Molecular Assembly and Gelating Behavior of Didodecanoylamides of α,ω-Alkylidenediamines

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We describe herein that didodecanoylamides of α,ω-alkylidenediamines self-complementarily assemble into microscopic structures through specific hydrogen bonding and van der Waals interactions, which are assignable to origins for the gelation of organic liquids.[1] Gelation by small quantities of a compound, usually a polymer,[2] has been known for several centuries.[3] Although the most important factors, self-complementary gelator aggregates, have been proposed from detailed spectroscopic and diffraction studies,[4] an understanding of the microscopic factors responsible for the gelation of organic liquids has not yet been thoroughly surveyed. Some attempts have been made to correlate the properties of the gels and the chemical structures of the gelators.[5] Hydrogen bonding and van der Waals interactions are representative fundamentals that determine the structures of organic molecules. The recent discovery and development of low molecular weight gelators have renewed interest in the determining factors for self-complementary assembly.[6] In particular, Hanabusa[7] and Feringa[8] have succeeded in the construction of gelators for organic liquids using a cyclic bisurea as donor and acceptor functionalities for hydrogen-bonding interactions.[9] More precise and deeper understandings of these interactions are necessary for the design of more efficient gelators and the application into sophisticated materials.[10] Here we describe systematic studies toward an appropriate arrangement of two amide groups for a self-complementary assembly.

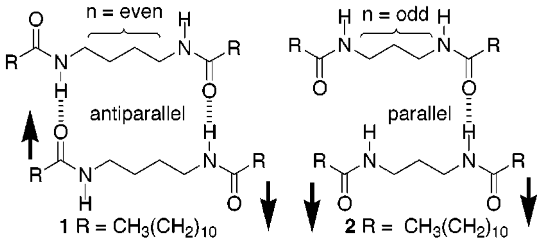
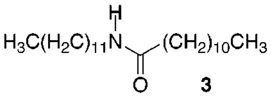


Figure 1. Parallel and antiparallel structures of diamides **1** and **2**. For clarification, diamides of $n = 4$ and 3 are presented.

It seems reasonable 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 10 didodecanoylamides **1** and **2** of diamines bridged by a straight carbon chain varying in length from 0 to 9 carbons were examined as possible gelator molecules. These diamides are classified into two categories with regard to the length of the carbon chain: one is diamide **1** bearing a bridging carbon chain of 0 or an even number, and the other is **2**, bearing a carbon chain of an odd number. The zigzag arrangement of the carbon chain of even number **1** directs the two amide carbonyl groups antiparallel (the opposite direction), while the carbon chain of the odd number **2** is parallel (the same direction) (Figure 1). Consequently, a diamide molecule of an even-numbered carbon chain **1** is able to form two pairs of hydrogen bonds with two other molecules in a plane. On the other hand, a diamide of an odd-numbered carbon chain **2** forms four independent hydrogen bonds with four other molecules not in a plane. Furthermore, the dodecanoyl moieties of diamides **1** and **2** favorably interact with each other within van der Waals contact. These analyses boldly predict the shape of self-complementary assembled structures of even- and odd-numbered diamides **1** and **2** to be ribbon and woven, respectively.

These diamides **1** and **2** of varying length from 0 and 2 to 9 methylene bridges were synthesized in high yields by the Schotten−Bauman acylation of the corresponding α,ω-diamines with dodecanoyl chloride in ether−water in the presence of sodium bicarbonate. The diamide of diamine ($n = 1$) was prepared by treatment with acid chloride in pyridine-THF. These diamides were recrystallizable to afford thin leaflets. As a reference, monoamide **3** was prepared by the acylation of dodecylamine with dodecanoyl choloride.



$H_3C(H_2C)_{11}\overset{H}{N}\underset{O}{C}(CH_2)_{10}CH_3$

3

Gel formation of these diamides with organic liquids was determined by the method "stable to inversion of the container".[11] A mixture of a crystalline diamide in an organic liquid in a container was heated to a solution and was then cooled back to room temperature. Benzene, toluene, mesitylene, and pyridine were suitable organic liquids in forming opaque gels. Hexane, diethyl ether, 1,4-dioxane, tetrahydrofuran, chloroform, ethyl acetate, acetone, acetonitrile, dimethylformamide, ethanol, and methanol were liquids that did not afford a gel and resulted in the crystallization of diamides. The gel was very stable and was converted to sol by heating, but upon cooling to room temperature, it reverted again to gel repeatedly, being reversible. The minimum concentration (MC) of diamides for gelation of mesitylene ranged from 1 to over 50 mg/mL (Table 1). The gelation power of diamides is not linearly correlated with the length of the carbon chain. Rather than the carbon chain length, the even and odd

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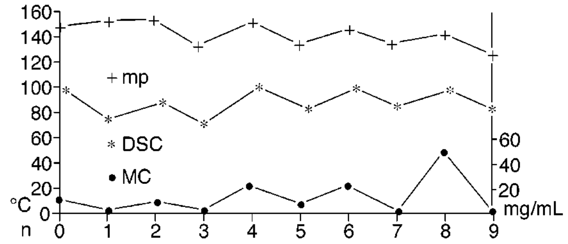
Table 1. Minimum Concentration of Diamides **1** and **2** for Gelation of Organic Liquid (mg/mL) (vs viscous solution)

	n =									
1 or **2**	0	1	2	3	4	5	6	7	8	9
benzene	20	5	25	8	40	13	50	4	>100	4
mesitylene	14	3	14	3	29	10	33	1	58	1
toluene			20	8	40	15	50			
pyridine			vs	33	vs	39	vs			

numbers of the carbon chain are decisive for the gelation. For **1**, with a carbon chain of 0 and even numbers, the longer the carbon chain is, the poorer the efficiency is. Diamide **1** with $n = 8$ required as much as 58 mg for gelation of 1 mL of mesitylene. In contrast, for **2** with an odd number carbon chain, the efficiency is generally highly capable of gelating mesitylene with less than 10 mg. It is impressive to find that 1 mg of **2** with $n = 7$ or 9 is enough to gel mesitylene. It is noteworthy that **3** did not gel organic liquids. A similar tendency was observed, when not only mesitylene, but also benzene, toluene, and pyridine were tested as organic liquids.

