Notes

Liquid Crystals Derived from Cholesterol Functionalized Poly(propylene imine) Dendrimers

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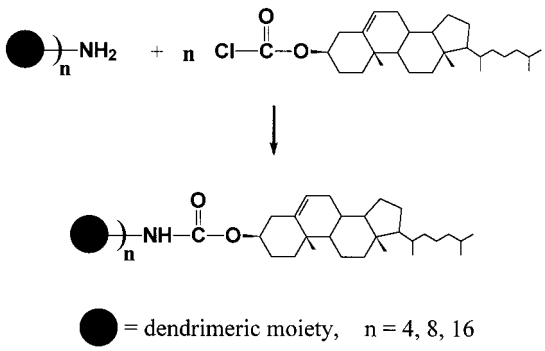
Introduction

The functionalization of the external groups of dendrimers[1] has proved a fruitful strategy[2] for the preparation of a diversity of novel materials including liquid crystals.[3] Functionalized dendrimers exhibit not only the conventional properties attributed to the presence of the specific moieties but also a behavior associated with their overall structural features primarily attributed to the accumulation of functional groups at their external spherical surface, collectively characterized as multivalent effects.[4] In several dendrimeric compounds thermotropic liquid crystalline character was induced by the introduction of mesogenic moieties in their external surface, and it is at least intriguing why the cholesteryl moiety was only employed in the case of carbosilane dendrimers.[5] It is exactly the purpose of this study to investigate whether the versatile cholesteryl moiety[6] is able to induce the formation of dendrimeric liquid crystals when introduced to poly(propylene imine) dendrimers. Diaminobutane poly(propylene imine) dendrimers of the first, second, and third generation were employed, and the introduction of the cholesteryl moiety was achieved by the interaction of cholesteryl chloroformate with the primary amino groups of the dendrimers as shown in Scheme 1. For comparison purposes, the dicholesteryl derivative *N,N*-butanediylbis(carbamic acid) dicholesteryl ester was also prepared.

Experimental Section

General Procedure for the Synthesis of Diaminobutane Poly(propylene imine) Cholesteryl Carbamate Dendrimers (G1−G3). To 0.001 mol of diaminobutane poly(propylene imine) dendrimer (DSM Fine Chemicals) of the first (DAB-4), second (DAB-8), and third (DAB-16) generation, dissolved in dry chloroform, 3-fold molar equivalent of triethylamine with respect to the primary amino groups was added. To this solution 5% molar excess of cholesteryl chloroformate dissolved in the same solvent was slowly added at 0° C. The reaction mixture was allowed to reach room temperature and stirred under inert gas atmosphere for 2−4 h depending on the dendrimers' generation. The solution containing the product was washed several times with water, and the separated organic solution was dried over sodium sulfate. The solvent was distilled off, and the remaining material was recrystallized from an ethyl acetate/chloroform mixture. The materials obtained were exhaustively dried under vacuum over phosphorus pentoxide, and their structure was established by NMR and elemental analysis. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.5−2.4 (m, cholesterol skeleton and central CH_2), 2.5 (m, $NCH_2CH_2CH_2CH_2N$, $NCH_2CH_2CH_2N$, $NCH_2CH_2CH_2NHCO$), 3.2 (m, $NCH_2CH_2CH_2NHCO$), 4.5 (m, H_{3a}), 5.4 (d, H_{6a}), 5.5 (broad s, N*H*). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 156.0 (*C*OO), 140.0 (C_5), 122.5 (C_6), 74.1 (C_3), 56.7 (C_{14}), 56.2 (C_{17}), 54.0 ($NCH_2CH_2CH_2CH_2N$), 52.2 ($NCH_2CH_2CH_2N$), 51.8 ($NCH_2CH_2CH_2NHCO$), 50.0 (C_9), 42.5 (C_{13}), 39.7 (C_{16}), 39.5(C_{24}), 38.7 ($NCH_2CH_2CH_2NHCO$), 37.0 (C_1), 36.5 (C_{10}), 36.0 (C_{22}), 35.8 (C_{20}), 32.0 (C_7, C_8), 28.3 ($NCH_2CH_2CH_2N$, $NCH_2CH_2CH_2NHCO$), 28.2(C_{12}), 28.0 (C_{25}), 27.2 (C_2), 25.0 ($NCH_2CH_2CH_2CH_2N$), 24.2 (C_{15}), 24.0 (C_{23}), 22.8 (C_{27}), 22.5 (C_{26}), 21.0 (C_{11}), 19.2 (C_{19}), 18.7 (C_{21}), 11.8 (C_{18}). Elemental analysis: G1, $C_{128}H_{216}N_6O_8$: Calcd: C, 78.15; H, 11.07; N, 4.27. Found: C, 78.09; H, 11.23; N, 3.81. G2, $C_{264}H_{448}N_{14}O_{16}$: Calcd: C, 77.82; H, 11.08; N, 4.81. Found: C, 77.21; H, 11.14; N, 4.95. G3, $C_{536}H_{912}N_{30}O_{32}$: Calcd: C, 77.66; H, 11.09; N, 5.07. Found: C, 77.40; H, 11.06; N, 5.31.

