Stabilization of enhanced chirality from pyrene-containing L-glutamide lipid in methyl methacrylate by photo-induced polymerization

Makoto Takafuji,[a,*] Arata Ishiodori,[a] Taisuke Yamada,[a] Toshihiko Sakurai[a] and Hirotaka Ihara[a,b,*]

[a] Department of Applied Chemistry and Biochemistry, Kumamoto University, 2-39-1 Kurokami, Kumamoto, Japan. Fax & Tel: 81-96-342-3662; E-mail: takafuji@chem.kumamoto-u.ac.jp
[b] Institute for Materials Chemistry and Engineering, Kyushu University, 6-10-1 Hakozaki, Higashi-ku, Fukuoka 812-8581, Japan. Tel: 81-92-642-2713; E-mail: ihara@kumamoto-u.ac.jp

*This submission was created using the RSC ChemComm Template (**DO NOT DELETE THIS TEXT**)*
*(**LINE INCLUDED FOR SPACING ONLY - DO NOT DELETE THIS TEXT**)*

Enhanced CD spectra based on chirally-oriented structures of pyrene-containing L-glutamc acid-derived lipid were observed in polymerizable monomers and CD strength was maintained after photo-induced polymerization of the monomer solvents.

Last decade, a number of low molecular weight organic compounds have been reported[1-5] to be effective gelators for organic solvents. In most of these cases, the gelator forms nanofibrous aggregates based on highly-ordered structures with inter-molecular interactions such as hydrogen bondings, van der Waals forces and π-π interactions. These fibrous aggregates form a three-dimensional network by entwining with themselves and gelation is brought by encapsulation of solvent molecules into the network. Therefore, this new organic system may have potential applications for various fields such as catalysis, sensor technology and materials science. To make these systems more amenable for such applications, introduction of polymerizable groups onto organogelators has often been performed to increase their physical strength and immobilize their aggregate morphology by polymerization.[6] Also, morphological features
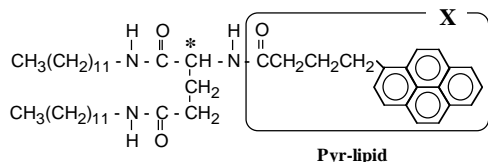
Scheme Chemical structure of L-glutamic acid-derived lipid.

are applicable for imprinting techniques. For example, a hollow fiber silica was prepared from sol-gel polymerization of tetraethoxysilane in cholesterol-based organogel[7] and polymer-block with strand-like pores was obtained by extraction of organogelators from polymerized organogel of methyl methacrylate or styrene.[8]

On the other hand, stabilization of molecular oriented structures has been attracting much interest from the field of optical materials science because some of the organogels induce specific enhanced chirality. For example, we have reported a versatility of a chiral L-glutamide unit for self-assembled organogelation (scheme).[2, 9-11] This key unit works not only as an effective intermolecular hydrogen bonding source but also induces specific functions, especially in enhanced chirality with a chromophoric head group (X) such as azobenzene, spiropyran, pyrene and isoquinoline. In this study, we demonstrate the stabilization of chirally-oriented structures formed from the L-glutamic acid-derived lipid with a pyrenyl head group (Pyr-lipid) in polymerizable monomer solvents.

The Pyr-lipid was prepared by coupling pyrene butylic acid with N^1, N^5-didodecyl-L-glutamide[11] using diethyl phospholocyanide
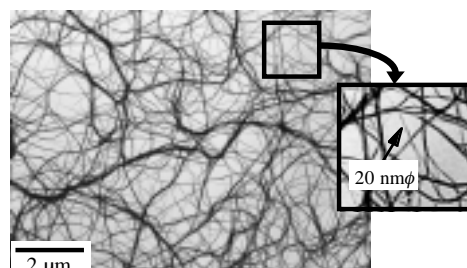
Fig. 1 Typical TEM image of **Pyr-lipid** in methyl methacrylate.

as a coupling agent. The Pyr-lipid was clearly dissolved in polymerizable monomers such as methyl methacrylate (MMA), styrene and divinylbenzene (DVB) at 80 °C and the solution was then cooled to 15 °C. The gel formation in the monomers was observed by an inversion fluid method. The Pyr-lipid formed clear or slightly turbid gels in styrene, MMA and DVB, though the critical gelation concentrations (cgc) were different for each monomer solvent.[†] TEM observations showed that well-developed fibrous aggregates were included in the organogels of MMA, styrene and DVB. Fig. 1 shows a typical electron micrograph of the organogel in MMA. On the contrary, neither gelation nor developed aggregates were observed in acrylic acid (AA) and methacrylic acid (MAA). These results indicate that the gelation is induced through network formation with nanofibrous aggregates (apparent diameters in MMA, 20 - 25 nm) and that acidic monomers suppress hydrogen bonding interactions among the lipids.

