 DOI: 10.1002/masy.200650504

Self-Assembled Nanofibrillar Aggregates with Amphiphilic and Lipophilic Molecules

Takashi Sagawa,[1] *Saleh Chowdhury,*[2] *Makoto Takafuji,*[2] *Hirotaka Ihara**[2]

Summary: This article gives a review on self-assembled nanofibrillar aggregates such as helical, twisted ribbon-like and tubular forms, those are produced in aqueous bilayer membrane and organogel systems. Two common features necessary for the chemical structure that yields special morphology are a chiral carbon atom and moieties feasible for intermolecular interactions although there are some exceptions. In aqueous systems, a hydrophobic effect is also an essential driving force for molecular aggregates in aqueous solution systems but almost disappear in organic media. More positive intermolecular interactions play an important role in molecular aggregation in organic media. Hydrogen bonding interaction is especially effective and many organogelators are classified into this category. Some lipophilic peptides have been investigated not only as organogelators but also with respect to their self-assembling behaviors. This latter property gives them distinct advantages compared with conventional gel systems because the gels include highly-ordered structures supramolecular functions like aqueous lipid membranes through molecular orientation. This article also introduces applicability of the organogel system.

Keywords: hydrogels; nanocomposites; organogels; peptides; self-assembly

Introduction

Self-assembly can easily produce intricate structures that would be difficult to make by conventional fabrication methods. The term ''Self-Assembled Nanofibers'' refers to strands with various shapes such as helices, ribbons and tubes. Biological organisms are constructed by molecular building blocks and these molecules assemble spontaneously through various intermolecular interactions.[1–6] On the other hand, many artificially self-assembled nanofibers have been reported in last two decades.[7–19] These self-assemblies show not only unique morphologies but also high molecular orientation toward special functions, for which molecular chirality is an especially important factor. Mirror images of morphologies are formed from enantiomer and racemates will often destroy developed aggregates.[20,21] This suggests that chirality is not unrelated with evolution of life. Well-designed self-assembled nanofibers are also expected to support nanoscopic technologies and their applications. In this article the authors would like to survey the self-assembled nanofibrillar aggregates, and specific attention will be paid to aqueous bilayer membrane systems and organogel systems. In particular, we focus on our previous and rescent studies on the molecular design and the applications of lipophilic L-glutamide derived lipids of low molecular-weight organogel (LMOG) system as functional soft-materials but also as well-defined nano-structured assemblies.

[1] Institute of Advanced Energy, Kyoto University, Gokasho, Uji, Kyoto 611-0011, Japan
[2] Department of Applied Chemistry & Biochemistry, Kumamoto University, 2-39-1 Kurokami, Kumamoto 860-8555, Japan
Fax: (+81) 96 342 3662
E-mail: ihara@kumamoto-u.ac.jp

Fabrication and Characterizations of Nanofibers

Self-assembled nanofibers are generally prepared by dispersing into aqueous or

non-aqueous (organic solvents) media with heating and sonication procedures and then allow to stand the solution at designated temperature for few minutes to several days. Some cases are accompanied by macroscopic transformations through formation of well-developed aggregates. A typical example is viscosity increase and thus the judgement of gelation of organic solvents are conventionally carried out by an inversion fluid method.[22]

Microscopic techniques are useful for observation of aggregation morphologies. Optical microscopes, scanning and transmission electron microscopes (SEM and TEM). Scanning probe microscopes such as atomic force microscope (AFM) have been also used to obtain detailed information on the self-assembled morphologies. A large number of photographs and images of self-assembled aggregates show various fiber-like morphologies such as rods, tubes, halices, ribbons, tapes and twisted multiple strands. The freeze-fracture and freeze-drying techniques can be combined with these microscopic observations. Small angle X-ray scattering (SAXS) and small angle neutron scattering (SANS) are important techniques to obtain the information of practical quantities such as diameter, thickness and length of aggregates. Jung et al. discussed the molecular packing mode.[23] Thermodynamic properties are in most case performed by differential scanning calorimeter (DSC).[24–35] Most self-assembled aggregates show phase transition phenomena such as gel (crystal)-to-liquid crystal and gel (crystal)-to-sol especially in aqueous systems and thus physicochemical properties of the aggregates drastically change at their transition temperatures. Spectroscopic observations provide information on molecular orientations, packing states and lateral diffusion behavior. UV-visible,[19,27,31–34] Fourier transform infrared (FT-IR), circular dichroism (CD),[8,9,19,31,34–36] fluorescence[37,38] and nuclear magnetic resonance (NMR)[39] spectrometers have been widely used for investigation and analysis on the molecular orientation. Typical investigations are found in chromophore-containing lipid systems. Shimomura et al. discussed on H- or J-aggregations with λ_{max}-shift of UV-visible spectra.[40] Ihara et al. discussed on chiral stacking behavior among the sorbyl groups of lipids with both UV-visible and CD spectra.[19] They also discussed on the photo-induced polymerization process by following the spectral changes. Hachisako et al. discussed on the crtical aggregation concentration with visible spectral change induce by isomerization of the spiropiran-containing lipid.[41] Schunur et al. discussed on the relationship between the molecular chirality of lipids and the helicity of aggregation morphology with CD spectra.[42] These suprastructural aggregates often provide specific binding behavior for guest molecules such as dyes. These phenomena can be also detected by UV-visible and CD spectra.[34,43–45] Fluorescence spectra are helpful for knowing microenvironment around lipids. Sagawa et al. reported excimer formation when a pyrenyl group-containing lipid forms highly-ordered aggregates in organic solvents.[38]

