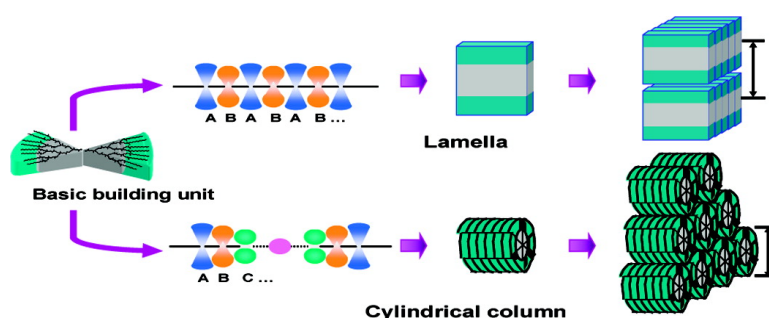## Research Article

Supramolecular Ordering of Amide Dendrons in Lyotropic and Thermotropic Conditions

Hye-Jin Jeon, Min Kwan Kang, Chiyoung Park, Kyoung Taek
Kim, Ji Young Chang, Chulhee Kim, and Hyun Hoon Song

More About This Article

Additional resources and features associated with this article are available within the HTML version:

- Supporting Information
- Access to high resolution figures
- Links to articles and content related to this article
- Copyright permission to reproduce figures and/or text from this article

View the Full Text HTML

Supramolecular Ordering of Amide Dendrons in Lyotropic and Thermotropic Conditions

Hye-Jin Jeon,[†] Min Kwan Kang,[†] Chiyoung Park,[‡] Kyoung Taek Kim,[‡] Ji Young Chang,[§] Chulhee Kim,*,[‡] and Hyun Hoon Song*,[†]

Department of Advanced Materials, Hannam University, Daejeon, Korea, Department of Polymer Science and Engineering, Inha University, Incheon, Korea, and College of Materials Science and Engineering, Seoul National University, Seoul, Korea

Self-assembled superstructures of amide dendrons, from first to third generation including monodendrons and covalently linked dimers, were extensively examined, and the supramolecular ordering processes in thermotropic and lyotropic conditions were compared. The superstructures as determined by X-ray diffraction and DSC revealed that the first and second generation dendrons showed nearly identical superstructures regardless of the assembly conditions. But, the third generation dendrons showed a more sensitive self-organizing behavior. The structure obtained from the gel state was lamellar with a more extended conformation, while the structure from the melt state revealed the columnar superstructures of contracted branches. The superstructure formed from the gel state also showed a structural change upon raising the temperature and assumed a structure similar to the thermotropically driven one, implying that the structure formed from the gel is thermodynamically unstable. The formation of lamellar- or cylinder-type superstructures from amide dendrons was primarily dependent on the shape of dendrons, which is associated with the branch size (generation) and the surrounding conditions.

Introduction

A material having an ordered structure in the nanometer scale provides unique physical and chemical properties. Among many techniques to fabricate nanostructured materials, one approach is based on the self-assembling nature of large molecules such as linear polymers or dendrimers. In particular, perfect monodisperse dendrimers and their self-assembling process have emerged as one of the main research area in such efforts.[1–7]

Self-assembly of dendron building blocks via secondary interactions such as hydrogen bonding, ionic interactions, hydrophilic properties, π–π interactions, and metal–ligand coordination has been reported by several researchers.[8–17] It has been demonstrated that the self-assembly of dendrons is a unique and useful method to create well-defined superstructures at the nanometer scale. These researchers also reported that the self-assembly of dendrons results in different superstructures depending on the assembly conditions including generation, molecular structures, solvent (or solubility), and temperature.[18–23] For example, Percec and co-workers published the self-assembly in which flat tapered and conical monodendrons generate cylindrical or spherical supramolecular structures depending on the size and shape of the monodendrons.[9–11] Self-organization behavior of some dendritic bolaamphiphiles in the aqueous phase was also elucidated by Newkome and co-workers.[13,14] Newkome reported that the introduction of rigidity or interactive internal functionality plays a critical role in the aggregation process for stacking an orthogonal or ordered helical array.[24]

Variation of superstructure formation via self-assembly is not restricted in dendrimers. Variations have been reported in phase transitions of block copolymers including rod–coil block copolymers and the self-assembly of amphiphilic materials.[25–30]

* To whom correspondence should be addressed. E-mail: (C.K.) chk@inha.ac.kr or (H.H.S.) songhh@hnu.kr.

† Hannam University.

‡ Inha University.

§ Seoul National University.

