

## Self-Organization of Dendrons with Focal Pyrene Moiety and Diacetylene-Containing Periphery

Min Ju Im, Chiyong Park, and Chulhee Kim\*

Department of Polymer Science and Engineering,  
Inha University, Incheon 402-751, Korea

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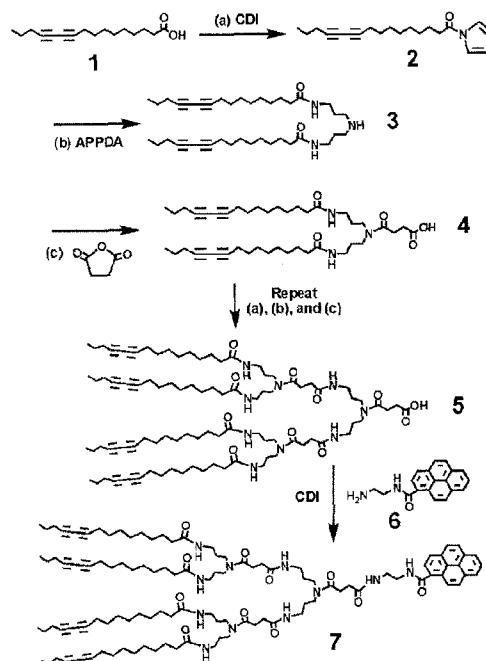
### Introduction

The creation of nanostructures through the self-assembly of amphiphiles is an efficient approach to reach functional nanomaterials which can find important applications in many areas of nanotechnologies.<sup>1</sup> Non-spherical nanostructures including cylinders, nanotubes, and helices have been prepared via self-assembly of well-defined amphiphiles such as polymeric and dendritic amphiphiles as well as peptide amphiphiles.<sup>2-8</sup> The chemical structures of these building blocks could be designed not only to control the morphology of the self-assembled structures but also to dictate the surface or internal functionalities of the assembled structures. We have investigated the self-assembly characteristics of the amphiphilic amide dendrons having peripheral hydrophobic chains, which self-assemble into well-defined structures such as fibers and ribbons in organic solvents by using hydrogen bonding and hydrophobic interactions as a main driving force.<sup>9-20</sup> In addition, in aqueous medium, the amide dendrons self-organize into vesicles and cylindrical micelles particularly depending on the nature of the functional group at the focal point of the dendron.<sup>10</sup> Our recent finding of the supramolecular transformation of self-assembled structures from vesicles to nanotubes induced by the host-guest complexation of the focal pyrene group of the amide dendron and cyclodextrins (CDs)<sup>11</sup> highlighted the importance of guiding the self-assembly process of the dendrons through their structural tuning. The self-assembled nanotubes of the amide dendrons could be a useful platform for applications such as biosensor, nanotemplate, and catalysis etc. Therefore, we are carrying out a comprehensive study to understand the detailed mechanism of supramolecular transformation with diverse dendritic building blocks so that we can provide a clear scope of the functional nanostructures which can be derived from self-assembly of amide dendrons.

In this note, we report the synthesis and self-organization behavior of amide dendrons with diacetylene-containing periphery and the focal pyrene moiety. In addition, we investigated the effect of the assembled structure of the dendron on the polymerizability of the peripheral diacetylene moiety and the possibility of the supramolecular transformation due to host-guest interactions between the dendron and CDs.

### Experimental

**Synthesis of 1.** A pyrrolidine solution (10 mL) of 1-pentynyl iodide (2.98 g, 15.3 mmol) was added dropwise to the solution of 10-undecynoic acid (2.0 g, 11 mmol) and copper iodide (0.21 g, 1.1 mmol) in pyrrolidine (5 mL) while the temperature was kept at 0 °C. After stirring at room temperature for 4 h, the mixture was treated with a saturated aqueous solution of ammonium chloride and extracted with chloroform. The organic extract was dried over MgSO<sub>4</sub> and the solvent was removed under reduced pressure. The product mixture was column chromatographed on silica gel with a mixture of n-hexane and methylene chloride (7:3, v/v). The product was recrystallized from n-hexane (Yield 1.8 g, 66%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 0.98 (t, *J*=7.3 Hz, 3H), 1.30-1.41 (m, 8H), 1.47-1.57 (m, 4H), 1.59-1.66 (m, 2H), 2.22 (t, *J*=6.2 Hz, 2H), 2.24 (t, *J*=6.2 Hz, 2H), 2.34 (t, *J*=7.3 Hz, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 13.56, 19.25, 21.26, 21.91, 24.69, 28.34, 28.79, 28.92, 29.04, 29.11, 34.00, 65.29, 65.37, 77.39, 77.43, 179.47.