Fig. 2 shows UV-visible and CD spectra of the gels (5 mmol l^{-1}) in MMA. An absorption spectrum with λ_{max}s of 314, 328 and 343 nm was observed in MMA solution at 70 °C. This corresponds to the spectrum in which a pyrenyl group is in a monomeric dispersion.[12] In support of this, almost no CD was detected at 70 °C. On the other hand, when the solution was cooled to 15 °C, a red-shift with broadening of peaks was observed with gelation of the solution. This red-shift was accompanied by distinct induction of CD around the new absorption band. The detailed temperature dependency showed that remarkable changes of UV and CD spectra occurred around the gel-to-sol phase transition temperature (T_{gel} = 60 °C, the T_{gel} was evaluated by an inversion fluid method). Similar phenomena have often been observed in aqueous bilayer membrane systems formed from chiral amphiphiles[13] which can be explained by the fact that enhancement of CD strength is based on chiral stacking among the chromophore groups. Therefore, it is estimated that the Pyr-lipid produces highly-ordered structures with chiral arrangement of pyrenyl head groups in MMA at temperatures below T_{gel}. Similar enhanced CD spectra were also observed in styrene and DVB although their CD strengths differed depending on the polymerizable monomer solvent (in styrene: θ_{353} = 3.0 x 10^5, in DVB: θ_{353} = 4.2 x 10^5, and in MMA: θ_{353} = 4.6 x 10^4 deg cm^2 $dmol^{-1}$). The CD strengths were much smaller in MAA and
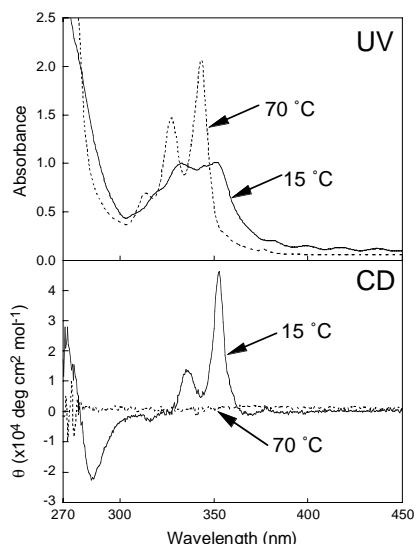
NO TEXT BELOW THIS LINE

Fig. 2 UV and CD spectra of **Pyr-lipid** in MMA at 15 ˚C and 70 ˚C.
[**Pyr-lipid**] = 1 mmol l^{-1}

AA (in MAA: θ_{353} = 1.7 x 10^3, and in AA: θ_{353} = 0.9 x 10^3 deg cm^2 dmol^{-1}). This indicates that these monomer solvents are not suitable for molecular assembling because of their acidic property, an assumption supported by the fact that trifluoroacetic acid works as an inhibitor for intermolecular hydrogen bonding interaction[9] and subsequently both gelation and CD enhancement are suppressed.

Photo-induced polymerization was accomplished by addition of 1 wt% of a photo-initiator (benzoin ethyl ether) to the MMA gel containing 5 mmol l^{-1} of Pyr-lipid and UV-light irradiation using a high-pressure mercury lamp for 10 hours at 15 °C. A transparent solid sheet (Fig. S-1) was obtained by photo-induced polymerization. As shown in Fig. 3, the shape and strength of the CD spectrum showed almost no change after polymerization of MMA at 15 °C. Furthermore, no decrease was observed in the CD strength even at 70 °C in spite of the almost no CD in the solution state before polymerization (the CD strength showed almost no change after being maintained at 70 ˚C for more than 1 day). These results indicate that highly-oriented structures were maintained by photo-induced polymerization of MMA and were stable even at temperatures above the original T_{gel}. Evidence for the stacking structure of pyrenyl groups was also obtained from fluorescence measurements of Pyr-lipid in MMA polymer (Fig. S-2). Excimer emission of pyrenyl moieties[12] was observed around 460 nm (excitation wavelength = 350 nm) in the solid sheets polymerized at 15 ˚C, while monomer emissions were observed at 378 and 398 nm in those polymerized at 70 ˚C. It has been reported[12,14] that similar excimer formation of pyrenyl moieties in the organogel system is provided through highly-oriented structures of organogelators. The remaining monomer
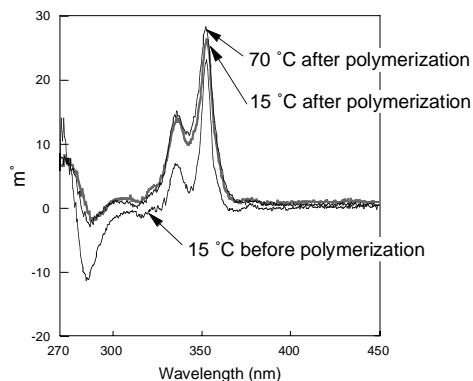

Fig. 3 CD spectra of **Pyr-lipid** in MMA before and after polymerization. Photo-induced polymerization was carried out in 0.1 mm quartz cell at 15 ˚C for 10 hours. [**Pyr-lipid**] = 1 mmol l^{-1}

in the transparent solid sheet was quantitated by HPLC.[††] It was confirmed that more than 95 % of MMA was polymerized after UV irradiation for 10 hours. The weight-average molecular weight (M_w) and polydispersity (M_w/M_n) of the resultant MMA polymer were estimated by SEC[†††] and these values were almost same for both with (10 x 10^4, 2.6) and without (5.5 x 10^4, 3.0) Pyr-lipid. Therefore, it is clear that fibrous aggregates of Pyr-lipid do not influence polymerization of MMA.

