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Optically active polymer film tuned by a chirally self-assembled molecular organogel

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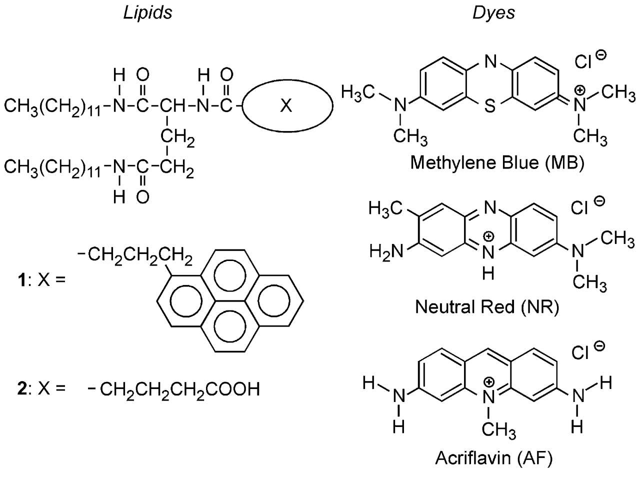
Abstract—Chirally-oriented lipid aggregates were doped into a solid polymer film, which was readily prepared by casting and removing a solvent from anionic L-glutamide-derived organogels and polystyrene. When a cationic achiral dye was mixed into this system, the resultant polymer film showed tunable circular dichroism (CD) due to chiral complex formation with the achiral dye on the highly-ordered structures based on the L-glutamide lipid.

1. Introduction

Organogel systems with self-assembling low molecular compounds have been attractive as a construction tool for bottom-up nanotechnology because they are essentially generated through three-dimensional network formation from nano-sized one-dimensional fibrillar aggregates, constructed of highly-ordered assemblies like aqueous lipid bilayer membranes. It is also known that a number of chiral compounds form nano-sized one-dimensional unique aggregates with large curvatures such as nanotubes, nanohelices, and nanoribbons.[1] These aggregates are morphologically interesting and applicable as templates for the creation of nanomaterials. Gu et al.[2] and Hafkamp et al.[3] reported mesoporous polymer materials by using organogel systems. They were prepared by polymerization of a monomer, which was used as a solvent to produce an organogel and subsequent extraction of the nanofibrillar aggregates from the polymer. The other application has been the construction of inorganic nanomaterials by condensation of alkoxysilane or chlorosilane with self-assembled fibrous/helical aggregates as templates.[4] This template method has been also developed to create various inorganic,[5] metal,[6] and polymer[7] nanomaterials.

A specific circular dichroism (CD) signal is often observed in organogel systems[8–10] because of the chirality of organogelators. These CD patterns are rather unique compared with molecular chirality because they are usually induced by long-range chiral orientation among the chromophoric groups. Therefore, observed CD spectra are useful as an indicator to estimate their oriented structures. The enhanced chirality is one of the attractive features of self-assembling molecules and useful for sensing and switching because the chiral orientation of the molecules is strongly affected by environmental factors such as temperature, pH, and additives. We have reported that L-glutamide-derived lipids (Scheme 1), as chiral self-assembling compounds, can form gels in organic solvents. This is brought about through nanofibrous network formation and entrapment of solvent.



Scheme 1. Chemical structures of L-glutamide-derived lipids and cationic dyes.

Keywords: L-Glutamic acid; Induced circular dichroism; Self-organization; Nanofibrils; Polymer composite.

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Here, when a pyrenyl group was introduced onto the head part (**1**) as a chromophoric group, an enhanced CD signal was observed around the absorption band of the pyrenyl group.[11] This indicates that the process is driven by chiral stacking of the pyrenyl groups into highly-ordered structures. However, unfortunately the assembly is not stable because a temperature-induced gel-to-sol transition is commonly accompanied by disappearance of chiral stacking. To increase mechanical strength and heat stability of enhanced chirality, we have investigated the immobilization and stabilization of specific chiral microenvironments from an L-glutamide lipid by using a polymerizable solvent and following photo-induced (UV-light) polymerization.[10] By this method, both the CD pattern and strength could be maintained in the resultant polymer film and was stable even at temperature above the original gel-to-sol phase transition temperature.