Scheme I. Synthesis of the amide dendrons.

\*Corresponding Author. E-mail: chk@inha.ac.kr

**Synthesis of 2.** A chloroform solution (20 mL) of compound **1** (1.4 g, 5.6 mmol) was added to a solution of 1,1'-carbonyldiimidazole (CDI) (1.1 g, 6.8 mmol) in chloroform (30 mL). After 12 h at 25 °C under nitrogen, the chloroform solution was washed with water and dried with magnesium sulfate. After evaporation of the solvent under reduced pressure (Yield 1.55 g, 92%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 0.98 (t, *J*=7.3 Hz, 3H, CH<sub>3</sub>-CH<sub>2</sub>-), 1.30-1.42 (m, 8H, -CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CO-NH-), 1.47-1.58 (m, 4H, -CH<sub>2</sub>-CH<sub>2</sub>-C≡C-, -C≡C-CH<sub>2</sub>-CH<sub>2</sub>-), 1.76-1.83 (m, 2H, -CH<sub>2</sub>-CH<sub>2</sub>-CO-), 2.22 (t, *J*=6.2 Hz, 2H, -CH<sub>2</sub>-C≡C-), 2.24 (t, *J*=6.2 Hz, 2H, -C≡C-CH<sub>2</sub>-), 2.85 (t, *J*=7.3 Hz, 2H, -CH<sub>2</sub>-CO-NH-), 7.09 (s, 1H, -CO-N-CH=CH-N-), 7.47 (s, 1H, -CO-N-CH=CH-N-), 8.15 (s, 1H, -CO-N-CH=N-); <sup>13</sup>C NMR (100.64 MHz, CDCl<sub>3</sub>) δ 13.57, 19.25, 21.26, 21.91, 24.12, 28.30, 28.74, 28.89, 28.97, 29.14, 35.28, 65.29, 65.39, 77.36, 77.45, 115.93, 130.96, 136.04, 169.34).

**Synthesis of 3.** A chloroform solution (20 mL) of compound **2** (1.4 g, 4.7 mmol) was added to a solution of *N*-(3-aminopropyl)-propanediamine (APPDA) (0.25 g, 1.9 mmol) in chloroform (30 mL). After the solution was stirred for 12 h at room temperature, the solvent was evaporated under reduced pressure and the product mixture was recrystallized from ethyl acetate (Yield 0.9 g, 81%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 0.98 (t, *J*=7.3 Hz, 6H, CH<sub>3</sub>-CH<sub>2</sub>-), 1.29-1.40 (m, 16H, -CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CO-NH-), 1.46-1.57 (m, 8H, -CH<sub>2</sub>-CH<sub>2</sub>-C≡C-, -C≡C-CH<sub>2</sub>-CH<sub>2</sub>-), 1.58-1.63 (m, 4H, -CH<sub>2</sub>-CH<sub>2</sub>-CO-), 1.64-1.69 (m, 4H, -CO-NH-CH<sub>2</sub>-CH<sub>2</sub>-), 2.15 (t, *J*=7.3 Hz, 4H, -CH<sub>2</sub>-CO-NH-), 2.21 (t, *J*=6.2 Hz, 4H, -CH<sub>2</sub>-C≡C-), 2.23 (t, *J*=6.2 Hz, 4H, -C≡C-CH<sub>2</sub>-), 2.62-2.65 (m, 4H, -CO-NH-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-), 3.32-3.37 (m, 4H, -CO-NH-CH<sub>2</sub>-CH<sub>2</sub>-), 6.30 (br, 2H, -CO-NH-CH<sub>2</sub>-); <sup>13</sup>C NMR (100.64 MHz, CDCl<sub>3</sub>) δ 13.57, 19.25, 21.26, 21.91, 25.88, 28.35, 28.83, 29.00, 29.25, 29.32, 29.46, 36.91, 37.76, 47.38, 65.29, 65.39, 77.39, 77.45, 173.07; MS (MALDI-TOF) calcd for C<sub>38</sub>H<sub>61</sub>N<sub>3</sub>O<sub>2</sub> 591.91, found 592.72 (M+H).