The intramolecular hydrogen bond in **1** and **2** is not the force that gels organic liquids. FTIR spectra of diamides indicated the presence of intramolecularly hydrogen-bonded and free NHs at a concentration of 1 mM. The ratio of intramolecularly hydrogen-bonded conformer of $n = 3$ diamide **2** was calculated to be ca. 96% based on the peak area of free NH of **3**.[12] The ratio of intramolecularly hydrogen-bonded conformation is decreased along with the length of the carbon chain, and is not correlated with the even and odd numbers of the carbon chain.[13] ^{1}H NMR of the diamides in $CDCl_3$ at 1 mM concentration indicated that the population of intramolecular hydrogen-bonded conformation decreased along with the elongation of the carbon chain.[14] This suggests that the important gelating factor is an intermolecular hydrogen bond, not an intramolecular hydrogen bond.

Linegraph 1. Minimum concentration (MC, mg/mL), gel to sol phase transfer point (DSC, °C), and melting point (°C).



It is very interesting to study linegraph 1 in which MC for gelation, gel to sol phase transfer points (DSC, mesitylene), and the melting points of diamides are presented. The valley and top of MC were repeated alternately according to the even and odd numbers of the carbon chain of **1** and **2**. The alternate valley and top were observed in gel to sol phase transfer points as well as melting points.

The high and low melting points of **1** and **2**, respectively, may be attributable to structural differences in the self-complementary assembly. One molecule of **1** of the even numbered carbon chain self-assembles by using two sets of two hydrogen bondings with two other molecules. In contrast, one molecule of **2** with an odd number carbon chain connects four molecules each through only one hydrogen bond. Consequently, cleavage of these hydrogen bonds in the crystal of **2** is easier than that of **1**, attributing to the lower melting point of **2** than **1**.

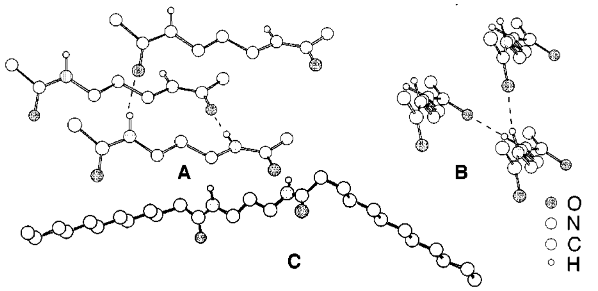


Figure 2. X-ray structure of **2** ($n = 3$). Hydrogen atoms attached to carbon atoms and alkyl chains were omitted for clarification in front view **A** and side view **B** of three molecules. A whole molecule is presented in **C**.

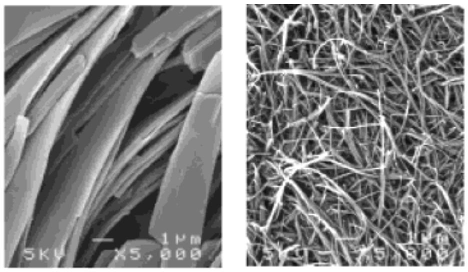


Figure 3. SEM photographs of xerogels (mesitylene) of **1** ($n = 6$) (left) and **2** ($n = 9$) (right).

Fortunately, **2** with $n = 3$ gave a crystal from ethanol suitable for X-ray crystallography (Figure 2). One molecule of **2** self-assembles with four other molecules through hydrogen bonds. α-Methylene carbons of both the amide carbonyl groups take gauche conformation to bend the chain, having the van der Waals attraction of the dodecanoyl moieties. These interactions support the basis for the alternate low and high melting points of even and odd numbered diamides.

A crystal structure-based gel structure would be meaningful for understanding and designing the molecular self-assembly into elongated fiberlike structures, which form a three-dimensional network encapsulating the organic liquids. The well-defined molecular arrangement within the fibers offers ample opportunity for the development of functional gels. The self-assembled woven structure was observed for xerogel (mesitylene) of **2** ($n = 9$) in the SEM photograph (Figure 3). It is interesting to observe the thin and flat ribbonlike structure of the xerogel of **1** ($n = 6$) as had been predicted in the bold design stage of the study.

In conclusion, the arrangement of two amide carbonyl groups bridged by even or odd carbon chains has been shown to be the basis for the design of the self-complementary assembly of molecules. Melting points, minimum concentration, gel to sol phase transfer points, X-ray structure, and SEM have been correlated with the pattern of hydrogen bonding originating from the parallel and antiparallel arrangement of amide carbonyl groups. These findings may become the basis for the design of sophisticated materials.

Supporting Information Available: Preparation, analytical data for **1**−**3**, and crystal data (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(12) The monoamide **3** did not show IR absorption of the intermolecular hydrogen bond at a concentration less than 1 mM.

(13) The IR peak area of free NH at 3455 cm^{-1} of **3** was used to estimate the percent population of a conformer bearing an intramolecular hydrogen bond. The hydrogen-bonded NH appeared at 3350 cm^{-1}. The amide **2** ($n = 3$) was estimated to be 96% intramolecular hydrogen bonded (eight-membered ring).

(14) Less than 38% of intramolecularly hydrogen-bonded conformer was observed in the amides of $n > 4$.