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Synthesis and Evaluation of Thermal Properties of Fluorinated Poly(aryl ether) Dendritic Structures Based on Calix[4]arenes

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By using a convergence approach two new poly(aryl ether) dendritic structures carrying 4-fluorobenzyl bromide on the surface and calix[4]arenes as a core with G1 were synthesized for the first time. Fluorinated dendritic structures are connected through ether bonds on the lower rim of the calix[4]arene unit. Its structure was determined by ^{1}H-NMR and elemental analysis. The thermal stabilities of fluorinated dendritic structures, based on calix[4]arenes, were investigated using thermogravimetric analysis. The activation energies and thermal degradation of the structures were calculated with the Ozawa Method.

Keywords: Dendrimer, dendron, calix[4]arene, fluorinated polymers, fluorinated dendrimers, thermal stability

1 Introduction

Organofluorine compounds are attractive materials due to exhibiting a variety of unique characteristics such as excellent chemical and thermal stability, low surface energy, and low refractive index and dielectric constant, which cannot be achieved in corresponding nonfluorinated ones (1–6). Dendrimers, as a new class of macromolecules, have attracted a great deal of attention in polymer chemistry in the two past decades (7–13). From the developmental viewpoints of new fluorinated functional materials, the preparation of dendritic polymers, having fluorine in some parts of their structure, is of particular interest, and the synthesis and applications of a variety of dendrimers and dendrons possessing fluorine atoms in some parts of their structure have been already studied in detail (14–22). The preparation of such branched structures demands the use of particular building blocks with the appropriate stereochemistry and multiple equivalent reaction centers. Calixarenes (23–27), with their multiple sites for functionalization on a conformationally restricted, macrocyclic scaffold, and are obvious substrates for such modular syntheses. Their chemistry is well-established and has engendered extensive research not only because of their capacity for forming complexes with a variety of guests, both charged and neutral, but also because of their ease of functionalization, enabling their use in the construction of sophisticated derivatives such as calixcrowns (23), calixcryptands and calixspherands (28). Calixarenes are considered to provide entities of excellent promise for incorporation within dendritic structures to generate new materials (29). To integrate calixarenes and dendrimers is an original idea, as well as their unique properties to form new structural hosts, and there have been several examples about dendrimers with calixarene as a core (29–32). Semifluorinated and perfluorinated molecules have had a significant impact in the field of chemistry and their use has provided new strategies in organic, biomolecular and supramolecular synthesis (33).

Thermogravimetric analysis (TGA) has been widely used to investigate the decomposition characteristics of many materials. Some methods have already been established to evaluate the kinetic parameters from thermogravimetric data (34–41). Previously we reported the synthesize fluorinated poly(aryl ether) dendritic structures via convergent methods (42). In this paper, we present the synthesis of new fluorinated poly(aryl ether) dendritic structures based on calix[4]arenes. In addition, the TGA technique is applied to new poly(aryl ether) dendritic structures based on calix[4]arenes. The apparent activation energy was evaluated by isothermal thermogravimetric methods. The energies of activation at different steps were calculated by the Ozawa method (39).

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2 Experimental

All commercially available reagents were used without further purification. $K_2CO_3$was activated by heating at 150°C overnight under vacuum and stored in a desiccator. Column chromatography was carried out with Merck silica gel 70–230 mesh. The FTIR spectra were recorded via the KBr pellet method by using a Perkin-Elmer 1605 FTIR spectrophotometer. ^{1}H-NMR and ^{13}C-NMR spectra were recorded on a BRUKER DPX-400 High Performance Digital FT-NMR, with tetramethylsilane (TMS) as the standard. The compounds were characterized by an Elementar Vario CHNS EL III elemental analysis instrument. UV-Vis absorption spectra were measured using a Shimadzu UV-1700 Pharma spectrophotometer. The thermal stability of the polymers was determined by Shimadzu TG60H. p-*tert*-Butylcalix[4]arene (43),3,5-bis[(4-fluorobenzyl)oxy]benzyl alcohol (42) **1** and 3,5-bis[(4-fluorobenzyl)oxy]benzyl methane-sulfonate **2** (42) were readily obtained according to the literature procedures.

