

A Novel Pentaerythritol-based Carbosilane Liquid Crystalline Dendrimer Containing 12 Nitroazobenzene Groups on the Periphery[†]

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A novel liquid crystalline dendrimer with peripheral mesogenic units was successfully prepared. Azo-reaction and Williamson synthesis were employed in the preparation of the mesogenic unit 4-[4-(6-hydroxyhexyloxy)-phenylazo]nitrobenzene (M-NO₂). A terminal Si—Cl functional carbosilane dendrimer based on pentaerythritol was used as dendritic scaffold and subsequently functionalized with the aforementioned groups. Investigation of the liquid crystalline properties of the mesogen-functionalized dendrimer PCSi-1G-NO₂ by polarizing optical microscopy, DSC, and X-ray diffraction showed that it exhibits smectic E (S_E) phase, different from the corresponding mesogenic unit, which shows nematic phase. Furthermore, the temperatures of both the melting point and the clearing point of the mesogen-functionalized dendrimer decrease, and the temperature region of the S_E phase is wider than that of the nematic phase.

Keywords pentaerythritol, carbosilane liquid crystalline dendrimer, nitroazobenzene, S_E phase

Introduction

The functionalization of the external groups of dendrimers has proved a fruitful strategy for the preparation of a diversity of novel materials including liquid crystals.¹ 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.² Thermotropic liquid crystalline materials with dendritic architecture have received a lot of attention in the past decade. In several dendrimeric compounds thermotropic liquid crystalline character was induced by the introduction of mesogenic moieties in the external surface. Due to their excellent chemical and thermal stability, and potentials for wide varieties of functions, carbosilane dendrimers have been used as molecular scaffolds for the construction of unusual molecular architectures, *e.g.*, liquid crystalline (LC) dendrimers. Some examples of such dendrimers have been reported using an appropriate choice of silane as the core molecule.³⁻⁸

We have been interested in the research of carbosilane dendrimers and their functionalization.⁹ Pentaerythritol

has been used for the synthesis of polyether dendrimers, polyamide dendrimers, polyamine dendrimers and organometallic dendrimers.¹⁰ Nevertheless not for carbosilane dendrimer construction, recently a series of pentaerythritol-based carbosilane dendrimers have been successfully synthesized.¹¹ These dendrimers center at carbon atom, different from conventional carbosilane dendrimers the center of which is silicon or siloxane. Based on these novel dendritic scaffolds, some liquid crystalline dendrimers have been synthesized. Herein, we report the functionalization of a pentaerythritol-based carbosilane dendrimer, bearing 12 nitroazobenzene groups on the periphery. The preparation and liquid crystalline properties of both the mesogenic unit M-NO₂ and the mesogen-functionalized dendrimer PCSi-1G-NO₂ are described in detail.

Experimental

General

Tetrahydrofuran (THF), trichlorosilane (HSiCl₃), allyl bromide, and pyridine were purified by distillation before use. Other reagents and solvents were obtained commercially and used as received. FT-IR spectra were measured on a Nicolet FTIR 5DX spectrophotometer. ¹H NMR and ¹³C NMR were recorded on a JOEL

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FX-90Q spectrometer. Perkin-Elmer 240C elemental analysis was employed. Liquid crystal textures were observed using a Leica polarizing microscope equipped with a Leica MPS 60 auto camera and a hot stage. DSC Q100 differential scanning calorimetry was employed with a DSC-thermal analysis apparatus under a DSC refrigerator system with heating and cooling rates of 10 °C/min. X-ray diffraction experiments were carried out on a Rigaku D/MAX2200 PC diffractometer equipped with a heating device.

Synthesis of 6-bromo-hexane-1-ol

11.8 g (0.1 mol) of hexane-1,6-diol, 12 mL of hydrobromic acid (48% aqueous solution), and 30 mL of toluene were added into a 100-mL three-necked round-bottom flask equipped with a stirrer, Dean-Stark trap, and a condenser. The mixture was heated at reflux for 5 h. The solvent was evaporated to give a colorless liquid. The yield was 16.7 g (92%). $^1\text{H NMR}$ (CDCl_3) δ : 1.19—1.75 (m, 8H, CH_2), 3.48 (t, $J=6$ Hz, 2H, BrCH_2), 3.61 (t, $J=6$ Hz, 2H, OCH_2); IR (KBr) ν : 3343 (OH), 2933 (CH_2) cm^{-1} .

