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Synthesis and thermal behavior of Janus dendrimers, part 2☆

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ABSTRACT

The thermal properties of twelve Janus-type dendrimers up to the second generation were evaluated by termogravimetric 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.

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_6 and C_{16} 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_{12} 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

☆ Janus dendrimers are C_{12} 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, $(OH)_2$-PE-[G1]-acetonide [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. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance DRX 500 NMR (500.13 and 125.76 MHz) spectrometer in $CDCl_3$ solution. The solvent signal was used as an internal standard. Mass spectral data was obtained with Micromass LCT Electronspray 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^{-1}) 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^{-1}). 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^{-1}) 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]-acetonide (**1**), 3,5-bis-dodecyloxybenzoic ester-PE-[G1]-acetonide (**2**), and 3,4,5-tris-dodecyloxybenzoic ester-PE-[G1]-acetonide (**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]-$(OH)_4$ (**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%). ^{1}H NMR ($CDCl_3$): δ_{ppm} = 0.88 (t, 12H, C*H*$_3$, *J* = 6.8 Hz), 1.08 (s, 6H, bis-MPA-C*H*$_3$), 1.26 (overlapped peaks, 64H, $CH_3(CH_2)_8$), 1.44–1.48 (m, 8H, $CH_2CH_2CH_2OAr$), 1.80–1.85 (m, 8H, CH_2CH_2OAr), 3.11 (br s, 4H, O*H*), 3.75 (d, 4H, bis-MPA-CH_2, *J* = 11.3 Hz), 3.87 (d, 4H, bis-MPA-CH_2, *J* = 11.3 Hz), 4.01 (t, 4H, CH_2OAr, *J* = 6.6 Hz), 4.03 (t, 4H, CH_2OAr, *J* = 6.6 Hz), 4.36 (s, 4H, CH_2), 4.50 (s, 4H, CH_2), 6.83 (d, 2H, Ar*H*, 5 position, *J* = 8.5 Hz), 7.49 (d, 2H, Ar*H*, 2 position, *J* = 2.0 Hz), 7.59 (dd, 2H, Ar*H*, 6 position, *J* = 8.4 Hz, *J* = 2.0 Hz). ^{13}C NMR ($CDCl_3$): δ_{ppm} = 14.1 (*C*H$_3$), 17.2 (*C*H$_3$), 22.7 (CH_3CH_2), 26.0 (*C*$H_2CH_2CH_2OAr$), 29.1 and 29.2 (CH_2CH_2OAr), 29.4–29.7 ($CH_3CH_2CH_2(CH_2)_6$), 31.9 ($CH_3CH_2CH_2$), 43.6 (*C*-PE), 49.9 (*C*-bis-MPA), 61.8 (*C*H_2-PE), 62.0 (*C*H_2-PE), 68.2 (bis-MPA-*C*H_2), 69.1 (*C*H_2OAr), 69.4 (*C*H_2OAr), 112.0 (Ar*C*, 5 position), 114.5 (Ar*C*, 2 position), 121.4 (Ar*C*, 1 position), 123.8 (Ar*C*, 6 position), 148.8 (Ar*C*, 3 position), 153.8 (Ar*C*, 4 position), 166.0 (*C*O), 175.2 (*C*O). ESI TOF MS: *m*/*z* calcd. for $C_{77}H_{132}O_{16}$ 1335.94 [M+Na]$^+$, found 1335.62 [M+Na]$^+$. Elem. Anal: Calcd. for $C_{77}H_{132}O_{16}\cdot H_2O$: C 69.44%, H 10.14%. Found: C 69.21%, H 10.26%.

2.2.3. 3,5-Bis-dodecyloxybenzoic ester-PE-[G1]-$(OH)_4$ (**5**)

Compound **2** (1.65 g, 1.18 mmol) was dissolved in CH_2Cl_2 (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_2Cl_2. Solvent was evaporated to give white solid (1.40 g, 90%). ^{1}H NMR ($CDCl_3$): δ_{ppm} = 0.88 (t, 12H, C*H*$_3$, *J* = 6.8 Hz), 1.08 (s, 6H, bis-MPA-C*H*$_3$), 1.26 (overlapped peaks, 64H, $CH_3(CH_2)_8$), 1.42–1.47 (m, 8H, $CH_2CH_2CH_2OAr$), 1.74–1.80 (m, 8H, CH_2CH_2OAr), 3.06 (br s, 4H, O*H*), 3.74 (d, 4H, bis-MPA-CH_2, *J* = 11.3 Hz), 3.88 (d, 4H, bis-MPA-CH_2, *J* = 11.3 Hz), 3.94 (t, 4H, CH_2OAr, *J* = 6.5 Hz), 4.37 (s, 4H, CH_2), 4.51 (s, 4H, CH_2), 6.64 (t, 2H, Ar*H*, 4 position, *J* = 2.3 Hz), 7.10 (d, 4H, Ar*H*, 2,6 positions, *J* = 2.3 Hz). ^{13}C NMR ($CDCl_3$): δ_{ppm} = 14.1 (*C*H$_3$), 17.1 (*C*H$_3$), 22.7 (CH_3CH_2), 26.0 ($CH_2CH_2CH_2OAr$), 29.2–29.7 (CH_2CH_2OAr and $CH_3CH_2CH_2(CH_2)_6$), 31.9 ($CH_3CH_2CH_2$), 43.5 (*C*-PE), 49.9 (*C*-bis-MPA), 61.7 (*C*H_2-PE), 62.4 (*C*H_2-PE), 68.2 (bis-MPA-*C*H_2), 68.4 (*C*H_2OAr), 106.7 (Ar*C*, 4 position), 107.8 (Ar*C*, 2,6 positions), 130.9 (Ar*C*, 1 position), 160.3 (Ar*C*, 3,5 positions), 166.0 (*C*O), 175.1 (*C*O). ESI TOF MS: *m*/*z* calcd. for $C_{77}H_{132}O_{16}$ 1335.94 [M+Na]$^+$, found 1335.75 [M+Na]$^+$. Elem. Anal: Calcd. for $2C_{77}H_{132}O_{16}\cdot 3H_2O$: C 68.97%, H 10.15%. Found: C 68.87%, H 10.06%.