Nanofibers in Aqueous Systems

Bio-membranes are spontaneously organized from many kinds of molecules such as phospholipids, proteins and polysaccharides. Some phospholipids (**1**–**4**) listed in Fig. 1, which are representative of amphiphiles, form bilayer membrane structures spontaneously in water and their hydrophobicity is a major driving force in the aggregation and maintenance of the bilayer structures. These lipids usually form small globules and vesicles in water. A typical example is the vesicular structures observed when soybean-derived phosphatidyl choline is dispersed in water, which was reported in 1965.[46]

In 1977, Kunitake et al. reported in a landmark study that didodecyldimetylammonium bromide as a totally synthetic lipid could form bilayer structures in water.[20] Since this turning point, a large number of double-chain alkyl amphiphiles have been synthetized and characterized by many

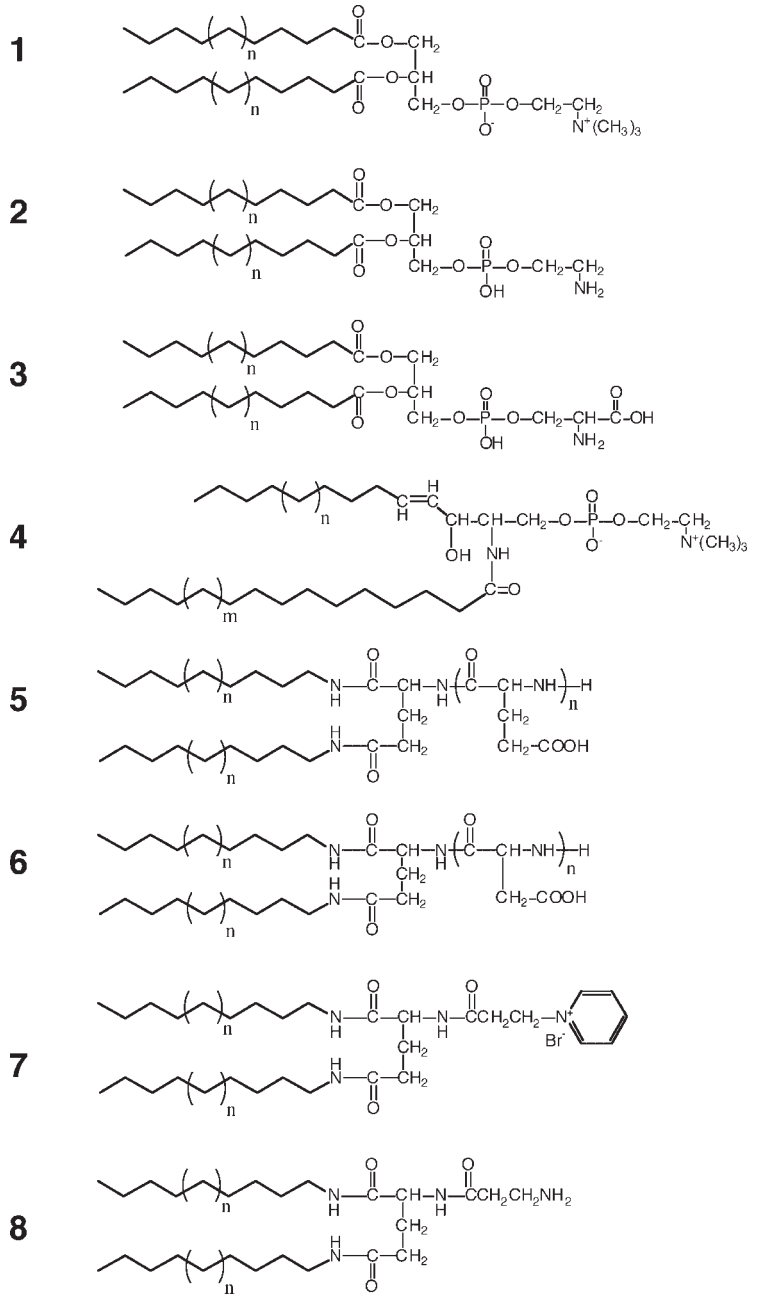

Figure 1.
Chemical structures of aqueous bilayer membrane-forming chiral lipids.

researchers. These findings led to the next step of lipid chemistry. Nobody doubts that the number of alkyl chains in a hydrophobic part is not directly related whether or not a lipid can form bilayer structures but its molecular shape and intermolecular interaction are rather important.

It has been recognized that bilayer membrane structures can be formed from single chains,[7,47] triple chains[48] and

others.[16] Also a hydrophilic part is not within the specified structure. It has been reported to form bilayer membrane structures from amphiphiles with anionic and nonionic groups as well as twitter ionic and cationic groups.

Through these investigations, in 1984, Ihara et al. who is one of the present authors found that special synthetic lipids (**5**) with hydrophilic oligo(L-glutamic acid) head groups can form helical or tubular structures in water (Fig. 2).[8] This finding is significant in light of fact that the thickness of the aggregates corresponds to that of single-walled bilayer structures and that the tubular and helical forms are closely related. Further investigation made it clear that the helical form (Fig. 2a) was rather an intermediate to the stabler tubular form (Fig. 2b) and that the formation of fibrillar structures with helices and tubules is deeply related to their chiral properties.[9,11,18] The detailed study on morphogenesis from low-molecular compounds to nano-size aggregates was done by them using the corresponding oligo(L-aspartic acid) derivatives. Amphiphilic compound **6** also formed fibrillar and twisted ribbon-like aggregates in aqueous systems and then the process of morphogenesis was moniterd by TEM observation and light scattering measurement[9]: (1) **6** formed globular aggregates with the largest curvature at the initial step; (2) these globules grew to fibrillar aggregates; (3) double- or multiple-strands were produced and then fused themselves to make ribbon-like aggregates. These findings indicate that even a very small difference between L-glutamic and L-aspartic acid in the head group strongly influences the morphology of the aggregates. This means that aggregation morphology is also very sensitive to temperature and pH factors because these can drastically change the secondary structures of the head groups.

