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New Approach to Chiral Conductive Materials. A Polymer Composite from Polypyrrole and an Optically Active Polyamide

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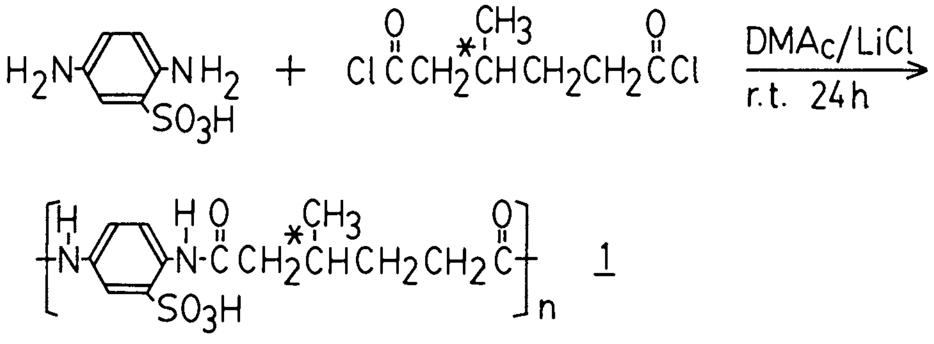
A new conductive polymer composite retaining an asymmetric structure in the solid state has been prepared by electropolymerization of pyrrole in the presence of a chiral aromatic polyamide containing a sulfonic acid group. The composite exhibits conductivity of 0.5 S/cm.

Conductive polymer composites of polypyrrole with anionic polymers have unique electrochemical and improved mechanical properties.1-6) These composites are prepared by electropolymerization of pyrrole in the presence of polyanions as dopants. Polymers containing sulfonic acid groups, e.g., poly(p-styrenesulfonic acid)1-3) and Nafion4,5) have been used as anionic polymer dopants for conductive polymer composites. Recently, poly[(p-phenyleneterephthalamide)propanesulfonate] was prepared and used as the polyanion to form a molecular complex with polypyrrole.6) However, a variety of structures of polymer dopants seems to be still limited. If various functional units designed properly are incorporated into polymer dopants, the composites of the functional polymer dopants with conductive polymers may result in the formation of new type of functional conductive materials, while various types of conducting polymers modified with functional units have been prepared by electropolymerization of pyrrole and thiophen derivatives.7)

Our aim is to develop new type of chiral conductive materials from polymer composites. Chiral conductive polymers modified with chiral units have been prepared by electropolymerization of pyrrole8) and thiophene9,10) derivatives because they have potential for asymmetric electrochemical reactions9,11) on an electrode and for new specific structures for chiral metals.

We herein report a new approach to chiral conductive polymer materials using electropolymerization technique for polymer composites



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from polypyrrole and a chiral polymer dopant. Chiral anionic polymer **1** has been designed as an optically active polymer dopant. Polymer **1** is an aromatic polyamide containing R-3-(+)-methyladipic acid unit[12] in the main chain and a sulfonic acid group on the aromatic ring. The polyamide was prepared by solution polycondensation from an equimolar amount of 2,5-diaminobenzene sulfonic acid and R-(+)-3-methyladipoyl chloride.[13] The polyanion **1** was soluble in water and methanol. To examine the ability of the chiral polymer to form asymmetric structure in the solid state, UV and CD spectra have been obtained for the film of **1** casted on a quartz plate with transmitted light (Fig. 1). The peak due to the π-π^* transition of the aromatic ring is observed at 265 nm in the UV spectrum. In the circular dichlorism (CD) spectrum, the first positive and the second negative Cotton effects are clearly observed at 285 and 254 nm, respectively. These effects demonstrate that the aromatic chromophores of **1** are arranged asymmetricaly in the solid film state.

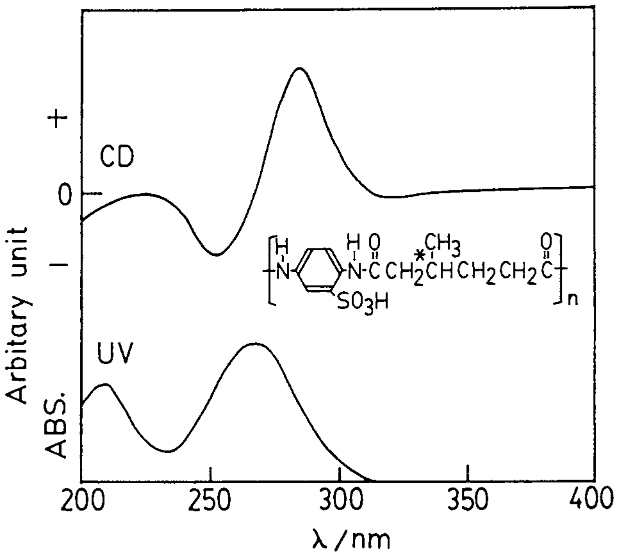

Fig. 1. CD (circular dichrolism) and UV spectra of chiral polyamide 1 in the solid film state. These spectra were obtained with transmitted light.