**Synthesis of 4.** A chloroform solution (20 mL) of dendron **3** (0.7 g, 1.2 mmol) and triethylamine (TEA) (0.18 g, 1.8 mmol) was added to a solution of succinic anhydride (0.18 g, 1.8 mmol) in chloroform (30 mL). After the solution was stirred for 12 h at room temperature, the solvent was removed under reduced pressure, and the product was recrystallized from ethyl acetate and diethyl ether (Yield 0.7 g, 86%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 0.98 (t, *J*=7.3 Hz, 6H, CH<sub>3</sub>-CH<sub>2</sub>-), 1.29-1.39 (m, 16H, -CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CO-NH-), 1.46-1.57 (m, 8H, -CH<sub>2</sub>-CH<sub>2</sub>-C≡C-, -C≡C-CH<sub>2</sub>-CH<sub>2</sub>-), 1.58-1.67 (m, 4H, -CH<sub>2</sub>-CH<sub>2</sub>-CO-), 1.79-1.86 (m, 4H, -CO-NH-CH<sub>2</sub>-CH<sub>2</sub>-), 2.17 (t, *J*=7.3 Hz, 4H, -CH<sub>2</sub>-CO-NH-), 2.22 (t, *J*=6.2 Hz, 4H, -CH<sub>2</sub>-C≡C-), 2.23 (t, *J*=6.2 Hz, 4H, -C≡C-CH<sub>2</sub>-), 2.61 (t, *J*=5.9 Hz, 2H, -N-CO-CH<sub>2</sub>-CH<sub>2</sub>-CO-OH), 2.71 (t, *J*=5.9 Hz, 2H, -N-CO-CH<sub>2</sub>-CH<sub>2</sub>-CO-OH), 3.10-3.30 (m, 4H, -CO-NH-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-), 3.32-3.43 (m, 4H, -CO-NH-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-), 6.25 (br, 1H, -CO-NH-CH<sub>2</sub>-), 6.72 (br, 1H, -CO-NH-CH<sub>2</sub>-); <sup>13</sup>C NMR (100.64 MHz, CDCl<sub>3</sub>) δ

13.57, 19.25, 21.25, 21.91, 25.82, 27.79, 28.37, 28.82, 29.14, 29.24, 29.32, 29.62, 35.67, 36.64, 36.99, 45.62, 65.31, 65.40, 77.43, 77.49, 172.40, 173.73, 175.45; MS (MALDI-TOF) calcd for C<sub>42</sub>H<sub>65</sub>N<sub>3</sub>O<sub>5</sub> 691.98 found 692.76 (M+H).

**Synthesis of 5.** For the preparation of second-generation dendron **4**, the convergent procedure identical to that employed for the synthesis of dendron **4** was repeated by using dendron **4** as the starting material. Dendron **4** was reacted with APPDA by using CDI as a coupling agent, and subsequently treated with succinic anhydride (Yield 0.4 g, 83%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 0.97 (t, *J*=7.3 Hz, 12H, CH<sub>3</sub>-CH<sub>2</sub>-), 1.28-1.37 (m, 32H, -CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CO-NH-), 1.45-1.56 (m, 16H, -CH<sub>2</sub>-CH<sub>2</sub>-C≡C-, -C≡C-CH<sub>2</sub>-CH<sub>2</sub>-), 1.58-1.64 (m, 4H, -CH<sub>2</sub>-CH<sub>2</sub>-CO-), 1.66-1.85 (m, 12H, -CO-NH-CH<sub>2</sub>-CH<sub>2</sub>-), 2.15 (t, *J*=7.3 Hz, 8H, -CH<sub>2</sub>-CO-NH-), 2.21 (t, *J*=6.2 Hz, 8H, -CH<sub>2</sub>-C≡C-), 2.23 (t, *J*=6.2 Hz, 8H, -C≡C-CH<sub>2</sub>-), 2.51 (t, *J*=5.9 Hz, 2H, -N-CO-CH<sub>2</sub>-CH<sub>2</sub>-COOH), 2.53 (t, *J*=5.9 Hz, 2H, -N-CO-CH<sub>2</sub>-CH<sub>2</sub>-COOH), 2.63 (t, *J*=5.9 Hz, 4H, -N-CO-CH<sub>2</sub>-CH<sub>2</sub>-CO-NH-), 2.65 (t, *J*=5.9 Hz, 4H, -N-CO-CH<sub>2</sub>-CH<sub>2</sub>-CO-NH-), 3.12-3.19 (m, 8H, -CO-NH-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-N-CO-, -CO-NH-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-N-CO-), 3.23-3.40 (m, 16H, -CO-NH-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-N-CO-, -CO-NH-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-N-CO-), 6.60 (br, 4H, -CO-NH-CH<sub>2</sub>-), 6.95 (br, 1H, -CO-NH-CH<sub>2</sub>-), 7.14 (br, 1H, -CO-NH-CH<sub>2</sub>-); <sup>13</sup>C NMR (100.64 MHz, CDCl<sub>3</sub>) δ 13.56, 19.24, 21.23, 21.90, 25.79, 27.58, 27.69, 28.28, 28.35, 28.61, 28.83, 28.99, 29.26, 29.34, 29.81, 31.42, 36.60, 36.78, 36.89, 42.81, 45.38, 65.30, 65.38, 77.21, 77.41, 172.21, 172.54, 173.49, 173.88, 175.05; MS (MALDI-TOF) calcd for C<sub>94</sub>H<sub>147</sub>N<sub>9</sub>O<sub>11</sub> 1579.23, found 1601.54 (M+Na).