(1) Fréchet, J. M. J. *Proc. Natl. Acad. Sci. U.S.A.* **2002**, *99*, 4787.
(2) Zimmerman, S. C.; Lawless, L. J. *Top. Curr. Chem.* **2001**, *217*, 95.
(3) Emrick, T.; Fréchet, J. M. J. *Curr. Opin. Colloid Interface Sci.* **1999**, *4*, 15.
(4) Genderen, M. H.; Meijer, E. W. *Supramolecular Materials and Technologies*; Wiley: New York, 1999; pp 47–88.
(5) Newkome, G. R.; Moorefield, C. N. *Chem. Rev.* **1999**, *99*, 1689.
(6) Zeng, F.; Zimmerman, S. C. *Chem. Rev.* **1997**, *97*, 1681.
(7) Hecht, S.; Fréchet, J. M. J. *Angew. Chem., Int. Ed.* **2001**, *40*, 74.
(8) Percec, V.; Glodde, M.; Bera, T. K.; Miura, Y.; Shiyanovskaya, I.; Singer, K. D.; Balagurusamy, V. S. K.; Heiney, P. A.; Schnell, I.; Rapp, A.; Spiess, H.-W.; Hudson, S. D.; Duan, H. *Nature (London, U.K.)* **2002**, *417*, 384.
(9) Hudson, S. D.; Jung, H.-T.; Percec, V.; Cho, W.-D.; Johansson, G.; Ungar, G.; Balagurusamy, V. S. K. *Science (Washington, DC, U.S.)* **1997**, *278*, 449.
(10) Percec, V.; Johansson, G.; Ungar, G.; Zhou, J. *J. Am. Chem. Soc.* **1996**, *118*, 9855.
(11) Balagurusamy, V. S. K.; Ungar, G.; Percec, V.; Johansson, G. *J. Am. Chem. Soc.* **1997**, *119*, 1539.
(12) Percec, V.; Cho, W.-D.; Möller, M.; Prokhorova, S. A.; Ungar, G.; Yeardley, D. J. P. *J. Am. Chem. Soc.* **2000**, *122*, 4249.
(13) Newkome, G. R.; Baker, G. R.; Saunders, M. J.; Russo, P. S.; Gupta, V. K.; Yao, Z.; Miller, J. E.; Bouilion, K. *J. Chem. Soc., Chem. Commun.* **1986**, 752.
(14) Newkome, G. R.; Moorfield, C. N.; Baker, G. R.; Behera, R. K.; Escamillia, G. H.; Saunders, M. J. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 917.
(15) Zimmerman, S. C.; Zeng, F.; Reichert, D. E. C.; Kolotuchin, S. V. *Science (Washington, DC, U.S.)* **1996**, *271*, 1095.
(16) Ungar, G.; Liu, Y.; Zeng, X.; Percec, V.; Cho, W.-D. *Science (Washington, DC, U.S.)* **2003**, *299*, 1208.
(17) Zubarev, E. R.; Parlle, M. U.; Sone, E. D.; Stupp, S. I. *J. Am. Chem. Soc.* **2001**, *123*, 4105.
(18) Isaacs, L.; Chin, D. N.; Bowden, N.; Xia, Y.; Whitesides, G. M.; Reinhoudt, D. N. *Supramolecular Materials and Technologies*; Wiley: New York, 1999; pp 1–23.
(19) Percec, V.; Cho, W.-D.; Ungar, G.; Yeardley, D. J. P. *J. Am. Chem. Soc.* **2001**, *123*, 1301.
(20) Percec, V.; Cho, W.-D.; Mosier, P. E.; Ungar, G.; Yeardley, D. J. P. *J. Am. Chem. Soc.* **1998**, *120*, 11061.
(21) Percec, V.; Cho, W.-D.; Ungar, G.; Yeardley, D. J. P. *Angew. Chem., Int. Ed.* **2000**, *39*, 1597.
(22) Percec, V.; Rudick, J. G.; Peterca, M.; Wagner, M.; Obata, M.; Mitchell, C. M.; Cho, W.-D.; Balagurusamy, V. S. K.; Heiney, P. A. *J. Am. Chem. Soc.* **2005**, *127*, 15257.
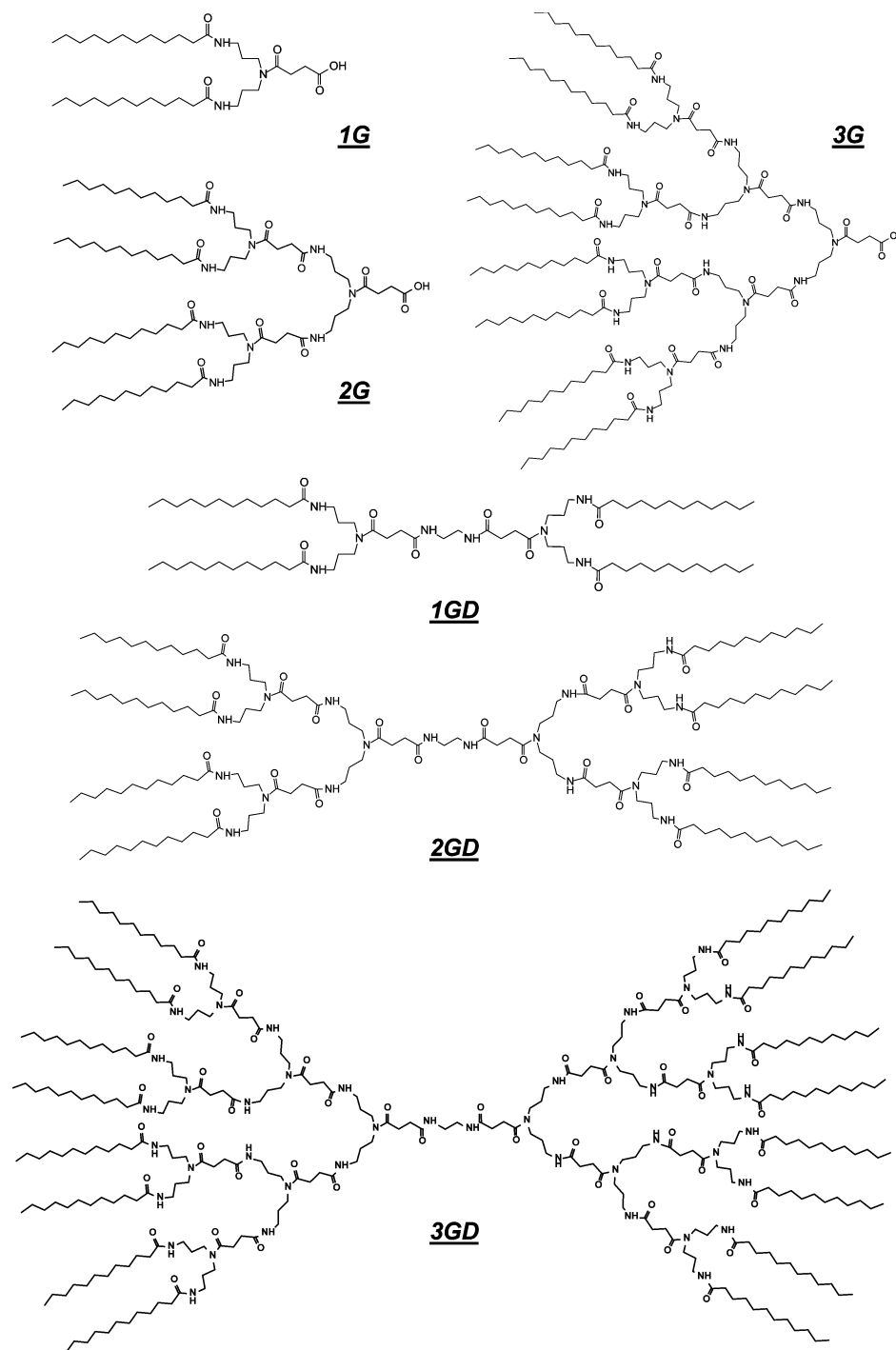(23) Peterca, M.; Percec, V.; Dulcey, A. E.; Nummelin, S.; Korey, S.; Ilies, M.; Heiney, P. A. *J. Am. Chem. Soc.* **2006**, *128*, 6713.
(24) Newkome, G. R.; Lin, X.; Yaxiong, C.; Escamilla, G. H. *J. Org. Chem.* **1993**, *58*, 3123.
(25) Lee, M.; Cho, B.-K.; Ihn, K. J.; Lee, W.-K.; Oh, N.-K.; Zin, W.-C. *J. Am. Chem. Soc.* **2001**, *123*, 4647.
(26) Vaidya, N. Y.; Han, C. D.; Kim, D.; Sakamoto, N.; Hashimoto, T. *Macromolecules* **2001**, *34*, 222.
(27) Lee, S.-H.; Char, K.; Kim, G. *Macromolecules* **2000**, *33*, 7072.