Scheme 1



For comparison reasons 1,4-diaminobutane, which may be regarded as the closest low molecular weight analogue, was also employed as a starting material, and the dicholesteryl carbamate derivative (G0) was prepared in an analogous manner. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.5−2.4 (m, cholesterol skeleton and central CH_2), 3.2 (m, 4H, $NH-CH_2$), 4.5 (m, 2H, H_{3a}), 4.6 (broad s, 2H, N*H*), 5.4 (d, 2H, H_{6a}). ^{13}C NMR (62.9 MHz $CDCl_3$): δ = 156.0 (*C*OO), 140.0 (C_5), 122.5 (C_6), 74.3 (C_3), 57.0 (C_{14}), 56.0 (C_{17}), 50.0 (C_9), 42.5 (C_{13}), 39.9 ($NH-CH_2$), 39.7 (C_{16}), 39.5 (C_{24}), 38.5 (C_4), 37.0 (C_1), 36.5 (C_{10}), 36.0 (C_{22}), 35.8 (C_{20}), 32.0 (C_7, C_8), 28.3 (central CH_2), 28.2 (C_{12}), 28.0 (C_{25}), 27.3 (C_2), 24.2 (C_{15}), 24.0 (C_{23}), 22.8 (C_{27}), 22.5 (C_{26}), 21.0 (C_{11}), 19.2 (C_{19}), 18.7 (C_{21}), 11.8 (C_{18}). Elemental analysis: G0, $C_{60}H_{100}N_2O_4$: Calcd: C, 78.89; H, 11.03; N, 3.07. Found: C, 78.64; H, 11.01; N, 3.46.

The completion of functionalization of the terminal primary NH_2 groups with the introduction of cholesteryl moieties was also confirmed by reacting the resulting compounds with fluorescamine, a reagent suitable for the detection of primary amines in the picomole range.[7] In all cases at least 99% of the primary amino groups were reacted.

Characterization. Liquid crystal textures were observed using a Leitz-Wetzlar polarizing microscope equipped with a Linkam hot stage. Thermotropic polymorphism was investigated by differential scanning calorimetry employing a DSC-

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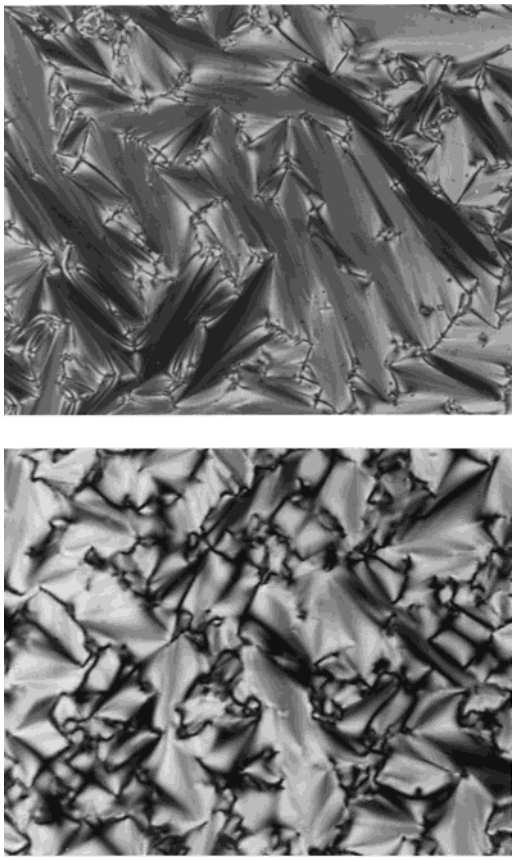

Figure 1. Optical textures of G0 (top, ×100) and G3 (bottom, ×250) in the smectic A phase observed by polarizing microscopy.

