Molecular Assembly of C_2-Symmetric Bis-(2S)-2-methyldodecanoylamides of α,ω-Alkylidenediamines into Coiled Coil and Twisted Ribbon Aggregates

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Abstract: A series of 10 didodecanoylamides of α,ω-alkylidenediamines bridged by a straight carbon chain varying in length from 0 to 9 carbons was examined as possible gelator molecules of organic liquids to gain information on the relationships between the spacial arrangement of two amide groups in a molecule and their effects on the microscopic structures of the gel. The structural characteristics of these amides are parallel and antiparallel arrangements of two amide carbonyl groups, which depend on the even and odd numbers of a bridging zigzag carbon chain. The linear alkyl chain moieties and a center carbon chain of diamides intermolecularly interact with each other within the van der Waals contact. Two amide moieties of an even number carbon chain diamide intermolecularly interact with each other by using two pairs of hydrogen bonds with two other molecules in a plane, which formed ribbonlike self-complementarily assembled aggregates. On the other hand, a diamide of an odd number carbon chain forms four independent hydrogen bonds with four other molecules not in a plane, which assembled into woven aggregates. Asymmetric introduction of a methyl group at the α-position of the amide groups successfully twists the two side chain van der Waals cores of the chiral diamides in the fixed direction, giving helically twisted ribbon and coiled coil aggregates. The helically twisted ribbon and coiled coil aggregates of these chiral diamides were directly observed by CD, SEM, and TEM, providing a basis for the design of a sophisticated small molecular gelator of a tailor-made shape.

Introduction

Gelation by small quantities of a polymer[1] has been known for several centuries.[2] Recently, many low molecular weight compounds have been reported as effective gelators for organic liquids and have renewed interest in the determining factors for self-complementary assembly.[3-5] The correlation of the properties to the chemical structure of gelators has been proposed from detailed spectroscopic and diffraction studies.[6]

Some small organic molecules self-complementarily assemble into microscopic structures through specific hydrogen bonding,[7] van der Waals interaction,[8] and π−π stacking,[9] which are assignable origins responsible for the gelation of organic liquids.[3] Tailor-made shapes, especially helical aggregates of these gelators, are of recent interest and are classified into helical fibers including coiled coil, twisted ribbon, and helical ribbon. The gelator compounds bearing α-amino acids,[10] glucose,[11] cyclohexanediamine,[12] and vancomycin[13] have been claimed to form helical fibers, those bearing chirally branched alkyl chains

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on the $\pi-\pi$ stacking cores[14] form coiled coil, those bearing tartrate, gluconate, malate,[15] and gluconamide[16] form twisted ribbon, and those bearing cholesterol[17] form helical ribbon aggregates. Of these modificators, chiral acceptor/donors of hydrogen bonds are impressive in dominant use as chiral cores, except for, for example, the approaches of Nolte,[14b] Shinkai,[17] and Maitra[14a] to helical coiled coil and ribbon aggregates by the use of chiral aliphatic tails as a chiral modificator on a crown ether and pyrene cores. For the sophisticated design of the specific shape and its application to materials, however, it is still necessary to understand the fundamental role of hydrogen bonding and van der Waals interaction cores of gelator molecules. Especially, it seems reasonable and important to gain information on the relationships between the spacial arrangement of two amide groups in a molecule and their effects on microscopic structures. A series of didodecanoylamides of α,ω-alkylidenediamines bridged by a straight carbon chain varying in length from 0 to 9 carbons were examined as possible gelator molecules. These amides self-complementarily assembled into microscopic woven and ribbon structures through hydrogen bonding and van der Waals interactions.[18] The SEM visible shape of the aggregate structures depends on the even and odd numbers of the bridging carbon chain of α,ω-alkylidenediamines. Further deductive logic led us to the assumption that introduction of chirality to the van der Waals interaction core of the diamides twists the ribbon and woven structures to the corresponding helically twisted ribbon and coiled coil aggregates. We describe herein these approaches in detail.