2.2.4. 3,4,5-Tris-dodecyloxybenzoic ester-PE-[G1]-$(OH)_4$ (**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. ^{1}H NMR ($CDCl_3$): δ_{ppm} = 0.89 (t, 18H, C*H*$_3$, *J* = 6.9 Hz), 1.08 (s, 6H, bis-MPA-C*H*$_3$), 1.26 (overlapped peaks, 96H, $CH_3(CH_2)_8$), 1.44–1.50 (m, 12H, $CH_2CH_2CH_2OAr$), 1.71–1.77 (4H, CH_2CH_2OAr, 4 position), 1.77–1.83 (8H, CH_2CH_2OAr, 3,5 positions), 3.04 (br s, 6H, O*H*), 3.76 (d, 4H, bis-MPA-CH_2, *J* = 11.3 Hz), 3.88 (d, 4H, bis-MPA-CH_2, *J* = 11.3 Hz), 3.98 (t, 8H, CH_2OAr, *J* = 6.4 Hz), 4.01 (t, 4H, CH_2OAr, *J* = 6.6 Hz), 4.36 (s, 4H, CH_2), 4.50 (s, 4H, CH_2), 7.21 (s, 4H, Ar*H*, 2,6 positions). ^{13}C NMR ($CDCl_3$): δ_{ppm} = 14.1 (*C*H$_3$), 17.2 (*C*H$_3$), 22.7 (CH_3CH_2), 26.1 ($CH_2CH_2CH_2OAr$, 4 position), 26.1 ($CH_2CH_2CH_2OAr$, 3,5 positions), 29.4–29.7 (*C*H_2CH_2OAr, 3,5 positions and $CH_3CH_2CH_2(CH_2)_6$), 30.4 (CH_2CH_2OAr, 4 position), 31.9 ($CH_3CH_2CH_2$), 43.7 (*C*-PE), 49.9 (*C*-bis-MPA), 61.6 (*C*H_2-PE), 61.9 (*C*H_2-PE), 68.5 (bis-MPA-*C*H_2), 69.3 (*C*H_2OAr, 3,5 positions), 73.6 (*C*H_2OAr, 4 position), 108.3 (Ar*C*, 2,6 positions), 123.6 (Ar*C*, 1 position), 143.1 (Ar*C*, 4 position), 153.0 (Ar*C*, 3,5 positions), 165.9 (*C*O), 173.3 (*C*O). ESI TOF MS: *m*/*z* calcd. for $C_{101}H_{180}O_{18}$ 1705.31 [M+Na]$^+$, found 1704.91 [M+Na]$^+$. Elem. Anal: Calcd. for $C_{101}H_{180}O_{18}\cdot 2H_2O$: C 70.59%, H 10.79%. Found: C 70.79%, H 10.89%.

2.2.5. 3,4-Bis-dodecyloxybenzoic ester-PE-[G2]-acetonide (**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_2Cl_2. The mixture was stirred at room temperature for 72 h. 1 mL of water was added with vigorous stir-

ring for 2 h to quench the anhydride. The mixture was then diluted with 100 mL of CH_2Cl_2, and washed with 10% $NaHSO_4$ (3 × 15 mL), 10% Na_2CO_3 (3 × 15 mL), and with brine (15 mL). Organic layer was dried over anhydrous $MgSO_4$ and solvent evaporated. The product was further purified by column chromatography (SiO_2) eluting with hexane/ethyl acetate (3:2) to give 1.00 g (74%) of glassy solid. ^{1}H NMR ($CDCl_3$): δ_{ppm} = 0.88 (t, 12H, C*H*$_3$, *J* = 6.9 Hz), 1.09 (s, 12H, G2-C*H*$_3$), 1.26 (overlapped peaks, 64H, $CH_3(CH_2)_8$), 1.28 (s, 6H, G1-C*H*$_3$), 1.32 (s, 12H, acetonide-C*H*$_3$), 1.36 (s, 12H, acetonide-C*H*$_3$), 1.44–1.50 (m, 8H, C*H*$_2$CH$_2$CH$_2$OAr), 1.79–1.86 (m, 8H, C*H*$_2$CH$_2$OAr), 3.56 (dd, 8H, G2-C*H*$_2$, *J* = 11.9 Hz, *J* = 2.2 Hz), 4.01 (t, 4H, C*H*$_2$OAr, *J* = 6.6 Hz), 4.03 (t, 4H, C*H*$_2$OAr, *J* = 6.6 Hz), 4.11 (d, 8H, G2-C*H*$_2$, *J* = 11.8 Hz), 4.34 (ABq, 8H, G1-C*H*$_2$, *J* = 11.1 Hz), 4.34 (s, 4H, C*H*$_2$), 4.46 (s, 4H, C*H*$_2$), 6.82 (d, 2H, Ar*H*, 5 position, *J* = 8.6 Hz), 7.48 (d, 2H, Ar*H*, 2 position, *J* = 2.0 Hz), 7.55 (dd, 2H, Ar*H*, 6 position, *J* = 8.4 Hz, *J* = 2.0 Hz). ^{13}C NMR ($CDCl_3$): δ_{ppm} = 14.1 (*C*H$_3$), 17.6 (G1-*C*H$_3$), 18.4 (G2-*C*H$_3$), 22.0 (acetonide-*C*H$_3$), 22.7 (CH$_3$*C*H$_2$), 25.1 (acetonide-*C*H$_3$), 26.0 (*C*H$_2$CH$_2$CH$_2$OAr), 29.1 and 29.2 (*C*H$_2$CH$_2$OAr), 29.3–29.7 (CH$_3$CH$_2$CH$_2$(*C*H$_2$)$_6$), 31.9 (CH$_3$*C*H$_2$CH$_2$), 42.0 (G2-*C*), 43.1 (*C*-PE), 47.1 (G1-*C*), 62.2 (*C*H$_2$-PE), 63.0 (*C*H$_2$-PE), 64.9 (G1-*C*H$_2$), 65.9 (G2-*C*H$_2$), 69.0 and 69.3 (*C*H$_2$OAr), 98.1 (*C*-acetonide), 112.0 (Ar*C*, 5 position), 114.4 (Ar*C*, 2 position), 121.5 (Ar*C*, 1 position), 123.6 (Ar*C*, 6 position), 148.8 (Ar*C*, 3 position), 153.7 (Ar*C*, 4 position), 165.6 (*C*O), 172.0 (G1-*C*O) 173.4 (G2-*C*O). ESI TOF MS: *m*/*z* calcd. for $C_{109}H_{180}O_{28}$ 1961.26 [M+Na]$^+$, found 1961.25 [M+Na]$^+$. Elem. Anal: Calcd. for $C_{109}H_{180}O_{28}\cdot 2H_2O$: C 66.30%, H 9.39%. Found: C 66.25%, H 9.29%.

