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

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

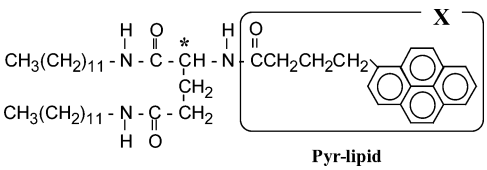
Over the last decade, a number of low molecular weight organic compounds have been reported[1–5] to be effective gelators for organic solvents. In most of these cases, the gelator forms nanofibrous aggregates based on highly-ordered structures with intermolecular interactions such as hydrogen bonding, van der Waals forces and π–π interactions. These fibrous aggregates form a three-dimensional network by entwining with themselves and gelation is brought about 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 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 orientated 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 the versatility of a chiral L-glutamide unit for self-assembled organogelation (Scheme 1).[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 or 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 butyric acid with N^1,N^5-didodecyl-L-glutamide[11] using diethyl phospholocyanide 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. In contrast, 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: $\theta_{353} = 3.0 \times 10^5$, in DVB: $\theta_{353} = 4.2 \times 10^5$, and in MMA: $\theta_{353} = 4.6 \times 10^4$ deg cm^2 dmol^{-1}). The CD strengths were much smaller in MAA and AA (in MAA: $\theta_{353} = 1.7 \times 10^3$, and in AA: $\theta_{353} = 0.9 \times 10^3$ 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



Scheme 1 Chemical structure of L-glutamic acid-derived lipid.

† Electronic supplementary information (ESI) available: photograph and fluorescence spectra of Pyr-lipid in PMMA solid sheet. See http://www.rsc.org/suppdata/cc/b3/b316673b/

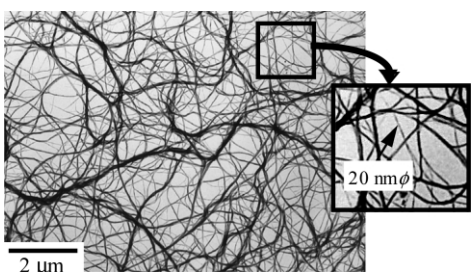


Fig. 1 Typical TEM image of Pyr-lipid in methyl methacrylate.

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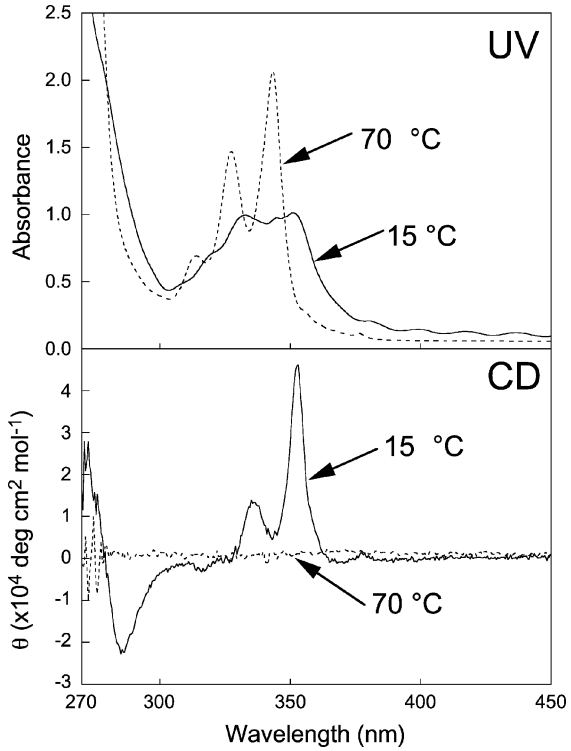

Fig. 2 UV and CD spectra of Pyr-lipid in MMA at 15 °C and 70 °C. [Pyr-lipid] = 1 mmol l^{-1}.

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, ESI) 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 are maintained by photo-induced polymerization of MMA and are 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, ESI). 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

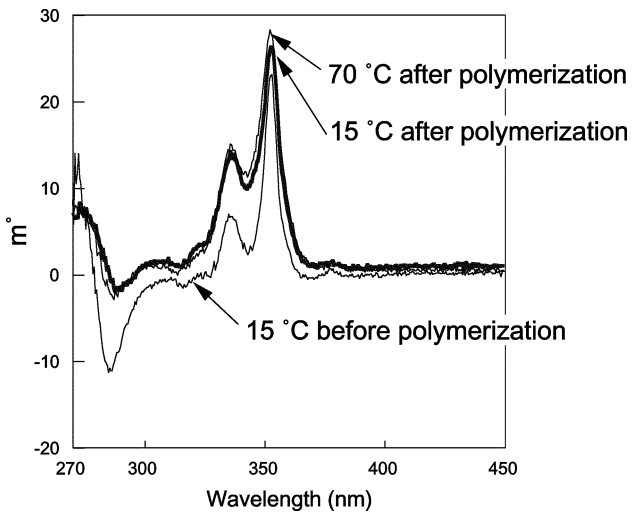

Fig. 3 CD spectra of Pyr-lipid in MMA before and after polymerization. Photo-induced polymerization was carried out in a 0.1 mm quartz cell at 15 °C for 10 hours. [Pyr-lipid] = 1 mmol l^{-1}.

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 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 the same for both with (10×10^4, 2.6) and without (5.5×10^4, 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 over a wide range of temperature. 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

‡ The cgc of Pyr-lipid in polymerizable monomers: 0.6–0.8 mmol l^{-1} in styrene, 0.8–1.0 mmol l^{-1} in MMA, 0.2–0.4 mmol l^{-1} in DVB.

§ HPLC was performed using a Grand pack 120STC column (MASIS Inc., Japan) thermostated at 30 °C. A JASCO PU-980 pump provided a constant flow of 0.5 ml min^{-1} of a mixture of methanol/water (50/50). A JASCO MD-910 multiwavelength detector was used for detection.

¶ SEC was performed using a TSKgel SuperHM-L column (Tosoh Co., Japan) thermostated at 30 °C. A JASCO PU-1580 pump provided a constant flow of 0.5 ml min^{-1} of tetrahydrofuran. A JASCO MD-1510 multi-wavelength detector was used for detection.

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