**Synthesis of 6.** A THF solution (20 mL) of pyrenecarbonyl chloride (1.8 g, 5.2 mmol) was added dropwise for 30 min into a THF (30 mL) solution of ethylenediamine (9.45 g, 15.7 mmol) while the temperature was kept at 0 °C. After stirring for 8 h at room temperature, the solvent was evaporated under reduced pressure. The product mixture was column chromatographed on silica gel with a mixture of *n*-hexane and methylene chloride (2:8, v/v), and the product was dried in vacuo (Yield 1.1 g, 73%). <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ 2.86 (t, *J*=6.2 Hz, 2H), 3.47 (t, *J*=6.2 Hz, 2H), 8.09-8.68 (m, 9H, py); <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>) δ 41.45, 43.20, 123.53, 123.65, 124.26, 124.62, 125.12, 125.42, 125.61, 126.41, 127.07, 127.59, 127.89, 128.06, 130.06, 130.57, 131.34, 132.12, 168.78.

**Synthesis of 7.** Dendron **5** was activated by using CDI as a coupling agent. Then chloroform solution (20 mL) of activated dendron **5** (0.16 g, 0.1 mmol) and **6** (0.057 g, 0.2 mmol) was stirred at room temperature for 12 h under nitrogen. After evaporation of the solvent under reduced pressure, the product mixture was column chromatographed on a silica gel with chloroform. And the product was recrystallized from THF/diethyl ether (1:9 v/v) (Yield 0.1 g, 55%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 0.97 (t, *J*=7.3 Hz, 12H, CH<sub>3</sub>-CH<sub>2</sub>-),