10 calorimeter (TA instruments) under nitrogen with heating and cooling rates of 10 °C min^{-1}. The thermal stability of the functionalized dendrimers was assessed by thermogravimetry employing a TGA-2050 instrument (TA instruments). Liquid crystalline phases were investigated by X-ray diffraction using Cu $K\alpha_1$ radiation from a Rigaku rotating anode X-ray generator (operating at 50 kV, 100 mA) and an R-AXIS IV image plate. Powder samples were sealed in Lindemann capillaries and heated employing an INSTEC hot stage.

Results and Discussion

Cholesteryl dendrimeric derivatives were prepared by a facile, one-step reaction with a method analogous to the one described for primary amines.[8] The thermal stability of the materials determined under nitrogen was satisfactory up to 210 °C (weight loss less than 0.25%) as assessed by thermogravimetry. The lower generation compounds were more stable while at temperatures above 250 °C the materials start degrading severely as also observed microscopically.

Diaminobutane cholesteryl carbamate derivative (G0) is a crystalline solid which on heating above 179.0 °C is transformed to a birefringent fluid, as evidenced by optical microscopy, becoming isotropic at 218.5 °C. On cooling, at temperatures below 212.5 °C, fan-shaped textures characteristic of smectic A phase are observed (Figure 1), while at temperatures below 140 °C the compound crystallizes. In a second heating/cooling run the material exhibits the same thermal behavior. The transition temperatures and the enthalpies involved were determined by DSC and presented in Table 1.

The dendrimeric derivatives G1−G3 exhibit T_g transitions at a temperature range between 63 and 78 °C (Table 1). The G1 compound exhibits a rather broad low-

Table 1. Phase Transition Temperatures *T* (Peak Values) and Enthalpies of Cholesteryl Dendrimeric Derivatives G0−G3 Obtained by DSC[a]

	T_g/°C	T_1/°C	T_2/°C	T_i/°C	ΔH_2/kJ mol^{-1}	ΔH_i/kJ mol^{-1}
G0			179.0	218.5	26.4	7.2
G1	63.6	118.9	149.0	170.1	11.2	5.9
G2	77.5	115.7[b]	158.5	209.4	58.5	12.2
G3	78.1	120.2[b]	162.2	209.5	126.6	∼25

[a] Subscript indices 1, 2, and i indicate transitions to ordered smectic phase, smectic A phase, and isotropic phase, respectively. T_g values reported are obtained during the second heating run. [b] Exothermic transition corresponding to cold crystallization.

enthalpy transition centered at 119 °C turning into a birefringent high-viscosity phase. On the other hand, G2 and G3 derivatives show an exotherm corresponding to a cold crystallization at 116 and 120 °C, respectively. The G1−G3 dendrimeric derivatives melt to birefringent fluids at temperatures 149−162 °C, depending on their generation and on further heating become isotropic at 170−210 °C. On cooling below the isotropization temperatures fan-shape textures are obtained under the polarizing microscope, typical of smectic A phases (Figure 1). It should be noted that as the generation increases, the development of smectic A textures is slower and less perfect. Microscopic observations between treated glass slides inducing homeotropic alignment show that on cooling from the isotropic phase the compounds do not develop textures, and therefore the existence of a SmC phase must be excluded. It should be noted in this respect that dicholesteryl carbamate derivatives exhibit only a SmA phase.[9]

On cooling below T_g, the smectic A phase of G1−G3 derivatives is transformed to a smectic A glass phase. Therefore, during the second heating/cooling DSC runs the dendrimers exhibit only a glass transition as well as a smectic−isotropic transition. However, the G3 cholesteryl dendrimer shows in addition an exothermic peak centered at 120 °C followed by an isoenergetic endothermic transition at 162 °C, which suggests a crystallization before melting into the smectic A phase.

