



## Synthesis and thermal behavior of Janus dendrimers, part 2<sup>☆</sup>

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### ABSTRACT

The thermal properties of twelve Janus-type dendrimers up to the second generation were evaluated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). Compounds consist of the dendritic bisMPA based polyester moieties, and either 3,4-bis-dodecyloxybenzoic acid, 3,5-bis-dodecyloxybenzoic acid or 3,4,5-tris-dodecyloxybenzoic acid moieties, attached to opposite sides of the pentaerythritol core. The thermal stability of the compounds was evaluated by TGA, displaying onset decomposition temperatures ( $T_d$ ) at around 250 °C. DSC measurements upon heating and cooling confirmed that OH terminated Janus dendrimers featuring large polarity difference in opposite sides display liquid crystalline phases with exception of 3,5-type G1 dendrimer; while acetonide terminated dendrimers displayed merely melting transitions. Dendrimers having terminal alkyl chains at positions 3,4 or 3,4,5 in aromatic moieties exhibited enantiotropic mesophases. However, the thermal behavior of the dendrimers with 3,5-substitution pattern was different: the 3,5-type G1 dendrimer exhibit a lack of mesomorphic transition, and in the case of the 3,5-type G2 dendrimer, the mesophase was absent in the first heating scan but was observed during the subsequent cooling and heating scans at the rate of 10 °C/min.

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### 1. Introduction

There exist an ever growing need for new materials in science and technology. Owing to the highly branched mono-disperse structures, dendrimers and dendrons have attracted researchers in designing and synthesizing these multifunctional compounds with various architectures and properties. Generally, dendrimers consist of three distinct regions: a central core, layered branching units, and terminal groups [1–3]. Two common stepwise synthetic methods, i.e. divergent [4] and convergent [5], have been utilized for the preparation of the dendrimers in order to control the shape, size, functionality, and as a result, properties of the dendrimers. Due to the unique features, the dendrimers have been widely investigated for various purposes, such as medical uses [6–11], light harvesting systems [12–14], and catalysis [15–18].

Alongside the conventional dendrimers, the interest in more specifically designed dendritic structures has arisen to meet the mounting demands of the modern technology. Recently, Janus dendrimers, also called bow-tie or block co-dendrimers, characterized by two differently functionalized segments on opposite sides, have been synthesized [19–27]. Owing to the possibility to tailor the opposite functional groups, the Janus-type dendrimers have gained interest, particularly in the design of liquid crystals [28–30] and amphiphilic self-assembling dendrimers [31–33]. In addition, the

use of bow-tie dendrimers in medical applications has provided promising results [34,35].

It is known that, altering the end group functionality [36–39] as well as other structural modifications [40] influence on the thermal properties of the dendritic molecules. Herein we report the thermal behavior study of the small Janus dendrimers up to the second generation. The synthesis the compounds have been described previously [41], but their thermal characterization was lacking. These two-faced dendrimers, emanating from the pentaerythritol core, consist of bisMPA based polyester wedges, having on one side either acetonide groups or hydroxyl groups in the periphery and on the other side monodendrons, namely, 3,4-bis-dodecyloxybenzoic acid, 3,5-bis-dodecyloxybenzoic acid or 3,4,5-tris-dodecyloxybenzoic acid moieties. The thermotropic liquid crystal mesophases of dendritic molecules containing above-mentioned, as well as other feasible monodendrons, have been studied extensively by Percec et al. [42–48]. In our previous study of the corresponding 3,4-type C<sub>6</sub> and C<sub>16</sub> alkylated dendrimers we observed that the combination of non-polar segments and polar hydroxyl terminated dendritic polyester moieties can form liquid crystalline mesophases [49]. The study is now extended to include also series of C<sub>12</sub> alkyl chain based polyester dendrimers.

### 2. Experimental

#### 2.1. Materials and instrumentations

All the starting materials were purchased from major suppliers and used without any further purification. Dichloromethane

<sup>☆</sup> Janus dendrimers are C<sub>12</sub> alkyl 7chain based polyester dendrimers.