1.21-1.31 (m, 32H,  $-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CO}-\text{NH}-$ ), 1.45-1.50 (m, 16H,  $-\text{CH}_2-\text{CH}_2-\text{C}\equiv\text{C}-$ ,  $-\text{C}\equiv\text{C}-\text{CH}_2-\text{CH}_2-$ ), 1.52-1.56 (m, 8H,  $-\text{CH}_2-\text{CH}_2-\text{CO}-$ ), 1.69-1.76 (m, 12H,  $-\text{CO}-\text{NH}-\text{CH}_2-\text{CH}_2-$ ), 2.01 (t,  $J=7.3$  Hz, 8H,  $-\text{CH}_2-\text{CO}-\text{NH}-$ ), 2.21 (t,  $J=6.2$  Hz, 8H,  $-\text{CH}_2-\text{C}\equiv\text{C}-$ ), 2.23 (t,  $J=6.2$  Hz, 8H,  $-\text{C}\equiv\text{C}-\text{CH}_2-$ ), 2.40 (t,  $J=5.9$  Hz, 2H,  $-\text{N}-\text{CO}-\text{CH}_2-\text{CH}_2-\text{CO}-\text{NH}-$ ), 2.48 (t,  $J=5.9$  Hz, 2H,  $-\text{N}-\text{CO}-\text{CH}_2-\text{CH}_2-\text{CO}-\text{NH}-$ ), 2.56 (t,  $J=5.9$  Hz, 4H,  $-\text{N}-\text{CO}-\text{CH}_2-\text{CH}_2-\text{CO}-\text{NH}-$ ), 2.62 (t,  $J=5.9$  Hz, 4H,  $-\text{N}-\text{CO}-\text{CH}_2-\text{CH}_2-\text{CO}-\text{NH}-$ ), 2.96-3.01 (m, 8H,  $-\text{CO}-\text{NH}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{N}-\text{CO}-$ ,  $-\text{CO}-\text{NH}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{N}-\text{CO}-$ ), 3.13-3.25 (m, 16H,  $-\text{CO}-\text{NH}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{N}-\text{CO}-$ ,  $-\text{CO}-\text{NH}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{N}-\text{CO}-$ ), 3.56-3.61 (m, 2H,  $-\text{CH}_2-\text{CH}_2-\text{NH}-\text{CO}-\text{py}$ ), 3.74-3.77 (m, 2H,  $-\text{CH}_2-\text{CH}_2-\text{NH}-\text{CO}-\text{py}$ ), 6.50 (br, 4H,  $-\text{CO}-\text{NH}-\text{CH}_2-$ ), 6.85 (br, 1H,  $-\text{CO}-\text{NH}-\text{CH}_2-$ ), 6.99 (br, 1H,  $-\text{CO}-\text{NH}-\text{CH}_2-$ ), 7.23 (br, 1H,  $-\text{CO}-\text{NH}-\text{CH}_2-\text{CH}_2-\text{NH}-\text{CO}-\text{py}$ ), 7.74 (br, 1H,  $-\text{CH}_2-\text{NH}-\text{CO}-\text{py}$ ), 8.03-8.61 (m, 9H, py);  $^{13}\text{C}$  NMR (100.64 MHz,  $\text{CDCl}_3$ )  $\delta$  13.52, 19.18, 21.19, 21.86, 25.71, 27.58, 27.61, 28.30, 28.35, 28.72, 28.76, 28.93, 29.19, 29.26, 29.81, 31.42, 36.48, 36.50, 36.69, 39.50, 40.16, 42.57, 45.10, 65.27, 65.36, 77.21, 77.38, 124.13, 124.47, 124.50, 124.70, 125.67, 125.81, 126.30, 126.99, 128.43, 128.60, 130.46, 130.84, 130.93, 132.28, 170.56, 171.98, 172.12, 172.54, 173.21, 173.57; MS (MALDI-TOF) calcd for  $\text{C}_{113}\text{H}_{161}\text{N}_{11}\text{O}_{11}$  1849.55, found 1872.53 ( $\text{M}+\text{Na}^+$ ).

## Results and Discussion

A convergent approach was employed to build the first and second generation dendrons with diacetylene-containing carboxylic acid (**1**) as a starting building material as described in Scheme I. 10,12-Hexadecadiynyl acid (**1**) was prepared by CuI-mediated coupling of 1-pentynyl iodide and 10-undecynoic acid at room temperature. For the synthesis of first-generation dendron **4**, compound **1** was treated with CDI in chloroform, and subsequently reacted with APPDA to generate secondary amine at the focal point, which was then reacted with succinic anhydride to yield dendron **4**. To prepare second-generation dendron **5**, dendron **4** was reacted with APPDA by using CDI as a coupling agent, and subsequently treated with succinic anhydride to yield dendron **5**. The second generation dendrons **5** were reacted with **6** to convert the focal carboxyl group of the dendron to the pyrene moiety (dendron **7**). The dendrons were characterized by  $^1\text{H}$  and  $^{13}\text{C}$  NMR and MALDI-TOF mass spectrometry.