Design of Self-Complementarily Assembling, Small, and Linear Diamide Molecules

The small and linear gelator molecule is constituted from three parts of van der Waals interaction cores, of which the center core is bridged by two hydrogen bonding cores, satisfying C_2-symmetric character for analytical simplification (Figure 1). Each core provides intermolecular hydrogen bonding and van der Waals interactions suitable for the self-complementary assembly of these structures. The diamides **1** of α,ω-alkylidenediamines bridged by a straight carbon chain varying in length from 0 to 9 carbons are the chemical structure corresponding to the image shown in Figure 1 (Figure 2).
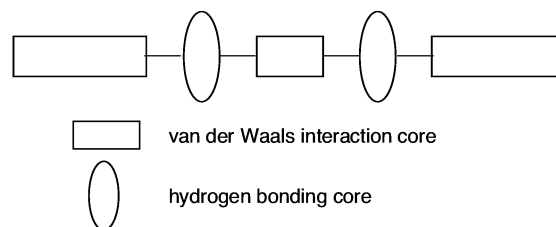

Figure 1. Self-complementarily assembling molecule.
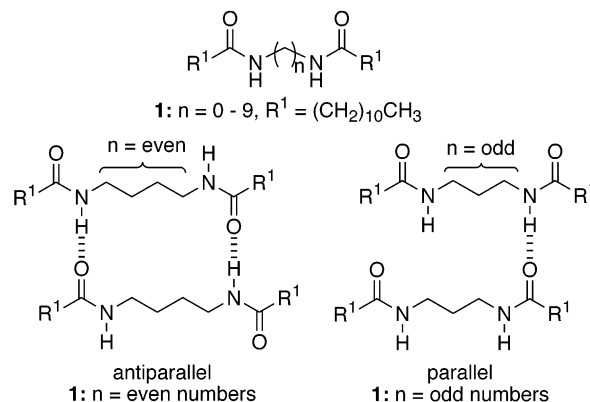

Figure 2. Bridging methylene chain number-dependent parallel and antiparallel two-amide groups and two types of assembly structures of diamides **1**.

These diamides **1** are classified into two categories with regard to the length of the carbon chain: one is the diamide **1** bearing a bridging carbon chain of 0 or an even number (n) (the left structure in Figure 2), and the other **1** bears a carbon chain of an odd number (the right structure in Figure 2). The zigzag arrangement of the carbon chain of even number directs the two amide carbonyl groups of **1** antiparallel (the opposite direction), while those of the carbon chain of the odd number are parallel (the same direction). Consequently, a diamide molecule **1** of an even number carbon chain forms two pairs of hydrogen bonds with two other molecules in a plane. On the other hand, **1** of an odd number carbon chain forms four independent hydrogen bonds with four other molecules not in a plane. Furthermore, the linear alkyl chain moieties (R^1) and a center carbon chain of diamide **1** intermolecularly interact with each other within van der Waals contact. These analyses predict the ribbon and woven shapes of self-complementarily assembled structures of even and odd number diamides **1**.

Gelation by Achiral Diamides 2 and 3

The didodecanoyl amides **2** (**1** of $n = 0$ or even number) and **3** (**1** of $n =$ odd number) were prepared by acylation of alkylidenediamines under standard conditions (Figure 3). Gel formation of **2** and **3** with organic liquids was determined by the method "stable to inversion of the container".[19] A mixture of a crystalline diamide and an organic liquid in a container was heated to a solution and was then cooled back to room temperature. Benzene, toluene, mesitylene, pyridine, ethyl acetate, and acetonitrile[20] were suitable organic liquids in forming opaque and reversible gels. The minimum concentration of **2** and **3** for gelation of mesitylene ranged from 1 to over 50

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(20) Although gelation of ethyl acetate and acetonitrile was not clear in a smaller container (7 mm diameter), these gelated in a bigger container (15 mm diameter).
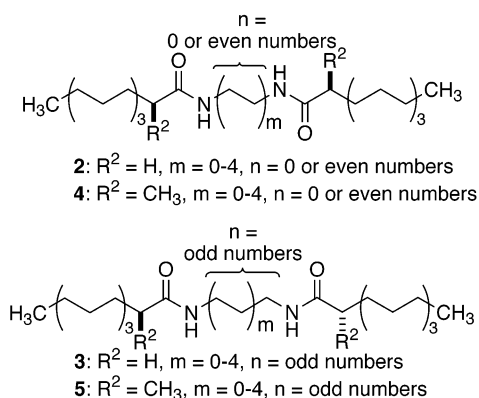
2: R^2 = H, m = 0-4, n = 0 or even numbers
4: R^2 = CH$_3$, m = 0-4, n = 0 or even numbers

3: R^2 = H, m = 0-4, n = odd numbers
5: R^2 = CH$_3$, m = 0-4, n = odd numbers

Figure 3. Achiral and chiral diamides **2**−**5**.