Figure 1. Chemical structures of amide dendrons (*n*G, no. of generations and D, dimeric dendrons).

Important factors to form various nanostructure are molecular size and shape, fraction or ratio between blocks, nature of solvents, concentration, temperature, etc.

In our recent works, we also reported that amide based dendritic molecules form superstructures via self-assembly in various conditions.[31−34] The key structural elements in the self-assembly of the amide dendron were 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. Our results demonstrated that the amide dendrons form thermoreversible gels through self-organization in organic media and result in the formation of lamella or columnar superstructures in the dry state depending on the structures of the dendron building blocks.[31,32] It was also claimed that formation of the dimer units either by the hydrogen bond at the carboxylic focal point or by the covalent linkage at the focal point was the key structural prerequisite for self-assembly into superstructures.

In this work, we carefully examined the effects of temperature variation on the self-assembly and assembled structures of amide

(28) Sakamoto, N.; Hashimoto, T. *Macromolecules* **1998**, *31*, 8493.
(29) Kimishima, K.; Koga, T.; Hashimoto, T. *Macromolecules* **2000**, *33*, 968.
(30) Hanley, K. J.; Lodge, T. P.; Huang, C.-I. *Macromolecules* **2000**, *33*, 5918.
(31) Kim, C.; Kim, K. T.; Chang, Y.; Song, H. H.; Cho, T.-Y.; Jeon, H.-J. *J. Am. Chem. Soc.* **2001**, *123*, 5586.

(32) Kim, C.; Lee, S. J.; Lee, I. H.; Kim, K. T.; Chang, Y.; Song, H. H.; Jeon, H.-J. *Chem. Mater.* **2003**, *15*, 3638.
(33) Ko, H. S.; Park, C.; Lee, S. M.; Song, H. H.; Kim, C. *Chem. Mater.* **2004**, *16*, 3872.
(34) Park, C.; Choi, K. S.; Song, Y.; Jeon, H.-J.; Song, H. H.; Chang, J. Y.; Kim, C. *Langmuir* **2006**, *22*, 3812.
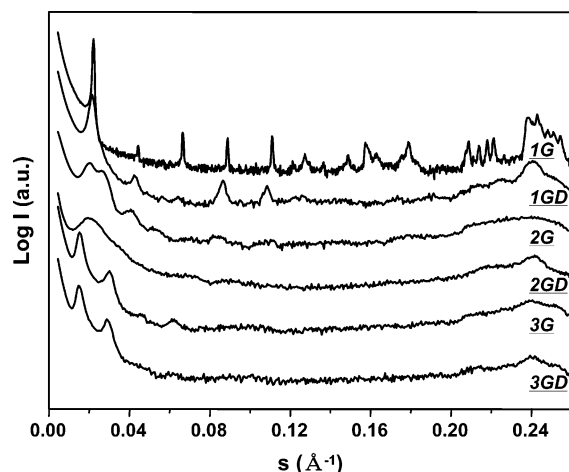
Figure 2. X-ray diffraction patterns of dendrons in the dry gel state at ambient temperature.

dendrons. The results were then compared with those of lyotropic conditions in organic media. In particular, for the detailed structural investigation associated with self-assembly, high resolution and time-resolved X-ray scattering was performed utilizing the intense synchrotron radiation source. DSC was also utilized to provide thermal responses of the self-assembled superstructures.

Experimental Procedures

Materials. The chemical structures of dendrons studied in this work are depicted in Figure 1. Each dendron consists of a carboxylic group at the focal point, amide branches in the middle, and alkyl tails. Synthesis of the dendrons has been described elsewhere.[31,35] The solvent utilized for the self-assembly of dendrons into the gel state was chloroform for the first and second generation dendrons and dichloromethane for the third generation ones.

Characterization. DSC (TA 2910) was used for the examination of thermal behavior of superstructures derived either from the gel state or from the melt state. For the DSC measurement, samples of ~3 mg were heated at 3 °C/min under a nitrogen atmosphere.

High resolution and time-resolved X-ray scattering was carried out at the Pohang Accelerator Laboratory and was operated at 2.0 GeV and 120 mA. The scattering intensities were measured using the diffractometer at the 3C2 beamline, but for the in situ scattering, a position sensitive area detector was utilized at the 4C2 beamline. Aluminum foil (12 μm thick) was used for the window material of the sample holder instead of using the ordinary Kapton film. This was done to eliminate the scattering hump arising from the Kapton film, which overlaps with the scattering peak of the dendrons. For X-ray scattering at an elevated temperature, the sample was heated to a predetermined temperature based on the DSC thermogram, and the temperature was maintained for 5 min to achieve temperature equilibration before the measurement. The scattering intensities were measured at diffraction angles of 0.4−23° with 0.05 and 0.02° intervals that cover both small angles and wide angles simultaneously. The exposure time was 1 s at each interval.

