TERMINATION OF DENDRITIC CARBOSILANE POLYMERS WITH PHENYLACETHYLENE, *p*-PHENYLPHENOXY AND *p*-BROMOPHENOXY GROUPS

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Abstract: Starting with allyl groups containing polycarbosilane as a core molecule, a succession of alternate platinum catalyzed hydrosilations of all allyl groups with HSiMeCl_2 as well as alkenylations with allylmagnesium bromide provided polycarbosilane-based dendrimers. The polymeric carbosilane dendrimer provided the materials with specific functions of intriguing supramolecular phenomena with phenylethynyl, *p*-bromophenoxy, and *p*-phenylphenoxy groups.

Introduction

The dendritic macromolecules have a unique structure which is characterized by a high degree of branch that emanates from a core molecule.^{1, 2} Recently, the emphasis has shifted from the simple construction of macromolecules with dendritic topology to the materials with specific functions and exhibiting intriguing supramolecular phenomena.³ Its applications have included catalysts, agents for delivering drugs, liquid crystals, and molecular antennae for absorbing light energy.⁴ To date, the syntheses and applications of dendritic macromolecules have sprung into two basic types. The first type has a globular unified structure in which well-defined branches emanate from a central core, becoming more branched and crowded as they extend out to the periphery.⁵ The second type of dendritic structure is based on polymer containing many functions, the development of which was pioneered by Y. H. Kim.⁶ This type of polymer also has random or fairly regular architectures. To date, most of the synthetic methodologies for silicon-containing dendrimers have been demonstrated by repeating units possessing considerable flexibilities.^{7, 8, 10} In the current paper, we described also a convenient synthetic way of carbosilane dendrimers, based on quantitative hydrosilation-alkenylation cycles.^{1, 10} As an extension of some of our previous studies,^{10e} we now report to demonstrate a detailed study on the reactions of chlorinated carbosilane polymer with *p*-bromophenol, *p*-phenylphenol and lithium phenylacetylides. Two well-known reactions involving Si-Cl bonds were provided for this model. Reactions were performed with *p*-bromophenol and *p*-phenylphenol in order to anchor ether groups on the periphery of dendrimers, respectively, while the reaction was also attempted with lithium phenylacetylides in order to cover the surface of dendrimers with phenylethynyl units.

Results and Discussion

Carbosilane polymer **4**, $(\text{Ph}_2\text{SiCH}_2\text{CH}_2\text{CH}_2)_n$ ($n > 10$), was obtained by the self-hydrosilation reaction of $\text{Ph}_2\text{SiH}(\text{CH}_2\text{CH}=\text{CH}_2)$ in the presence of a platinum catalyst (Pt in activated C, 10% Pt content) at 200 °C in toluene.^{10e}

The reaction of carbosilane polymer **4** with 2 equiv. triflic acid ($\text{CF}_3\text{SO}_3\text{H}$) in toluene at -78 °C followed by trapping with allylmagnesium bromide resulted in the isolation of allylated polymer **6** (**G0**). The 0th generation could be converted into a **G1P** generation with HSiMeCl_2 or HSiCl_3 by the use of hydrosilation cycles. Repeating the reaction of **8** with HSiCl_3 and allylmagnesium bromide by the use of hydrosilation-alkenylation cycles gave the third generation dendrimer **12**.^{10e} In the course of repeating reactions, higher generation dendrimers could not be unified due to the

phenomenon of surface congestion which was observed by ^1H NMR spectroscopic views.

Scheme 1

The treatment of **7** with lithium phenylacetylide at refluxing THF for 4 h gave rise to the dendrimer **11**. Reactions were monitored by ^1H NMR which showed the disappearance of the signal due to the MeSiCl_2 groups of **7** on behalf of a new signal at 0.77 ppm corresponding to the terminal MeSi groups. The treatment of **7** with an excess solution of *p*-bromophenol and TMED mixture in toluene at room temperature yielded *p*-bromophenoxy groups containing the dendrimer **9**, quantitatively. The same reactions were conducted with **7** and *p*-phenylphenol leading in quantitative yield to dendrimer **10**; here also, the reaction needed TMED to go to completion. The purification of the terminated dendrimers (**9**, **10**, and **11**) was obtained by careful chromatography after each reaction step. The glass transition (T_g) temperature was measured for a number of dendritic molecules.