Table 1. Minimum Concentration (mg/mL) of Diamides **2** (n = 0 or Even Number) and **3** (n = Odd Number) for Gelation of Organic Liquid (p, Precipitation; i, Insoluble)

2, 3/n	0	1	2	3	4	5	6	7	8	9
hexane									i	i
benzene[a]	20	5	25	8	40	13	50	4	>100	4
mesitylene[a]	14	3	14	3	29	10	33	1	58	1
methyl oleate	21	20	p	19	34	23	28	22	20	22
soy bean oil	19	16	28	15	27	22	24	17	16	14
AcOEt	37	25	15	19	53	15	34	15	52	5
MeCN								27	48	24

[a] Minimum concentration of **2** and **3** quoted from ref 18.

mg/mL (Table 1). Although hexane was a liquid that did not afford a gel, long aliphatic oils bearing alkyl chains, for example, soy bean oil (a mixture of triglycerides of fatty acids) and methyl oleate, were successfully converted to gel.

The gelation power of **2** and **3** is not linearly correlated with the length of the carbon chain (n in **1**). The even and odd numbers of the carbon chain of **2** and **3** are decisive for the gelation. For gelation of mesitylene by **2**, the longer the carbon chain is, the poorer the efficiency is. In contrast, **3** is generally highly capable of gelating mesitylene with less than 10 mg. A similar tendency was observed for gelation of long aliphatic chain esters and other liquids; that is, **3** (n = odd number) is superior to **2**.

The high and low efficiency of **2** and **3** in gelation was predictable from the SEM pictures of mesitylene gels.[18] The self-assembled thin and flat ribbonlike structure was observed for xerogel (mesitylene) of **2** (m = 3, n = 6 for **1**) in the SEM photograph as had been predicted in the design stage of the study (Figure 2). On the contrary, the fine woven structure of the xerogel of **3** (m = 4, n = 9 for **1**) was observed. It is also important to note that the crystal structure of **3** (m = 1, n = 3 for **1**) indicates self-assembly of one molecule with four other molecules through hydrogen bonds as had been predicted in the design stage of the study (Figure 2).[18] These characteristics of the aggregate structures are nicely correlated to the finer network by **3** rather than by **2**.

Design of Chiral Diamides for Helical Shape Aggregate

The design of a tailor-made helical shape stems from the above findings that antiparallel (n = even number) and parallel (n = odd number) arrangements of two amide groups, CONH, of diamides of α,ω-alkylidenediamines **2** and **3** (R = H) direct a specific shape formation of the ribbon and woven aggregates in gelation of organic liquids (Figures 1 and 2).[21] It is possible
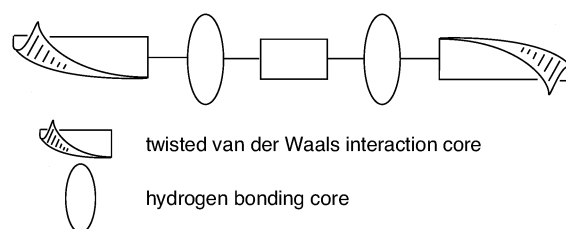

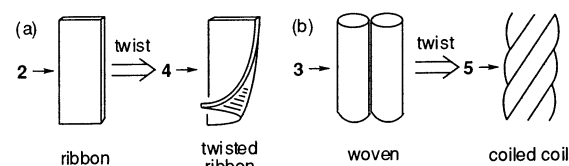**Figure 4.** Self-complementarily assembling molecule with a twisted van der Waals interaction core.