Synthesis of 4-(4-hydroxyphenylazo)nitrobenzene

6.9 g (0.05 mol) of *p*-nitroaniline was dissolved in 15 mL of conc. hydrochloric acid and 15 mL of water. For the diazotation 3.5 g (0.05 mol) of sodium nitrite dissolved in 20 mL of water was slowly added at temperature below 5 °C. To the cooled solution, 0.1 mol of 2 mol/L sodium hydroxide solution with 4.7 g (0.05 mol) of phenol were added and the reaction mixture was stirred for 1 h at room temperature. The precipitated azo dye was isolated by filtrating and washing with water. The residue was dissolved in 150 mL of ethanol/water (1 : 1, V/V) and acidified with conc. hydrochloric acid. The precipitate was isolated by filtrating and dried. Yield 8.0 g (66%); m.p. 219 °C; $^1\text{H NMR}$ (CDCl_3) δ : 8.31 (d, $J=9$ Hz, 2H), 7.95 (d, $J=9$ Hz, 4H), 6.95 (d, $J=9$ Hz, 2H); IR (KBr) ν : 3417 (OH), 1585 (CH), 1505 (N=N), 1284 (C—O), 1337 (NO_2), 846 (C—N) cm^{-1} .

Synthesis of 4-[4-(6-hydroxyhexyloxy)phenylazo]-nitrobenzene (M-NO₂)

2.0 g (0.008 mol) of 4-(4-hydroxyphenylazo)nitrobenzene, 1.38 g (0.01 mol) of potassium carbonate, and 1.66 g (0.01 mol) of KI were dissolved in 30 mL of absolute acetone, and 1.8 g (0.01 mol) of 6-bromo-1-hexanol was then added dropwise. The reaction mixture was refluxed for 24 h. 20 mL of chloroform was added to the mixture. The residual solid was washed twice by chloroform after filtrating. The chloroform solution was extracted three times with water and evaporated. The crude product was recrystallized from 50 mL of acetone. Further purification by column chromatography of a silica gel eluted with hexane/EtOAc (1 : 5, V/V) yielded 0.86 g of the pure product, a red crystalline solid in 31% yield. IR (KBr) ν : 3555 (O—H), 2933 (CH_2), 1580 (CH), 1512 (N=N), 1334 (NO_2), 1241 (C—O), 842

(C—N) cm^{-1} . $^1\text{H NMR}$ (CDCl_3) δ : 8.33 (d, $J=9$ Hz, 2H), 7.94 (d, $J=9$ Hz, 4H), 7.01 (d, $J=9$ Hz, 2H), 4.07 (t, $J=6$ Hz, 2H), 3.67 (t, $J=6$ Hz, 2H), 1.86—1.26 (m, 8H).

Synthesis of pentaerythritol-based tetraallyl ether

5.1 g (37.5 mmol) of pentaerythritol, 7.5 g (187.5 mmol, excess 25%) of NaOH, and 50 mL of anhydrous THF were added into a 100-mL flask. 17.3 mL (0.20 mol, excess 33%) of allyl bromide was dropped at a rate sufficient to maintain a moderate reflux. The reaction mixture was heated at reflux for 10 h. After being filtrated, the solid was washed twice with Et_2O , and the combined organic layers were washed twice with water and twice with saturated aqueous NaCl and dried over anhydrous MgSO_4 . The volatile components were removed on the rotary evaporator, leaving 7.0 g (63%) of pentaerythritol-based tetraallyl ether, a clear, colorless liquid. $^1\text{H NMR}$ (CDCl_3) δ : 6.03—5.67 (m, 4H), 5.30—5.06 (m, 8H), 3.94 (d, $J=6$ Hz, 8H), 3.46 (s, 8H); $^{13}\text{C NMR}$ (CDCl_3) δ : 134.71, 136.25, 71.98, 70.00, 44.99.