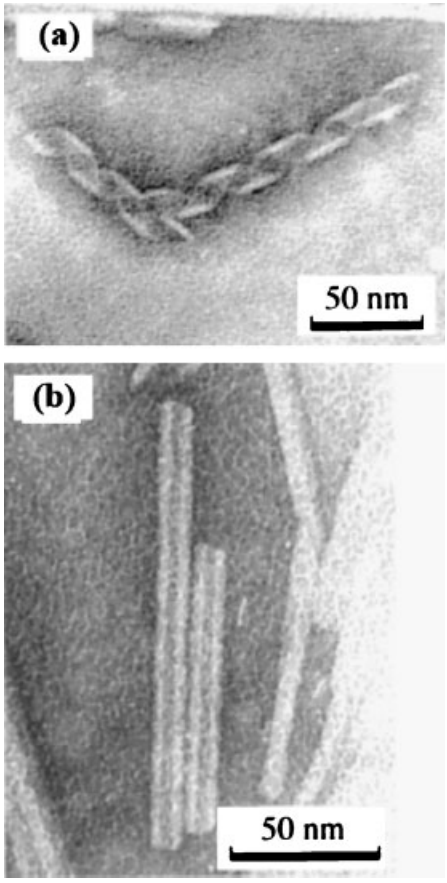

Figure 2.
TEM images of (a) helical and (b) tubular aggregates from lipid membrane of **5**.

These findings encouraged the development of self-assembling nanoarchitecture. Since 1984, many researchers have designed and synthesized chiral lipids that produce nanofibrillar structures in water. They can be roughly classified into two categories: (1) micellar-based aggregates and (2) bilayer sheet-based aggregates. So far, a large number of bilayer-forming lipids have been reported, including some which can form helical and twisted ribbon-like aggregates. Their assemblies are based on distorted sheet-like bilayer membranes with large curvature and are morphologically divided into helical and tubular structures with cylindrical curvature and twisted ribbons with Gaussian, saddle-like curvature.

Two common features necessary for the chemical structure yields special morphology are a chiral carbon atom and moieties feasible for intermolecular interactions although there are some exceptions. Therefore, thousands of amphiphilic compounds

forming bilayer membrane-based nanofibrills are now reported. It includes single chain,[32] quadriplex chain,[16] and cholesterol group[13] as hydrophobic part, and nucleotide group[15] as a hydrophilic part. Moreover, polymerizable moieties such as diacetyrene group,[12] acrylate group,[49] methacrylate[13] and sorbate group-containing lipids[19] have been also reported. So far, no consensus has been established, because supramolecular assemblies-forming compounds include many different chemical structures. Several questions still remain; for instance, the nature of the edge of the bilayers has not been clarified. Future work in both experimental and theoretical studies will develop technologies for order-made self-assembling nanofibers.

Nanofibers in Organic Media

Hydrogels can often be formed from aqueous solutions of hydrophilic polymers, biomolecules such as proteins, and inorganic materials such as silicates. They have been studied in detail, and related books[50,51] and reviews[52] have been published by many researchers. Some of these gels and gelators are widely used in industries, food science and cosmetic science. Recently, it has been found that some specific low molecular weight compounds formed gels in organic media.[53] These can be referred to as organogels (organic gels). Organogels are very unique not only in that the gelation is induced by three-dimensional network formation with well-developed fibrous aggregates, but also in that these aggregates are on the basis of highly-oriented structures like aqueous lipid bilayer membranes. Therefore, they attract our interest in spite of their instability, and we further label them ''self-assembled organogels'' to distinguish them from conventional gels. Self-assembled organogels include various fibrillar aggregates such as rods, helices and sheets, and the challenge of stabilizing their morphologies and molecular orientation to widen their applications is now being met. Here we focus on nanofibrillar aggregates formed in organic solvents.

Low molecular weight compounds that can produce gels from organic solvents have been known since 50 years ago. However the gelation of organic solvents and oils as macroscopic phenomena has been a main subject of interest for several decades thereafter. From the late '80s to the early '90s, several kinds of organogels were discovered simultaneously. In this period, many researchers joined the research field of nano-sized molecular architectures to develop molecular devices for supersensitive sensors, high density memory storage and so on. It appears that a point of view toward organogels has been shifted into explication and control of molecular buildings formed from low molecular weight organogelators, spontaneously. The original root compounds of organogelators (Fig. 3) have been discovered serendipitously by researchers who were working in various research fields.[28,54–57] Therefore the chemical structures of most organogelators are derived from intermediate molecules designed for specific functions.

A hydrophobic effect is the most essential driving force for molecular aggregates in aqueous solution systems but almost disappear in organic media. More positive intermolecular interactions play an important role in molecular aggregation in organic media. Hydrogen bonding interaction is especially effective and many organogelators are classified into this category.