The present work is aimed to develop this method for the preparation of optically active polymer composites because there are still some disadvantages: for instance, the chromophoric group of an organogelator is decomposed by photo (UV-light) irradiation. Also a mechanical property of the resultant polymer film is hardly controllable because of difficulty in controlling the polymerization degree. In this article, we introduce a facile method to create an optically active polymer composite using an L-glutamide lipid-derived organogel and also demonstrate that the resultant optical activity is quite tunable by induced chirality based on a doped achiral dye.

2. Results and discussion

2.1. Pyrenyl group-induced chirality

The lipid **1** (0.5 mM) and poly(methylmethacrylate) (PMMA, 500 unit-mM) were dissolved in benzene at 70 °C and then cooled to 10 °C to form a gel. Fibrous network formation was observed both in the cast film and xerogel[12] by TEM and SEM, respectively. No similar aggregates were found in the absence of **1**. The TEM image (Fig. 1a) indicates that the minimum diameter of the fibrous aggregates is approximately 30 nm, which corresponds to almost 10 lipid molecules. Therefore, it is estimated that the aggregates entangle each other, which leads to three-dimensional network structures.

The critical aggregation concentration (cac) and critical gelation concentration (cgc) of **1** in a benzene solution exist at 0.2–0.5 mM and 2.0–3.0 mM at room temperature, respectively.[11] No significant change in these values was found in the mixed system with PMMA. Figure 2 (left) shows UV and CD spectra of the mixed system. It is found that a strong CD signal was detected at 10 °C but not at 70 °C. This is due to the fact that the mixed system underwent a gel-to-sol phase transition at temperature around 60 °C. To support this, DSC measurement showed distinct endothermic peaks at 59 °C and 67 °C. These phenomena are very close to those in the absence of PMMA. This indicates that PMMA does not disturb the aggregation of **1** and that the gelation due to **1** is brought about through the formation of chirally-ordered aggregates at temperatures below their phase transition temperature.

The solid film was prepared by casting the mixture on a glass plate and removal of solvent. The resultant film was almost transparent and colorless. Figure 2 includes UV and CD spectra of the film. The CD pattern was similar to that in the gel at 10 °C but no change was observed, even at 70 °C. These results indicate that the specific chirality from the aggregates of **1** remains, even after casting, and is stable at elevated temperature. Here, we have established a facile method to immobilize specific chirality based on a **1**-organogel into a polymer solid film.

2.2. Chirality tune with induced chirality

It would be supposed that the CD pattern would be tunable by changing the head group of the L-glutamide-derived lipid.

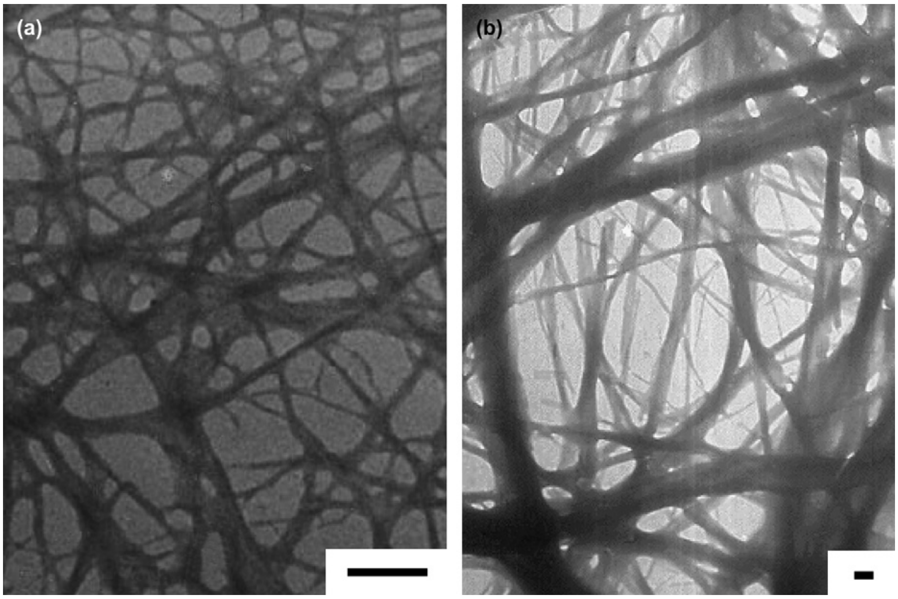

Figure 1. TEM images of **1** (a) and **2** (b) aggregates prepared from benzene solutions. Scale bars indicate 200 nm.