2.1 5,11,17,23-Tetra-*tert*-butyl-25,27-bis-(3,5-bis[(4-fluorobenzyl)oxy]benzyloxy)-26,28-dihydroxy-calix[4]arene 3

p-*tert*-Butylcalix[4]arene (1 eq., 0.20 g, 0.31 mmol), dry K_2CO_3 (2.11 eq., 0.09 g, 0.65 mmol), KI (1 eq., 0.05 g, 0.31 mmol) in CH_3CN (40 mL) was heated for 30 min. 3,5-Bis[(4-fluorobenzyl)oxy]benzyl methanesulfonate (2.11 eq., 0.28 g, 0.65 mmol) was then added and the reaction mixture refluxed for 6 days under N_2. After being cooled to room temperature, the reaction mixture was poured into water (100 mL) and extracted with CH_2Cl_2 (3 × 50 mL). The combined organic extracts were dried over $MgSO_4$. The solvent was evaporated in vacuum. The crude product was purified by column chromatography on silica gel (20:3, hexane/diethyl ether) followed by recrystallization to give 0.26 (%62) of compound **3** as a white solid. Mp: 177–178°C.

IR (KBr): 3430 (O—H), 2961, 2868 (C—H), 1605 (C=C), 1225 (C-F), 1205, 1064 (C—O—C) cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$)δ (ppm) = 0.97 (s, 18H, Bu^t), 1.34 (s, 18H, Bu^t), 3.32 (d, 4H, J = 13.15 Hz ArCH_2Ar), 4.31 (d, J = 13.06 Hz, 4H, ArCH_2Ar), 4.83 (s, 8H, FArCH_2O), 4.98 (s, 4H, ArCH_2O), 6.52 (t, 2H, J = 2.18 Hz, ArH), 6.82 (s, 4H, ArH), 6.96–7.01 (m, 12H, FArHCH$_2$), 7.11 (s, 4H, ArH), 7.24–7.29 (m, 8H, CH$_2$ArHCH$_2$), 7.32 (s, 2H, OH). Anal. Cald. for $C_{86}H_{88}O_8\,F_4$: C, 77.74; H, 6.90. Found: C, 77.15; H, 6.44.

2.2 5,11,17,23-Tetra-*tert*-butyl-25,27-bis-(4-fluoro benzyloxy)-26,28-dihydroxy-calix[4]arene 4

p-*tert*-Butylcalix[4]arene (1 eq., 1 g, 1.54 mmol), dry K_2CO_3 (2.11 eq., 0.45 g, 3.25 mmol) in CH_3CN (70 mL) was heated for 30 min. 4-Fluorobenzyl bromide (2.11 eq., 0.62 g, 3.25 mmol) was then added and the reaction mixture refluxed for additional 3 h under N_2. After being cooled to room temperature, the reaction mixture was poured into water (100 mL) and extracted with CH_2Cl_2 (3×50 mL). The combined organic extracts were dried over $MgSO_4$. The solvent was evaporated in vacuum. The crude product was dissolved in a small amount of $CHCl_3$ and the pure product was obtained after precipitation with hexane to give 1.05 g (79%) of compound **4** as a white powder. Mp: 177°C.

IR (KBr): 3420 (O—H), 2962, 2868 (C—H), 1602 (C=C), 1227 (C-F), 1208, 1096 (C—O—C) cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$)δ (ppm) = 0.98 (s, 18H, Bu^t), 1.31 (s, 18H, Bu^t), 1.57 (s, 2H, OH), 3.30 (d, 4H, J = 13.10 Hz, ArCH_2Ar), 4.27 (d, 4H, J = 13.03 Hz, ArCH_2Ar), 5.02 (s, 4H, FArCH_2O), 6.82 (s, 4H, ArH), 7.03–7.08 (m, 8H, FArHO), 7.61–7.64 (m, 4H, ArH). Anal. Cald. for $C_{58}H_{66}O_4F_2$: C, 80.52; H, 7.69. Found: C, 79.01; H, 7.33.