Peptide-based derivatives will be useful as organogelators because their amide bonds work as a stronger driving force for molecular aggregation. Peptide-based organogelators have a plural number of hydrogen bondable moieties. **10**[28,31] as a typical example possesses three amide bonds around an L-glutamic moiety, which works as a good organogelator. TEM and SEM observations showed a three-dimensional network with fibrillar aggregates in its organogel and xerogel. The minimum diameter of the aggregates in the picture is 20 nm, which is 2–3 times larger than the molecular length estimated by SAXS.[31] However, if two of the three amide bonds are replaced by the ester bonds, no gelation

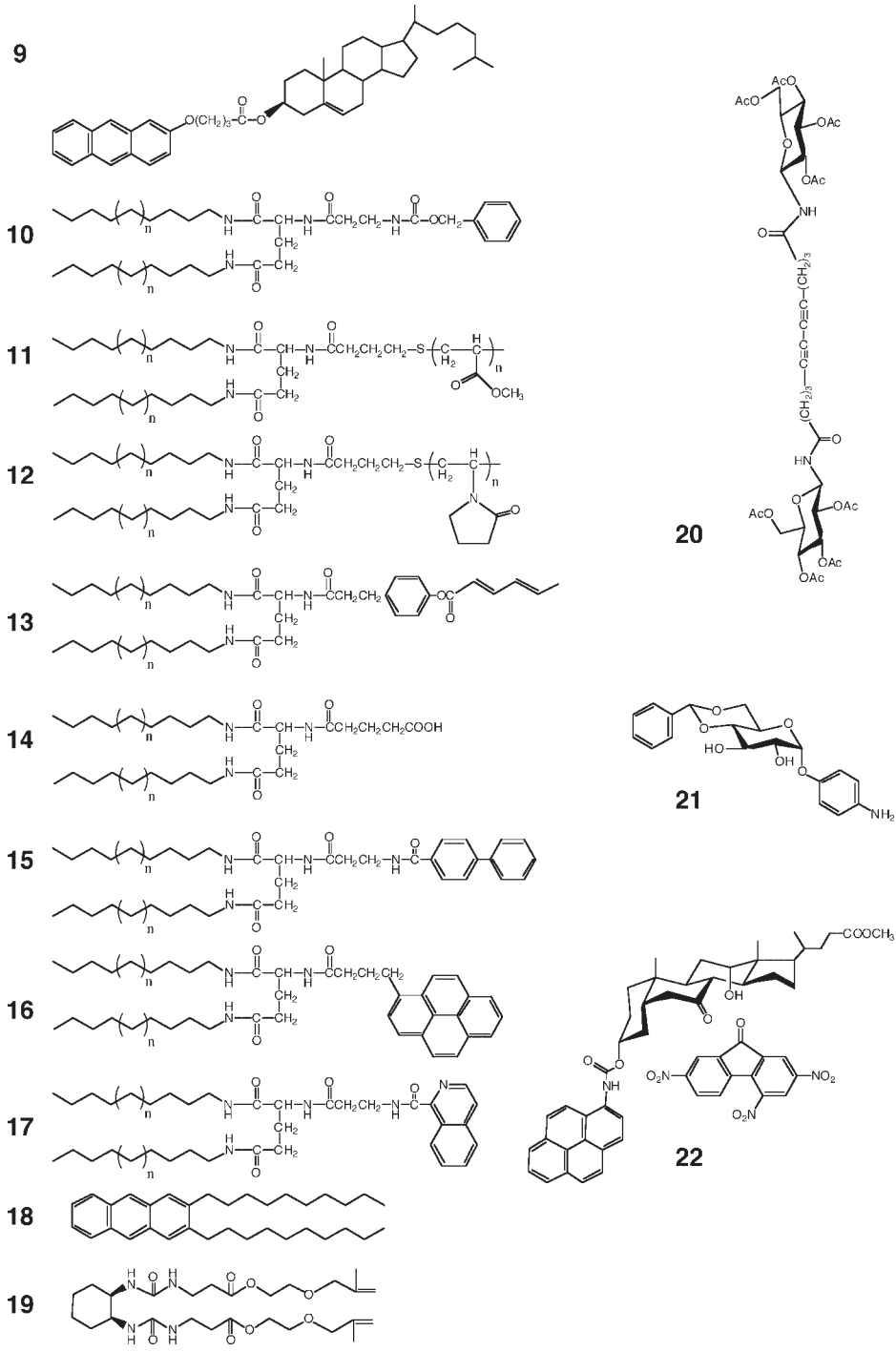

Figure 3.
Chemical structures of various low molecular-weight organogelators.

is observed even when their concentration is 10 times higher than former. It was also confirmed that addition of trifluoroacetic acid as an inhibitor for hydrogen bonding causes gel-to-sol transition. MOPAC calculation indicated that the three amide bonds around the L-glutamic acid moiety provided a proper conformation for intermolecular interaction. The compounds **11**[58] and **12**[59] are based on the L-glutamide moiety with oligomeric head groups. This molecular design is advantageous due to the facts that the function is not only tunable but also versatile only by choosing a monomer, which can be converted into a head group. **11** and **12** have oligo(methyl acrylate) and (vinyl-2-pyrrolidone), respectively. They were also derived from lipophilic L-glutamides and formed fibrous aggregations in organic media. For example, **12** formed tubular aggregates in methanol.