Figure 5. Twist of ribbon (a) and woven (b) aggregates of **2** and **3** into twisted ribbon and coiled coil aggregates of **4** and **5**.
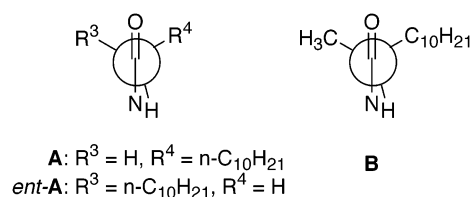

A: R^3 = H, R^4 = n-C$_{10}$H$_{21}$ **B**
ent-**A**: R^3 = n-C$_{10}$H$_{21}$, R^4 = H

Figure 6. Bisecting conformations **A** and *ent*-**A** of achiral diamide **3** (m = 1) and **B** of chiral diamide **5**.

to twist the side chain arms into the twisted ribbon and helical coiled coil aggregate structures by the introduction of chirality on the van der Waals interaction moieties when the hydrogen bonding cores are preserved as shown in Figure 4. Consequently, the ribbon and woven structures are capable of being twisted to the corresponding twisted ribbon and coiled coil aggregate structures depending on the parallel and antiparallel arrangements (Figure 5).

Because the X-ray crystallographic structure of achiral **3** (m = 1, n = 3 for **1**) shows a zigzag arrangement of all carbon chain, except for the bisecting conformations **A** and *ent*-**A** around two amide groups (Figure 6),[18] replacement of R^2 = H in **2** and **3** with a methyl group (R^2 = CH$_3$) renders molecular chirality to the diamides and fixes the conformation to **B**.[22] On the basis of this idea, we prepared and examined a series of 10 C_2-symmetric chiral diamides **4** and **5** bridged by a straight carbon chain varying in length from 0 to 9 carbons (n in **1**) in which two methyl groups were asymmetrically introduced at the α-positions of amides **2** and **3** (Figure 3).

Synthesis of Chiral Diamides 4 and 5

The nine chiral diamides **4** and **5** (m = 1−4, n = 0, 2−9 for **1**) were synthesized in high yields by acylation of the diamines with (2S)-2-methyldodecanoyl chloride[23] in ether−water in the presence of sodium bicarbonate. The diamide **5** (m = 0, n = 1 for **1**) was prepared by treatment of diaminomethane with the acid chloride in pyridine−THF. The optically pure chiral acid

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(23) Morigaki, K.; Dallavalle, S.; Walde, P.; Colonna, S.; Luisi, P. L. *J. Am. Chem. Soc.* **1997**, *119*, 292−301.

Table 2. Minimum Concentration (mg/mL) of Chiral Diamides **4** and **5** for Gelation of Organic Liquid (p, Precipitation)

4, 5/n	0	1	2	3	4	5	6	7	8	9
hexane	13	p	3	p	14	14	12	7	62	4
benzene	14	18	6	p	10	18	9	11	15	88
mesitylene	15	18	3	p	10	15	7	11	16	92
methyl oleate	15	16	7	32	19	13	16	11	13	14
AcOEt	14	15	6	p	40	40	20	30	11	21
MeCN	18	8	5	17	20	19	16	12	14	12
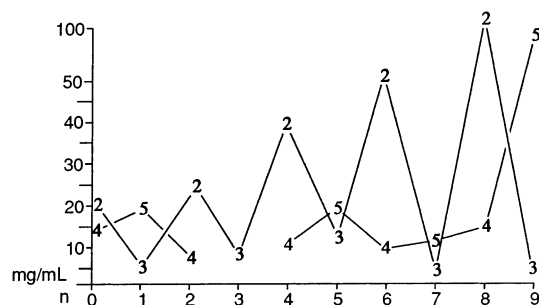
Figure 7. Minimum concentration (mg/mL) of diamides **2**–**5** for gelation of benzene.

chloride was successfully prepared in quantity by an asymmetric methylation reaction according to the Evans chiral oxazolidinone procedure.[24]

Gelation of Organic Liquids by Chiral Diamides 4 and 5

In addition to liquids such as benzene, mesitylene, ethyl acetate, and acetonitrile, hexane that was not gelated by achiral **2** and **3** was also a suitable organic liquid in forming opaque gels by the chiral diamides **4** and **5**. The gel was stable and reversible upon repeated heating and cooling. The minimum concentration of **4** and **5** for gelation of mesitylene ranged from 3 to 18 mg/mL, except for that it was 92 mg/mL for **5** with $n = 9$ ($m = 4$) (Table 2). Although the tendency of the gelation was equally averaged even in which chiral diamides and liquids were used, the striking difference from achiral diamides is the higher efficiency of chiral **4** than the corresponding achiral **2**. Introduction of only two extra methyl groups improved the efficiency of gelation by **4**.

