

## Supramolecular Assembly of Amide Dendrons

Chulhee Kim,\* Kyoung Taek Kim, and Youngkyu Chang

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

Hyun Hoon Song, Tai-Yon Cho, and Hye-Jin Jeon

Department of Polymer Science and Engineering  
Hannam University, Daejeon 300-791, Korea

Received February 18, 2001

Revised Manuscript Received April 10, 2001

Recently, self-assembly of dendritic molecules has been of great interest to create functional materials with nanoscale supramolecular structures.<sup>1</sup> In particular, self-aggregation of dendrons into supramolecular assemblies has been highlighted by Percec's discovery of self-assembling dendrons in a thermotropic fashion and by Newkome's results on the self-assembly characteristics of the bola-form of "arborols" in aqueous phases.<sup>2,3</sup> Recently, Aida et al. reported the gel formation of peptide-core poly(benzyl ether) dendrons in organic solvents.<sup>4</sup>

In our recent research efforts, special emphasis has been placed on the elucidation of structural driving forces in the self-assembly of dendritic molecules. Here we report the self-assembly characteristics of amide dendrons in organic media. The key structural elements of the amide dendrons in this study consist of amide branches for hydrogen bonding, carboxyl functionality at the focal point, and alkyl tails for the stabilization of assembled structures via van der Waals interactions. The amide dendrons (Figure 1) were synthesized via a convergent pathway.<sup>5</sup> For the synthesis of first generation amide dendron (**1**), lauric acid was treated with 1,1'-carbonyldiimidazole (CDI), and subsequently reacted with *N*-(3-aminopropyl)-1,3-propanediamine to generate a secondary amine at the focal point, which was then reacted with succinic anhydride to yield a carboxyl group at the focal point. The identical procedure was repeated for the preparation of the second generation dendron, **2**.<sup>6</sup> The dendrons formed self-aggregates in

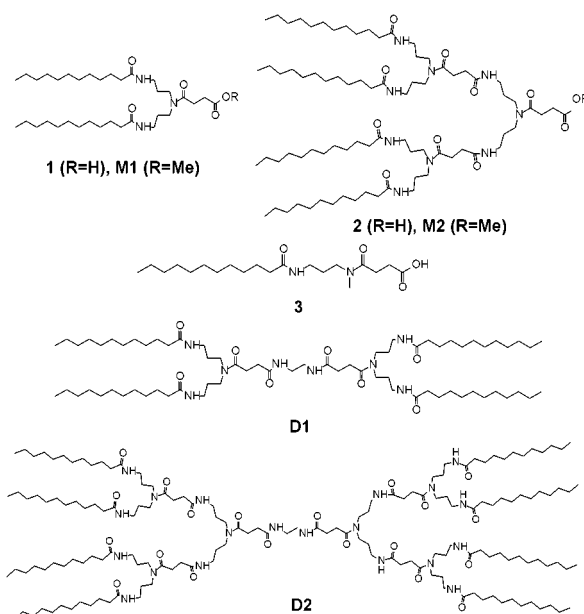


Figure 1. Amide dendrons, linear analogue and dimer forms of dendrons.

organic solvents such as  $\text{CHCl}_3$  and THF.<sup>7</sup> The dendron **1** formed a translucent immobile gel in  $\text{CHCl}_3$  and THF.<sup>8</sup> On the other hand, the second generation dendron (**2**) exhibited a transparent gel in  $\text{CHCl}_3$  and THF. The formation of self-assembled gels was thermoreversible in organic media. For example, the gels in  $\text{CHCl}_3$  redissolve at 58–59 °C for **1** and 42–43 °C for **2**. After cooling to room temperature, all the solutions turned into immobile gels after a certain period of time.