2.3 5,11,17,23-Tetra-*tert*-butyl-25,27-bis-(3,5-bis[(4-fluorobenzyl)oxy]benzyloxy)-26,28-bis-(4-fluoro benzyloxy)-calix[4]arene 5

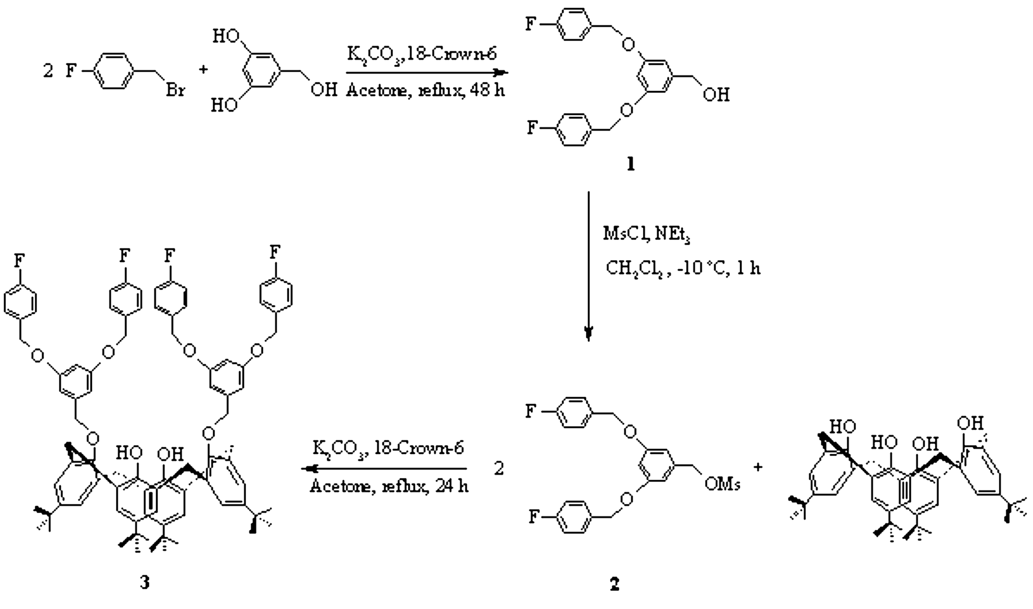
5,11,17,23-Tetra-*tert*-butyl-25,27-bis-(4-fluoro benzyloxy)-26,28-dihydroxy-calix[4]arene **4** (1 eq., 0.20 g, 0.23 mmol), dry K_2CO_3 (2.11 eq., 0.07 g, 0.49 mmol), KI (0.07 g, 0.23 mmol) in CH_3CN (50 mL) was heated for 30 min. 3,5-Bis[(4-fluorobenzyl)oxy] benzyl methanesulfonate (2.11 eq., 0.21 g, 0.49 mmol) was then added and the reaction mixture refluxed for additional 7 days under N_2. After being cooled to room temperature, the reaction mixture was poured into water (100 mL) and extracted with CH_2Cl_2 (3×50 mL). The combined organic extracts were dried over $MgSO_4$. The solvent was evaporated in vacuum. The crude product was purified by column chromatography on silica gel (1:20, diethyl ether/hexane) followed by recrystallization to give 0.22 g (62%) of compound. Mp: 98–99.5°C.

IR (KBr): 3045, 2873 (C—H), 1605 (C=C), 1226 (C-F), 1205, 1046 (C—O—C) cm^{-1}.

^{1}H-NMR (400 MHz, $CDCl_3$)δ (ppm) = 0.98 (s, 18H, Bu^t), 1.31 (s, 18H, Bu^t), 3.30 (d, 4H, J = 13.12 Hz, ArCH_2Ar), 4.27 (d, 4H, J = 13.01 Hz, ArCH_2Ar), 5.00 (s, 12H, FArCH$_2$O), 5.02 (s, 4H, ArCH$_2$O), 6.49 (t, 2H, J = 2.23 Hz, ArH), 6.64 (d, 4H, J = 2.22 Hz ArH), 7.08–7.12 (m, 24H, FArHCH$_2$), 7.39–7.43 (m, 8H, CH$_2$ArHCH$_2$). Anal. Calcd. for $C_{100}H_{98}O_8F_6$: C, 77.90; H, 6.41. Found: C, 75.13; H, 6.84.