Synthesis of carbosilane liquid crystalline dendrimer PCSi-1G-NO₂

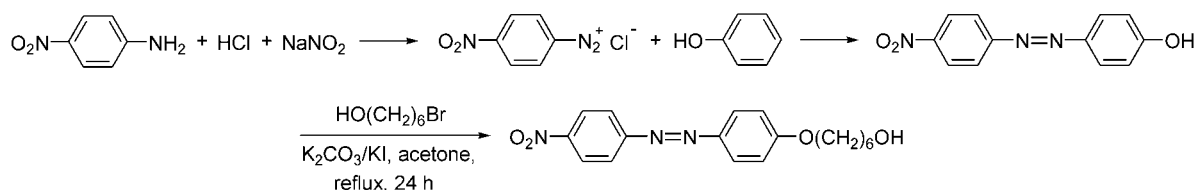
Into a 50-mL flask was added 1.5 g (5 mmol) of pentaerythritol-based tetraallyl ether, 3.0 mL (20 mmol, excess 50%) of HSiCl_3 , 20 mL of anhydrous THF, and five drops of Karstedt catalyst solution. The mixture was stirred for 30 min at room temperature and subsequently for 4 h at 50 °C. Volatiles were removed at reduced pressure, and 20 mL of fresh anhydrous THF was transferred to the flask through the vacuum system. Then 0.4 mL of this solution was dropwise added into the mixture of 0.45 g (1.32 mmol) of 4-(4-(6-hydroxyhexyloxy)phenylazo)nitrobenzene and 1 mL of pyridine in 10 mL of fresh anhydrous THF. The reaction mixture was heated at reflux for 24 h. After filtration, 100 mL of water was added to the THF solution. The precipitate was isolated by filtration and dried. Further purification by column chromatography on a silica gel eluted with hexane/EtOAc (1 : 4, V/V) afforded 0.24 g of pure product in 54% yield as a red crystalline solid. IR (KBr) ν : 2922 (CH_2), 1602 (CH), 1516 (N=N), 1343 (NO_2), 1242 (C—O), 843 (C—N) cm^{-1} ; $^1\text{H NMR}$ (CDCl_3) δ : 8.31 (d, $J=9$ Hz, 24H), 7.92 (d, $J=9$ Hz, 48H), 6.98 (d, $J=9$ Hz, 24H), 4.07 (t, $J=6$ Hz, 24H), 3.72 (t, $J=6$ Hz, 24H), 3.35 (t, 16H), 1.70—1.36 (m, 104H), 0.81 (m, 8H). Anal. calcd for $\text{C}_{233}\text{H}_{272}\text{N}_{36}\text{O}_{52}\text{Si}_4$: C 61.91, H 6.02, N 11.16; found C 62.01, H 6.11, N 10.98.

Results and discussion

Carbosilane liquid crystalline dendrimer

Depending on the location of mesogenic unit, liquid crystalline dendrimers with terminal mesogenic groups^{3-8,12,13} and those with mesogen-containing branching units¹⁴ have received much attention. Both

Scheme 1



liquid crystalline dendrimers with terminal mesogenic groups and side chain liquid crystalline polymers consist of molecules built up from the following general structure units: polymeric chain, spacer, and terminal (or side chain) mesogenic groups. The main difference between these liquid crystalline compounds is the different topology of the polymer chain. It is linear in the case of side chain liquid crystalline polymers, while in the case of liquid crystalline dendrimers it has superbranched architecture. It should be noted that liquid crystalline dendrimers are monodisperse compounds. This is an important distinction from side chain liquid crystalline polymers, which are usually polydisperse, as are most synthetic polymers.⁴

As a relatively flexible dendritic scaffold, pentaerythritol-based carbosilane dendrimer, a kind of novel carbosilane dendrimer synthesized firstly by us, was selected because of its well-defined structure. The preparation of mesogen-functionalized dendrimer is divided into three parts, (a) preparation of the mesogenic unit possessing a hydroxyl terminal group (Scheme 1), (b) synthesis of dendritic scaffold with 12 terminal Si—Cl groups, and (c) coupling of the mesogenic unit to the dendritic scaffold via substitution reaction yielding the mesogen-functionalized dendrimer (Scheme 2).

General characterization

The chemical structures of M-NO₂ and PCSi-1G-NO₂ were confirmed by IR, elemental analysis, and ¹H NMR spectroscopies.

The disappearance of the spike at 3555 cm⁻¹, which corresponds to the hydroxyl group, in the IR spectrum of PCSi-1G-NO₂ confirmed that all hydroxyl groups were functionalized. Moreover, the spike between 1140 cm⁻¹ and 1040 cm⁻¹ in the spectrum of the dendrimer turned broad showing that Si—O bonds were formed.

¹H NMR spectroscopy data of M-NO₂ and PCSi-1G-NO₂ were in agreement with the structures proposed (see Experimental Section).