The gelating behavior of chiral diamides is not linearly correlated with the length and the odd and even numbers (n) of the carbon chain (Figure 7). Unlike the achiral diamides **2** and **3**, of which odd and even numbers of the carbon chain are decisive for the gelation, there is little difference in the ability of **4** and **5** based on the odd and even numbers, gelating at a similar concentration, except for **5** ($n = 9$).

Thermotropic Behavior of Chiral Diamides

The influence of the extra methyl groups was also observed in other properties. Melting points of **4** and **5** were lower than those of the corresponding achiral **2** and **3** by a factor of 12–36 °C, probably due to the unfavorable intermolecular steric repulsion by a methyl group (Figure 8). However, the valley and top of the melting points of achiral and chiral diamides **2**–**5** were alternately repeated according to the odd and even numbers of the carbon chain, suggesting the same type of the molecular packing structure.

(24) Gage, J. R.; Evans, D. A. *Org. Synth.* **1990**, *68*, 83–91.
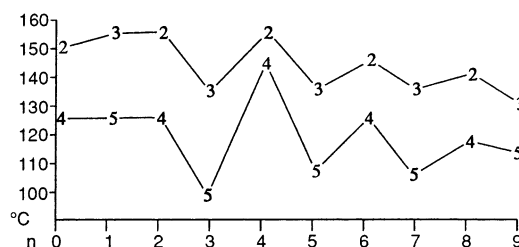
Figure 8. Melting points (°C) of diamides **2**–**5**.
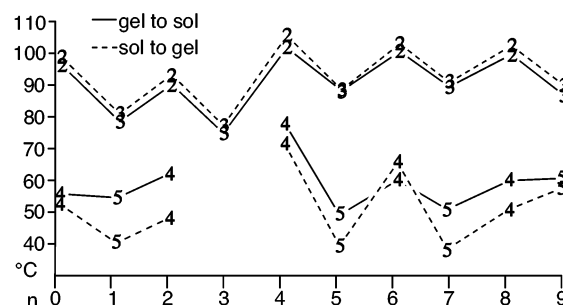
Figure 9. Gel-to-sol and sol-to-gel phase transition temperatures of the mesitylene gels of diamides **2**–**5** (DSC, °C, 50 mg/mL). (No gelation was observed for **5** ($n = 3$).)

The gel-to-sol and sol-to-gel phase transition temperatures of the mesitylene gels of **4** and **5**, determined by differential scanning calorimetry (DSC), were lower than those of achiral diamides **2** and **3** of the corresponding number (n) of the carbon chain by a factor of 22–40 °C (Figure 9). However, the valley and top of the gel-to-sol and sol-to-gel phase transition temperatures were alternately repeated according to the odd and even numbers of the carbon chain. The high and low melting points and gel-to-sol and sol-to-gel phase transition temperatures of **4** and **5** are attributable to the parallel and antiparallel arrangements of the two amide groups and subsequent structural differences in the self-complementary assembly as had been observed with **2** and **3**.[18] The relatively lower transition points of **4** and **5** than those of **2** and **3** are due to the unfavorable steric repulsion by the introduction of the extra methyl groups.