3 Results and Discussion

In order to obtain fluorinated poly(aryl ether) dendritic structures based on calix[4]arenes our studies began with the synthesis of p-*tert*-butylcalix[4]arene (43), compound **1** (42) and compound **2** (42) to the literature procedures.



Sch. 1. Synthesis of fluorinated poly(aryl ether) dendritic structures **1, 2** and dendritic structures based on calix[4]arenes **3**.

3.1 Synthesis of Dendritic Structures

The synthesis of dendritic structures are shown in Scheme 1. We used mesylate activation route (42, 44) as an alternative to the bromide route (45). The apparent advantages of the mesylate route over bromide route in the synthesis of fluorinated dendrons are reduced reaction times and simple purification of first generation mesylate dendritic structure by crystallization; therefore, chromatographic separations can be avoided. Under typical Williamson ether synthesis conditions in the presence of K_2CO_3, 4-fluorobenzyl bromide was reacted with 3,5-dihydroxbenzyl alcohol to synthesize compound **1** in a yield of 76%. Compound **1** was converted to the compound **2** in 81% yield using methanesulphonyl chloride in the presence of excess NEt_3 at −10°C (Sch. 1) (42).

3.2 Synthesis of Dendritic Structures Based on Calix[4]arene

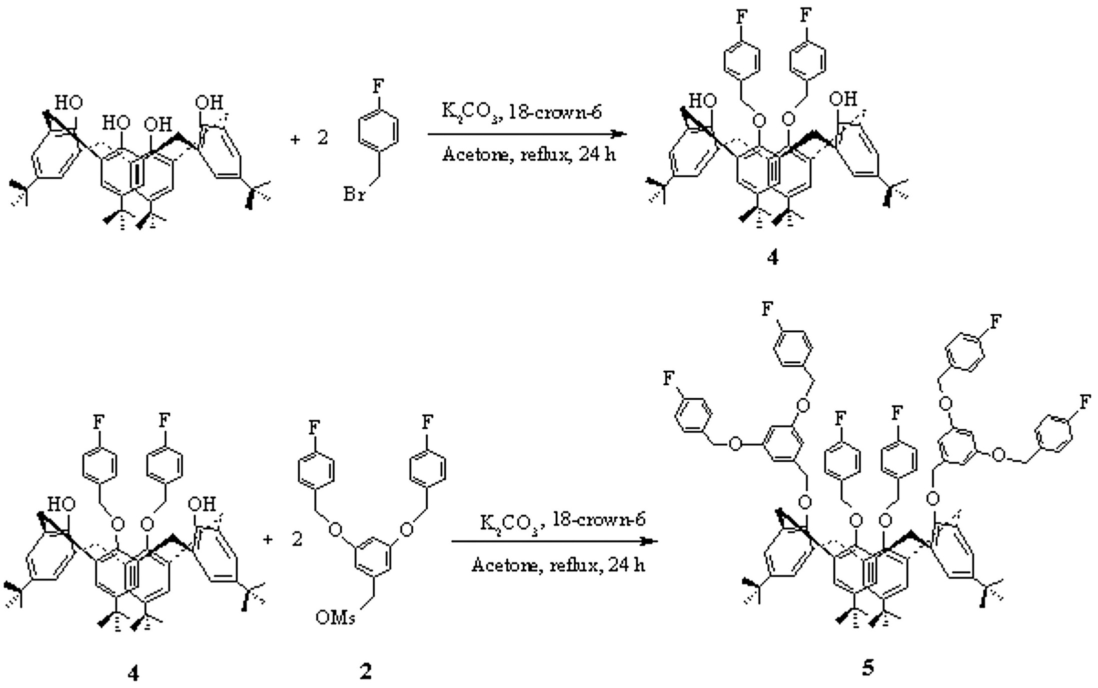
Synthesis of dendritic structures based on calix[4]arene is soluble in common organic solvents such as dichloromethane, chloroform, and acetonitrile, which are helpful for separation and purification. All dendritic structures based on calix[4]arenes were characterized by FTIR, elemental analysis, ^{1}H-NMR spectroscopy.