Experimental

All reactions were carried out under a dried nitrogen atmosphere. NMR spectra were measured by using samples in the CDCl_3 solution: ^1H NMR spectra at 200.13 MHz and ^{13}C NMR spectra at 50.32 MHz by Bruker AC-200 Spectrophotometer. FT-IR spectra were measured by IFS 55 (Bruker). UV spectra were measured by HP 8452A Diode Array UV/Vis. Spectrophotometer. Elemental analysis was performed by the Pusan Branch of the Korean Basic Science Institute.

Calorimetry: DSC (Setaram DSC 92) was used to monitor glass transitions at the scan rate of 5 °C/min. Sample weights were typically chosen between 10 and 15 mg. Ether and THF were dried by distillation from a blue solution of sodium-benzophenone ketyl. Solvents such as pentane and hexane were dried and distilled from Na/K₂ amalgam. Hydrosilanes (HSiMeCl₂ and HSiCl₃) were used by vacuum distillation before the experiment. Platinum catalysts (Pt on activated carbon, 10 % Pt content) were used after vacuum dry at room temperature.

Spectroscopic data of compounds **2**–**5**, **8** and **12** were performed in ref. 10e.

6. 60 mmol of allylmagnesium bromide (42 ml of 1.4 M solution in ether, 1.3 equiv.¹¹) was slowly added to 5.14 g (22.91 mmol) of **5** in 50 ml toluene. After the addition was finished, the reaction mixture was stirred for 2 h. When the reaction was completed by ¹H NMR, solvents were removed under reduced pressure. The magnesium salt was precipitated in 150 ml pentane and filtered off. The volatile components were removed under vacuum, leaving 2.03 g (13.33 mmol, 58%) of a colorless liquid. All portions of the yielded compounds were chromatographed on silica gel with chloroform as an eluent. The product, **G1**, was obtained as a clear, colorless oil or glass. ¹H NMR (CDCl₃): δ (ppm) 0.40–0.82 (m), 0.84–1.13 (m), 1.12–1.74 (m) (CH₂), 4.70–5.02 (m), 5.52–5.86 (m) CH₂=CH).

7. A mixture of 2.03 g (13.33 mmol) of **6**, 4.60 g (40.00 mmol, 1.5 equiv.¹¹) of HSiMeCl₂, and 0.08 g of a dried platinum catalyst in 25 ml THF was stirred for 12 h at room temperature. The reaction mixture was refluxed for 1 h. When the reaction was completed by ¹H NMR, excessive HSiMeCl₂ and THF were removed under vacuum. The catalyst was filtered off in pentane and the pentane was evaporated, leaving 4.16 g (10.88 mmol, 81%) of **7** as a clear, colorless oil, which was very sensitive to moisture. ¹H NMR (CDCl₃): δ (ppm) 0.44–0.83 (m), 0.83–1.12 (m), 1.12–1.42 (m), 1.42–1.78 (m) (CH₂).