Small-Angle X-ray Scattering of Mesitylene Gels of Diamides 2–5

Bragg reflections were unambiguously observed in the small-angle X-ray scattering (SAXS) of the mesitylene gels of **2**–**5**. These peaks had a periodicity of $^1/_1$, $^1/_2$, $^1/_3$, and $^1/_4$ that is attributed to a lamellar structure, indicating regularly arranged molecular layers. The d values, which correspond to the interlayer distance, of the mesitylene gels showed the similar and alternately repeated top and valley according to the odd and even numbers of the carbon chain (Figure 10). The top and valley are reverse to those of the melting points and phase transition temperatures, indicating that efficiency in both gelation and molecular self-complementary assembly are directly proportionate to the interlayer distance. It is also interesting to find that d values of chiral diamides **4** and **5** are shorter than the achiral **2** and **3** of the corresponding number of the carbon chain (n), suggesting the winded-molecular structure of **4** and **5** by the extra methyl group. The helical structure of the aggregates seems responsible for such smaller d values and molecule winding.
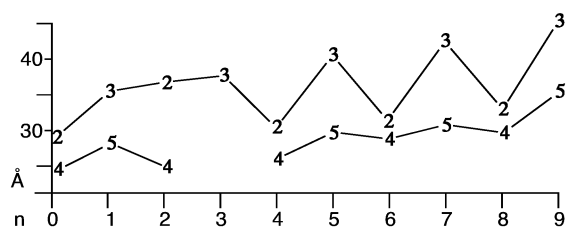
Figure 10. The d values of the mesitylene gels of diamides **2**−**5**. No Bragg reflection was observed for **5** ($n = 3$).
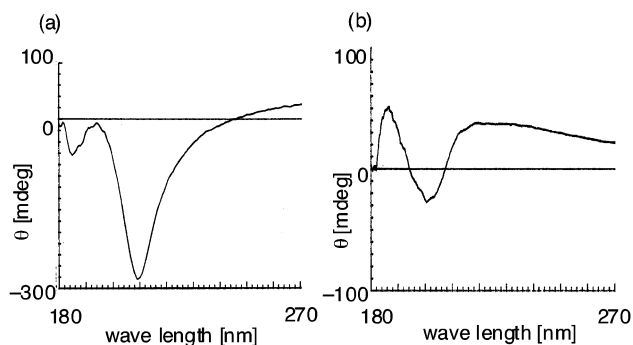

Figure 11. The CD spectra of (a) the hexane gel of **4** ($m = 4$, $n = 8$, 3.3 mg/mL, 25 °C) and of (b) the hexane gel of **5** ($m = 3$, $n = 7$, 8.6 mg/mL, 25 °C).

Circular Dichroism of Hexane Gels of Diamides 4 and 5

The CD spectrum (a in Figure 11) of the hexane gel of **4** ($m = 4$, $n = 8$) at 25 °C exhibited a strong negative peak at 210 nm. The spectrum b of the hexane gel of **5** ($m = 3$, $n = 7$) exhibited a positive peak around $210-220$ nm and a negative peak at 201 nm, and a $\lambda_{\theta=0}$ value appeared at 207 nm. These strong peaks disappeared upon heating and in the trifluoroethanol solution of **4** and **5** ($n = 7$, 8) at 25 °C. These results indicate that the peaks were attributable to the helical aggregates, not to the chirality of the molecule,[12a] and that chiral diamides **4** and **5** self-assembled into different structured aggregates, respectively. The CD spectrum of the hexane gel of **4** ($m = 4$, $n = 8$) is similar to that of the twisted ribbon aggregates observed by Shimizu,[25] indicating that **4** ($m = 4$, $n = 8$) self-assembled into twisted ribbon aggregates as we designed. The peaks of hexane gel of **5** ($m = 3$, $n = 7$) are assigned to the exciton coupling bands. The positive sign for the first Cotton effect indicated that the dipole moments are oriented in a clockwise direction as has been described by Shinkai[12b] in the right-handed helical coiled coil aggregates, suggesting the right-handed coiled coil aggregates of **5** ($m = 3$, $n = 7$).

Scanning Electron Micrograph (SEM) and Transmission Electron Micrograph (TEM)

The twisted ribbon aggregates (a in Figure 12) with $2000-3000$ nm widths of **4** ($m = 4$, $n = 8$) and coiled coil aggregates (b and c) with $200-300$ nm widths of **5** ($m = 3$, $n = 7$) were observed by the SEM pictures of the mesitylene xerogels. The coiled coil aggregates of **5** ($m = 3$, $n = 7$) are composed of helical fibers with $50-80$ nm widths. The twisted ribbon aggregates (a in Figure 13) with $2000-3000$ nm widths of **4** ($m = 4$, $n = 8$) and coiled coil aggregates (b and c) with $200-300$ nm widths of **5** ($m = 3$, $n = 7$) were also clearly observed