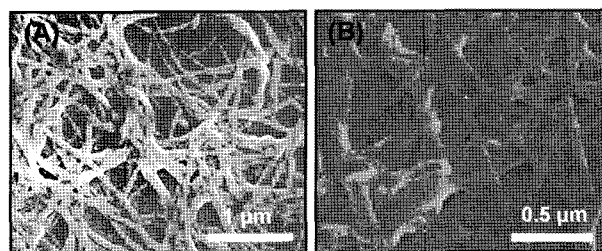
In our previous attempt of stabilizing the self-assembled structure of the dendrons,<sup>12</sup> we observed that the ordering of peripheral diacetylene-containing chains in the hydrophobic domain of the self-assembled structures plays a crucial role in the photopolymerization of diacetylene moieties. In order to induce a long-range photopolymerization of diacetylene units, the topological requirements have to be satisfied by crystalline ordering of the alkyl chains. Higher efficiency in photopolymerization of diacetylene units was achieved

from the lamellar platelet and the bilayer membrane of the vesicles in which the peripheral alkyl chains reside in an ordered fashion.<sup>12</sup>

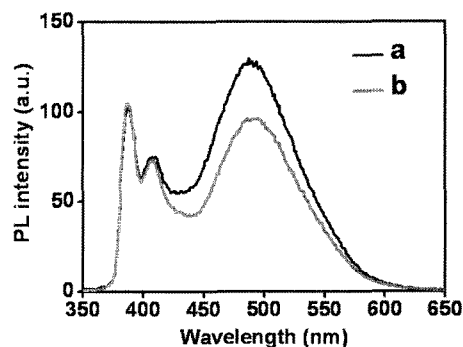
When the saturated hydrocarbons such as dodecyl chains were used as the peripheral group, a variety of second generation amide dendrons including the one with a focal pyrene moiety self-assemble into vesicles in aqueous phase.<sup>9-11,14-17</sup> The self-assembled vesicle transforms into the CD-covered nanotube upon CD complexation on the focal pyrene unit.<sup>11</sup> We expected that dendron **7** might also self-assemble into vesicle in water in a fashion similar to the self-assembly of the amide dendrons with saturated alkyl chains as peripheral groups. Dendron **7** was dispersed in water (10 mL) by slowly adding the THF solution of **7** (1 mg of **7** in 1 mL of THF). After 1 h of gentle stirring of the aqueous solution, THF was evaporated. However, the scanning electron microscopy (SEM) images of the self-aggregate of **7** in aqueous solution revealed a densely packed nanofiber network (Figure 1). The fibrous structures turned out to be bundles of thinner fibers.

The extensive  $\pi-\pi$  interaction between the focal pyrene groups in the self-aggregates was also identified by fluorescence measurements. We observed a broad fluorescence emission peak at ca. 480 nm in Figure 2, which is an indication of excimer formation of the focal pyrenes in the fibrous aggregate. This result suggests that the majority of the focal pyrenes are pre-associated within a close proximity as the dendron building blocks are stacked in a cylindrical aggregate.

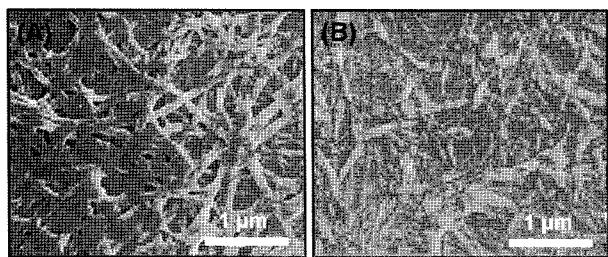
In order to check the possibility of transforming the self-



**Figure 1.** SEM images of the fibrous assembly of dendron **7** formed in water.



**Figure 2.** Fluorescence emission spectra of the aqueous micellar solution of **7** (a) and **7**/ $\beta$ -CD (b).



**Figure 3.** SEM images of the self-aggregate of **7**/ $\beta$ -CD complex (A) and **5** (B) obtained in water.

assembled structure of **7** via the host-guest complexation between pyrene and  $\beta$ -CD, we prepared the aqueous solutions of **7**/CD with various molar ratios of **7** to  $\beta$ -CD. Even with a 10 fold excess of  $\beta$ -CD to **7**, however, the fibrous self-aggregate did not undergo transformation of the morphology (Figure 3(A)). The inclusion of the focal pyrene into the hydrophobic cavity of CD prevents the included pyrene moiety from participating in excimer formation.<sup>11</sup> As shown in Figure 2, the excimer emission decreased upon addition of CD into the micellar solution of **7**, possibly because only a fraction of pyrenes on the exposed surface of fibrous bundles could be included in CD due to the extensive bundle formation. The remaining pyrene units within the bundles of the fibrous aggregates still exhibited the excimer emission at ca. 480 nm as shown in Figure 2.