Results and Discussion

Superstructures of Amide Dendrons from Gel State. In Figure 2, X-ray diffraction patterns of dry gels taken at an ambient temperature are plotted. The plots reveal that the dendrons of first generation (1G and 1GD) and third generation (3G and 3GD) form lamellar superstructures, while those of second generation (2G and 2GD) form cylindrical columns of hexagonal packing. Here, 1G stands for first generation monodendron and 1GD for the first generation dimer. The results of first generation

and second generation are consistent with our previous reports.[31] The lamellar spacings and cylinder diameters derived from the main diffraction peak are summarized in Table 1. The monodendrons show somewhat higher packing order than the dimeric units. However, the monodendrons and dimers share the same superstructures with similar sizes, confirming that the dimer units linked either by covalent bond or by hydrogen bond at the focal carboxylic group are the basic building blocks for self-assembly as has been reported earlier.[31−34] The results also suggest that the formation of symmetrical unit is critically required for the molecules to organize into ordered superstructures.

The formation of self-assembled superstructures is associated with the structural characteristics of the dendrons and their interactions with the surrounding molecules. As already discussed in the previous section, the driving forces of self-assembly of these amide dendrons are intermolecular hydrogen bonds between the amide groups and at the focal carboxylic group as well as the van der Waals interactions of the alkyl tails. For the first generation (1G and 1GD), the dendrons are relatively small with two amide branches. The steric hindrance is, therefore, minimal, and the low viscosity allows for easy packing. As can be noted in Table 1, the first generation dendrons form the lamellar structure with a nearly extended conformation ($l/l_0 = \sim 0.9$). The X-ray patterns of first generation dendrons also exhibit many reflections at high angles, demonstrating that the crystalline order exists within the lamellar domains. The dendrons of the third generation (3G and 3GD) also show a lamellar structure but with a much less ordered feature. The third generation dendrons are large and bulky, and the overall molecular shape becomes globular. The value $l/l_0 = \sim 0.7$ shown in Table 1 suggests the contracted form of the dendrons in the superstructure formation.

Formation of Lamellar- or Cylinder-Type Superstructures. We have seen that first and third generation dendrons form the lamellar-type superstructure, while the second generation dendrons assemble into columnar cylinders. As was emphasized previously, the formation of the dimer unit is an essential process for the self-assembly of monodendrons into an ordered super-structure. The chemical structures of the dendrons depicted in Figure 1 reveal that the dimer unit takes a dumbbell shape, where the central linkage core has a relatively low density. We can envisage that this causes some frustration in the packing of the molecules side by side, which becomes more distinct with the increase of generation. For the dimers to pack efficiently, dimer units must cross-pack one another. The cross-packed units must stack side-by-side along the long axis to yield a lamellar structure. On the other hand, for cylindrical column formation, each dumbbell-shaped dimer unit must cross-pack continuously along the long (cylinder) axis, resulting in a spiral structure and thus a cylindrical superstructure. The assembly processes are sche-matically described in Figure 3.

With regard to forming the lamellar or cylindrical super-structure, it is worth mentioning that the gelation time of the third generation is rather shorter than the second generation dendrons. A high number of branches and thus hydrogen bonding sites may promote the gelation process and the assembly process. The second generation, on the other hand, taking the molecular shape between the first and the third generation, shows the slowest gelation time among the three generations. The number of branches and, therefore, the hydrogen bonding sites are higher than those of the first generation but may not be high enough to compensate for the steric hindrance arising from the bulky size. The size and shape of the branch units and their interactions within the surrounding solvents are all important parameters in determining the ordering process.

---

(35) See Supporting Information.

Table 1. Molecular Dimensions of Dendrons and Interdomain Distances of Self-Assembled Superstructures

		1G	1GD	2G	2GD	3G	3GD
	superstructure[a]	L	L	C	C	L	L
	molecular dimension[b] l_0 (Å)	26	53	36	73	45	91
Interdomain distance[c]	l_g (Å)	45	47	57	59	65	67
	l_g/l_0	0.87[d]	0.89	0.79[d]	0.81	0.72[d]	0.74
	l_m (Å)		46	52	53	52	53
	l_m/l_0		0.87	0.71	0.73	0.57	0.58

[a] L, lamella and C, cylinder. [b] Stretched molecular dimension (l_0) of the dendrons was obtained by using a Cerius[2] on a Silicon Graphics O_2 workstation. [c] Interdomain distances (lamellar thickness or cylinder diameter) were derived from the X-ray results; l_g denotes the dimension of gel-state-driven structure and l_m for the melt-induced one. [d] $2l_0$ was used for the calculation of monodendrons (1G, 2G, and 3G).
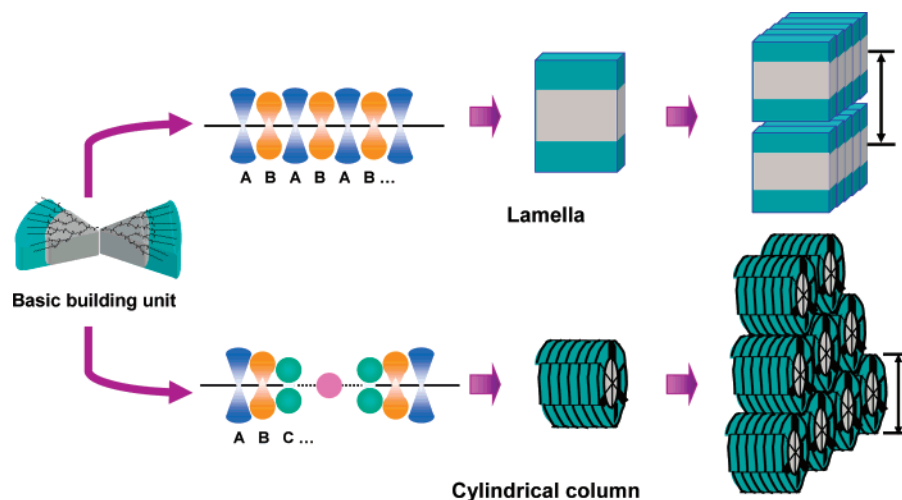
Figure 3. Schematic representation of supramolecular ordering of amide dendrons into lamellae or cylindrical columns.
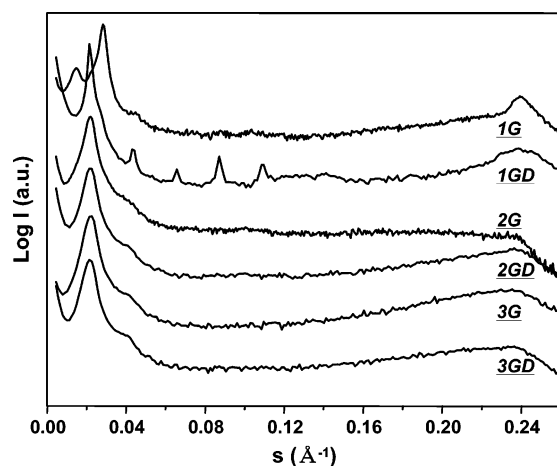
Figure 4. X-ray diffraction patterns of thermally induced superstructures of amide dendrons at ambient temperature.

