterns were obtained using a pinhole camera (Anton-Paar) operating with a point-focused Ni-filtered Cu K α beam. The samples were held in Lindemann glass capillaries (1-mm diameter) and heating, when necessary, was achieved with a high-temperature attachment. The diffraction patterns were collected on flat photographic film.

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