Notes

Synthesis of Chiral Conjugated Polymers Bearing Azobenzene Moieties Using Cholesterics

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Early studies on chiral polyacetylene derivatives suggested that the polyacetylenes form one-handed helical structures,[1−4] and more recent studies of helical polyaniline,[5−10] a host−guest type substituted polyacetylene,[11] and polyacetylene bearing optically active substituents[12] have indicated that the chirality of the main-chain type conjugated polymers derives from a helical conformation.[13−15] A range of syntheses for obtaining chiral conjugated polymers have been proposed to date, including polymerization using a chiral catalytic system[16] and the introduction of chiral substituents into the main chain[3,5,8] by covalent bonding,[10,17−25] static interactions,[5−9] or hydrogen bonding[11] to achieve a helical structure.

The synthesis of chiral conjugated polymers prepared from achiral monomers in a chiral liquid crystalline medium without a chiral initiator was previously reported.[26] Through the preparation of chiral polymers having functional groups in the monomer repeat unit, it is possible to obtain optically active polymers with functions such as light isomerization. In the present research, the polymerization of achiral monomers in a cholesteric liquid crystal medium is similarly performed to obtain chiral conjugated polymers containing azobenzene, which is a well-known chromophore.

The interest of the present study is in the use of a chiral liquid-crystalline material as a reaction solvent. Such an approach allows chiral polymers to be obtained without chiral catalysts or chiral monomers through the use of cholesteric liquid crystal as a chiral polymerization method. Chiral polymers prepared in this way typically exhibit stable optical activity. Furthermore, the cholesteric liquid crystalline field provides a simple means of molecular design for chiral polymers with functional groups, and the solvents themselves are repeatedly reusable.

Chiral conjugated polymers consisting of three thiophene rings with an azobenzene moiety in the monomer repeat unit are prepared in the present study. Thiophene monomers are adopted for the polymerization reaction because the linearity of the molecular forms in both the monomer and the corresponding polymer are expected to have good affinity for the cholesteric liquid-crystalline reaction solvents used in the reaction. This new synthetic method can be applied for the preparation of chiral polymers having various functions.

Cholesteric liquid crystalline materials (**1** and **2**) for the reaction medium were synthesized according to the method reported in the literature,[26] and then a monomer having an azobenzene moiety as a bulky substituent is prepared. The achiral monomer thus synthesized is finally polymerized in the cholesterics to afford chiral conjugated polymers.

The cholesteric liquid crystalline phases of compounds **1** and **2** are stable over a wide temperature range and remain stable upon the addition of aromatic compounds such as dibromobenzene and dibromothiophene. The phase-transition behavior of compounds **1** and **2** was determined by differential scanning calorimetry and polarizing optical microscopy (POM).[26] Compounds **1** and **2** both exhibit frustrated platelet textures of blue phases and the oily streak textures of cholesteric liquid crystalline phases under POM.

The 2,2′-position of 3-thenoic acid was brominated using *N*-bromosuccinimide (NBS) in *N*,*N*-dimethylformamide (DMF) for 24 h at 60 °C, as shown in Scheme 1. The mixture was then added to a large volume of aqueous sodium thiosulfate solution to terminate residual bromine. The crude product was purified by recrystallization from ethanol to afford 2,5-dibromothiophene-3-carboxylic acid (compound **3)**.

Dibromothiophene containing azobenzene was synthesized by coupling compound **3** with 4-(phentylazo)phenol in the presence of *N*,*N*′-dicyclohexylcarbodiimide (DCC) and 4-dimethylaminopyridine (DMAP). After the reaction, the mixture was filtered off, washed with water several times, and extracted using dichloromethane. Evaporation followed by recrystallization from acetone afforded orange crystals of 2,5-dibromothiophene-3-carboxylic acid 4-phenylazophenyl ester (**4**).

A polycondensation reaction between **4** and bis(trimethyltin)-substituted bithiophene derivative was carried out using compound **1** or **2** (cholesteric solvent) at 92 °C (in the temperature of cholesteric liquid crystalline phase) in a small Schlenk flask. After visual confirmation of the selective reflection of light, achiral monomers were added to the medium. Following further confirmation of the selective reflection of the mixture, $Pd(PPh_3)_4$ (a catalyst) was added. During this process, the mixture was stirred continuously at 75 rpm in order to maintain the cholesteric liquid crystal phase. After 24 h, the visible selective reflection again confirmed that the mixture maintained the chiral cholesteric liquid crystal phase. Both mixtures thus prepared exhibited the oily streak texture of the cholesteric liquid crystal phase under the POM, before and after polymerization. It can thus be concluded that the cholesteric liquid crystal phase was maintained throughout the polymerization reaction.