There are some derivatives that can produce organogels without intermolecular hydrogen bonding interaction. A typical example is the steroid derivative with polyaromatic group (**9**), first reported in 1987 by Weiss et al., who investigated the gelation ability of the isoandrosterone derivatives.[54,60–62] The kinetics were investigated in detail by using electron paramagnetic resonance (EPR), SANS, infrared (IR), and CD spectroscopies. After this finding, more than 40 derivatives including steroid and aromatic groups have been reported. They are sometimes classified by the abbreviations ALS, where A, L and S correspond to aromatic (A), linking (L) and steroid (S) groups, respectively. Effects of chemical structures of each part on the gelation were investigated in detail; for instance, (1) stereo-chemistry at C-3 and the nature of the chain at C-17 of the steroidal part, (2) various aromatic groups such as 9,10-anthraquinones, cinnamate, 2-naphtyl, 1-pyrenyl, phenyl and their substituted compounds, and (3) the length and functionality of the linking groups.[63–65] Inductions of functional groups such as crown ether and azo-benzene into cholesterol were performed by Shinkai et al.[66–68]

We estimate that a steroid group will give limited solubility to organic solvents compared to a long chain alkyl group and thus may work as a sorbophobic moiety. Positive interaction can probably be induced by polyaromatic groups. Supporting this, anthryl derivatives connected to dialkyl chains have been studied as organogelators[55,69–71] 2,3-Bis-*n*-decyloxyanthracene, **18**, produced organogels in many organic solvents.[55] Since 2,3-dialkoxynaphthalene showed no ability of gelation for any organic solvents, increasing aromaticity promoted gelation ability. Even if the anthracene moiety was replaced by anthrax quinone and phenazine, effective gelation was observed. The number and length of alkyl chains were also sensitive to gelation abilities. Freeze-fracture electron micrographs of **18**-propanol gels indicated a three-dimensional network of fibrous rigid bundles with 60–70 nm diameters.

Chemical Stabilization of Organogels

Some lipophilic peptides have been investigated not only as organogelators but also with respect to their self-assembling behaviors. This latter property gives them distinct advantages compared with conventional gel systems. The fibrillar aggregates are based on highly-ordered structures and thus show aqueous lipid membrane-like behaviors such as phase transition, phase separation and chirality enhancement through molecular orientation. Although these features are advantageous for extended applications, it is also clear that their thermal and mechanical instabilities are a disadvantage in some application fields.

Some approaches have been proposed for stabilization of organogels. Introducing a polymerizable group into a gelator is a reasonable method for this purpose as the instability of the organogel derived from assembled structure via non-covalent bonds. The first example of polymerizable organogelator was a sorboyl group-introduced peptide (**13**) in 1995. In this case, significant stabilization was not observed by photo-induced cross-linking among the peptides because oligomerization was pre-

dominant reaction in the process.[72] On the other hand, de Loos et al. reported a bis(ureido)cyclohexane derivative containing a methacrylate moiety as a polymerizable organogelator (**19**).[73] This compound produce organogels with developed fibrous aggregates in various organic solvents. Gel formation was maintained after polymerization by UV irradiation in the presence of photo-initiator and the resultant gel showed highly thermal stability up to temperatures above the boiling point of the solvents. Polymerization of photo-induced polymerizable groups containing organogelators (**20**) was demonstrated by Masuda et al.[74,75] Diacetylene containing organogelator (bolaamphiphile) was used for the purpose of stabilizing. Polymerization could be monitored by UV spectroscopic observations, and was induced by photo or γ-ray irradiation. In each case, stability of the organogel preserving fibrous aggregates rose in several samples after polymerization. However, reversibility of sol-to-gel transition and most properties based on molecular fluidity disappeared.

Sometimes metal ions increase the mechanical strength of organogels. 1-O-(*p*-Aminophenyl)-4,6-O-benzylidene-α-D-glucopyranoside (**21**) behaves as a good gelator for various organic solvents.[36,76] The T_{gel} values for ethanol gel were markedly improved by the addition of $AgNO_3$, $CoCl_2$ or $CdCl_2$. The T_{gel}s for 1 wt/vol% of organogel in ethanol are $-10\,^{\circ}C$ and $71\,^{\circ}C$ respectively in the absence and presence of equimolar $CoCl_2$. This remarkable change is due to cross-linking of **21** molecules by Co(II)-amino group interaction. It seems that hydrogen bonds and coordination bonds work cooperatively for reinforcement of organogels. Similar observations were obtained using a diketonate ligand-containing organogelator.[77] Maitra et al. reported that the donor-acceptor interaction promoted organogels (**22**).[65]

Approach for Nano-Structures Materials

Organogel systems can be applied as liquid organic media. Gu et al.[78] and Hafkamp et al.[76] described morphological imprinting of fibrous aggregates using tetraoctadecylammonium bromide and gluconamide derivatives coordinated with metal ion, respectively. Each organogelator can produce organogels with fibrous aggregates in styrene and methyl methacrylate. Polymerization of the solvents was carried out with UV light in the presence of a photo-initiator. Fibrous aggregates with similar diameters were observed before and after photopolymerization and the gelator molecules could be removed from the resultant polymer matrix by the solvent extraction method.[76] According to optical and electron microscopic measurements, the diameters of the strand-like pores were bigger than those of the original fibrous aggregates. It was expected that the monomers which exist near the surface of fibrous aggregates could not react since their mobility and fluidity were restricted. Similar observations were obtained with organogels from a pyrenyl group-containing peptide lipid (**16**) in styrene and methylmethacrylate. In this study, we obtained significant information on the molecular orientation states before and after polymerization of the bulk solution. Enhanced CD spectra around the pyrenyl group was observed after polymerization and maintained even at $70\,^{\circ}C$, a temperature even higher than its sol state temperature. These results indicate that highly-oriented structures can be stabilized by polymerization of a bulk solution.[79]

Control of Highly-Ordered States

Some organogelators form highly-ordered structures like those in aqueous bilayer membranes. Therefore it is a convenient method to arrange the functional groups in the molecular assemblies. The arrangement and controls of functional groups will certainly be an invaluable technique in many application fields such as sensors, molecular devices and nano fabrication.