2.2.6. 3,5-Bis-dodecyloxybenzoic ester-PE-[G2]-acetonide (**8**)

The procedure is the same as the synthesis of **7**. Compound **5** (0.85 g, 0.65 mmol), anhydride of bis-MPA (1.11 g, 3.36 mmol), and DMAP (0.05 g, 0.39 mmol) were used. The product was purified by column chromatography (SiO_2) eluting with hexane/ethyl acetate (7:4) to give 1.01 g (81%) of glassy solid. ^{1}H NMR ($CDCl_3$): δ_{ppm} = 0.88 (t, 12H, C*H*$_3$, *J* = 6.9 Hz), 1.09 (s, 12H, G2-C*H*$_3$), 1.26 (overlapped peaks, 64H, CH$_3$(C*H*$_2$)$_8$), 1.28 (s, 6H, G1-C*H*$_3$), 1.32 (s, 12H, acetonide-C*H*$_3$), 1.36 (s, 12H, acetonide-C*H*$_3$), 1.40–1.47 (m, 8H, C*H*$_2$CH$_2$CH$_2$OAr), 1.74–1.79 (m, 8H, C*H*$_2$CH$_2$OAr), 3.56 (dd, 8H, G2-C*H*$_2$, *J* = 11.9 Hz, *J* = 2.4 Hz), 3.93 (t, 8H, C*H*$_2$OAr, *J* = 6.5 Hz), 4.10 (d, 8H, G2-C*H*$_2$, *J* = 11.9 Hz), 4.33 (ABq, 8H, G1-C*H*$_2$, *J* = 11.2 Hz), 4.34 (s, 4H, C*H*$_2$), 4.46 (s, 4H, C*H*$_2$), 6.62 (t, 2H, Ar*H*, 4 position, *J* = 2.3 Hz), 7.07 (d, 4H, Ar*H*, 2,6 positions, *J* = 2.3 Hz). ^{13}C NMR ($CDCl_3$): δ_{ppm} = 14.1 (*C*H$_3$), 17.7 (G1-*C*H$_3$), 18.4 (G2-*C*H$_3$), 22.0 (acetonide-*C*H$_3$), 22.7 (CH$_3$*C*H$_2$), 25.2 (acetonide-*C*H$_3$), 26.0 (*C*H$_2$CH$_2$CH$_2$OAr), 29.2–29.7 (*C*H$_2$CH$_2$OAr and CH$_3$CH$_2$CH$_2$(*C*H$_2$)$_6$), 31.9 (CH$_3$CH$_2$*C*H$_2$), 42.0 (G2-*C*), 43.1 (*C*-PE), 47.1 (G1-*C*), 62.4 (*C*H$_2$-PE), 62.8 (*C*H$_2$-PE), 64.9 (G1-*C*H$_2$), 65.9 (G2-*C*H$_2$), 68.4 (*C*H$_2$OAr), 98.1 (*C*-acetonide), 106.6 (Ar*C*, 4 position), 107.8 (Ar*C*, 2,6 positions), 131.0 (Ar*C*, 1 position), 160.3 (Ar*C*, 3,5 positions), 165.6 (*C*O), 172.0 (G1-*C*O), 173.4 (G2-*C*O). ESI TOF MS: *m*/*z* calcd. for $C_{109}H_{180}O_{28}$ 1961.26 [M+Na]$^+$, found 1961.33 [M+Na]$^+$. Elem. Anal: Calcd. for $C_{109}H_{180}O_{28}\cdot 2H_2O$: C 66.30%, H 9.39%. Found: C 66.41%, H 9.33%.

2.2.7. 3,4,5-Tris-dodecyloxybenzoic ester-PE-[G2]-acetonide (**9**)

The procedure is the same as the synthesis of **7**. Compound **6** (1.39 g, 0.83 mmol), anhydride of bis-MPA (1.42 g, 4.30 mmol), and DMAP (0.06 g, 0.50 mmol) were used. The product was purified by column chromatography (SiO_2) eluting with hexane/ethyl acetate (7:4) to give 1.44 g (75%) of glassy solid. ^{1}H NMR ($CDCl_3$): δ_{ppm} = 0.88 (t, 18H, C*H*$_3$, *J* = 6.9 Hz), 1.08 (s, 12H, G2-C*H*$_3$), 1.26 (overlapped peaks, 96H, CH$_3$(C*H*$_2$)$_8$), 1.28 (s, 6H, G1-C*H*$_3$), 1.31 (s, 12H, acetonide-C*H*$_3$), 1.36 (s, 12H, acetonide-C*H*$_3$), 1.44–1.50 (m, 12H, C*H*$_2$CH$_2$CH$_2$OAr), 1.71–1.76 (4H, C*H*$_2$CH$_2$OAr, 4 position), 1.77–1.83 (8H, C*H*$_2$CH$_2$OAr, 3,5 positions), 3.55 (dd, 8H, G2-C*H*$_2$, *J* = 11.8 Hz, *J* = 2.1 Hz), 3.97 (t, 8H, C*H*$_2$OAr, 3,5 positions, *J* = 6.4 Hz), 4.00 (t, 4H, C*H*$_2$OAr, 4 position, *J* = 6.6 Hz), 4.10 (d, 8H, G2-C*H*$_2$, *J* = 11.8 Hz), 4.33 (s, 4H, C*H*$_2$), 4.34 (ABq, 8H, G1-C*H*$_2$, *J* = 11.1 Hz), 4.44 (s, 4H, C*H*$_2$), 7.19 (s, 4H, Ar*H*, 2,6 positions). ^{13}C NMR ($CDCl_3$): δ_{ppm} = 14.1 (*C*H$_3$), 17.7 (G1-*C*H$_3$), 18.4 (G2-*C*H$_3$), 21.9 (acetonide-*C*H$_3$), 22.7 (CH$_3$*C*H$_2$), 25.3 (acetonide-*C*H$_3$), 26.1 (*C*H$_2$CH$_2$CH$_2$OAr, 4 position), 26.2 (*C*H$_2$CH$_2$CH$_2$OAr, 3,5 positions), 29.4–29.8 (*C*H$_2$CH$_2$OAr, 3,5 positions and CH$_3$CH$_2$CH$_2$(*C*H$_2$)$_6$), 30.4 (*C*H$_2$CH$_2$OAr, 4 position), 31.9 (CH$_3$CH$_2$*C*H$_2$, 3,5 positions + CH$_3$CH$_2$*C*H$_2$, 4 position), 42.0 (G2-*C*), 43.3 (*C*-PE), 47.1 (G1-*C*), 62.1 (*C*H$_2$-PE), 62.7 (*C*H$_2$-PE), 64.8 (G1-*C*H$_2$), 65.9 (G2-*C*H$_2$), 66.0 (G2-*C*H$_2$), 69.2 (*C*H$_2$OAr, 3,5 positions), 73.5 (*C*H$_2$OAr, 4 position), 98.1 (*C*-acetonide), 108.2 (Ar*C*, 2,6 positions), 123.8 (Ar*C*, 1 position), 143.0 (Ar*C*, 4 position), 153.0 (Ar*C*, 3,5 positions), 165.5 (*C*O), 171.9 (G1-*C*O), 173.44 (G2-*C*O). ESI TOF MS: *m*/*z* calcd. for $C_{133}H_{228}O_{30}$ 2329.62 [M+Na]$^+$, found 2329.70 [M+Na]$^+$. Elem. Anal: Calcd. for $C_{133}H_{228}O_{30}\cdot H_2O$: C 68.70%, H 9.97%. Found: C 68.43%, H 10.09%.

