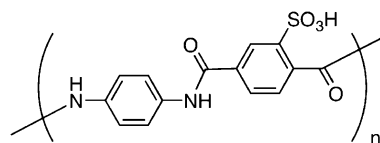


A Sulfonated Polyamide: Stir-induced Chirality in Its Aqueous Solution

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We demonstrated that aqueous solutions containing a sulfonated polyamide exhibited stir-induced chirality detected by circular dichroism (CD) spectroscopy. This phenomenon can be visualized as dynamics of supramolecular structure comprising hydrogen-bonded polyaramides. We further show that the sign of the CD response can be tuned using vortex direction, stirring-rate, and concentration.

**Chart 1.**

Determination of the origin of the homochirality in naturally occurring organic molecules is a problem that is yet to be solved in molecular biology, organic chemistry, and supramolecular chemistry.¹ Previous studies on this subject have examined the amplification of enantiomeric imbalances that occur as a result of the existence of achiral precursors that are generalized by circularly polarized light, chiral inorganic crystal, and so on. Moreover, in 1976, Honda et al. reported the induction of CD sign in a vortex flow of J-aggregated isocyanine chloride.² However, this system was controversial as the combinations of linear dichroism (LD) and birefringence can lead to artifactual CD signals. In a recent study performed for reexamining these results, Muller matrix spectroscopy, which is an advanced measurement method, showed true CD signal excluded artificial polarizations in a stirred sample.³ Moreover, several types of porphyrin derivatives, which is a representative structure showing stir-induced chirality, have been examined.⁴ A plausible mechanism of the effect is twisting the supramolecular structures in solution, and this gives the possibility that other molecular structures also exhibit chirality in vortex flow. In fact, an organo gelator forming 3D networks in solution exhibits stir-induced chirality, and it can transfer the chiral information to guest dyes.⁵

Herein, we show a polyamide lyotropic liquid crystal (LLC) solution exhibiting chirality in vortex flow. Polyamide derivatives are used in broad applications in industry owing to their extremely high durability and strength. However, for conventional polyaramides, the hydrophobic nature of their aromatic backbones in combination with strong intermolecular hydrogen bonding between chains reduces their solubility, thereby restricting their application in solution. This problem is solved by introducing an ionic sulfonyl group to a polyamide backbone (PPSA) (Chart 1), and this can be dissolved in aqueous solution.⁶ The aqueous polyamide solution exhibits a LLC phase, and this means that supramolecular structure formed. Thus, it is expected that the ionic polyamide solutions exhibit stir-induced chirality.

The PPSA that we used in this study was synthesized by polycondensation between 2-sulfoterephthalic acid and 1,4-phenylenediamine (see Supporting Information¹⁰). PPSA could

be dissolved in water because of the hydrophilic nature of its sulfonic acid moiety. Self-assembly of PPSA in aqueous solution results in H-bonding and gives rise to an LLC phase of over 0.8 wt % at 20 °C. Moreover, PPSA is particularly useful owing to its simple molecular structure, which can be obtained by carrying out rudimentary chemical syntheses. We measured the CD of this system in a 10 × 10 × 40 mm³ quartz optical cell in which 4 mL of sample solutions were stirred mechanically using a magnetic stirring bar (φ2.0 × 5.0 mm³) placed at the bottom of the cell, 13 mm below the center of an φ8.0 mm wide polarized beam of light.

Unstirred aqueous PPSA at 0.5 wt % exhibited a stagnant CD sign, but it became optically active upon mechanical stirring (Figure 1a). When we stirred the solution at 1000 rpm in a clockwise (CW) direction, the sample solution showed negative CD bands in the absorbance region at approximately 440 nm. When the stirring direction was reversed the CD spectral sign was inverted perfectly. Therefore, it is possible to select the optical activity by specifying the stirring direction. Furthermore, when the stirring was stopped, the optical activity disappeared. As shown in Figure 1b, the sample solution underwent quick chiroptical responses to changes in the stirring directions. We also observed that the CD intensity increased in a sigmoidal fashion with increasing stirrer rotation rate (Figure S3 of SI).¹⁰ From the data of Figure 1, one question that arises is whether or not the CD that is observed during stirring is an artifact of measurement instrumentation such as fiber alignment in the vortex. In the next experiment, we measured linear dichroism (LD) spectra detecting linearly artifactual elements in the sample (Figure S4 of SI).¹⁰ The sample solution used in this study has molecular order caused from an LLC phase, thereby LD signal was observed even in a stagnant state and this sign was enhanced to negative value from -0.017 to -0.046 by stirring. This indicates that the stir-induced CD signal contains linear artifacts. Analogous with other supramolecular systems showing chirality in vortex flows, our system could also contain chiral elements even in highly birefringent solution.

