

Interfacial Conversion for Poly(*para*-phenylenevinylene) at a Cholesteric Liquid Crystal Surface

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ABSTRACT

A new approach for the preparation of poly(*para*-phenylenevinylene) (PPV) with an ordered structure is presented. PPV is synthesized by a precursor method using a cholesteric liquid crystal medium. The resultant PPV film is observed to have a cholesteric fingerprint-like texture, indicating replication of the cholesteric liquid crystal medium. Infrared absorption measurements confirm that the PPV has essentially the same molecular structure as normal PPV film. Ultraviolet-visible absorption measurements show that the absorption band due to π - π^* transition of the conjugated main-chain is located at 403 nm. The conversion is found to occur at the interface with the cholesteric liquid crystal medium as a mechanical process.

Key words: chiral, conjugated polymers, films, liquid crystals, UV-vis spectroscopy

INTRODUCTION

Poly(*para*-phenylenevinylene) (PPV) is one of the most useful of the conjugated polymers, with application as the emission layer in polymer electroluminescent devices.¹⁻⁴ The preparation of PPV can be achieved by many routes, including Knöevenagel polycondensation between a cyano-substituted precursor and a dialdehyde compound,⁵⁻⁶ Wittig-type reaction between an aromatic bisphosphonium salt and bisaldehyde,⁷⁻⁸ Heck reaction,⁹ and McMurry polycondensation with the aid of a titanium catalyst to afford a linear polymer.¹⁰ Several different precursor routes to PPV have also been reported, such as benzoine condensation,¹¹ ring-opening metathesis polymerization,^{12,13} chemical vapor deposition,¹⁴⁻¹⁷ the alkoxy precursor method,¹⁸⁻²⁰ the Gilch route,²¹⁻²⁷ and the xanthate precursor method.²⁹ The most well-known and widely used precursor method was discovered by Wessling and Zimmerman,^{29,30} and involves treatment of a sulfonium salt with a base to yield a water-soluble material. Although the product of this synthetic route can be efficiently purified by dialysis, the final material is of low molecular weight. Murase et al. developed another sulfonium precursor method for the preparation of stable PPV film,^{31,32} and polymers prepared by this method exhibit very high electrical conductivity with SO₃ or AsF₅ doping compared with previous reports.³³ The Louwet-Vanderzande route provides an excellent approach that promises further interesting developments in this field.³⁴ Their method, which has overcome many of the drawbacks of the precursor routes for PPV,³⁵⁻³⁷ involves heat treatment under vacuum conditions and allows for the preparation of insoluble and infusible fluorescent films or fibers with good mechanical strength.

Shirakawa and Akagi developed a novel method for preparing non-substituted polyacetylene with a one-handed helical structure.^{38,39} Polyacetylene synthesized in a cholesteric liquid crystal field displays a clearly defined helical structure under scanning electron microscopy (SEM) observation, and exhibits distinct positive or negative Cotton effects at the molecular level due to the one-handed helical structure. The helical polyacetylene has quite stable chirality, being insoluble and infusible. The chiral liquid crystal field thus provides a strong control on the

polymer structure, from the molecular level to the macroscopic morphology of the polymer.

In our previous work, a new electrochemical polymerization method employing a cholesteric liquid crystal electrolyte was presented for the preparation of non-substituted optically active and chiral poly(3,4-ethylenedioxythiophene) (PEDOT).^{40,41} The polymers thus prepared exhibit a fingerprint optical texture and spiral physical texture similar to that of the cholesteric liquid crystal. Circular dichroism measurements also revealed a Cotton effect for the PEDOT film, suggesting that an asymmetric reaction field such as cholesteric liquid crystal can be used to obtain polymers with well-defined chiral structures.

Although PPV precursor methods have yet to be used to produce an ordered structure, if a PPV precursor is capable of transforming in a cholesteric environment, the resultant polymer may replicate the macroscopic structure of the reaction environment, and the structure should be maintained due to its insolubility and infusibility. Thus, it is expected that PPV with an ordered structure can be prepared using the precursor method through the use of a cholesteric liquid crystal medium.