Thermotropically Induced Superstructures of Amide Dendrons. The dry gels of dendrons having a supramolecular order were raised above the disordering temperature, and a new thermotropically driven structure was obtained upon cooling the dendrons. X-ray scattering patterns of the dendrons taken at ambient temperature are plotted in Figure 4. The first generation dendrons, 1G and 1GD, show similar lamellar patterns to those of the dry gel. When compared with the patterns of the dry gel, the patterns of the first generation dendrons exhibit a broad main peak and a lack of diffraction peaks at high angles, illustrating the reduced packing order both in superstructure and in local structures. In particular, we also further note an extra peak at the very small angles of the 1G pattern. This interesting structure will be discussed in the following section. For the second and third generations, on the other hand, both the monodendron (2G and 3G) and the dimer (2GD and 3GD) show a hexagonally

packed supramolecular order but with a much broader main peak and absence of high order peaks. It is also noted that the dendrons of thermotropically driven structures are more contracted than those of the gel state, which is more distinctive for the third generation dendrons as indicated in Table 1. The reduced packing order and contracted conformation observed in these thermotropically driven structures are associated with the sluggish motion of the dendrons in the crowded melt state. We also emphasize that the third generation dendrons (3G and 3GD) show the superstructure of hexagonally packed cylinders (we recall that the dry gel has shown the lamellar structure). It is very interesting to observe that the third generation dendrons can form either the lamellar structure or the cylinders depending on the assembly conditions. As discussed in the previous section, for the cylindrical superstructure to be formed, the dimeric dendrons must stack with continuous rotation along the cylinder axis. The cylinder-type superstructure appears to be more favored for the contracted dendrons of higher steric hindrance in this crowded environment.

Thermal Effects on Superstructures. Now, we examine the structural change induced upon elevating the temperature for both samples derived from the gel state of the lyotropic environment and from the melt of the thermotropic environment. The former is called the first heating and the latter the second heating, hereafter. X-ray scattering patterns were measured at the predetermined temperatures upon raising the temperature, and the thermal data of DSC in Figure 5 were used as a guideline. Before measuring the X-ray pattern, the predetermined temperature was brought to an equilibrium by maintaining the sample for 5 min at each temperature.

In Figure 6 (1G-1), X-ray patterns of 1G at various temperatures are plotted, while the corresponding DSC thermogram is shown in Figure 5 (1G). The initial lamellar structure is maintained without any marked change until it melts into a disordered liquid. We also note that the primary peak of the superstructure and
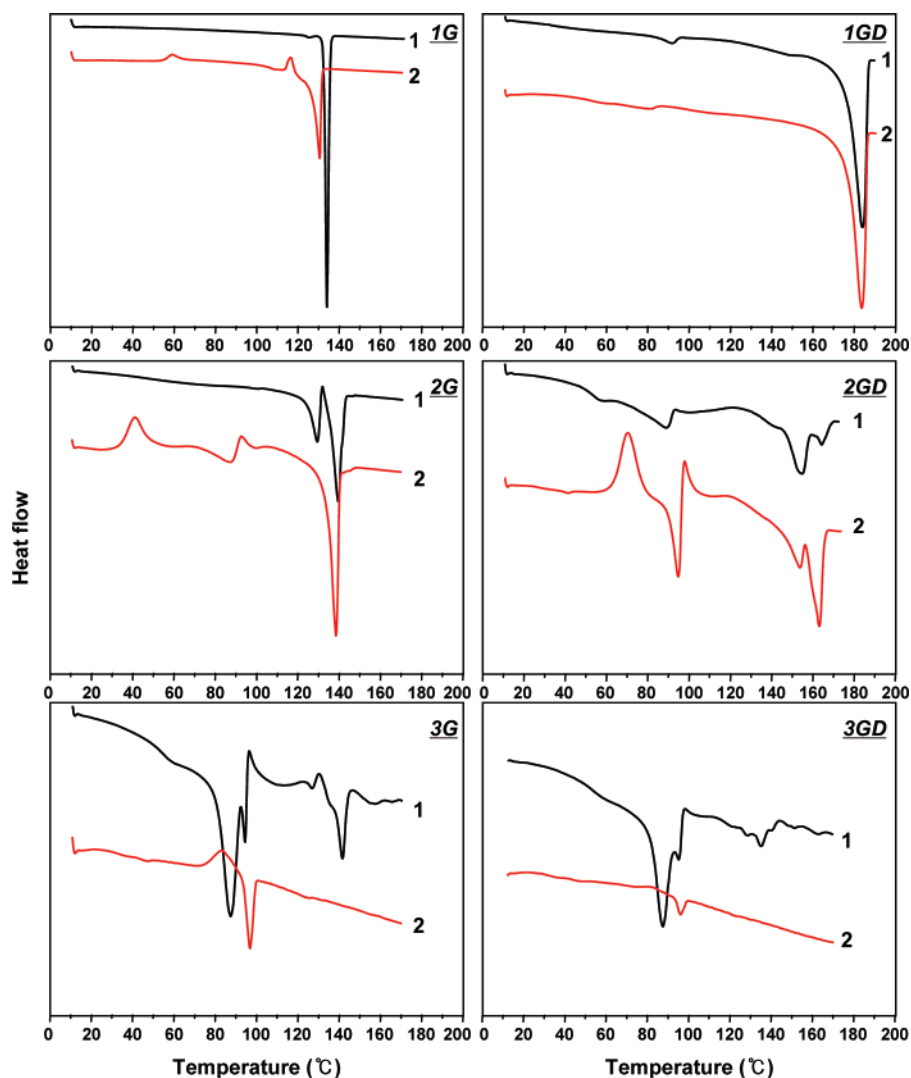
Figure 5. DSC thermograms of dendrons; curve 1 denotes the first heating (heating of dendrons derived from the gel state) and curve 2 the second heating (heating of thermally induced dendrons, exo up).