Lipophilic peptide-derived organogelators such as **15** and **16** show specific chirality which is detectable by CD spectroscopic measurement around the chromophore groups. We have made some examinations to confirm whether or not specific proper-

ties observed in aqueous bilayer membranes can be reproduced in organic solvents. Phase separation behavior was observed in a mixture of **10** and an azobenzene-attached **8** derivative in benzene. Distinct CD spectra based on the azobenzene moiety were observed below T_{gel}.[27] The cotton effect of this mixture disappeared above T_{gel} and thermal reversibility was observed. On the other hand, a carboxylic acid-containing L-glutamate derivative (**14**) produced organogel with developed fibrous aggregates in several organic solvents.[80]

This specific chiral properties stimulated us to implement optical resolution with chiral organogels. We reported the first example in 1995. When dansylphenyl alanine as a chiral guest molecule was dissolved in organogels from **10** and **7**, distinct enantioselective elution to an alkaline solution was observed. Interestingly, CD and DSC measurements showed that the best result was obtained through **7** domain formation phase separated from **10** aggregates.[81]

This finding encouraged us to control the chirality of organogels. For this purpose, we synthesized a double-chain alkyl L-glutamide derivative with an isoquinoline-head group (**17**).[82,83] This behaves as an organogelator with developed twisted fibers. It was confirmed that chelation with metal chloride in cyclohexane-ethanol (100:1) solution remarkably perturbed the chirality and morphology of the aggregates. Addition of copper ion ($CuCl_2$), which can form a square planar coordination, induced the chirality enhancement with morphological change from twisted fibrous aggregates to ribbon-like aggregates. On the contrary, cobalt ion ($CoCl_2$) and zinc ion ($ZnCl_2$), which can form an octahedral coordination state, caused serious morphological change with remarkable decrease of the chirality.[82,83]

Conclusion

"**Self-assembled nanofibers**" are formed from miscellaneous synthetic compounds and show various charming shapes as describe herein. Although it is hard to completely understand the relationships between their morphologies and chemical structures, experimental and theoretical approaches indicate several important factors such as a) moderate solubility into media, b) intermolecular interaction moieties and their sterical position, c) molecular shapes for highly-ordered molecular packing and d) molecular chirality. Many reports also indicate a wide range of possible applications for these self-assembled nanofibers, from morphological applications such as preparation and utilization of replica of them to molecular level applications of specific molecular orientation. In this article, we introduced self-assembled nanofibers constructed mainly by relatively simple compounds, but oligomers and polymers such as cyclic polypeptide, cyclodextrin and cyclic polysaccharide are also known to form self-assembled nanofibers.[84]

It is prospected that self-assembling nano architectures including fibrillar aggregates have many potential applications because nature, especially human, is excellent example of hierarchical product of self-assembling molecules, there are so many excellent examples of hierarchical products of self-assembling molecules in nature itself, not the least of which is the human body. We sincerely hope that research on self-assembled nano architectures will be helpful in the development of molecularly precise materials and devices. The diversity of self-assembled nanofiber systems including a large number of molecules provides much opportunity to modify the chemical structures of self-assembling molecules. With the present rapid progress and expansion of this field, we feel a premonition that many applications will be found for nanofibers in the near future, including using combinations of morphologies and functions to provide suggestions for the origin of life.

[1] J. Inglese, J. F. Glickman, W. Lorenz, M. G. Caron, R. J. Lefkowitz, *J. Biol. Chem.* **1992**, *267*, 1422.
[2] J. E. Tousa, W. Baehr, R. L. Martin, J. Hirsh, W. L. Pak, *Cell* **1985**, *40*, 839.