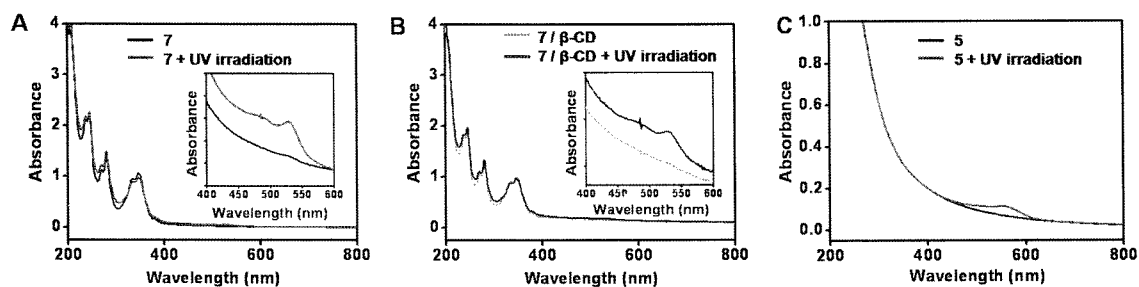
The photopolymerization of the diacetylene units of the dendrons in their self-aggregate state was carried out by irradiating the micellar solution of the dendrons with the UV light (500 W mercury lamp). Upon irradiation for 5 min at 0 °C, the solutions changed to very light red color, suggesting the appearance of the conjugated ene-yne species through a short range photopolymerization. The UV-vis spectra of the micellar solutions of **7** and **7**/ $\beta$ -CD after irradiation exhibited a very weak absorption at 528 nm, which is a characteristic absorption band for the formation of very short conjugated ene-yne bridges (Figures 4(A) and 4(B)). Prolonged UV irradiation on the sample also provided very similar UV-vis spectra without further increase of the absorption. The morphology of the self-assembled fibrous aggregates was not noticeably changed even after prolonged

UV irradiation. These results suggested that the degree of the photopolymerization of the diacetylene units in the fibrous aggregates was very low possibly because the diacetylene peripheries of the dendron may adopt an amorphous state when aggregated as a hydrophobic core. The lack of crystalline order of the hydrophobic alkyl chains in the core of the nanofibers has been observed from the peptide amphiphiles with oligopeptide head group and C-16 single tail, and the amorphous nature of the core of the nanofiber was theoretically described.<sup>8</sup>

Unlike the long fibrous aggregate of **7**, dendron **5** formed fibrous aggregates with much shorter aspect ratio in water, as shown in Figure 3(B). We are currently investigating why the nanofiber is favored over other possible nanostructures with the amide dendrons which contain C-16 diacetylene periphery. Figure 4(C) showed the increased absorption at 580 nm from the solution of **5** after UV irradiation compared to the absorption from the solutions of **7** and **7**/ $\beta$ -CD.

## Conclusions

We have synthesized the amide dendrons with diacetylene-containing periphery and the focal pyrene moiety to investigate their self-organization behavior in aqueous phase. We investigated the effect of the assembled structure of the dendron on the polymerizability of the peripheral diacetylene moiety and the possibility of the supramolecular transformation due to host-guest interactions between the dendron and  $\beta$ -CD. The second generation dendron with a focal pyrene group self-assembled into the fibrous aggregates in water. We observed a low degree of polymerization of diacetylene units upon photopolymerization from the fibrous aggregates possibly due to the amorphous nature of the hydrophobic core. After addition of  $\beta$ -CD into the aqueous solution of dendron **7**, only a fraction of pyrenes of fibrous bundles could be included in  $\beta$ -CDs with maintaining a fibrous structure. We are currently carrying out a comprehensive study to understand the detailed mechanism of formation of different supramolecular structures with the modified amide dendrons and their supramolecular transformation so that we can provide a clear scope of the functional nanostructures which can be derived from self-



**Figure 4.** UV-Vis spectra of before and after photopolymerization of the micelles of **7** (A), **7**/ $\beta$ -CD (B) and **5** (C).

assembly of the amide dendrons.

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**Supporting Information:** Materials and the experimental details for fluorescence measurements, UV-VIS absorption measurements, and SEM analysis. The materials are available via the Internet at <http://www.polymer.or.kr>.

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