those of the local order within the superstructure domain disappears nearly simultaneously at temperatures of 109−128 °C. But, in the second heating shown in Figure 6 (1G-2), somewhat different patterns are revealed. Before discussing the temperature effect, we begin with the X-ray patterns of the melt grown sample at room temperature. The X-ray pattern of 1G obtained at room temperature (Figure 6 (1G-2)) reveals the first two peaks located at $s = 0.0144$ and 0.0283 Å^{-1}, which correspond to 70 and 36 Å, respectively. The first peak intensity is much lower than the second peak, and the 70 Å spacing is far beyond the extended length of the dimer unit. It is apparent that the two peaks do not arise from single structural units, in this case the lamellae. The pattern implies that the thermotropically driven structure consists of lamellae of two different layer thicknesses. The population of the lamellae with larger thicknesses is relatively minor. As the temperature is raised, however, the two peaks merge into one that represents a well-ordered lamellar structure with spacing of 41.3 Å. The structure is very similar to that of the dry gel (Figure 2). When increasing the temperature further, the spacing increases to 44. 6 Å with the advent of higher order peaks, illustrating an improvement of the supramolecular packing order.

It is very interesting to observe that two different lamellar units of 70 and 36 Å form when the structure is derived from the disordered melt. We recall that forming the dimer unit is an essential process for the supramolecular ordering and also that the extended molecular length of the dimer unit of 1G is 53 Å (Table 1). In a dilute solution, hydrogen bonding between the carboxylic units at the focal point appears to be preferred over other possible hydrogen bondings between carboxylic group and amide branches, yielding a primary building block of the dimer unit as demonstrated by the structures formed from solution. But, in a melt of a molecularly crowded situation, the structural rearrangement is rather restricted and may not be fast enough to follow the temperature change, allowing hydrogen bonding between carboxylic units and amide branches. In Figure 7a, a possible packing mode to result in the lamellar structure of two different layer spacings (70 and 36 Å) is depicted. The severely contracted alkyl branches are expected in these two lamellar units as illustrated in the figure. When sufficient thermal energy is supplied at an elevated temperature, the structure, however, restores itself to the stable one (Figure 7b) that is linked by hydrogen bonding between the carboxylic groups at the focal point and with more extended alkyl branches. The exothermic hump at 50−60 °C in the heating curve of the DSC thermogram (Figure 5 (1G-2)) can be associated with the structural rearrangement to form a new lamellar structure of single layer thickness. The X-ray patterns of 1GD (first generation dimer) are depicted in Figure 6 (1GD-1 and 1GD-2). The pattern 1GD-1 from the gel state reveals that the structure is not as ordered as
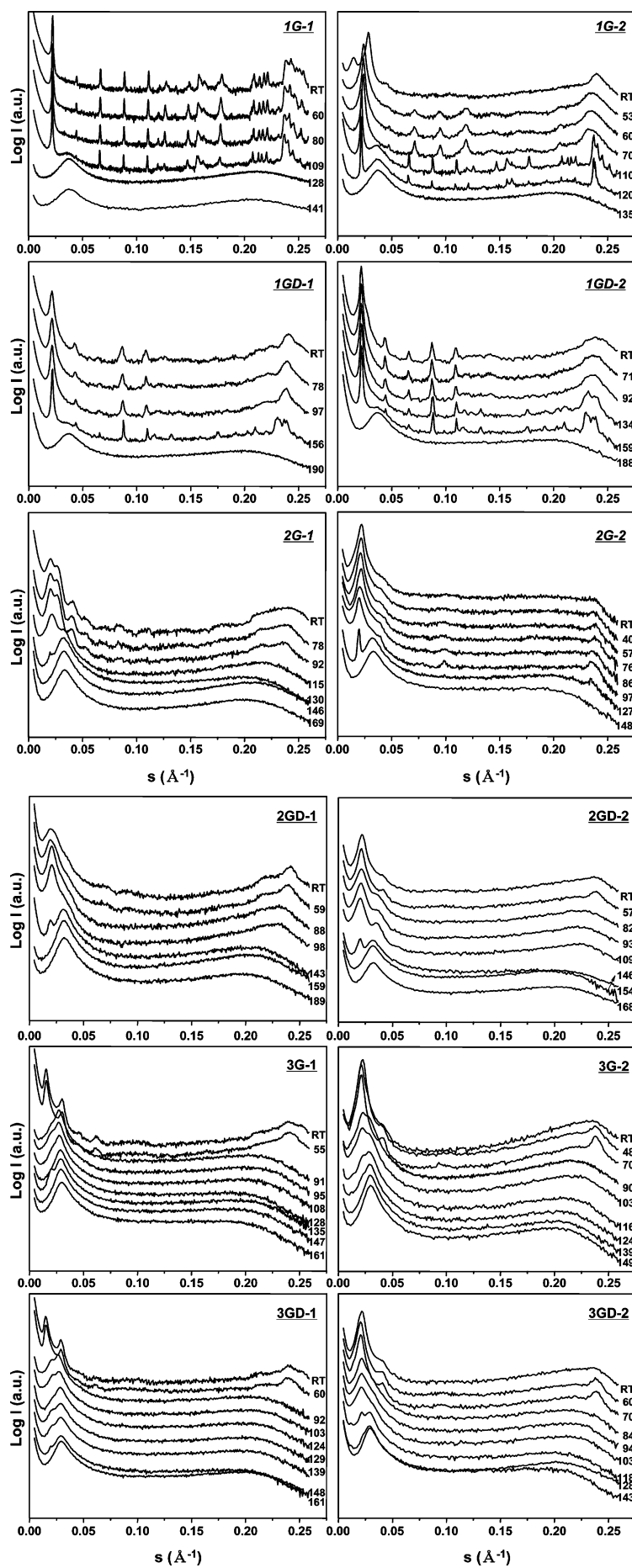
Figure 6. X-ray diffraction patterns obtained with temperature variation; *nG*-1 denotes the first heating and *nG*-2 for the second heating.
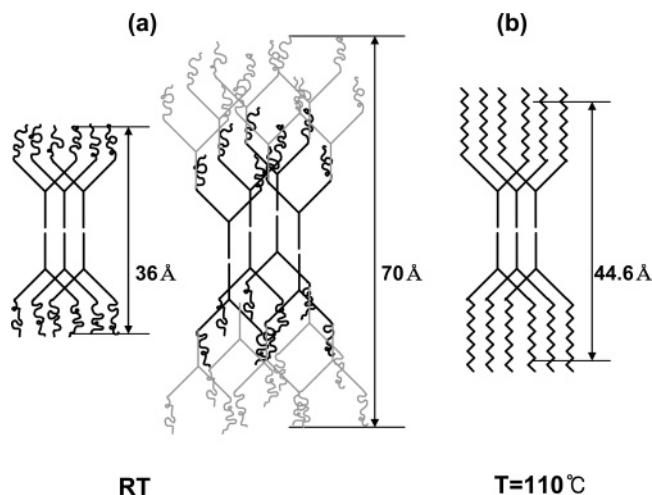
Figure 7. Schematic representation of thermotropically induced superstructure of 1G showing dual lamellar thickness (a) and rearranged structure at an elevated temperature (b). Note that dendrons on right in panel a are arranged to emphasize hydrogen bonds between the focal carboxyl groups and the amide branches.
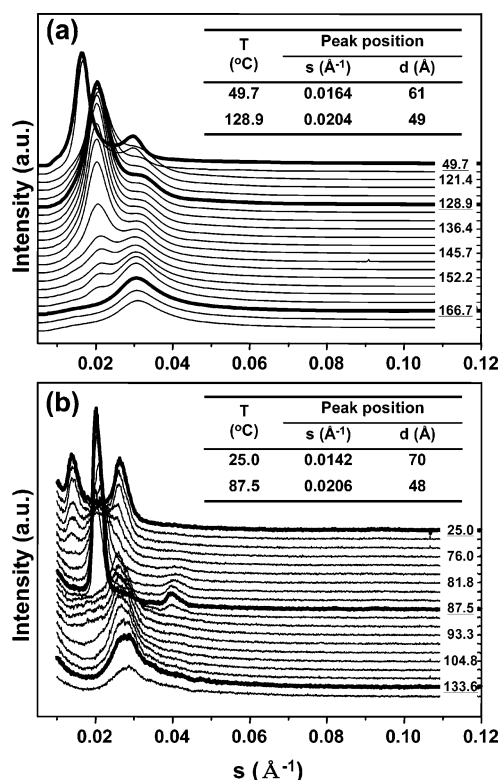
Figure 8. Structural change of third generation dendrons with temperature variation: 3G (a) and 3GD (b).