[3] A. F. Cowman, C. S. Zuker, G. M. Rubin, *Cell* **1986**, *44*, 705.
[4] C. S. Zuker, A. F. Cowman, G. M. Rubin, *Cell* **1985**, *40*, 851.
[5] S. S. Karnik, T. P. Sakmar, H. Chen, H. Khorana, *Proc. Natl. Acad. Sci. U. S. A.* **1988**, *85*, 8459.
[6] I. Nishie, K. Anzai, T. Yamamoto, Y. Kirino, *J. Biol. Chem.* **1990**, *265*, 2488.
[7] T. Kunitake, Y. Okahata, S. Shimomura, S. Yasunami, K. Takarabe, *J. Am. Chem. Soc.* **1981**, *103*, 5401.
[8] K. Yamada, H. Ihara, T. Ide, T. Fukumoto, C. Hirayama, *Chem. Lett.* **1984**, 1713.
[9] H. Ihara, T. Fukumoto, C. Hirayama, K. Yamada, *Polym. Commun.* **1986**, *27*, 282.
[10] T. Kunitake, N. Yamada, *J. Chem. Soc., Chem. Commun.* **1986**, 655.
[11] H. Ihara, T. Fukumoto, C. Hirayama, K. Yamada, *J. Chem. Soc. Jpn.* **1987**, 543.
[12] J. H. Georger, A. Shingh, R. R. Price, J. M. Schnur, P. Yager, P. E. Schoen, *J. Am. Chem. Soc.* 109, 6169 (1987).
[13] I. Cho, J. G. Park, *Chem. Lett.* **1987**, 977.
[14] J.-H. Fuhrhop, P. Schnieder, E. Boekema, W. Helfrich, *J. Am. Chem. Soc.* **1988**, *110*, 2861.
[15] H. Yanagawa, Y. Ogawa, H. Furuta, K. Tsuno, *J. Am. Chem. Soc.* **1989**, *111*, 4567.
[16] N. Kimizuka, H. Ohira, M. Tanaka, T. Kunitake, *Chem. Lett.* **1990**, 29.
[17] H. Ihara, M. Yamaguchi, M. Takafuji, H. Hachisako, C. Hirayama, K. Yamada, *J. Chem. Soc. Jpn.* **1990**, 1047.
[18] H. Ihara, K. Yoshikai, M. Takafuji, C. Hirayama, K. Yamada, *Jpn. J. Polym. Sci. Tech.* **1991**, *48*, 377.
[19] H. Ihara, M. Takafuji, C. Hirayama, D. F. O'Brien, *Langmuir* **1992**, *8*, 1548.
[20] R. Jetter, M. Riederer, *Planta* **1994**, *195*, 257.
[21] M. Lohmeyer, P. Workman, *Biochem. Pharmacol.* **1992**, *819*, 44.
[22] K. Hanabusa, T. Miki, Y. Taguchi, T. Koyama, H. Shirai, *J. Chem. Soc., Chem. Commun.* **1993**, 1382.
[23] J. H. Jung, S. Shinkai, *J. Incl. Phenom. Macrocyc. Chem.* **2001**, *41*, 53.
[24] S. Mabrey, J. M. Sturtevant, *Proc. Natl. Acad. Sci. U. S. A.* **1976**, *73*, 3862.
[25] T. Kajiyama, A. Kumano, M. Takayanagi, Y. Okahata, T. Kunitake, *Chem. Lett.* **1979**, 645.
[26] Y. Okahata, T. Kunitake, *Ber. Bunsenges. Phys. Chem.* **1980**, *84*, 550.
[27] T. Kunitake, H. Ihara, Y. Okahata, *J. Am. Chem. Soc.* **1983**, *105*, 6070.
[28] H. Ihara, H. Hachisako, C. Hirayama, K. Yamada, *J. Chem. Soc. Chem. Commun.* **1992**, 1244.
[29] T. Kimura, S. Shinkai, *Chem. Lett.* **1998**, 1035.
[30] T. Kato, G. Kondo, K. Hanabusa, *Chem. Lett.* **1998**, 193.
[31] H. Ihara, M. Yoshitake, M. Takafuji, T. Yamada, T. Sagawa, C. Hirayama, H. Hachisako, *Liq. Cryst.* **1999**, *26*, 1021.
[32] T. Kunitake, N. Nakashima, M. Shimomura, Y. Okahata, K. Kano, T. Ogawa, *J. Am. Chem. Soc.* **1980**, *102*, 6642.
[33] M. Shimomura, T. Kunitake, *Chem. Lett.* **1981**, 1001.
[34] H. Ihara, H. Hachisako, C. Hirayama, K. Yamada, *Liq. Cryst.* **1987**, *2*, 215.
[35] J. E. Sohna, F. Fages, *J. Chem. Soc. Chem. Commun.* **1997**, 327.
[36] N. Amanokura, K. Yasumasa, S. Shinkai, *J. Chem. Soc. Perkin Trans. 2* **1999**, 1995.
[37] K. Kano, A. Romero, B. Djermouni, H. J. Ache, J. H. Fendler, *J. Am. Chem. Soc.* **1979**, *101*, 4030.
[38] T. Sagawa, S. Fukugawa, T. Yamada, H. Ihara, *Langmuir* **2002**, *18*, 7223.
[39] T. Nagamura, S. Mihara, Y. Okahata, T. Kunitake, T. Matsuo, *Ber. Bunsenges. Phys. Chem.* **1978**, *82*, 1093.
[40] M. Shimomura, R. Ando, T. Kunitake, *Ber. Bunsenges. Phys. Chem.* **1983**, *87*, 1134.
[41] H. Hachisako, H. Ihara, T. Kamiya, C. Hirayama, K. Yamada, *J. Chem. Soc. Chem. Commun.* **1997**, 19.
[42] J. M. Schnur, B. R. Ratna, J. V. Seliger, A. Singh, G. Jyothi, K. R. K. Easwaran, *Science* **1994**, *264*, 945.
[43] N. Nakashima, H. Fukushima, T. Kunitake, *Chem. Lett.* **1981**, 1207.
[44] N. Nakashima, T. Kunitake, *J. Am. Chem. Soc.* **1982**, *104*, 4261.
[45] T. Arimura, M. Shibata, H. Ihara, C. Hirayama, *Anal. Sci.* **1993**, *9*, 401.
[46] A. D. Bungham, M. M. Standish, J. C. Watkins, *J. Mol. Biol.* **1965**, *13*, 238.
[47] K. Yamada, H. Shosenji, H. Ihara, O. Hotta, *Chem. Lett.* **1983**, 43.
[48] T. Kunitake, N. Kimizuka, N. Higashi, N. Nakashima, *J. Am. Chem. Soc.* **1984**, *106*, 1978.
[49] T. Kunitake, N. Nakashima, M. Kunitake, *Macromolecules* **1989**, *22*, 3544.
[50] Y. Osada, A. R. Khokhlov, *Polymer Gels and Networks*, Marcel Dekker, Inc., New York (**2001**).
[51] J. P. Cohen Addad, *Physical Properties of Polymeric Gels*, John Wiley & Sons, Inc., Hoboken (**1996**).
[52] K. Almdal, J. Dyre, S. Hvidt, O. Kramer, *Polym. Gels Networks* **1993**, *1*, 5.
[53] P. Terech, R. Weiss, *Chem. Rev.* **1997**, *97*, 3133.
[54] Y.-C. Lin, R. G. Weiss, *Macromolecules* **1987**, *20*, 414.
[55] T. Brotin, R. Utermohlen, F. Fages, H. Bouas-Laurent, J. P. Desvergne, *J. Chem. Soc., Chem. Commun.* **1991**, 416.
[56] Y. Ishikawa, H. Kuwahara, T. Kunitake, *J. Am. Chem. Soc.* **1989**, *111*, 8530.
[57] N. Ide, T. Fukuda, T. Miyamoto, *Bull. Chem. Soc. Jpn.* **1995**, *68*, 3423.
[58] H. Ihara, M. Takafuji, T. Sakurai, M. Katsumoto, N. Ushijima, T. Shirosaki, H. Hachisako, *Org. Biomol. Chem.* **2003**, *1*, 3004.
[59] S. Chowdhury, H. Ihara, *to be submitted*.
[60] I. Furman, R. G. Weiss, *Langmuir* **1993**, *9*, 2084.