The formation of self-assembled gels must be associated with the structural characteristics of the amide dendrons as described previously. One of the driving forces for self-assembly of dendrons would be the intermolecular hydrogen bonding between the amide groups in the dendritic structure. Addition of a drop of methanol into the gel of dendrons **1** and **2** in  $\text{CHCl}_3$  gives rise to clear solutions, confirming that the intermolecular hydrogen bonding between amide groups is one of the main driving forces for the gel formation in  $\text{CHCl}_3$ . From FT-IR study, for example, the second generation dendron **2** in  $\text{CHCl}_3$  solution (10 mg/mL) showed amide I, II, and NH-stretching bands at 1654, 1541, and 3334  $\text{cm}^{-1}$ , respectively. However, these bands were shifted in the dried gel state to 1639, 1553, and 3308  $\text{cm}^{-1}$ , respectively, which corroborated the presence of hydrogen bonding of the amide groups between dendrons.<sup>4,9</sup> In addition, the dendritic architecture is also critical in forming the self-assembled gel. For example, the linear model compound for the dendrons, **3**, did not form a gel in chloroform but was totally soluble.

The structure of the gels of **1** and **2** formed in  $\text{CHCl}_3$  were investigated by using transmission electron microscopy (TEM) and X-ray diffraction (XRD) techniques. The TEM image of the gel from compound **1** (Figure 2A) showed a thin platelike morphology, and XRD results showed a lamellar structure with

(7) Typical procedure: A pulverized sample of **2** (80 mg) was placed in a vial and  $\text{CHCl}_3$  (1 mL) was added. Upon heating to 50 °C, the mixture turned to a transparent solution. After 36 h at room temperature, a transparent immobile gel formed.

(8) (a) Terech, P.; Weiss, R. G. *Chem. Rev.* **1997**, *97*, 3133–3159. (b) Esch, J. v.; Feringa, B. L. *Angew. Chem., Int. Ed.* **2000**, *39*, 2263–2266.

(9) (a) Loos, M. d.; Esch, J. v.; Stokroos, I.; Kellogg, R. M.; Feringa, B. L. *J. Am. Chem. Soc.* **1997**, *119*, 12675–12676. (b) Esch, J. v.; Feyter, S. D.; Kellogg, R. M.; Schryver, F. D.; Feringa, B. L. *Chem. Eur. J.* **1997**, *3*, 1238–1243. (c) Hanabusa, K.; Yamada, M.; Kimura, M.; Shirai, H. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1949–1951. (d) FT-IR spectra of consolidated wet gel and dry gel exhibited identical characteristic bands.

\* To whom correspondence should be addressed. E-mail: chk@inha.ac.kr.

(1) (a) Zeng, F.; Zimmerman, S. C. *Chem. Rev.* **1997**, *97*, 1681–1712. (b) Emerick, T.; Fréchet, J. M. J. *Curr. Opin. Colloid Interface Sci.* **1999**, *4*, 15–23. (c) Genderen, M. H.; Meijer, E. W. *Supramolecular Materials and Technologies*; Wiley: New York, 1999; pp 47–88. (d) Tomalia, D. A.; Majoros, I. *Supramolecular Polymers*; Marcel Dekker: New York, 2000; pp 359–434. (e) Newkome, G. R.; He, H.; Moorefield, C. N. *Chem. Rev.* **1999**, *99*, 1689–1746. (f) Tsukruk, V. V. *Adv. Mater.* **1998**, *10*, 253–257.