that of 1G as can be expected as the dimer units covalently linked at the focal point are relatively restricted in the movement of the assembly process. However, the pattern 1GD-2 (1GD from the melt state) shows a somewhat more ordered packing state than that from the gel state (1GD-1), which is contradictory to the results of 1G. Also, in this case, a single lamellar spacing is observed throughout the whole temperature range. It is apparent that the covalently linked dimer units are no longer able to form the structure suggested in Figure 7a and that they are able to form better packing than 1G before the structural reorganization takes place at an elevated temperature.

DSC results of second generation dendrons, depicted in Figure 5 (2G and 2GD), show more complicated thermal behavior than
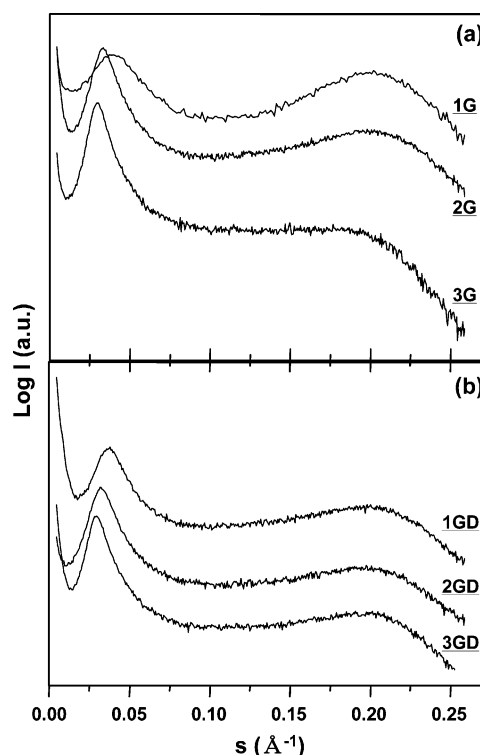

Figure 9. X-ray diffraction patterns of dendrons above the disordering temperature: (a) 1G, 2G, and 3G and (b) 1GD, 2GD, and 3GD.

those of the first generation. Corresponding X-ray patterns of second generation dendrons (2G and 2GD) upon heating are denoted as 2G-1, 2G-2, 2GD-1, and 2GD-2 in Figure 6. Results of second generation dimers (2GD-1 and 2GD-2) are very similar to those of monodendrons (2G-1 and 2G-2). All patterns exhibit the hexagonally packed cylinder-type supramolecular order without distinctive high angle peaks. It is certain that the local order within the supramolecular domain is not required for the formation of the superstructure. Careful comparison between the patterns, however, reveals that the structure of monodendron from the gel state (2G-1) shows a somewhat better packing order than thermotropically driven structures and also those of dimeric dendrons. We also note that the main peak sharpens with the temperature increase, illustrating that the supramolecular order is improving. The ordering effect is more distinct in the heating of the melt quenched samples (second heating). The exotherms observed in the DSC thermograms are apparently associated with the ordering of the structures. When the temperature was raised further above the final endotherms in DSC, the main peak at small angles disappeared, leaving a new broad hump representing the disordered structure.