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(DCM) was dried over 4 Å sieves. Isopropylidene-2,2-bis(hydroxymethyl)propionic acid anhydride (anhydride of bisMPA) [50]; the pentaerythritol based core molecule, (OH)<sub>2</sub>-PE-[G1]-acetone [26]; and mini dendrons 3,4-bis-dodecyloxybenzoic acid, 3,5-bis-dodecyloxybenzoic acid, and 3,4,5-tris-dodecyloxybenzoic acid were prepared according to literature [42]. Column chromatography was performed with Merck 60 F254 silica gel, particle size 0.040–0.063 mm. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Bruker Avance DRX 500 NMR (500.13 and 125.76 MHz) spectrometer in CDCl<sub>3</sub> solution. The solvent signal was used as an internal standard. Mass spectral data was obtained with Micromass LCT Electrospray ionization time-of-flight (ESI TOF) instrument with either positive-ion or negative-ion mode. Thermal behavior of the compounds was determined on power compensation type PerkinElmer PYRIS DIAMOND DSC. The measurements were carried out under nitrogen atmosphere (flow rate 50 mL min<sup>-1</sup>) using 50 μL sealed aluminum sample pans. The sealing was made by using a 30 μL aluminum pan with capillary holes to ascertain good thermal contact between a sample and pan, and to minimize free volume inside the pan. The temperature calibration was made using two standard materials (*n*-decane and Indium metal) and energy calibration by an Indium standard (28.45 J g<sup>-1</sup>). Typically, following temperature profile was used for each sample: a sample was heated from -40 to desired end temperature (from 120 to 200 °C) with a heating rate of 10 °C/min, followed by 1 min hold at the end temperature, and cooled down to -40 °C with a rate of 10 °C/min. The sample was held at -40 °C for 5 min and heated for a second time, respectively. Sample weights of 3–6 mg were used on the measurements. Finally, the sample weight was checked afterwards to monitor weight losses that may have occurred during the scans. The uncertainty for measured temperatures was less than 0.8 °C for all measurements. Preliminary studies with polarizing optical microscope (POM) were accomplished to confirm the presence of mesomorphic phases. More detailed characterization of the mesomorphic phases will be presented later on elsewhere.

The thermal decomposition was examined with PerkinElmer TGA7 thermogravimetric analyzer. Measurements were carried out in platinum pans under synthetic air atmosphere (flow rate of 50 mL min<sup>-1</sup>) with heating rate of 10 °C/min on temperature range of 25–700 °C. The temperature calibration of instrument was carried out using Curie-point calibration technique (Alumel, Ni, Perkalloy, Fe). The weight balance was calibrated by measuring the standard weight of 50 mg at room temperature. The sample weights used in the measurements were about 4–5 mg. The decomposition onset was obtained using step-tangent method at which 5% decomposition is occurred, taken account the possible initial weight loss occurred due to removal of water/solvent.

## 2.2. Synthesis

### 2.2.1. 3,4-Bis-dodecyloxybenzoic ester-PE-[G1]-acetone (1), 3,5-bis-dodecyloxybenzoic ester-PE-[G1]-acetone (2), and 3,4,5-tris-dodecyloxybenzoic ester-PE-[G1]-acetone (3)

Compounds 1–3 were prepared according to literature procedures, and spectroscopic data agreed with those reported [41].

### 2.2.2. 3,4-Bis-dodecyloxybenzoic ester-PE-[G1]-(OH)<sub>4</sub> (4)

Compound 1 (1.60 g, 1.15 mmol) was dissolved in THF (20 mL), and 20 mL of 6 M HCl was added. The mixture was stirred at room temperature for 3 h. Formed white solid was filtered, washed with water, and dried in vacuo (1.42 g, 94%). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ<sub>ppm</sub> = 0.88 (t, 12H, CH<sub>3</sub>, *J* = 6.8 Hz), 1.08 (s, 6H, bis-MPA-CH<sub>3</sub>), 1.26 (overlapped peaks, 64H, CH<sub>3</sub>(CH<sub>2</sub>)<sub>8</sub>), 1.44–1.48 (m, 8H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OAr), 1.80–1.85 (m, 8H, CH<sub>2</sub>CH<sub>2</sub>OAr), 3.11 (br s, 4H, OH), 3.75 (d, 4H,