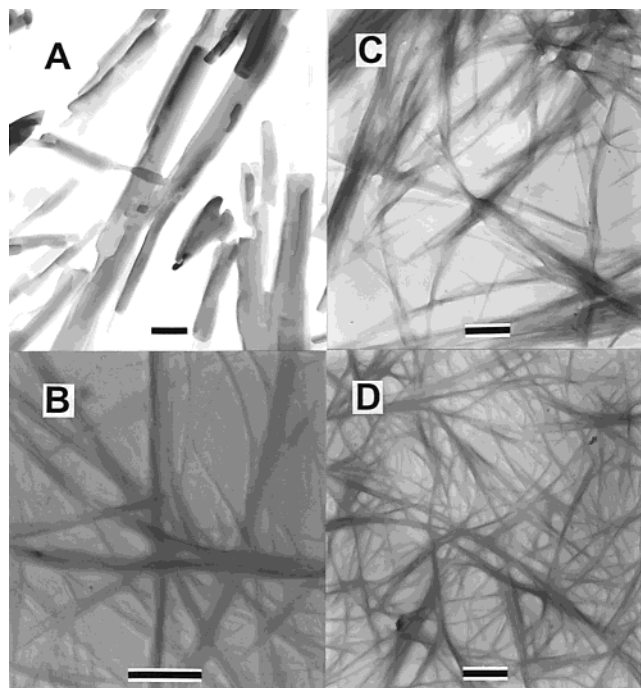
(2) (a) Percec, V.; Johansson, G.; Heck, J.; Ungar, G.; Batty, S. V. *J. Chem. Soc., Perkin Trans. 1* **1993**, 1411–1420. (b) Percec, V.; Johansson, G.; Ungar, G.; Zhou, J. *J. Am. Chem. Soc.* **1996**, *118*, 9855–9866. (c) Balagurusamy, V. S. K.; Ungar, G.; Percec, V.; Johansson, G. *J. Am. Chem. Soc.* **1997**, *119*, 1539–1555. (d) Hudson, S. D.; Jung, H.-T.; Percec, V.; Cho, W.-D.; Johansson, G.; Ungar, G.; Balagurusamy, V. S. K. *Science* **1997**, *278*, 449–452. (e) Percec, V.; Cho, W.-D.; Mosier, P. E.; Ungar, G.; Yearley, D. J. P. *J. Am. Chem. Soc.* **1998**, *120*, 11061–11070.

(3) (a) Newkome, G. R.; Baker, G. R.; Saunders, M. J.; Russo, P. S.; Gupta, V. K.; Yao, Z.; Miller, J. E.; Bouillion, K. *J. Chem. Soc., Chem. Commun.* **1986**, 752–753. (b) Newkome, G. R.; Baker, G. R.; Arai, S.; Saunders, M. J.; Russo, P. S.; Theriot, K. J.; Moorefield, C. N.; Rogers, L. E.; Miller, J. E.; Lieux, T. R.; Murry, M. E.; Phillips, B.; Pascal, L. *J. Am. Chem. Soc.* **1990**, *112*, 8458–8465. (c) Newkome, G. R.; Moorefield, C. N.; Baker, G. R.; Behera, R. K.; Escamillia, G. H.; Sanders, M. J. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 917–919.

(4) Jang, W.-D.; Jiang, D. L.; Aida, T. *J. Am. Chem. Soc.* **2000**, *122*, 3232–3233.

(5) Hawker, C. G.; Fréchet, J. M. J. *J. Am. Chem. Soc.* **1990**, *112*, 7638–7647.

(6) (a) Rannard, S. P.; Davis, N. J. PCT/GB96/03189. (b) Rannard, S. P.; Davis, N. J. *Polym. Mater. Sci. Eng.* **1997**, *77*, 160–161. (c) Rannard, S. P.; Davis, N. J. *Org. Lett.* **2000**, *2*, 2117–2120. (d) Rannard, S. P.; Davis, N. J. *Org. Lett.* **1999**, *1*, 933–936. (e) For similar structure, see: Linares, M.; Roy, R. *Chem. Commun.* **1997**, 2119.



**Figure 2.** TEM images of aggregates of **1** (a), **2** (b), **D1** (c), and **D2** (d). Bars represent 500 nm, respectively.