The synthesis of dendritic structures based on calix[4]arene is shown in Scheme 1 and 2. Under typical Williamson ether synthesis conditions in the presence of K_2CO_3, *p-tert*-calix[4]arene was reacted 3,5-bis[(4-fluorobenzyl)oxy]benzyl methanesulfonate **2** in acetonitrile at reflux temperature to give the narrow-rim 1,3-disubstituted compound **3** in good yields (62%) (Sch. 1). The ^{1}H-NMR spectrum of compound **3** is shown in Figure 1. Compound **3** shows the expected NMR pattern, with two signals being obtained for both the aromatic protons of the calix[4]arene and the tert-butyl groups, indicative of 1,3-disubstitution on the narrow rim of calix[4]arene. Furthermore, the cone conformation of the calix[4]arenes is also confirmed by the presence of two doublets at 3.32 and 4.31 ppm.

Substitution of p-*tert*-butylcalix[4]arene with 4-fluorobenzyl bromide has been carried out in the presence of K_2CO_3 in acetone to afford the cone conformer **4** in 89%. The ^{1}H NMR spectrum of compound **3** is shown in Figure 2. The ^{1}H-NMR spectrum of compound **4** has a typical AB pattern for the methylene bridge protons ($ArCH_2Ar$) of the calixarene moiety at 3.30 and 4.27 ppm. The aromatic methylene and aromatic protons at 5.02 and 7.03–7.08 and 7.61–7.64 indicates that substitution of 4-fluorobenzyl groups has occurred. Following a standard convergent strategy, in the presence of K_2CO_3 and KI, compound **4** was reacted compound **2** in acetonitrile at reflux temperature to give the narrow rim 1,3-disubstituted compound **5** in good yields (Sch. 2). The ^{1}H-NMR spectrum of compound **3** is shown in Figure 2. Compound **5** was easily identified ^{1}H-NMR spectrum, with two signals being obtained for both the aromatic protons of the calix[4]arene and the tert-butyl groups, indicative of 1,3-disubstitution on the narrow rim of calix[4]arene. Additionally, the cone conformation of the calix[4]arenes is also confirmed by the presence of two doublets at 3.30 and 4.27 ppm.

3.3 Thermal Analysis

One of the properties of fluorinated dendrimers frequently studied concerns their thermal behavior, in particular their thermogravimetric analysis (14, 17). The thermal stabilities



Sch. 2. Synthesis of fluorinated poly(aryl ether) dendritic structures based on calix[4]arenes **4, 5**.

of the compounds **3** and **5** were investigated by thermogravimetric analysis (TGA) in a nitrogen stream at a heating rate of 20°C.min^{-1}. The initial decomposition temperatures of 5,11,17,23-tetra-*tert*-butyl-25,27-bis-(3,5-bis[(4-fluorobenzyl)oxy]benzyloxy)-26,28-bis-(4-fluoro benzyloxy)-calix[4]arene **5** and 5, 11, 17, 23-tetra-*tert*-butyl-25,27-bis-(3,5-bis[(4-fluorobenzyl)oxy]benzyloxy)-26,28-dihydroxy-calix[4]arene **3** around 230 and 280°C, respectively