bis-MPA-CH<sub>2</sub>, *J* = 11.3 Hz), 3.87 (d, 4H, bis-MPA-CH<sub>2</sub>, *J* = 11.3 Hz), 4.01 (t, 4H, CH<sub>2</sub>OAr, *J* = 6.6 Hz), 4.03 (t, 4H, CH<sub>2</sub>OAr, *J* = 6.6 Hz), 4.36 (s, 4H, CH<sub>2</sub>), 4.50 (s, 4H, CH<sub>2</sub>), 6.83 (d, 2H, ArH, 5 position, *J* = 8.5 Hz), 7.49 (d, 2H, ArH, 2 position, *J* = 2.0 Hz), 7.59 (dd, 2H, ArH, 6 position, *J* = 8.4 Hz, *J* = 2.0 Hz). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ<sub>ppm</sub> = 14.1 (CH<sub>3</sub>), 17.2 (CH<sub>3</sub>), 22.7 (CH<sub>3</sub>CH<sub>2</sub>), 26.0 (CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OAr), 29.1 and 29.2 (CH<sub>2</sub>CH<sub>2</sub>OAr), 29.4–29.7 (CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>6</sub>), 31.9 (CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>), 43.6 (C-PE), 49.9 (C-bis-MPA), 61.8 (CH<sub>2</sub>-PE), 62.0 (CH<sub>2</sub>-PE), 68.2 (bis-MPA-CH<sub>2</sub>), 69.1 (CH<sub>2</sub>OAr), 69.4 (CH<sub>2</sub>OAr), 112.0 (ArC, 5 position), 114.5 (ArC, 2 position), 121.4 (ArC, 1 position), 123.8 (ArC, 6 position), 148.8 (ArC, 3 position), 153.8 (ArC, 4 position), 166.0 (CO), 175.2 (CO). ESI TOF MS: *m/z* calcd. for C<sub>77</sub>H<sub>132</sub>O<sub>16</sub> 1335.94 [M+Na]<sup>+</sup>, found 1335.62 [M+Na]<sup>+</sup>. Elem. Anal: Calcd. for C<sub>77</sub>H<sub>132</sub>O<sub>16</sub>·H<sub>2</sub>O: C 69.44%, H 10.14%. Found: C 69.21%, H 10.26%.

### 2.2.3. 3,5-Bis-dodecyloxybenzoic ester-PE-[G1]-(OH)<sub>4</sub> (5)

Compound 2 (1.65 g, 1.18 mmol) was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (15 mL), and diluted with MeOH (15 mL). 2 teaspoons of Dowex 50W-X8 resin was added, and the mixture stirred at 50 °C until reaction was complete. Resin was filtered off, and washed with small amount of CH<sub>2</sub>Cl<sub>2</sub>. Solvent was evaporated to give white solid (1.40 g, 90%). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ<sub>ppm</sub> = 0.88 (t, 12H, CH<sub>3</sub>, *J* = 6.8 Hz), 1.08 (s, 6H, bis-MPA-CH<sub>3</sub>), 1.26 (overlapped peaks, 64H, CH<sub>3</sub>(CH<sub>2</sub>)<sub>8</sub>), 1.42–1.47 (m, 8H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OAr), 1.74–1.80 (m, 8H, CH<sub>2</sub>CH<sub>2</sub>OAr), 3.06 (br s, 4H, OH), 3.74 (d, 4H, bis-MPA-CH<sub>2</sub>, *J* = 11.3 Hz), 3.88 (d, 4H, bis-MPA-CH<sub>2</sub>, *J* = 11.3 Hz), 3.94 (t, 4H, CH<sub>2</sub>OAr, *J* = 6.5 Hz), 4.37 (s, 4H, CH<sub>2</sub>), 4.51 (s, 4H, CH<sub>2</sub>), 6.64 (t, 2H, ArH, 4 position, *J* = 2.3 Hz), 7.10 (d, 4H, ArH, 2,6 positions, *J* = 2.3 Hz). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ<sub>ppm</sub> = 14.1 (CH<sub>3</sub>), 17.1 (CH<sub>3</sub>), 22.7 (CH<sub>3</sub>CH<sub>2</sub>), 26.0 (CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OAr), 29.2–29.7 (CH<sub>2</sub>CH<sub>2</sub>OAr and CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>6</sub>), 31.9 (CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>), 43.5 (C-PE), 49.9 (C-bis-MPA), 61.7 (CH<sub>2</sub>-PE), 62.4 (CH<sub>2</sub>-PE), 68.2 (bis-MPA-CH<sub>2</sub>), 68.4 (CH<sub>2</sub>OAr), 106.7 (ArC, 4 position), 107.8 (ArC, 2,6 positions), 130.9 (ArC, 1 position), 160.3 (ArC, 3,5 positions), 166.0 (CO), 175.1 (CO). ESI TOF MS: *m/z* calcd. for C<sub>77</sub>H<sub>132</sub>O<sub>16</sub> 1335.94 [M+Na]<sup>+</sup>, found 1335.75 [M+Na]<sup>+</sup>. Elem. Anal: Calcd. for 2C<sub>77</sub>H<sub>132</sub>O<sub>16</sub>·3H<sub>2</sub>O: C 68.97%, H 10.15%. Found: C 68.87%, H 10.06%.