We also investigated the effect of the PPSA concentration on the stir-induced optical activity (see Figure S5 of SI).¹⁰ The intensity of the CD signal increased with increasing PPSA

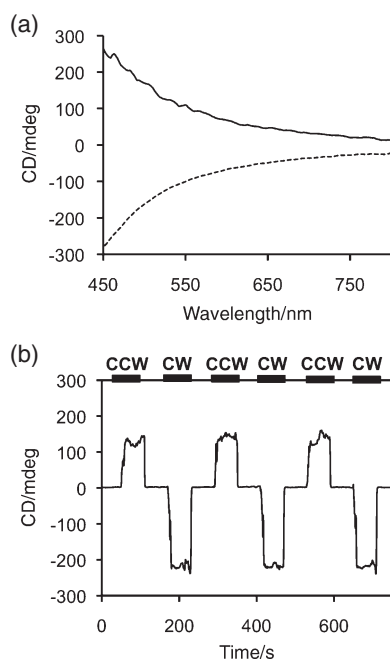


Figure 1. (a) Circular dichroism (CD) spectra of PPSA at 0.5 wt % upon stirring at 1000 rpm in clockwise direction (CW; dashed line) and counterclockwise direction (CCW; solid line). (b) Change in signal intensities by repeating the stirring cycles: CW at 1000 and 0 rpm and CCW at 1000 rpm.

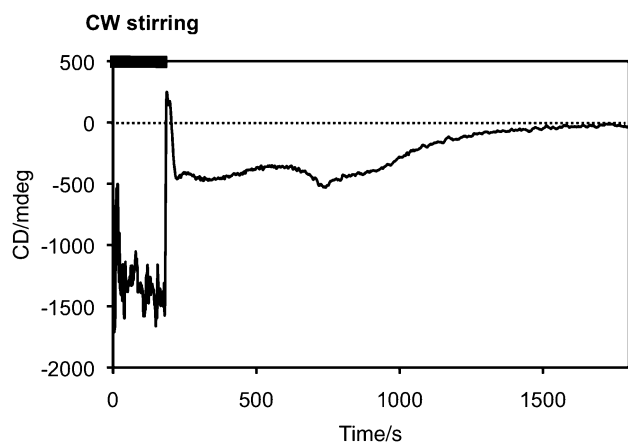


Figure 2. Relaxation in a 0.8 wt % lyotropic liquid crystalline phase for a stir-induced optical activity after stopping CW stirring at 1000 rpm. CD spectra were measured at 500 nm.

concentration owing to the high ratio of the supramolecular structure that induced the optical activity. Moreover, decay in an LLC phase is strongly dependent on the sample phase. For example, an isotropic solution of 0.5 wt % exhibits rapid decay in its stir-induced CD sign toward a stagnant state, as shown in Figure 1b. Conversely, an LLC phase of 0.8 wt % exhibits an instant memory effect (Figure 2), which occurs in the following steps: i) rapid decay of the CD signal to the stagnant state after stirring has been stopped, ii) recovery of the CD signal to the initial direction, and iii) slow decay of the recovered CD signal. This implies that chiral supramolecular structures in an LLC