The electropolymerization was conducted in a single compartment cell containing pyrrole (0.1 M) and the anionic polyamide **1** (0.015 M) in water at 5 °C under galvanostatic condition (1.0 mA/cm^2). A platinum plate or a tin-oxide(SnO_2)-coated glass substrate was used as the working electrode. As the counter electrode, a platinum wire was used. The polymer composite was obtained as a black and shiny free standing film. The film thickness was 30 μm after 1.5 C had passed. The conductivity of the composite measured with the four probe method was 0.5 S/cm. Elemental analysis indicated that 0.35 repeating unit of the polyamide per one pyrrole unit was incorporated into the composite. SEM observation revealed that the surface of the polymer composite film was very smooth compared to that of polypyrrole film containing ClO_4^- as a dopant. The polymer composite exhibited electrochemical activity in KCl solution.

To determine the formation of an asymmetric structure in the solid composite film, we have recorded a CD spectrum of the film formed on a platinum plate with electropolymerization.[14] In this experiment, reflected light was used for the measurement because no free standing film which is thin enough to transmit the beam, is obtained, and the SnO_2-coated glass substrate which supports the thin film does not transmit the beam whose wavelength is shorter than 300 nm. The setup for the reflected beam is illustrated in Fig. 2. Figure 3A clearly demonstrates the Cotton effect for the composite of polypyrrole/chiral polyamide **1**. It is similar to the spectrum obtained for the polyamide **1** film using the transmitted light shown in Fig. 3C. The Cotton effect is confirmed in comparison with a deviated background when the CD spectrum is obtained from a bare platinum plate using the reflected light (Fig. 3B). Thermogravimetric analyses have shown that the composite is thermally more stable than polypyrrole with ClO_4^- dopant or poly-

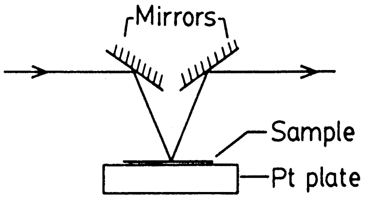

Fig. 2. Schematic illustration of the setup for the CD measurement of the chiral conductive composite film on a platinum plate using reflected light.

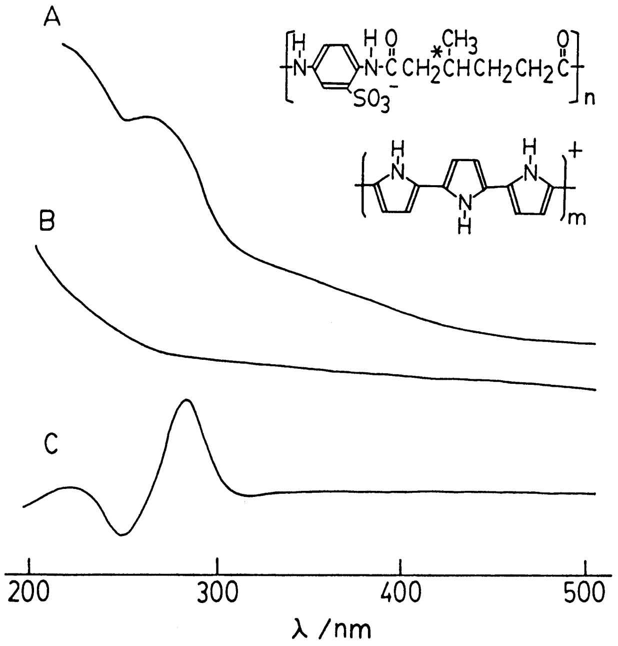

Fig. 3. CD spectra of (A) polyamide **1**/polypyrrole complex on a platinum plate, (B) a platinum plate, and (C) polyamide **1** on a quartz plate. Spectra A and B were obtained with reflected light. Transmitted light was used for spectrum C.

amide **1**. These results suggest that polyamide **1** retains a stable asymmetric structure complexing with polypyrrole in the solid film state. The approach reported here provides a new method to chiral and conductive organic materials.

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12) (R)-3-(+)-Methyladipic acid moiety has been used for a unit of liquid crystalline polyesters which exhibit chiral mesophases. For example: A. Blumstein, S. Vilasagar, S. Ponrathnam, S. B. Clough, and R. B. Blumstein, J. Polym. Sci., Polym. Chem. Ed., 20, 877 (1982).
13) Polycondensation was performed in dimethylacetamide/LiCl (5% w/v of LiCl) at room temperature for 24 h. The polymer was precipitated in cold acetone. Yield, 94%.
14) CD spectra were recorded on a JASCO J-500 spectrometer. The thin composite film for the CD measurement was electrochemically prepared by the passage of 50 mC.

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