### 2.2.4. 3,4,5-Tris-dodecyloxybenzoic ester-PE-[G1]-(OH)<sub>4</sub> (6)

The procedure is the same as the synthesis of 5. Compound 3 (2.00 g, 1.13 mmol), and 2 teaspoons of Dowex 50W-X8 resin were used to give 1.85 g (97%) of white solid. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ<sub>ppm</sub> = 0.89 (t, 18H, CH<sub>3</sub>, *J* = 6.9 Hz), 1.08 (s, 6H, bis-MPA-CH<sub>3</sub>), 1.26 (overlapped peaks, 96H, CH<sub>3</sub>(CH<sub>2</sub>)<sub>8</sub>), 1.44–1.50 (m, 12H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OAr), 1.71–1.77 (4H, CH<sub>2</sub>CH<sub>2</sub>OAr, 4 position), 1.77–1.83 (8H, CH<sub>2</sub>CH<sub>2</sub>OAr, 3,5 positions), 3.04 (br s, 6H, OH), 3.76 (d, 4H, bis-MPA-CH<sub>2</sub>, *J* = 11.3 Hz), 3.88 (d, 4H, bis-MPA-CH<sub>2</sub>, *J* = 11.3 Hz), 3.98 (t, 8H, CH<sub>2</sub>OAr, *J* = 6.4 Hz), 4.01 (t, 4H, CH<sub>2</sub>OAr, *J* = 6.6 Hz), 4.36 (s, 4H, CH<sub>2</sub>), 4.50 (s, 4H, CH<sub>2</sub>), 7.21 (s, 4H, ArH, 2,6 positions). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ<sub>ppm</sub> = 14.1 (CH<sub>3</sub>), 17.2 (CH<sub>3</sub>), 22.7 (CH<sub>3</sub>CH<sub>2</sub>), 26.1 (CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OAr, 4 position), 26.1 (CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OAr, 3,5 positions), 29.4–29.7 (CH<sub>2</sub>CH<sub>2</sub>OAr, 3,5 positions and CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>6</sub>), 30.4 (CH<sub>2</sub>CH<sub>2</sub>OAr, 4 position), 31.9 (CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>), 43.7 (C-PE), 49.9 (C-bis-MPA), 61.6 (CH<sub>2</sub>-PE), 61.9 (CH<sub>2</sub>-PE), 68.5 (bis-MPA-CH<sub>2</sub>), 69.3 (CH<sub>2</sub>OAr, 3,5 positions), 73.6 (CH<sub>2</sub>OAr, 4 position), 108.3 (ArC, 2,6 positions), 123.6 (ArC, 1 position), 143.1 (ArC, 4 position), 153.0 (ArC, 3,5 positions), 165.9 (CO), 173.3 (CO). ESI TOF MS: *m/z* calcd. for C<sub>101</sub>H<sub>180</sub>O<sub>18</sub> 1705.31 [M+Na]<sup>+</sup>, found 1704.91 [M+Na]<sup>+</sup>. Elem. Anal: Calcd. for C<sub>101</sub>H<sub>180</sub>O<sub>18</sub>·2H<sub>2</sub>O: C 70.59%, H 10.79%. Found: C 70.79%, H 10.89%.

### 2.2.5. 3,4-Bis-dodecyloxybenzoic ester-PE-[G2]-acetone (7)

Compound 4 (0.92 g, 0.70 mmol), anhydride of bis-MPA (1.20 g, 3.62 mmol) and DMAP (0.05 g, 0.42 mmol) were dissolved in 1.1 mL of pyridine and 4 mL of CH<sub>2</sub>Cl<sub>2</sub>. The mixture was stirred at room temperature for 72 h. 1 mL of water was added with vigorous stir-

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