The elemental analysis data of PCSi-1G-NO₂ were in accordance with the calculations (see Experimental).

Liquid crystalline properties

The mesomorphic and thermal properties of the mesogen-functionalized dendrimer PCSi-1G-NO₂ were investigated by polarizing optical microscopy (POM) and differential scanning calorimetry (DSC). DSC curves of PCSi-1G-NO₂ were shown as Figure 1 and phase transition data of the compound were listed in Table 1.

Scheme 2

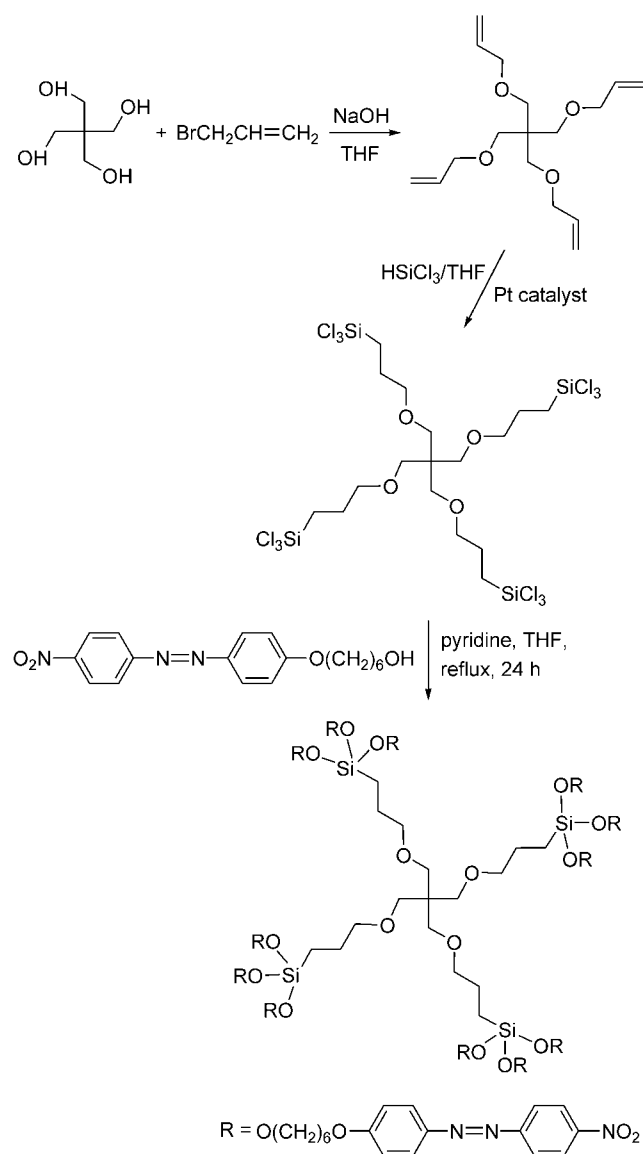


Table 1 Phase transition data of the mesogenic unit and the mesogen-functionalized dendrimer^a

	Heating	Cooling
<i>t</i> /°C	K59.6S _E 105.0I	I102.0S _E 56.0K
PCSi-1G-NO ₂ Δ <i>H</i> /(J•g ⁻¹)	K11.6S _E 8.12I	I—7.1S _E —13.6K
Δ <i>S</i> /(J•g ⁻¹ •K ⁻¹)	K0.035S _E 0.031I	I—0.027S _E —0.042I
<i>t</i> /°C	K129.6I	I120.6N114.1K
M-NO ₂ Δ <i>H</i> /(J•g ⁻¹)	K73.84I	I—1.30N64.0K
Δ <i>S</i> /(J•g ⁻¹ •K ⁻¹)	K0.183I	I—0.003N—0.165K

^a K: Crystal; S: Smectic; I: Isotropic.

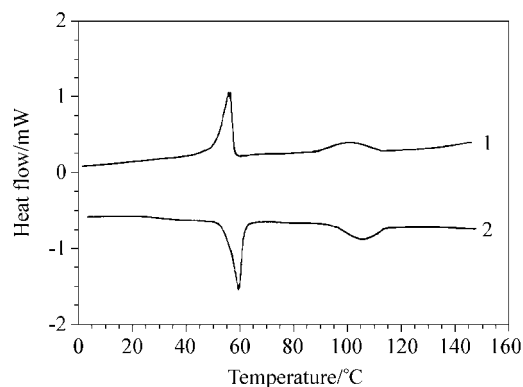


Figure 1 DSC curves of the mesogen-functionalized dendrimer: 1, the first cooling run; 2, the second heating run.