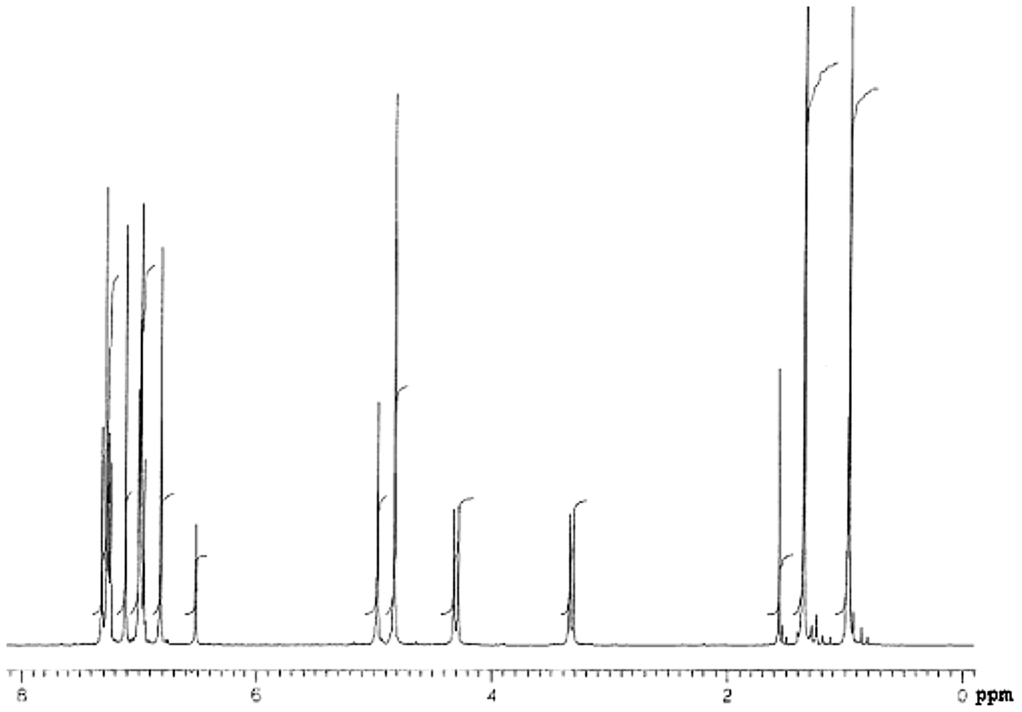


Fig. 1. ^{1}H-NMR spectrum of compound **3** (5,11,17,23-tetra-*tert*-butyl-25,27-bis-(3,5-bis[(4-fluorobenzyl)oxy]benzyloxy)-26,28-dihydroxy-calix[4]arene).