X-ray patterns of third generation dendrons, 3G and 3GD, are also plotted in Figure 6. Here, 3G-1 and 3GD-1 denote the dry gels obtained from the solution, while 3G-2 and 3GD-2 denote the samples from the melt state. The patterns of the dry gels (3G-1 and 3GD-1) exhibit a lamellar structure, while the structure from the melt state (3G-2 and 3GD-2) confirms the hexagonal cylinders as already discussed in the previous section. The initially formed supramolecular order becomes improved upon heating until the DSC endotherm appears as was observed with the previous first and second generation dendrons. One particular observation, however, noted in the heating of the dry gel is that a transition of the superstructure appears to take place at the elevated temperatures during the heating process. For detailed examination, time-resolved X-ray scattering using a synchrotron
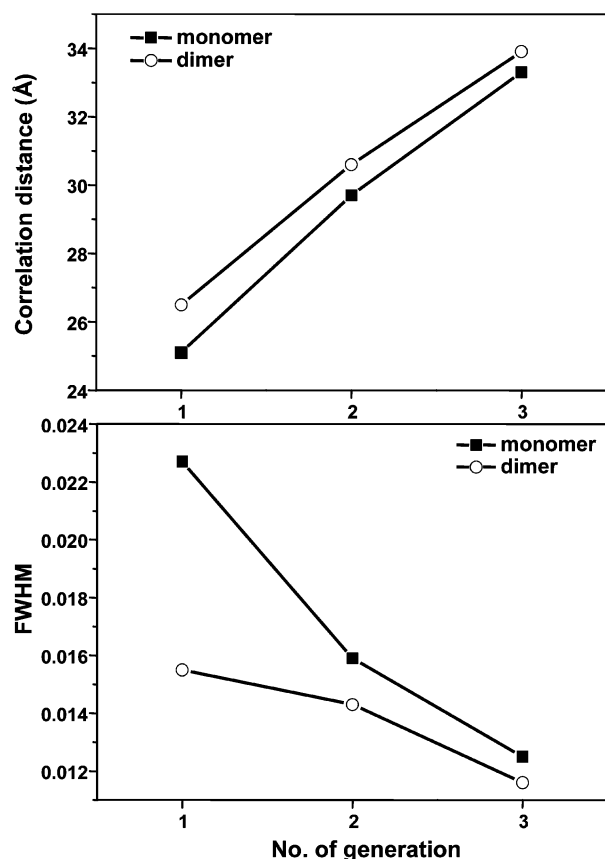
Figure 10. Correlation distance and fwhm estimated from X-ray patterns of the disordered melt.

radiation source and a position sensitive area detector was performed upon heating the samples (3 °C/min). The results of 3G and 3GD are depicted in Figure 8a,b, respectively. In both figures, we indeed note a drastic change of the diffraction peaks at temperatures between 60 and 90 °C, which is apparently responsible for the first endothermic peak of DSC thermograms shown in Figure 5 (3G-1 and 3GD-1). The main peak representing the lamellar structure of ∼70 Å thickness rapidly shifts to a higher angle, which also represents another lamellar structure but with a much reduced thickness of ∼48 Å. Therefore, the changes noted in the diffraction pattern are associated with the internal rearrangement within the super domains while maintaining the original skeleton. The thickness of the second lamella (48 Å) is extraordinarily small, considering the initial lamellar thickness (∼70 Å) and the molecular dimension of the third generation dendrons (91 Å), implying that the branches of the dendrons are severely contracted. The dendrons assembled into the superstructure from the solution are in a more extended conformation, which seems to be thermodynamically unstable. Once the thermal energy is available at an elevated temperature, the branches undergo rearrangement to a more stable contracted conformation. At this point, we recall that the structure formed from the melt state was the hexagonally packed cylinder, where the cylinder diameter was 55 Å. The lamellar structure with contracted branches observed during the heating might be the intermediate stage of transition from the lamellar to the equilibrium cylindrical domains.

Disordered Melt State. As discussed in the previous section, all dendrons showed a transition from the ordered supramolecular structure to a disordered state at temperatures above the final melting endotherms, seen in the DSC thermal scans (Figure 5). It is noted that the melting endotherms of dimers are located at higher temperatures than those of monodendrons. The result is

consistent with all generations and can be attributed to the low entropy gain in the melting of the superstructures of the dimer units. At the disordered melt state, the molecules are randomly dispersed with a uniform density distribution throughout the entire sample. However, in X-ray scattering patterns taken from the melt state shown in Figure 9, we note a broad but strong hump at the small angles (∼30 Å), implying the existence of a structure possessing a somewhat strong correlation even in the melt state. The pattern with a strong correlation of ∼30 Å also suggests that each dendron molecule isolates itself from the others and forms an individual particle. The correlation distance and fwhm estimated from the hump are shown in Figure 10. The correlation distance increases with the generation from 26 to 33 Å. The fwhm of the peak, on the other hand, decreases with the increase of generation, indicating the higher coherency in the high generation dendrons. Dimers apparently show the higher coherence over the monodendrons, which is more marked in the first generation dendron. As already was discussed, the hydrogen bonds at the focal point and between the amide branches are the main driving forces to form the superstructure. The transition of the ordered superstructure to a disordered melt at high temperature must be accompanied by the breakage of these hydrogen bonds. It is, however, interesting to note that both monodendrons and covalently linked dimers show nearly the same correlation distances in the melt state. Even in the covalently linked dimers (1GD, 2GD, and 3GD), the dendronic branches in either side of the focal linkage behave like the individual monodendrons.

Conclusion

Dendronic molecules containing amide branches including monodendrons and covalently linked dimers (up to the third generation) were studied for their supramoleular ordering in both lyotropic and thermotropic environments. The supramolecular ordering of these dendrons differs depending on the assembling conditions as well as the generations. The differences associated with the two different passages are more distinct with the higher generation dendrons. The dendrons assembled in the lyotropic conditions showed a better supramolecular ordering, but the dendrons forming the superstructure appear to be thermodynamically unstable. When sufficient thermal energy is supplied, the dendrons relax to the more stable state, which is similar to the behavior of those in thermotropic conditions.

The formation of symmetric molecular entities is the key process for monodendrons to self-organize into superstructures. As has been claimed previously, the dimer units formed either by hydrogen bonding between the carboxylic units of monodendrons or the covalently linked units at the focal points are the basic building blocks for ordered superstructures. The dimer units of amide dendrons, however, result in an unfavorable shape for efficient packing. The dimer units must cross-pack to one another to avoid steric hindrance of the bulky branches. The cross-packed dendrons stack to result in either lamellar or columnar superstructures.

Supporting Information Available: Synthesis of third generation dendrons (3G and 3GD). This information is available free of charge via the Internet at http://pubs.acs.org.

LA7023555