2.2.8. 3,4-Bis-dodecyloxybenzoic ester-PE-[G2]-(OH)$_8$ (**10**)

The procedure is the same as the synthesis of **5**. Compound **7** (0.84 g, 0.43 mmol) and 2 teaspoons of Dowex 50W-X8 resin was used. The product was purified by column chromatography (SiO_2) eluting with ethyl acetate to give 328 mg (43%) of white solid. ^{1}H NMR ($CDCl_3$): δ_{ppm} = 0.87 (t, 12H, C*H*$_3$, *J* = 6.9 Hz), 1.04 (s, 12H, G2-C*H*$_3$), 1.26 (overlapped peaks, 64H, CH$_3$(C*H*$_2$)$_8$), 1.29 (s, 6H, G1-C*H*$_3$), 1.44–1.49 (m, 8H, C*H*$_2$CH$_2$CH$_2$OAr), 1.78–1.86 (m, 8H, C*H*$_2$CH$_2$OAr), 3.09 (br s, 8H, O*H*), 3.67 (dd, 8H, G2-C*H*$_2$, *J* = 11.3 Hz, *J* = 4.8 Hz), 3.78 (dd, 8H, G2-C*H*$_2$, *J* = 11.2 Hz, *J* = 3.2 Hz), 4.00 (t, 4H, C*H*$_2$OAr, *J* = 6.6 Hz), 4.03 (t, 4H, C*H*$_2$OAr, *J* = 6.6 Hz), 4.32(s, 4H, C*H*$_2$), 4.34 (ABq, 8H, G1-C*H*$_2$, *J* = 11.1 Hz), 4.47 (s, 4H, C*H*$_2$), 6.83 (d, 2H, Ar*H*, 5 position, *J* = 8.5 Hz), 7.48 (d, 2H, Ar*H*, 2 position, *J* = 2.0 Hz), 7.56 (dd, 2H, Ar*H*, 6 position, *J* = 8.4 Hz, *J* = 2.0 Hz). ^{13}C NMR ($CDCl_3$): δ_{ppm} = 14.1 (*C*H$_3$), 17.1 (G2-*C*H$_3$), 18.0 (G1-*C*H$_3$), 22.7 (CH$_3$*C*H$_2$), 26.0 (*C*H$_2$CH$_2$CH$_2$OAr), 29.1 and 29.2 (*C*H$_2$CH$_2$OAr), 29.3–29.7 (CH$_3$CH$_2$CH$_2$(*C*H$_2$)$_6$), 31.9 (CH$_3$*C*H$_2$CH$_2$), 42.9 (*C*-PE), 46.8 (G1-*C*), 49.8 (G2-*C*), 62.6 (*C*H$_2$-PE), 63.7 (*C*H$_2$-PE), 64.9 (G1-*C*H$_2$), 67.2 and 67.4 (G2-*C*H$_2$), 69.1 and 69.4 (*C*H$_2$OAr), 112.0 (Ar*C*, 5 position), 114.4 (Ar*C*, 2 position), 121.2 (Ar*C*, 1 position), 123.7 (Ar*C*, 6 position), 148.8 (Ar*C*, 3 position), 153.9 (Ar*C*, 4 position), 166.0 (*C*O), 172.6 (G1-*C*O), 175.0 (G2-*C*O). ESI TOF MS: *m*/*z* calcd. for $C_{97}H_{164}O_{28}$ 1801.13 [M+Na]$^+$, found 1801.27 [M+Na]$^+$. Elem. Anal: Calcd. for $C_{97}H_{164}O_{28}\cdot 3H_2O$: C 63.58%, H 9.35%. Found: C 63.85%, H 9.26%.

2.2.9. 3,5-Bis-dodecyloxybenzoic ester-PE-[G2]-(OH)$_8$ (**11**)

The procedure is the same as the synthesis of **5**. Compound **8** (0.90 g, 0.46 mmol), and 2 teaspoons of Dowex 50W-X8 resin was used. The product was further purified by column chromatography (SiO_2) eluting with ethyl acetate to 371 mg (45%) of white solid. ^{1}H NMR ($CDCl_3$): δ_{ppm} = 0.88 (t, 12H, C*H*$_3$, *J* = 6.9 Hz), 1.04 (s, 12H, G2-C*H*$_3$), 1.26 (overlapped peaks, 64H, CH$_3$(C*H*$_2$)$_8$), 1.30 (s, 6H, G1-C*H*$_3$), 1.41–1.47 (m, 8H, C*H*$_2$CH$_2$CH$_2$OAr), 1.74–1.80 (m, 8H, C*H*$_2$CH$_2$OAr), 3.04 (s br, 8H, O*H*), 3.68 (dd, 8H, G2-C*H*$_2$, *J* = 11.2 Hz, *J* = 4.4 Hz), 3.79 (dd, 8H, G2-C*H*$_2$, *J* = 11.1 Hz, *J* = 3.4 Hz), 3.94 (t, 8H, C*H*$_2$OAr, *J* = 6.6 Hz), 4.35 (ABq, 8H, G1-C*H*$_2$, *J* = 11.1 Hz), 4.37 (s, 4H, C*H*$_2$), 6.63 (t, 2H, Ar*H*, 4 position, *J* = 2.3 Hz), 7.08 (d, 4H, Ar*H*, 2,6 positions, *J* = 2.3 Hz). ^{13}C NMR ($CDCl_3$): δ_{ppm} = 14.1 (*C*H$_3$), 17.1 (G2-*C*H$_3$), 18.0 (G1-*C*H$_3$), 22.7 (CH$_3$*C*H$_2$), 26.0 (*C*H$_2$CH$_2$CH$_2$OAr), 29.2–29.7 (*C*H$_2$CH$_2$OAr and CH$_3$CH$_2$CH$_2$(*C*H$_2$)$_6$), 31.9 (CH$_3$CH$_2$*C*H$_2$), 42.9 (*C*-PE), 46.9 (G1-*C*), 49.8 (G2-*C*), 62.8 (*C*H$_2$-PE), 63.5 (*C*H$_2$-PE), 64.9 (G1-*C*H$_2$), 67.5 and 67.7 (G2-*C*H$_2$), 68.4 (*C*H$_2$OAr), 106.7 (Ar*C*, 4 position), 107.8 (Ar*C*, 2,6 positions), 130.8 (Ar*C*, 1 position), 160.3 (Ar*C*, 3,5 positions), 166.0 (*C*O), 172.5 (G1-*C*O), 175.1 (G2-*C*O). ESI TOF MS: *m*/*z* calcd. for $C_{97}H_{164}O_{28}$ 1801.13 [M+Na]$^+$, found 1801.27 [M+Na]$^+$. Elem. Anal: Calcd. for $C_{97}H_{164}O_{28}\cdot 2H_2O$: C 64.21%, H 9.33%. Found: C 64.41%, H 9.32%.