After allowing the reaction mixture to cool to room temperature, a small amount of acetone was added. The liquid crystal solution was then poured into a large volume of acetone and washed for ca. 4 h to remove the cholesteric solvent. The acetone was then decanted off, and the crude product was washed in a large volume of methanol. The insoluble fraction was collected by decanting off the methanol to afford the desired polymer (poly1 and poly2). The synthetic yields of the polymers were ca. 47%.

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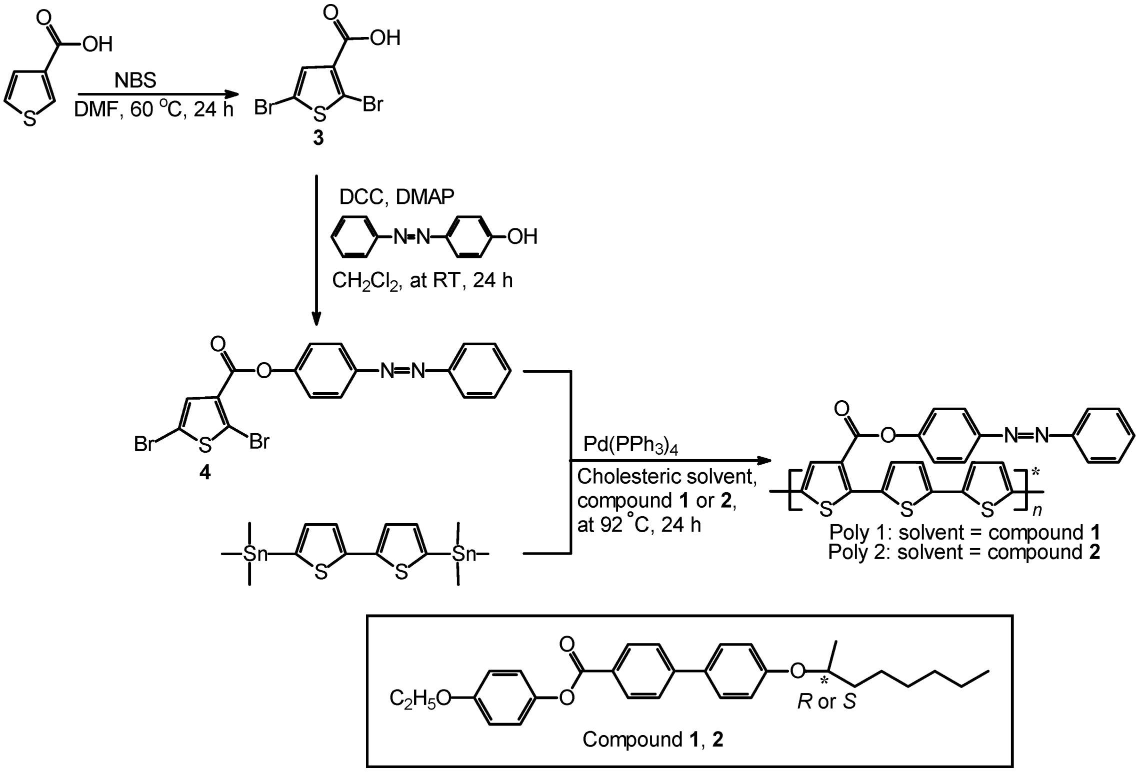
Scheme 1



The number-average molecular weights of poly1 and poly2 are 1800 and 2200 g/mol, and the weight-average molecular weights are 2400 and 3200 g/mol, respectively. The number-average and weight-average molecular weights were determined by gel permeation chromatography (GPC) relative to a polystyrene (PS) standard. Samples for GPC were prepared by filtration in tetrahydrofuran (THF) solution using a 0.1 μm membrane filter to exclude insoluble material. The molecular weights thus represent only the THF-soluble fraction of the polymer and are somewhat lower than expected (the polymers are partially soluble in THF and chloroform). The insoluble fraction in THF is considered to consist of high molecular weight chains or large aggregates. Estimation of the number-average molecular weight by ^{1}H NMR end-group analysis of the polymer was difficult due to peak broadening of the spectra. The insolubility of the polymers in acetone indicates that the molecular weights value can be satisfactory, and the polymer shows a monopeak in the GPC measurement. This result suggests that the purification procedure of the polymer, washed by large amount acetone, was valid.

Infrared absorption spectroscopy of poly2 was performed using a KBr. Stretching vibrations due to benzene−N and N═N of the azo moiety were observed at 1110 and 1436 cm^{-1}, respectively, confirming that the polymer contains azobenzene.