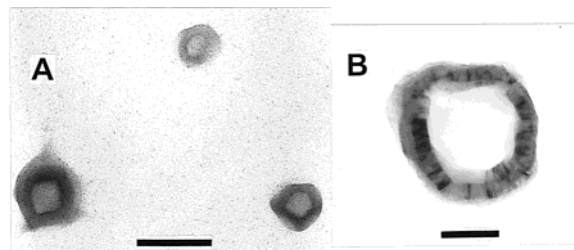
interlamellar spacing of 48 Å. Considering the molecular dimension of **1** (26 Å),<sup>10</sup> each lamellar layer consists of two dendron molecules of **1** which probably are hydrogen bonded at the focal carboxyl groups. The gel of **2**, on the other hand, exhibited a fibrous morphology (Figure 2B), whose diameter ranged from 30 to 100 nm. The XRD results, in this case, showed a hexagonal columnar structure with the column diameter of 61 Å. Therefore, considering the molecular dimension of dendron **2** (36 Å), it is most likely that the column was also formed by stacking the dimeric species of dendron **2**, where the hydrogen bonded carboxyl groups are in the middle of the column with alkyl chains stretched outward. TEM images of fibrous rods with fine fibers indicate that the fibers are bundles of such columnar units. The results of TEM and XRD strongly suggest that the dimeric forms of **1** and **2**, induced by hydrogen bonding at the focal carboxyl groups, are the primary building blocks in the self-aggregation process. Indeed, transformation of the carboxyl groups of **1** and **2** to methyl ester (**M1** and **M2**) did not induce gelation in CHCl<sub>3</sub>, demonstrating that the carboxyl groups at the focal point of the amide dendrons play the key role in the self-assembly. The results also suggest that covalently bridged dendron dimers **D1** and **D2** should be able to form similar self-assembled supramolecular structures. Model dendron dimers **D1** and **D2** were synthesized by coupling **1** and **2** with ethylene diamine by using CDI as a coupling agent. These dimeric species, **D1** and **D2**, also formed thermoreversible gels in CHCl<sub>3</sub> (50 mg/mL). The gels in CHCl<sub>3</sub> dissolve at 60–61 °C for **D1** and 44–45 °C for **D2**. At room temperature, immobile gels formed after a certain period of time. The TEM image of **D1** gel (Figure 2C) showed a flattened fibrous

(10) Stretched molecular dimensions of the dendrons were obtained by using Cerius<sup>2</sup> on a Silicon Graphics O<sub>2</sub> workstation.

**Table 1.** Summary of Results from XRD and Molecular Modeling

| compd     | $d$ (Å) <sup>a</sup> | molecular dimension (Å) <sup>b</sup> | lattice form <sup>a</sup> |
|-----------|----------------------|--------------------------------------|---------------------------|
| <b>1</b>  | 48 <sup>c</sup>      | 26                                   | lamella                   |
| <b>D1</b> | 47 <sup>c</sup>      | 48                                   | lamella                   |
| <b>2</b>  | 61 <sup>d</sup>      | 36                                   | hexagonal                 |
| <b>D2</b> | 60 <sup>d</sup>      | 73                                   | hexagonal                 |

<sup>a</sup> Measured from XRD. <sup>b</sup> Measured from molecular modeling. <sup>c</sup> Inter-lamellar spacing. <sup>d</sup> Column diameter.



**Figure 3.** TEM images of vesicle structures of **M2** in water. Bars represent 200 nm (A) and 50 nm (B), respectively.

structure and the XRD pattern revealed a lamellar structure with interlamellar spacing of 47 Å, which approximately corresponds to the molecular dimension of **D1**. The structure of the self-assembled aggregate of **D2**, on the other hand, exhibited fibrous rods with fine fibers (Figure 2D) and columnar hexagonal structure with the column diameter of 60 Å. The results support the hypothesis that the dimeric species of **1** and **2** are the primary building blocks in the self-assembly process.

It is also interesting to note that the amphiphilic **M2** forms vesicular assemblies in the aqueous phase. The average diameter of the vesicle determined by TEM and dynamic light scattering was about 160 nm. The assembly characteristics of higher generation dendrons are being investigated for comprehensive understanding of supramolecular aggregation of these types of amide dendrons.

In summary, the amide dendrons, **1** and **2**, with focal carboxyl functionality and peripheral alkyl tails form supramolecular assemblies in organic media. Several structural factors, such as formation of hydrogen bonded dimer species through focal carboxyl units, hydrogen bonding of amide groups, and van der Waals interaction of alkyl tails, played key roles in building the supramolecular structures ranging from lamella to columnar hexagonal arrays (Table 1). We also have demonstrated that the covalently coupled dendron dimer species, **D1** and **D2**, formed self-assembled supramolecular structures analogous to those of **1** and **2**. The self-assembly characteristics of the amide dendrons in organic media could provide a new methodology for the construction of supramolecular nanostructured functional materials.

**Acknowledgment.** This work was supported by HOMRC. C.K. also thanks Inha Research Fund (2000) for support. The X-ray diffraction was performed at the Pohang Accelerator Laboratory.

**Supporting Information Available:** Spectral characterization and XRD details for **1**, **2**, **3**, **M1**, **M2**, **D1**, and **D2** (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

JA015687H