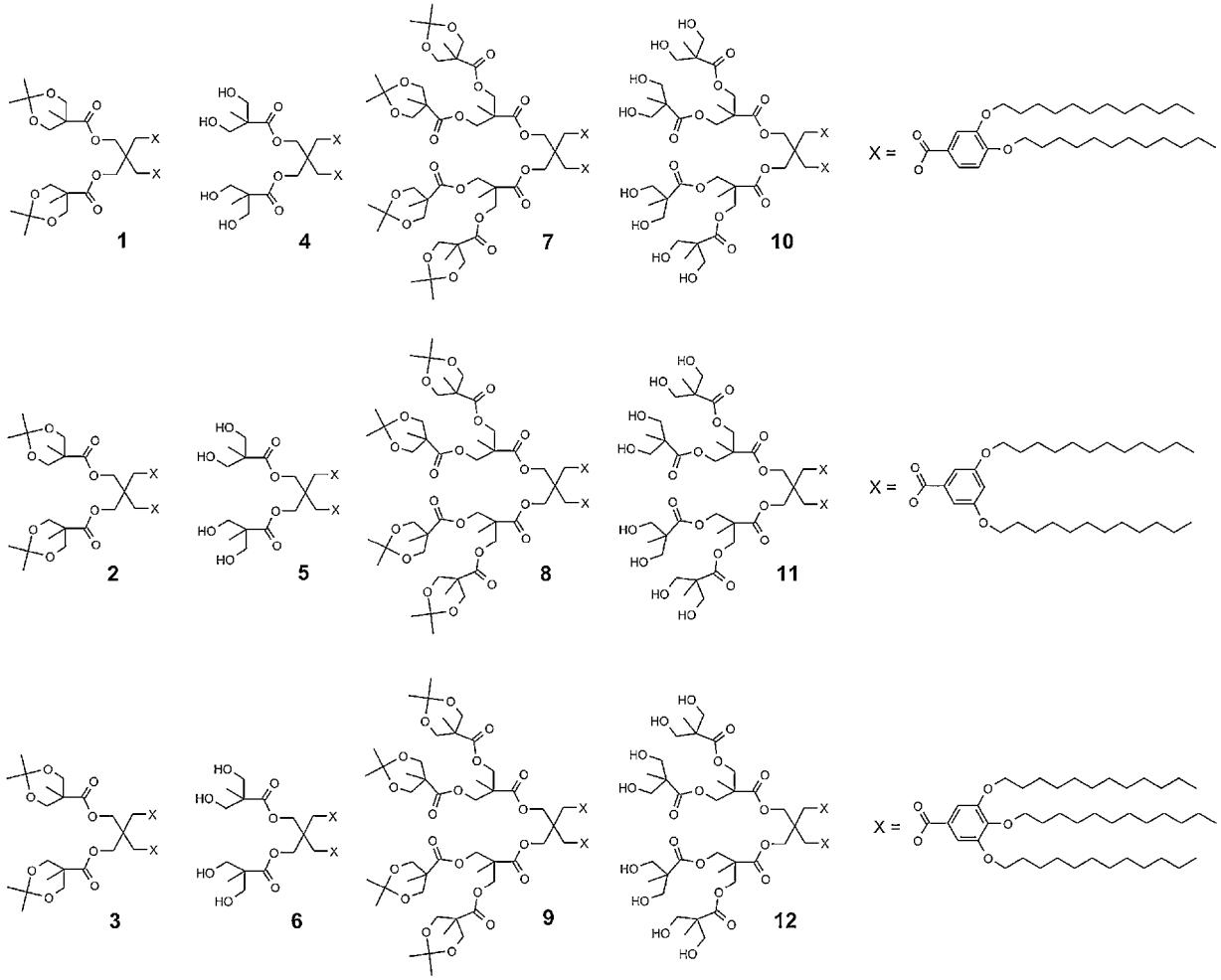
*2.2.10. 3,4,5-Tris-dodecyloxybenzoic ester-PE-[G2]-(OH)$_8$ (**12**)*

The procedure is the same as the synthesis of **5**. Compound **9** (1.30 g, 0.456 mmol) and 2 teaspoons of Dowex 50W-X8 resin were used. The product was purified by column chromatography (SiO_2) eluting with ethyl acetate to give 822 mg (68%) of white solid. ^{1}H NMR ($CDCl_3$): δ_{ppm} = 0.88 (t, 18H, C*H*$_3$, *J* = 6.9 Hz), 1.03 (s, 12H, G2-C*H*$_3$), 1.26 (overlapped peaks, 96H, CH$_3$(C*H*$_2$)$_8$), 1.31 (s, 6H, G1-C*H*$_3$), 1.44–1.49 (m, 12H, C*H*$_2$CH$_2$CH$_2$OAr), 1.70–1.76 (4H, CH$_2$C*H*$_2$OAr, 4 position), 1.76–1.82 (8H, C*H*$_2$CH$_2$OAr, 3,5 positions), 3.11 (br s, 8H, O*H*), 3.67 (dd, 8H, G2-C*H*$_2$, *J* = 11.3 Hz, *J* = 5.5 Hz), 3.78 (dd, 8H, G2-C*H*$_2$, *J* = 11.2 Hz, *J* = 3.4 Hz), 3.97 (t, 8H, C*H*$_2$OAr, 3,5 positions, *J* = 6.4 Hz), 4.00 (t, 4H, C*H*$_2$OAr, 4 position, *J* = 6.6 Hz), 4.35 (ABq, 8H, G1-C*H*$_2$, *J* = 11.1 Hz), 4.36 (s, 4H, C*H*$_2$), 4.47 (s, 4H, C*H*$_2$), 7.19 (s, 4H, Ar*H*, 2,6 positions). ^{13}C NMR ($CDCl_3$): δ_{ppm} = 14.1 (*C*H$_3$), 17.1 (G2-*C*H$_3$), 18.0 (G1-*C*H$_3$), 22.7 (CH$_3$*C*H$_2$), 26.1 (*C*H$_2$CH$_2$CH$_2$OAr, 4 position), 26.1 (*C*H$_2$CH$_2$CH$_2$OAr, 3,5 positions), 29.4–29.7 (*C*H$_2$CH$_2$OAr, 3,5 positions and CH$_3$CH$_2$CH$_2$(*C*H$_2$)$_6$), 30.4 (*C*H$_2$CH$_2$OAr, 4 position), 31.9 (CH$_3$CH$_2$*C*H$_2$), 43.0 (*C*-PE), 46.9 (G1-*C*), 49.8 (G2-*C*), 62.6 (*C*H$_2$-PE), 63.5 (*C*H$_2$-PE), 64.8 (G1-*C*H$_2$), 67.4 and 67.5 (G2-*C*H$_2$), 69.3 (*C*H$_2$OAr, 3,5 positions), 73.6 (*C*H$_2$OAr, 4 position), 108.2 (Ar*C*, 2,6 positions), 123.5 (Ar*C*, 1 position), 143.2 (Ar*C*, 4 position), 153.0 (Ar*C*, 3,5 positions), 165.9 (*C*O), 172.5 (G1-*C*O), 175.0 (G2-*C*O). ESI TOF MS: *m*/*z* calcd. for $C_{121}H_{212}O_{30}$ 2169.50[M+Na]$^+$, found 2169.68 [M+Na]$^+$. Elem. Anal: Calcd. for $C_{121}H_{212}O_{30}\cdot 2H_2O$: C 66.57%, H 9.97%. Found: C 66.71%, H 10.15%.