The mesogen-functionalized dendrimer PCSi-1G-NO₂ is a red crystalline solid at room temperature. On being heated above 60 °C, the compound turns into a birefringent viscous phase and melts to birefringent fluid, as evidenced by polarizing microscopy, and becomes isotropic at 105 °C. On cooling below the isotropic temperatures, focal-conics textures appeared and were improved, inequidistant concentric arc fan-shaped textures were observed under the polarizing microscopy, typical of smectic E (S_E) phase (Figure 2). While at temperature below 56 °C, the compound crystallizes. As shown in Figure 1, during the heating DSC run, the compound exhibits two endothermic peaks at 60 °C and 106 °C, and during the cooling run, there are two exothermic peaks at 102 °C and 56 °C, which indicate the transition from isotropic phase to smectic E phase and the transition corresponding to cold crystallization, respectively.



Figure 2 Optical texture of the mesogen-functionalized dendrimer in the smectic E phase at $T=80$ °C ($\times 200$).

The X-ray diffraction (XRD) curve of the mesogen-functionalized dendrimer PCSi-1G-NO₂ at 70° was shown in Figure 3. The XRD trace indicates some reflections at $2\theta=18^\circ$, 24° , and 26° . It suggests that a highly ordered smectic phase formed. If a hexatic phase is formed in the sample, the d spacings (d_{hkl}) of the X-ray reflections observed at the wide-angle area exhibit the relationship of the hexagonal packing mode: $d_{110} : d_{110} : d_{210} = 1 : 1/\sqrt{3} : \sqrt{7}$.¹² But, their d spacings obtained did not show the above relationship, and

the smectic phases were not assigned to hexatic smectic B. Therefore, it might be a highly ordered smectic E (S_E) phase.

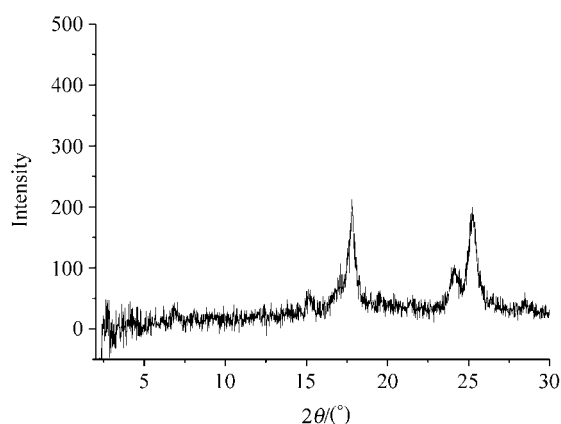


Figure 3 X-ray diffraction trace of the mesogen-functionalized dendrimer.

In summary, POM, DSC, and XRD results display that the mesogen-functionalized dendrimer exhibits smectic E (S_E) phase, different from the mesogenic unit which shows nematic phase.¹⁵

Comparing the phase transition temperature of the mesogen-functionalized dendrimer with that of the mesogenic unit, it is known that the melting point of the dendrimer (56 °C) is 58 °C lower than that of the mesogen unit (114 °C), and the clearing point of the dendrimer (102 °C) is 19 °C lower than that of the mesogen unit (121 °C). The mesophase region temperature of the dendrimer is 46 °C (56—102 °C), otherwise that of the mesogenic unit is 7 °C (114—121 °C), and the former is 39 °C wider than the latter.

Conclusion

A novel liquid crystalline dendrimer has been successfully prepared. A nitroazobenzene mesogenic unit was synthesized and subsequently coupled to a pentaerythritol-based carbosilane dendrimer possessing 12 terminal Si—Cl groups. The mesogenic unit and the mesogen-functionalized dendrimer showed nematic and smectic E phase, respectively. They are different in terms of melting point, clearing point, and mesophase region. Compared to the mesogenic unit, the mesogen-functionalized dendrimer has more advantages and potential applications. Meanwhile because the materials containing photochromic azobenzene moieties have been of great interest for applications to photomemories, light-driven displays, optical data storage, optical switching, opto-mechanical actuation, and optoelectronics, this novel nitroazobenzene mesogen-functionalized dendrimer is promising in some area. Further research is now under way.

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