(25) Jung, J. H.; John, G.; Yoshida, K.; Shimizu, T. *J. Am. Chem. Soc.* **2002**, *124*, 10674−10675.
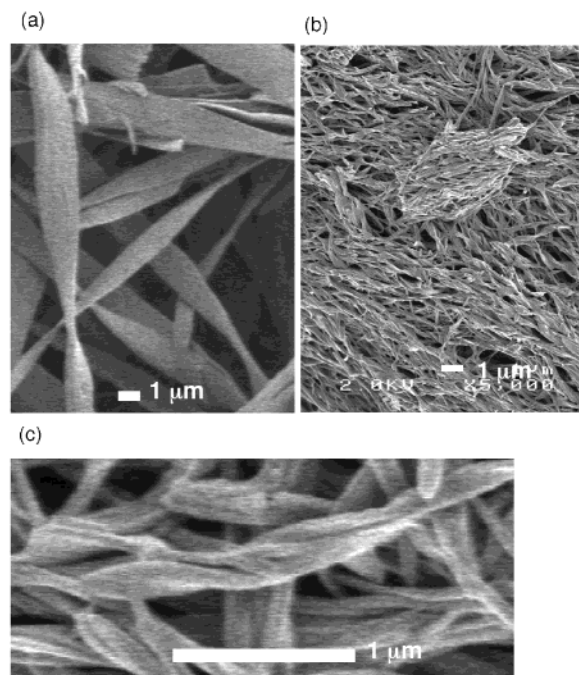

Figure 12. SEM pictures of the mesitylene xerogel of **4** ($m = 4$, $n = 8$) ((a) twisted ribbon) and **5** ($m = 3$, $n = 7$) ((b, c) coiled coil). The pictures (a) and (b) are presented in the same scale. The picture (c) is an 8-fold expanded picture of (b).
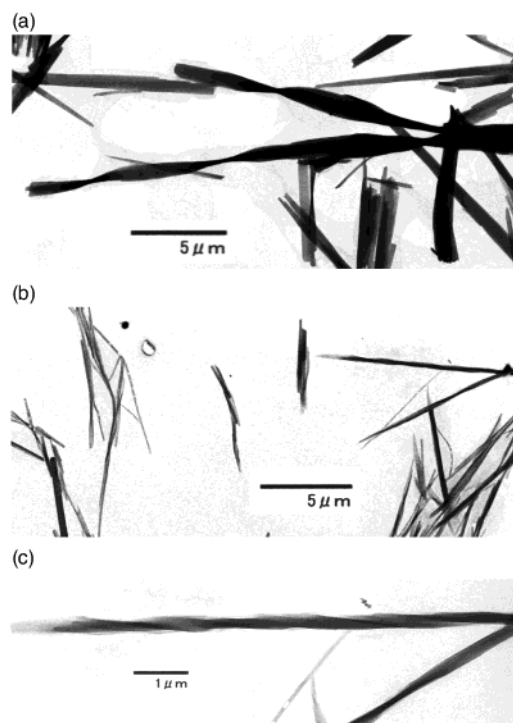

Figure 13. TEM pictures of the mesitylene xerogel of **4** ($m = 4$, $n = 8$) ((a) twisted ribbon) and **5** ($m = 3$, $n = 7$) ((b, c) coiled coil). The pictures (a) and (b) are presented in the same scale. The picture (c) is a 3-fold expanded picture of (b).

by the TEM pictures of the mesitylene xerogels. The twisted ribbon and coiled coil aggregates have the right-handed helical structures. The ribbon and woven aggregates of achiral **2** and **3** were twisted by asymmetrically introducing two methyl groups on van der Waals interaction cores to the twisted ribbon and coiled coil aggregates of chiral **4** and **5**, respectively.[18]

Conclusion

The characteristics of didodecanoyl amides of α,ω-alkylidenediamines are parallel and antiparallel arrangements of two amide carbonyl groups, which are dependent on the even and odd numbers of a bridging zigzag carbon chain. The linear alkyl chain moieties and a center carbon chain of the diamides intermolecularly interact with each other within van der Waals contact. Two amide moieties of an even number carbon chain diamide interact with each other by using two pairs of hydrogen bonds with two other molecules in a plane, which forms ribbonlike self-complementarily assembled aggregates. On the other hand, a diamide of an odd number carbon chain forms four independent hydrogen bonds with four other molecules not in a plane, which forms woven aggregates. Asymmetric introduction of a methyl group at the α-position of two amide groups successfully twists the two side chain van der Waals cores in the fixed direction, giving helically twisted ribbon and coiled coil aggregates. The shape-controlled self-complementary assembly of the diamides opens a new way for the design of a sophisticated small molecular gelator of a tailor-made shape.

Supporting Information Available: Preparation and analytical data of **4** and **5**, and experimental procedures (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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