3. Results and discussion

3.1. Synthesis

The synthesized compounds are presented in Scheme 1. The procedure for the synthesis of the compounds **1**–**12** was published originally by Ropponen et al. [41], however, we did some modifications to the synthetic procedure: branching was obtained by anhydride coupling of bisMPA instead of DCC/DPTS coupling, and the deprotection of the acetonide terminal groups were removed by Dowex resin instead of THF–HCl mixture. The synthesis of the dendrimers started from pentaerythritol to construct a partly protected dendritic core molecule, (OH)$_2$-PE-[G1]-acetonide [26]. 3,4-Bis-dodecyloxybenzoic acid, 3,5-bis-dodecyloxybenzoic acid, and 3,4,5-tris-dodecyloxybenzoic acid, were attached to the dendritic core utilizing DCC/DPTS coupling to obtain the protected first generation dendrimers **1**–**3** [41]. The removal of the acetonide groups was performed by Dowex 50W-X8 resin in 1:1 CH_2Cl_2–MeOH solution. The first approach to remove the protection groups of compound **4** at room temperature failed probably due to too mild conditions, and therefore the deprotection was eventually done by THF–HCl (6 M) [41]. However, in the case of other acetonide protected G1 dendrimers (**5** and **6**), the reaction temperature was increased to 50 °C, which was enough to remove protecting groups with Dowex resin in CH_2Cl_2–MeOH solution in 90 and 97% yields, respectively. The acetonide terminated second generation dendrimers **7**–**9** were prepared in 74–81% yields, by



Scheme 1. The synthesized dendrimers **1**–**12**.

adding another layer of bisMPA through the divergent synthetic method. Instead of using DCC/DPTS in the addition of bisMPA layer, we preferred anhydride coupling, in order to avoid problematic purification of DCC-urea by-product. Dowex resin was again utilized to the deprotection of the acetonide groups to obtain hydroxyl terminated G2 dendrimers **10**–**12**. The final purification of the dendrimers **10**–**12** was accomplished by column chromatography eluting with ethyl acetate, after which compounds were obtained in 43–68% yields.

3.2. Thermogravimetric studies

Thermogravimetric analysis (TGA) was utilized to evaluate the thermal stability of the compounds in terms of onset decomposition temperatures (T_d). The curves of the TGA measurements are shown in Fig. 1, and T_d-values are collected in Table 1. Due to a rather slow decomposition rate of the dendrimers the onset decomposition temperatures were obtained by the step-tangent method, in which a tangent was set at point were 5% mass loss was observed, taken into account of possible mass loss caused by removal of solvent or water. This method was chosen in order to not overestimate the thermal stability of the dendrimers. All the compounds were thermally stable up to around 250 °C, at which temperature decomposition started, and compounds were completely decomposed at 600 °C. According to TGA measurement, the nature of the terminal groups or size of the polyester segments or the position of the alkyl chains on the opposite aromatic moieties of the dendrimers had little effect on the T_d-values.

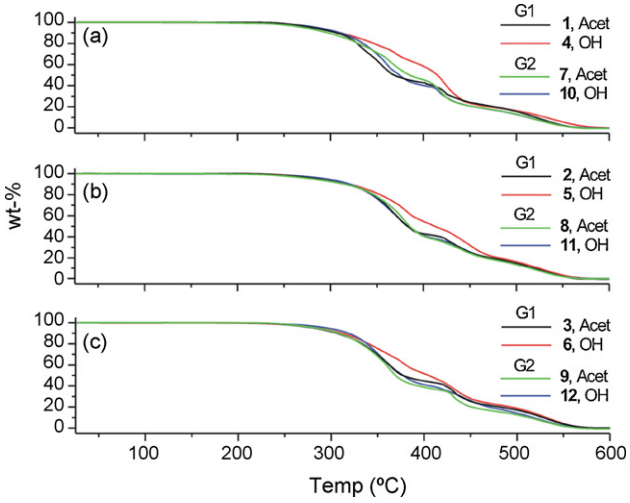


Fig. 1. The TGA curves of the acetonide (Acet) and hydroxyl (OH) terminated dendrimers **1**–**12**: (a) 3,4-, (b) 3,5-, and (c) 3,4,5-type dendrimers.

3.3. Differential scanning calorimetric studies

Thermal transitions of the dendrimers **1**–**12** were studied by the differential scanning calorimetry (DSC). The curves from the measurements are shown in Figs. 2–4, and phase transition temperatures and associated enthalpy changes (ΔH) from the heating–cooling–heating cycles are collected in Table 1. The OH

Table 1
Thermal properties of compounds **1**–**12**.