Figure 1 shows the ultraviolet−visible (UV−vis) absorption and circular dichroism (CD) spectra of the polymer films cast from chloroform solution. The polymer films exhibit two absorption bands in the UV−vis region, near wavelengths of 316 and 465 nm. The absorption at 316 nm is attributable to the π−π* transition of the aromatic rings,[27,28] while the absorption at 465 nm is due to overlap of the π−π* transition of the conjugated main chain and the n−π* transition of azobenzene of the side chain. The absorption tails off toward the near-infrared region. The long tailing of the absorption suggests that this polymer consists of conjugated main chain. In addition, the azobenzene side chain may be arranged in a one-handed helical manner in the aggregation. The CD signal reflects both chirality of the main-chain and side-chain aggregation.

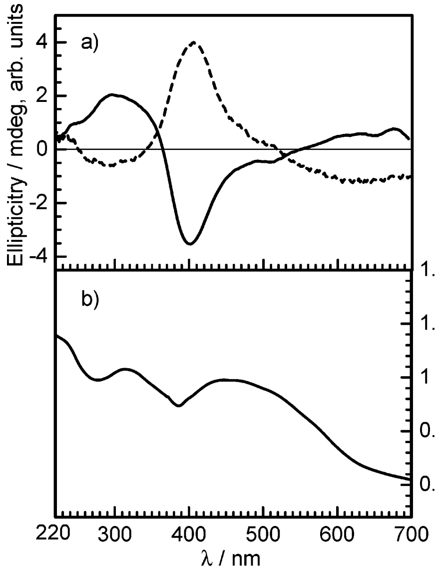


Figure 1. (a) CD absorption spectra and (b) UV−vis absorption spectrum of poly1 (solid line) and poly2 (dashed line).

Poly1 and poly2 display complementary mirror-image signals in the respective CD spectra. Berova and Nakanishi reported that chiral materials in solvents produce an exciton coupling pattern.[29] The polymers synthesized in the present study display an exciton couple type bisignate CD pattern, which can be reasonably explained by chiral aggregation. Poly1 exhibits a positive first (at longer wavelength) Cotton effect (CE), a negative second CE, and a positive third CE, while poly2 displays the opposite sequence. This result indicates that poly1 and poly2 are chiral aggregates with clockwise and anticlockwise formation, respectively.

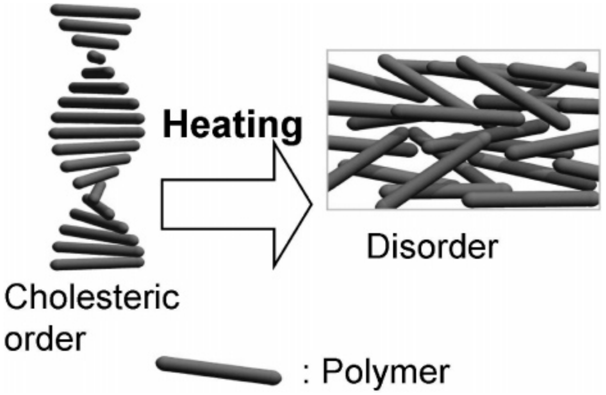


Figure 2. Possible model of disaggregation of polymer upon heating.

Poly1 and poly2 melted at ca. 265 and 228 °C under nitrogen, respectively. The difference of melting points of the polymers may depend on the degree of polymerization. The polymers allowed to cool back to room temperature before observation of optical textures. The polymers thus prepared exhibited a mesophase optical texture. Although the polymers displayed birefringence under POM at room temperature, no optical textures related to the cholesteric liquid crystal could be observed by POM during the course of heating and cooling. This may indicate that such heat treatment released the chiral aggregation, resulting in racemization. Thermally induced racemization has also been observed in the case of helicene and binol. A possible model for the chiral aggregation produced by polymerization in cholesteric liquid crystal and decomposition by heating is shown in Figure 2.

We also investigated light-induced isomerization behavior for the polymers thus synthesized in this study. However, clear photoinduced isomerization of the azobenzene moiety was no observed upon ultraviolet light or visible light irradiation. This may be due to the fact that tight packing derived from the chiral aggregation of the individual main chains restricts free movement of the molecules. Therefore, geometrical motion at the azobenzene moiety cannot be performed by the ultraviolet light irradiation. Furthermore, the main chain absorbs ultraviolet light as well. The azobenzene group in the side chain may not sufficiently receive light energy required for the isomerization. Introduction of long flexible alkyl spacer between the azobenzene group and the main chain may improve isomerization behavior of the system.

In conclusion, chiral conjugated polymers bearing bulky groups (azobenzene) were prepared for the first time from achiral monomers in a cholesteric liquid crystal medium. The polymers thus prepared display aggregation and complementary mirror-image Cotton effects. New chiral conjugated polymers with other functions prepared by this method may also be reported in the near future.

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