X-ray diffraction data for the G0 derivative in the crystalline state reveal a lamellar arrangement of the molecules. In the small-angle region more than three equidistant reflections are observed, indicating a lamellar spacing of 37.2 Å, while in the wide-angle region a number of sharp reflections suggest a long-range ordering of the molecule. At temperatures above 180 °C, two equidistant reflections in the small-angle region and a diffuse band at 5.6 Å indicate the presence of a SmA phase. The lamellar spacing, 40.0 Å, observed at 185 °C, is very close to the length of the dimeric compound, taking into consideration that the length of one cholesteryl moiety is about 18 Å.[10] This finding supports the results from microscopic observations with treated glass slides, which ruled out a tilted smectic phase.

The X-ray diffraction patterns of G1−G3 dendrimeric derivatives on heating at temperatures below isotropization, as well as on cooling from their isotropic phases, show up to three equidistant reflections in the small-angle region and a diffuse band in the wide-angle region located at 5.5 Å (Figure 2). The observed lamellar spacings (Figure 3) suggest, as previously established for the G0 derivative, that in each layer the cholesteryl moieties are standing almost upright with the dendrimeric moiety filling the space between them. Some overlapping of the cholesterol terminal chains, as already proposed for low molecular weight cholesteric

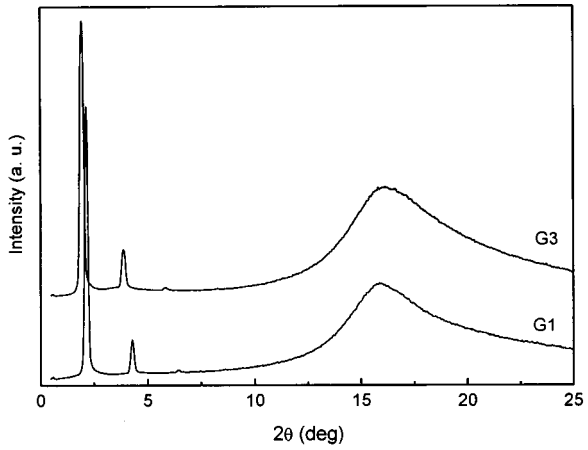

Figure 2. X-ray diffraction patterns of the G1 and G3 dendrimeric derivatives in the SmA phase.

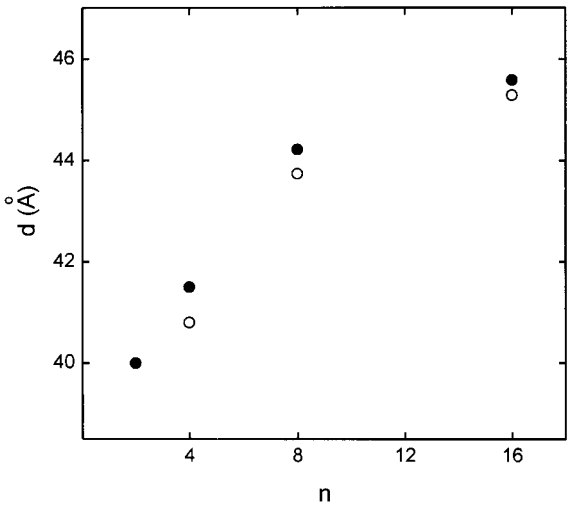

Figure 3. Smectic periods of the Gn compounds in the smectic A phase (100 °C, closed circles) and in the glassy smectic A phase (20 °C, open circles) obtained on cooling, as a function of the number of cholesteryl groups.

compounds,[10,11] can be envisaged since the cholesterol cross-sectional area (36.6 Å^2) is almost twice that of melted aliphatic chain.[10,12] From the data presented in Figure 3 it becomes clear that as the dendrimer generation increases, the lamellar spacings do not increase analogously, but instead they tend to reach a plateau value. For space-filling reasons the dendrimeric moieties are broadened to account for the significantly high cholesteric cross-sectional area. By considering the density of the compounds[13] (approximately 1 g cm^{-3}) and the experimental lamellar spacings, we can deduce the cross-sectional area of each dendrimeric derivative in the layers. The molecular area obtained divided by the molecular area of cholesterol is almost equal to one-half of the number of cholesteryl groups in each molecule. The cholesteryl groups are therefore located above and below the dendrimeric moieties (Figure 4). Finally, from the same data it can also be concluded that the glassy phase obtained at room temperature has a similar structure to the high-temperature SmA phase. The lamellar values at room temperature are essentially the same of those at 100 °C if one takes into consideration the thermal contraction of the materials.