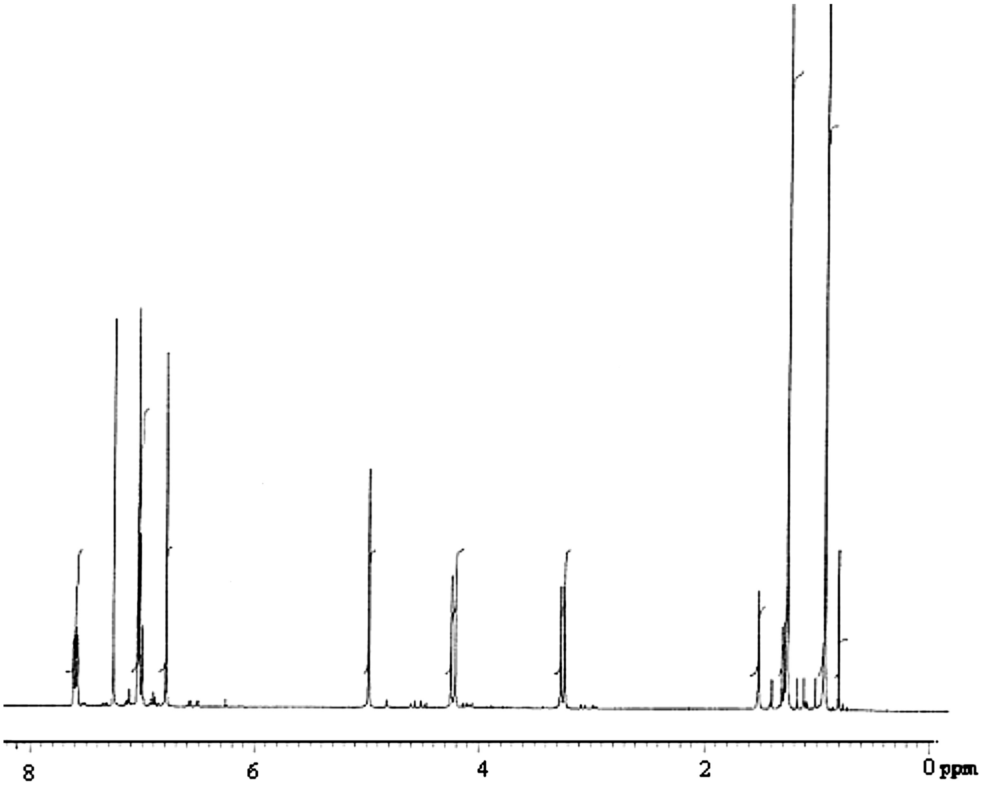


Fig. 2. ^{1}H-NMR spectrum of compound **4** (5,11,17,23-tetra-*tert*-butyl-25,27-bis-(4-fluoro benzyloxy)-26,28-dihydroxy-calix[4]arene).

(Figure 3). This result shows that main-chain scission is an important reaction in the degradation of compounds, at least in the beginning. The degradation of compound **5** occurred in two stages. The first stage was observed 240–290°C and the last stage was observed 395–470°C. Compound **3** undergoes a two stage decomposition. The first stage was observed at 290–385°C, and the last stage was observed at 390–480°C. The residue at 450°C for the compound **5** is about 20% and for the compound **3,** it is about 50%. The compound **3** is more stable than that of compound **5**. Compound **3** has two hydroxyl groups and fluorine atoms. The strong hydrogen bonding occurred between the hydroxyl group and fluorine atoms. For this reason, compound **3** has good thermal stability. Fluorinated carbosilane dendrimers have thermally poor stability (17). However, the fluorinated polyphenylene dendrimers are stable up to 505°C (14). We have also compared the stability of our fluorinated dendrimers with that of the dendrimer and we observed that our structures showed similar properties.

3.4 Decomposition Kinetics

The activation energies on the thermal decomposition of dendrimers were determined by thermogravimetric analysis. The activation energies can be obtained using Ozowa's method. For the study on the kinetics of thermal degradation of polymers, we can select the isothermal thermogravimetry (ITG) or the thermogravimetry (TG) at various heating rates. ITG is superior to obtain an accurate activation energy for thermal degradation, although it is time consuming. In the case of thermal degradation of polymers, in which depolymerization is competing with cyclization or crosslinking due to the side groups, the TG at various heating rates is much more convenient than ITG for the investigation of thermal degradation kinetics. Therefore, in the present work, TG curves at various heating rates were obtained and the activation energies (Ed) for thermal degradation of dendrite's were calculated by Ozawa's plot, which is a widely used method. Degradations were performed in the scanning mode, from 35 up to 500°C, under nitrogen flow (20 mL.min^{-1}), at various heating rates (β: 5,7,10, 15 and 20°C min^{-1}). Samples of 5–8 mg held in alumina open crucibles were used and their weights were measured as a function of temperature and stored in the list of data of the appropriate built-in program of the processor. The TGA

Table 1. The apparent activation energies of compounds 3 and 5 under thermal degradation in N_2

	Activation energy Ed (kj/mol) *Conversion (%)*							
Sample	10	20	30	40	50	60	70	80
Compound 3	102.6	91.5	97.5	89.1	—	—	—	—
Compound 5	99.7	94.1	98.8	101.3	102.3	88.9	88.7	—