[61] R. Mukkamala, R. G. Weiss, *J. Chem. Soc., Chem. Commun.* **1995**, 375.
[62] R. Mukkamala, R. G. Weiss, *Langmuir* **1996**, *12*, 1474.
[63] D. J. Abdallah, R. G. Weiss, *Adv. Mater.* **2000**, *12*, 1237.
[64] L. Lu, D. L. Cocker, R. E. Bachman, R. G. Weiss, *Langmuir* **2000**, *16*, 20.
[65] U. Maitra, P. V. Kumar, N. Chandra, L. J. D'Souza, M. D. Prasanna, A. R. Raju, *J. Chem. Soc. Chem. Commun.* **1999**, 595.
[66] K. Murata, M. Aoki, T. Nishi, A. Ikeda, S. Shinkai, *J. Chem. Soc., Chem. Commun.* **1991**, 1715.
[67] K. Murata, M. Aoki, T. Suzuki, T. Harada, H. Kawabata, T. Komori, F. Ohseto, K. Ueda, S. Shinkai, *J. Am. Chem. Soc.* **1994**, *116*, 6664.
[68] S. Shinkai, K. Murata, *J. Mater. Chem.* **1998**, *8*, 485.
[69] F. Placin, M. Colomes, J.-P. Desvergne, *Tetrahedron Lett.* **1997**, *38*, 2665.
[70] J.-L. Pozzo, G. M. Clavier, J.-P. Desvergne, *J. Mater. Chem.* **1998**, *8*, 2575.
[71] G. M. Clavier, J.-F. Brugger, H. Bouas-Laurent, J.-L. Pozzo, *J. Chem. Soc., Perkin Trans. 2* **1998**, 2527.
[72] H. Ihara, K. Shudo, M. Takafuji, C. Hirayama, H. Hachisako, K. Yamada, *Jpn. J. Polym. Sci. Technol.* **1995**, *52*, 606.
[73] M. de Loos, J. van Esch, I. Stokroos, R. M. Kellogg, B. L. Feringa, *J. Am. Chem. Soc.* **1997**, *119*, 12675.
[74] M. Masuda, T. Honda, K. Yase, T. Shimizu, *Macromolecules* **1998**, *31*, 9403.
[75] M. Masuda, T. Honda, Y. Okada, K. Yase, T. Shimizu, *Macromolecules* **2000**, *33*, 9233.
[76] R. J. H. Hafkamp, B. P. A. Kokke, I. M. Danke, H. P. M. Geurts, A. E. Rowan, M. C. Feiters, R. J. M. Nolte, *J. Chem. Soc. Chem. Commun.* **1997**, 545.
[77] K. Hanabusa, Y. Maesaka, M. Suzuki, M. Kimura, H. Shirai, *Chem. Lett.* 2000, 1168.
[78] W. Gu, L. Lu, G. B. Chapman, R. G. Weiss, *J. Chem. Soc. Chem. Commun.* **1997**, 543.
[79] M. Takafuji, A. Ishiodori, T. Yamada, T. Sakurai, H. Ihara, *J. Chem. Soc. Chem. Commun.* **2004**, 1122.
[80] M. Takafuji, H. Ihara, C. Hirayama, H. Hachisako and K. Yamada, *Liq. Cryst.* **1995**, *18*, 97.
[81] H. Ihara, K. Shudo, H. Hachisako, K. Yamada, C. Hirayama, *Liq. Cryst.* **1996**, *20*, 807.
[82] M. Takafuji, T. Sakurai, T. Hashimoto, N. Kido, T. Yamada, T. Sagawa, H. Hachisako, H. Ihara, *Chem. Lett.* **2002**, 7223.
[83] H. Ihara, T. Sakurai, T. Yamada, T. Hashimoto, M. Takafuji, T. Sagawa, H. Hachisako, *Langmuir* **2002**, *18*, 7120.
[84] D. T. Bong, T. D. Clark, J. R. Granju, M. R. Ghadiri, *Angew. Chem. Int. Ed.* **2001**, *40*, 988.