9. 2.20 mmol of a *p*-bromophenol solution (1M in THF) was slowly added to 2.17 g (1.04 mmol)¹¹ of **7** in 25 ml toluene (in the presence of 5 ml of TMED). After the addition was completed, the reaction mixture was stirred for 3 h. When the reaction was done by ¹H NMR, solvents were removed under reduced pressure. The TMED·HCl salt was precipitated in pentane and filtered off. All yielded compounds were chromatographed on silica gel with chloroform as an eluent. The product, **9**, was obtained as a clear, colorless glass (3.08 g, 3.24 mmol, 100 %). ¹H NMR (CDCl₃): δ (ppm) 0.18–0.33 (m, Me), 0.33–0.68 (m, CH₂), 0.68–1.00 (m, CH₂), 1.00–1.77 (m, CH₂), 6.58–6.82 (m, Ph), 7.04–7.17 (m, Ph). ¹³C NMR (CDCl₃): δ (ppm) -3.75 (MeSi), 14.00–21.00 (CH₂), 114.50 (C-*i*), 121.45 (C-*o*), 132.60 (C-*m*), 153.13 (C-*p*). FT-IR (KBr): 3065 (νC-H), 2917.6 (νC-H), 1585.3 (νC=C). UV: λ_{max} 285 nm, ε_{max} 2845 l·mole⁻¹·cm⁻¹. Anal. Calcd. for (C₃₅H₄₀Si₃O₄Br₄)_n: C, 45.50; H, 4.36. Found C, 45.65, H, 4.68. Tg: -9.51 °C

10. ¹H NMR (CDCl₃): δ (ppm) 0.20–0.39 (m, MeSi), 0.39–0.78 (m, CH₂), 0.78–1.09 (m, CH₂), 6.80–7.06 (m, Ph), 7.12 (m, Ph). ¹³C NMR (CDCl₃): δ (ppm) -3.73 (MeSi), 16.00–21.00 (CH₂), 120.56 (C-*i*), 127.11 (C-*o*), 128.84 (C-*m*), 129.02 (C-*p*), 153.65 (C-*i*), 154.98 (C-*o*), 160.24 (C-*p*), 173.50 (C-*m*). FT-IR (KBr): 3032.2 (νC-H), 2917.4 (νC-H), 1605.4 (νC=C). UV: λ_{max} 288 nm, ε_{max} 7765 l·mole⁻¹·cm⁻¹. Anal. Calcd. for (C₅₉H₅₆Si₂O₄)_n: C, 77.67; H, 6.19. Found C, 76.72, H, 6.73. Tg: 20.24 °C

11. 17.28 mmol (1 M in THF)¹¹ of a lithium phenylacetylide solution was slowly added to 2.17 g (1.04 mmol) of **7** in 25 ml THF. After the addition was completed, the reaction mixture was refluxed for 4 h. When the reaction was done by ¹H NMR, solvents were removed under reduced pressure. All of the yielded compounds were chromatographed on silica gel with chloroform as an eluent. The product **11** was obtained as a clear, yellow-brown glass (2.78 g, 4.32 mmol, 100 %). ¹H NMR (CDCl₃): δ (ppm) 0.32, 0.43 (d, MeSi), 0.43–0.80 (m, CH₂), 0.80–1.18 (m, CH₂), 1.18–1.92 (m, CH₂), 7.12–7.39 (m, Ph), 7.39–7.62 (m, Ph). ¹³C NMR (CDCl₃): δ (ppm) -1.06 (MeSi), 14.00–22.00 (CH₂), 90.16 (C≡), 106.40 (≡CPh), 122.78 (C-*i*), 128.19 (C-*o*), 128.41 (C-*p*), 132.12 (C-*m*).

FT-IR (KBr): 3058.5 ($\nu_{\text{C-H}}$), 2915.6 ($\nu_{\text{C-H}}$), 2159.30 ($\nu_{\text{C}\equiv\text{C}}$), 1487.8 ($\nu_{\text{C}=\text{C}}$). UV: λ_{max} 309 nm, ϵ_{max} 4591 l/mole-cm, λ_{max} 288 nm, ϵ_{max} 4043 l/mole-cm, λ_{max} 330 nm, ϵ_{max} 3840 l/mole-cm. Anal. Calcd. for $(\text{C}_{43}\text{H}_{44}\text{Si}_3)_n$: C, 80.16; H, 6.88. Found C, 79.88, H, 6.85. Tg: -4.02 °C

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