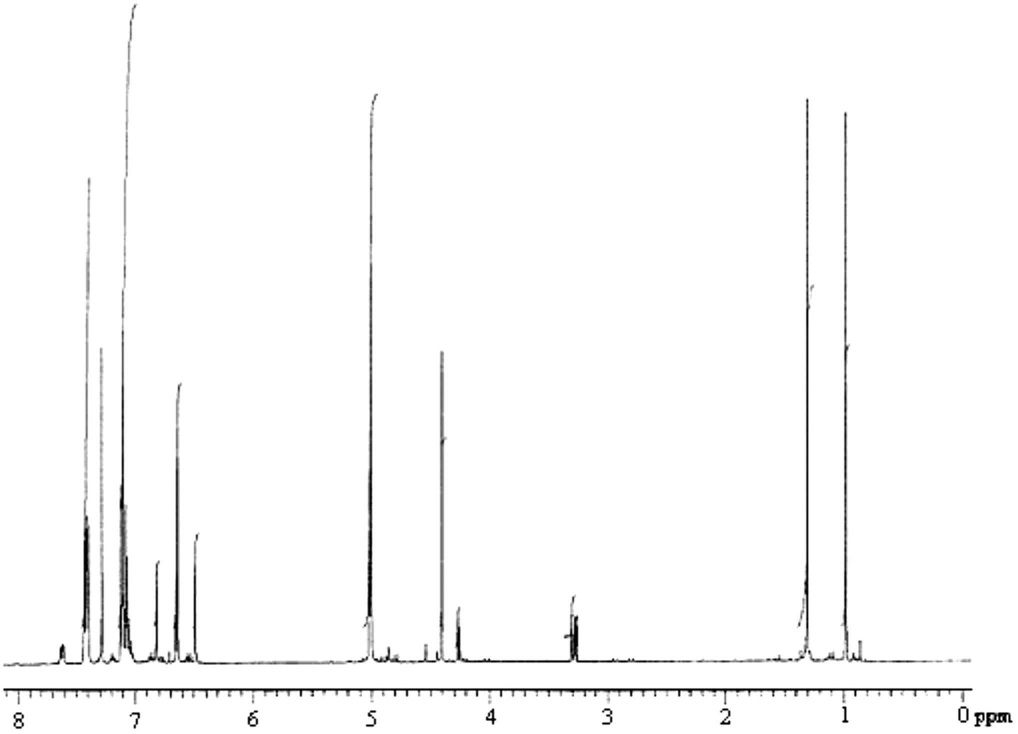


Fig. 3. ^{1}H-NMR spectrum of compound **5** (5,11,17,23-tetra-*tert*-butyl-25,27-bis-(3,5-bis[(4-fluorobenzyl)oxy]benzyloxy)-26,28-bis-(4-fluoro benzyloxy)-calix[4]arene).

curves were immediately printed at the end of each experiment and the weights of the sample at various temperatures were then transferred to a PC.

According to the Ozawa method, the apparent thermal decomposition activation energy, *E*d, can be determined from the TGA thermograms under various heating rates, and the following equation:

$$E_d = -\frac{R}{b}\left[\frac{d\log\beta}{d(1/T)}\right]$$

Where R is the gas constant; b, a constant (0.4567); and β, the heating rate (°C/min). According to the equation, the activation energy of degradation can be determined from the slope of the linear relationship between log β and $1/T$. The *E*d values for compound **3**, **5** are given in Table 1. *E*d calculated from the Ozawa method is superior to other methods for complex degradation, since it does not use the reaction order in the calculation of the decomposition activation energy (39). Therefore, *E*d calculated from the Ozawa method was superior to the former methods for complex degradation. The average activation energies corresponding to the different stages have been calculated and listed Table 2.

Table 2. Thermal decomposition data and activation energies of the compounds 3 and 5 by Ozowa method

Sample	*Stage of decomposition*	*Temperature range (°C)*	*Average activation energy (kj/mol)*
Compound 3	Stage 1	290–385	103.45
	Stage 2	390–480	99.70
Compound 5	Stage 1	240–290	98.65
	Stage 2	395–470	95.70

4 Conclusions

The potential use of fluorinated materials in a wide variety of research and application areas increases the importance of fluorinated poly(aryl ether) dendrons as one of the major building blocks for the synthesis of dendrimers. We have synthesized two new poly(aryl ether) dendritic structures carrying 4-fluorobenzyl bromide on the surface and calix[4]arene as a core through a convergent synthetic strategy. The TGA studies concluded that the thermal stability of the compound **3** is more stable than compound **5**. The decomposition activation energies of the compound **3** and **5** were calculated with Ozawa method.

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