Compound	Mw (g mol^{-1})	Thermal transitions (°C) and their corresponding enthalpy and/or heat capacity changes (kJ mol^{-1}) [kJ mol^{-1} °C^{-1}][a]		DSC scan range (°C)	TGA T_d (°C)[b]
		Heating scans	Cooling scans		
1	1394.03	1st: k 60.5 (100.01) i 2nd: k {10.0 (9.11), 22.5 (42.64)} i	1st: i 11.6 (−48.82) k	−40 to 120	250
2	1394.03	1st: k {1.7 (1.15), 16.7 (1.60), 30.1 (66.24)} i 2nd: g −37.0 [0.38], k {−8.3 (−16.76), 18.8 (21.36)} i	1st: –	−40 to 160	249
3	1762.68	1st: k 34.4 (124.12) i 2nd: k 9.9 (64.57) i	1st: i 2.9 (−60.63) k	−50 to 160	250
4	1313.90	1st: k 48.3 (74.96) LC 95.9 (2.35) i 2nd: k 38.2 (25.31) LC 97.0 (2.27) i	1st: i 96.3 (−2.34) LC 33.8 (−32.22) k	−40 to 160	250
5	1313.90	1st: k {56.2 (43.39), 86.3 (56.12)} i 2nd: g −13.2 [0.47], 15.2 (−15.79), k 85.4 (51.33) i	1st: i {33.1 (−3.85), 31.1 (−5.39)} k	−40 to 150	252
6	1682.55	1st: k 60.6 (56.58)} LC 86.0 (0.89) i 2nd k 16.2 (23.99) LC 86.3 (0.74) i	1st: i 82.7 (−0.44) LC 13.5 (−22.26) k	−40 to 105	251
7	1938.63	1st: k 39.6 (86.36) i 2nd: k {−15.6 (10.37), 0.29 (−3.33), 6.7 (16.33)}[c] i	1st: –	−40 to 140	252
8	1938.63	1st: k 28.5 (56.73) i 2nd: g −26.3 [0.38] i	1st: –	−40 to 140	232
9	2307.28	1st: k {−20.3 (12.12), 32.2 (3.12), 56.5 (99.64)} i 2nd: k 5.2 (47.11) i	1st: i −4.6 (−43.32) k	−40 to 140	240
10	1778.37	1st: k 112.2 (48.99) LC 133.9 (2.55) i 2nd: g 35.1 [0.97], 56.4 (−39.74) k 111.6 (50.03) LC 133.7 (2.68) i	1st: i 132.2 (−2.57) LC	−40 to 160	268
11	1778.37	1st: k {54.4 (110.41)[d], 85.1 (33.15)} i 2nd: g 5.4 [0.49] k 67.4 (4.70) LC 79.8 (0.94) i	1st: i 79.0 (−1.27) LC	−40 to 160	266
12	2147.02	1st: k 95.3 (62.55) LC 138.0 (2.12) i 2nd: g 17.8 [0.56] k 94.5 (42.81) LC 137.7 (1.96) i	1st: i 136.8 (−1.82) LC	−40 to 160	259

Abbreviations: k, crystalline, I, isotropic liquid, g, glass, LC, liquid crystal phase.
[a] The glass transition temperatures are taken as half ΔCp extrapolated.
[b] Decomposition temperatures determined from onset at 5 wt% mass loss.
[c] Overlapping transitions in order of endo–exo–endo.
[d] Two overlapping endothermic transitions.

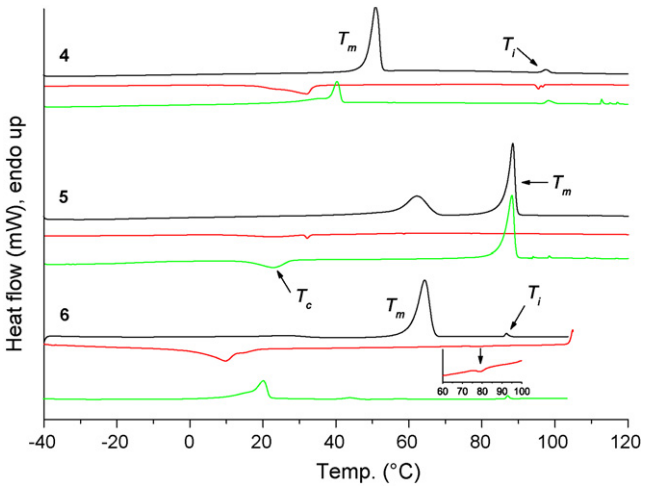


Fig. 2. The DSC curves of the hydroxyl terminated G1 dendrimers. Black: the first heating, red: the first cooling, and green: the second heating. For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.

terminated G1 dendrimers **4** and **6** having alkyl chains in positions 3,4 and 3,4,5, respectively, formed enantiotropic liquid crystalline phases, whereas 3,5-substituted dendrimer **5** exhibit the absence of a mesomorphic phase transition (Fig. 2.). The initial heating scan of compound **4** showed melting transition to LC-phase at 48.3 °C followed by transition to isotropic liquid (T_i = 95.9 °C). Upon cooling, reversible transition from isotropic liquid to LC-phase and crystallization were observed (confirmed by POM studies). In the subsequent heating scan, transition to LC-phase was observed at 38.2 °C, indicating that the compound crystallized to a different polymorph from a melt. A clearing point in the second heating scan was consistent with the T_i of the first heating scan. Upon the first heating, compound **6** displayed transition from crystal phase to LC-phase at 60.6 °C and subsequent clearing point at 86.0 °C. A cooling scan revealed that a peak corresponding to the transition to LC-phase was broadened and shifted to a slightly lower temperature (82.7 °C), indicating that the transition from isotropic liquid to LC-phase was sluggish compared to the transition during the heating scan. Upon second heating, transition to LC-phase occurred at 16.2 °C followed by clearing point at 86.3 °C. Transition to LC-phase at a significantly lower transition temperature is due to the formation of a different polymorph from a melt. In first heating scan of compound **5**, two distinct endothermic peaks at 56.2 and 86.3 °C were shown. Upon cooling small but sharp exothermic peak at 33.1 °C was observed, which was immediately followed by broad peak corresponding to crystallization. The second heating scan showed glass transition followed by broad exothermic peak corresponding to cold crystallization, and melting transition to isotropic liquid. In order to find out whether the small exotherm at 33.1 °C upon cooling represents mesomorphic transition, additional DSC measurements with different temperature profiles were accomplished (see Supplementary information, Figs. S1 and S2). The supplementary DSC measurements revealed that small exotherm exist actually between two crystalline transitions and was observed only at a cooling rate 10 °C/min. On a basis of additional DSC observations, we assume that this exotherm stems from a crystallization event rather than mesomorphic transition. The thermal behavior of this 3,5-type dendrimer corresponds with the study of Bury et al. stating that 3,5-substitution pattern disfavors the induction of mesomorphism [21].

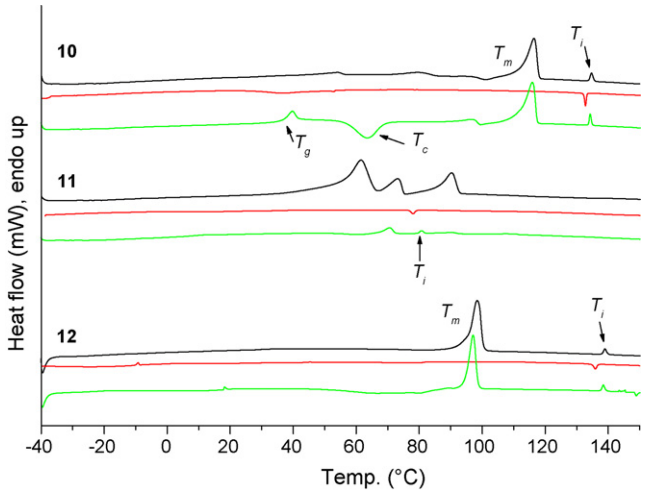


Fig. 3. The DSC curves of the hydroxyl terminated G2 dendrimers. Black: the first heating, red: the first cooling, and green: the second heating. For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.