In conclusion, we have described chiral orientation of Pyr-lipid in polymerizable monomer solvents and photo-induced polymerization of the solvent (MMA). The chiral microenvironment formed from Pyr-lipid aggregates in MMA was maintained after photo-induced polymerization of the solvent and was stable at wide range temperatures. It should be emphasized that solid polymer sheets with enhanced optical activity were obtained by use of a small amount of chiral compound and this would expand their possible applications as optical materials.

Notes and references

1   P. Terech and R. G. Weiss, *Chem. Rev.,* 1997, **98**, 3133.
2   D. J. Abdallah and R. G. Weiss, *Adv. Mater.,* 2000, **12**, 1237.
3   H. Ihara, M. Takafuji and T. Sakurai, "*Encyclopedia of Nanoscience and Nanotechnology*", American Scientific Publishers, California, 2004.
4   O. Gronwald, E. Snip and S. Shinkai, *Curr. Opin. Colloid Interf. Sci,*, 2002, **7**, 148.
5   T. Shimizu, *Macromol. Rapid Commun.,* 2002, **23**, 311.
6   M. D. Loos, J. V. Esch, I. Stokroos, R. M. Kellogg and B. L. Feringa, *J. Am. Chem. Soc.,* 1997, **119**, 12675; M. Masuda, T. Hanada, K. Yase and T. Shimizu, *Macromolecules*, 1998, **31**, 9403; K. Inoue, Y. Ono, Y. Kanekiyo, K. Hanabusa and S. Shinkai, *Chem. Lett.*, **1999**, 429; H. Ihara, M. Takafuji, T. Sakurai, M. Katsumoto, N. Ushijima, T. Shirosaki and H. Hachisako, *Org. Biomol. Chem.,* 2003, **1**, 3004.
7   Y. Ono, K. Nakashima, M. Sano, J. Hojo and S. Shinkai, *Chem. Lett.,* **1999**, 1119; Y. Ono, K. Nakashima, M. Sano, J. Hojo and S. Shinkai, *J. Mater. Chem.,* 2001, **11**, 2412.
8   W. Gu, L. Lu, G. B. Chapman and R. G. Weiss, *Chem. Commun.,* 1997, 543; R. J. H. Hafkamp, B. P. A. Kokke, I. M. Danke, H. P. M. Geurts, A. E. Rowan, M. C. Feiters and R. J. M. Nolte, *Chem. Commun.,* **1997**, 545.
9   H. Ihara, H. Hachisako, C. Hirayama and K. Yamada, *Chem. Commun.,* **1992**, 1244.
10 M. Takafuji, H. Ihara, C. Hirayama, H. Hachisako and K. Yamada, *Liq. Cryst.,* 1995, **18**, 97; H. Hachisako, H. Ihara, T. Kamiya, C. Hirayama and K. Yamada, *J. Chem. Soc., Chem. Commun.,* **1997**, 19; H. Ihara, T. Sakurai, T. Yamada, T. Hashimoto, M. Takafuji, T. Sagawa and H. Hachisako, *Langmuir*, 2002, **18**, 7120.
11 H. Ihara, M. Yoshitake, M. Takafuji, T. Yamada, T. Sagawa and C. Hirayama, *Liq. Cryst.,* 1999, **26**, 1021
12 T. Sagawa, S. Fukugawa, T. Yamada and H. Ihara, *Langmuir*, 2002, **18**, 7223. H. Ihara, T. Yamada, M. Nishihara, T. Sakurai, M. Takafuji, H. Hachisako and T. Sagawa, *J. Mol. Liq.,* 2004, **111**, 73.
13 J. M. Schnur, B. R. Ratna, J. V. Seliger, A. Singh, G. Jyothi and K. R. K. Easwaran, *Science,* 1994, **264**, 945; M. S. Specter, J. V. Selinger, A. Singh, J. M. Rodriguez, R. R. Price and J. M. Schnur, *Langmuir*, 1998, **14**, 3493; H. Ihara, M. Takafuji, C. Hirayama and D. F. O'Brien, *Langmuir*, 1992, **8**, 1548-1553.
14 P. Babu, N. M. Sangeetha, P. Vijaykumar, U. Maitra, K. Rissanen and A. R. Raju, *Chem. Eur. J.,* 2003, **9**, 1922.

NO TEXT BELOW THIS LINE