Diffraction studies during the first heating run for the G1 derivative show the coexistence of two different lamellar phases. Specifically, at room temperature a

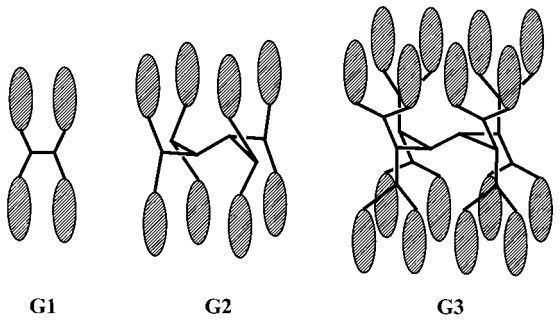

Figure 4. Schematic representation of the molecular structure in the smectic A phase: thick lines represent the dendrimeric branches, and ellipses depict the cholesteryl carbamate moieties.

number of sharp peaks in the wide-angle region were observed while in the small-angle region two reflections and their second harmonics were present, resulting from the coexistence of two lamellar periodicities of 41.0 and 32.1 Å. Apparently, the first period is equal to the molecular length while the second one probably originates from an intercalated phase. At temperatures above the first transition, in the small-angle region two sharp reflections are observed at 41.9 and 32.9 Å and their second harmonics. In the wide-angle region a rather sharp peak characteristic of SmB phase centered at 5.5 Å is observed. The two periodicities can be induced by steric frustrations[14] or by packing differences originally present in the recrystallized sample which cannot be compensated at this high-viscosity phase on moving from low to high molar mass systems.[15] On the other hand, the X-ray patterns of the G2 and G3 derivatives at temperatures below the SmA phase suggest the existence of an incommensurate phase. For the G2 derivative two high-intensity peaks are present at 44.5 Å ($q_1 = 2\pi/d = 0.141$ Å^{-1}) and at 23.9 Å ($q_2 = 0.263$ Å^{-1}) while less intense peaks at $q_1 + q_2$ and at $2q_2$ can also be observed. For the G3 derivative the two high-intensity peaks are located at 46.3 Å ($q_1 = 0.136$ Å^{-1}) and 26.5 Å ($q_2 = 0.237$ Å^{-1}). As pointed out by Hardouin et al.[16] and Kumar et al.,[17] these patterns are characteristic of an incommensurate liquid crystalline phase. In the wide-angle region a number of rather sharp peaks, especially for the G3 derivative, suggest the existence of a more ordered smectic phase—more likely a crystal E phase.[17]

The exhibition of liquid crystallinity by systems in which mesogenic units are attached to a molecular scaffold of a globular conformation certainly raises the question of molecular conflict between the preferentially lamellar ordering of the mesogens located on the periphery and the entropically favored spherical shape of the dendrimer. A similar problem has already been addressed in polymeric liquid crystalline and block copolymer systems. Thermodynamically, the positive free energy of ordering (stretching) of the polymer chains or dendrimers over a short distance is more than compensated by the negative free energy of phase separation.[18] Therefore, the alternating incompatible segments undergo nanophase separation and mesophases are induced. In this process the rigidity of the dendrimeric scaffold obviously plays a predominant role, and as a consequence, the mesomorphic properties are affected. This has already been discussed in the literature by comparing poly(amidoamine) and poly(propylene imine) liquid crystalline dendrimeric systems.[19] In the case under investigation both experimental and molec-

ular dynamics simulation studies[20] clearly prove that the employed poly(propylene imine) dendrimers are considered as flexible molecules. As a result, their conformation can be easily flattened at no great expense of free energy.

In summary, the functionalization of poly(propylene imine) dendrimers with cholesteryl moieties through a carbamate linkage results in the formation of smectic A phases at a broad thermal range, i.e., from 150 to 160 °C up to about 210 °C. Within each layer the cholesterol moieties, standing almost upright, are located above and bellow the dendrimeric part of the molecule. On cooling the materials are transformed into liquid crystalline glasses retaining the structural characteristics of the SmA phase. During the first heating run, at temperatures below the smectic A phase transition, the coexistence of two different lamellar phases and incommensurate smectic phases is observed.

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