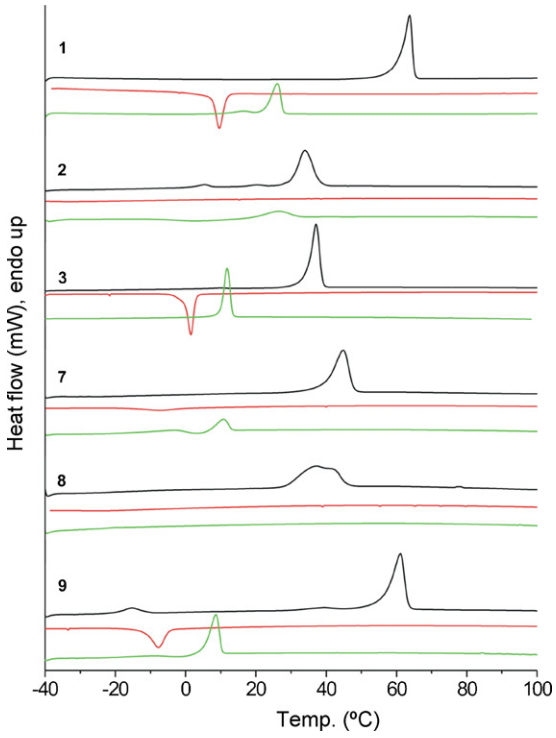


Fig. 4. The DSC curves of the acetonide functionalized G1 dendrimers (**1**–**3**) and G2 dendrimers (**7**–**9**). Black: the first heating, red: the first cooling, and green: the second heating. For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.

All the hydroxyl terminated G2 dendrimers exhibited liquid crystalline phase in DSC measurements. The curves from the measurements are shown in Fig. 3. The initial heating of compound **10** showed transition to LC-phase at 97.4 °C and clearing point at 133.9 °C. In addition, two minor melting transitions at 44.6 and 71.8 °C, and subsequent crystallization just before mesomorphic transition were also observed, corresponding to the existence of different polymorphs. Reversible transition from isotropic liquid to LC-phase is shown in the cooling scan at 133.4 °C. In the subsequent heating scan, glass transition (T_g) is followed by cold crystallization at 56.4 °C. Minor melting transition and immediate crystallization was observed prior to transition to LC-phase at a temperature relative to that of the first heating scan. The clearing point was observed at 133.7 °C corresponding well with previous heating and cooling

scans. During the first heating scan of the compound **11** a cluster of endothermic peaks corresponding to melting transitions of three different polymorphs were observed. However, the cooling scan displays only exothermic peak at 79.0 °C, assumed to represent a transition from isotropic liquid to LC-phase. Following heating scan shows mesomorphic transition of the polymorph II at 67.4 °C, and clearing point at 79.8 °C analogous to peak found in the cooling scan. The phase transitions of the compound **11** were further studied with different temperature profiles to verify the thermal behavior (see Supplementary information, Fig. S3) When the turning point of the measurement was above the melting of polymorph I, the melting of polymorph II was also commenced, as upon the subsequent heating only melting of polymorph III at around 85 °C was observed. Once the polymorph III had melted, subsequent cooling and heating scans displayed the reversible mesomorphic transition. It was observed that the vitreous state, obtained from 10 °C/min cooling rate, tend to crystallize into the metastable polymorph (II) which was associated with the formation of the mesophase. Compound **12** exhibit simple thermal behavior showing transition to LC-phase at 95 °C and subsequent clearing point at around 138 °C both in the first and the second heating scans, as well as transition from isotropic liquid to LC-phase during the cooling scan.

All the OH terminated G2 dendrimers exhibit glass transition, but the glass transition of the corresponding G1 dendrimers was observed only for the compound **5** in the temperature range of the measurements. This behavior is in agreement with our previous studies stating that increasing branching increases the glass transition temperature [40]. The mesomorphic transition temperatures as well as isotropization temperatures of the OH terminated dendrimers were also found to increase with increasing polyester generation, as the stability of the dendrimers improved. In the case of G2 dendrimer with 3,5-dialkyl substitution the isotropization temperature was significantly lower than those of 3,4- and 3,4,5-substituted analogues, which is not surprising as it has been reported, that 3,5-substitution pattern in dendritic compounds have decreasing effect on their isotropization temperatures [45].

The phase transitions of the acetonide terminated dendrimers were also studied. DSC curves of the acetonide terminated G1 and G2 dendrimers shown in Fig. 4, exhibit only melting transitions, and added to that, glass transitions in the case of 3,5-type dendrimers. The melting transitions of the acetonide terminated dendrimers were at higher temperatures in the first heating scan compared to the second heating scan, which is due to the formation of metastable phases via crystallization or cold crystallization. In the case of compound **8** only glass transition was observed in the second heating scan. On the basis of DSC curves, 3,5-type compounds had lowest crystallinity with broad melting transitions in heating scan and absence of crystallization in cooling scan. This is probably due to more flexible character of the 3,5-substituted alkyl chain packing compared to 3,4- and 3,4,5-substituted analogues.

4. Conclusions

The thermal transitions of the Janus dendrimers were examined by the differential scanning calorimetric measurements. The hydroxyl terminated dendrimers having alkyl chains at positions 3,4 and 3,4,5 of the aromatic moieties displayed enantiotropic liquid crystal phases. In the case of the G2 dendrimer **11** with 3,5-substitution pattern, the mesomorphic transition occurred below the melting of the polymorph with the highest melting point—the mesophase was observed in the cooling scan, and thereafter crystallized into a metastable polymorph which was associated with the reversible formation of mesophase at a constant heating/cooling rate of 10 °C/min. The corresponding 3,5-substituted G1 dendrimer **5**, was the only OH terminated dendrimer that displayed the absence of mesomorphic phases. The acetonide terminated dendrimers exhibited only melting transitions. Thermal stability of the dendrimers in terms of onset decomposition was evaluated by thermogravimetry. All the studied dendrimers exhibited similar thermal stability – decomposition of the dendrimers started at around 250 °C and compounds were completely decomposed by 600 °C – regardless of the number and the position of alkyl chains, or the branching and terminal functionality of the dendritic polyester moieties.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tca.2009.08.019.

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