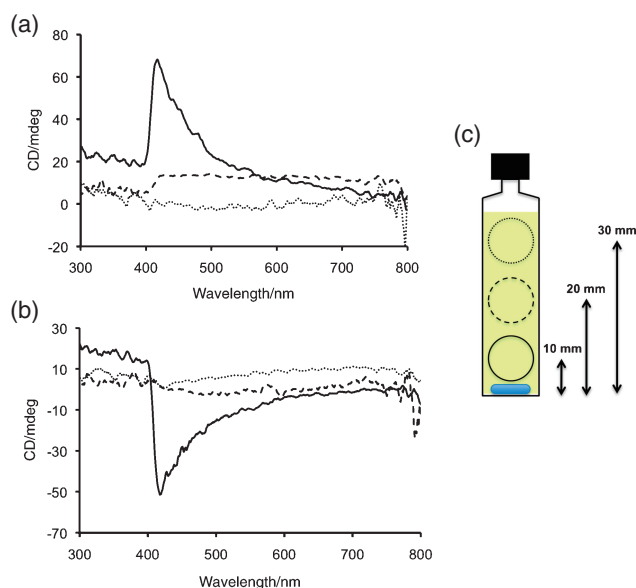


Figure 3. CD spectra of a 4 mL aqueous solution of 0.5 wt % PPSA upon CW (a) and CCW (b) stirring at 1000 rpm using a coated magnetic stirring bar ($\phi 2.0 \times 5.0 \text{ mm}^3$) in a $10 \times 10 \times 40 \text{ mm}^3$ quartz optical cell. (c) Illustration of the experiment: a probe beam was used to irradiate the cell at different positions from bottom to top.

phase show signs of fluid molecular alignment and memorize chiral structures instantly.

As mentioned above, the effects of vortex direction, stirring rate, and sample concentration on optical activity were examined. Since mechanical rotation achieved by using a stirring bar gives rise to locally variable fluidic situations, the CD signal that occurs in a cuvette is positionally dependent.^{5a} To investigate how optical activity varies depending on the location in the cuvette, we irradiated the sample with a CD probe beam from its bottom to its top. The solution was stirred at 600 rpm in the clockwise (CW) or counterclockwise (CCW) direction and was irradiated with CD probe beam at different positions (Figure 3). As expected, for the same stirring direction, each measurement position had the same CD directionality even at different signal intensities. We noticed that the CD signal near the bottom was largest, which means that supramolecular chirality occurs around the stirring bar. A previous study reported that a dilute solution of 10^{-5} M ionic porphyrine exhibited stir-induced CD at the center of the cuvette from the bottom to the top.⁷ In our system, the relatively high viscosity of the sample could restrict vortex flow propagation to the top region of the cuvette. This could also support the instant memory of stir-induced chirality as shown in Figure 2. That is, the chirality induced around the stirring region decayed because the supramolecular structure showing CD signal in LLC could be relaxed from bottom to top in the cuvette.

In this study, we showed that an aqueous solution containing sulfonated polyaramide exhibits stir-induced optical activity and that this activity arises from chiral supramolecular structures present in the vortex. The system exhibited the following characteristics: i) the sense of the CD sign could be specified by

fixing the stirring direction and rate, ii) the optical activity of the LLC phase retains its supramolecular chirality just after stopping of stirring, and iii) optical activity occurs around the stirring region. The physical chirality of the vortex flow can be used to impart selective optical activity to an aqueous polyaramide solution. The sample solutions that were used in this study were composed of approximately 99 wt% water and an ionic oligomer that was obtained easily by synthesis. Therefore, our results show the possibility for studying stir-induced supramolecular chirality by using a conventional polymer compound that is of general interest and can be created easily. Previous results implied supramolecular nanostructures (particles and fibers) cause the stir-induced chirality. That is, supramolecular assemblies can be deformed to a chiral structure in a vortex flow, which shows a CD signal even if the assemblies are achiral. Therefore, in view of the molecular structure, characteristics of noncovalent interactions, such as hydrogen bonding, J-aggregation, and so on, should be incorporated.⁸ Moreover, in recent studies, a Langmuir–Blodgett film which is molecularly ordered forms chiral assemblies by a vortex-like flow.⁹ This study showed the first example of stir-induced chirality by using an LC system. Although at the moment, vortex flow gives rise to chirality which can be detected by CD spectroscopy, the mechanism through which chirality is transferred on a molecular or macroscopic level is not clear. Therefore we are preparing experiments to clarify the detailed mechanism to advance the field.

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