EXPERIMENTAL

Technique

All experiments were performed under an argon atmosphere using Schlenk/vacuum line techniques. Tetrahydrofuran (THF), ethanol, acetone, and ether were distilled prior to use. High purity chloroform (Wako) was used without purification for optical measurements of the polymer. Proton nuclear magnetic resonance (¹H NMR) spectra were measured in CDCl₃ using a Bruker AV-600 Fourier transform NMR spectrometer. Gas chromatography analysis was carried out using a Shimadzu model GC-14B equipped with a flame photonic detector and a separation column (β,β'-ODPN).

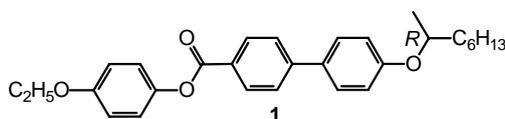
Chemical shifts are represented in parts per million downfield from tetramethylsilane (TMS) as an internal standard. Infrared spectra were measured using a Jasco FT-IR 550 spectrometer with KBr configuration. Optical absorption spectra were measured at room temperature using a Hitachi

U-2000 spectrometer with quartz cell. Thermogravimetry and differential thermal analysis of the polymer were performed using a Seiko Instruments EXSTRAR6000 platform. Phase transition temperatures were determined using a TA Instruments Q-100 differential scanning calorimeter with a constant heating/cooling rate of 10 °C/min. Texture observations were made using a Nikon ECLIPS E 400 POL polarizing microscope equipped with a Linkam TM 600PM heating and cooling stage. Circular differential interference contrast microscopy observations were carried out using a Carl Zeiss Axioskop 40 Pol microscope. Temperature calibration of the heating stage was carried out by differential scanning calorimetry. Optical phase-contrast microscopy (PCM) observations were performed using a Wraymer BX-3500T microscope equipped with an optical phase-contrast unit.

Synthesis of cholesteric liquid crystal compound for asymmetric reaction medium

Cholesteric liquid crystal compounds having a three-ring system with terminal alkyl groups having an (*R*) configuration (**1**) as a cholesteric liquid crystal matrix for conversion of the PPV precursor was prepared by the method previously reported in the literature.^{42-43,45}

Chemical structure of the synthesized compound was confirmed with a NMR. The sextet signals of protons attached to the chiral center are exactly observed at 4.4 ppm in ¹H NMR. Both ¹H NMR and ¹³C NMR measurements confirm molecular structure of compound **1**.



The phase transition behavior of these compounds was determined by DSC and POM, giving K 97 (72) Ch*135 (133) BP (134) Iso* (K: crystal, Ch*: cholesteric liquid crystal, BP: blue phase, Iso*: isotropic; parentheses denote cooling transition temperature).

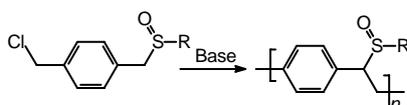
Preparation of PPV

The PPV film was prepared by the sulfonium precursor method in a cholesteric liquid crystal

field at 105–110 °C, as shown in Scheme 1.

Scheme 1.

The precursor polymer was prepared by the method described in the literature.³⁶ The number-average molecular weight (M_n) of the precursor was 113000 g/mol, the weight-average molecular weight (M_w) was 401500 g/mol, and the molecular weight distribution was 3.6. Here, M_n and M_w were evaluated by gel permeation chromatography (GPC) relative to a polystyrene standard (eluent: THF).



The film of the precursor, cast from a chloroform solution onto a quartz substrate, was prepared prior to conversion to PPV. The film was dried for 24 h under vacuum. The substrate was enveloped by aluminum foil, leaving the top open, and ca. 0.5 g of **1** (cholesteric liquid crystal) was placed on the film. The sample cell was then placed very carefully in a large separable vessel (Figure 1), which was heated in a vacuum at 110 °C on an oil bath. The cholesteric liquid crystal on the precursor polymer displayed iridescence due to the selective reflection of light, which strongly suggests that the liquid crystal exhibited a cholesteric phase with a helical structure. After 12 h, the visible selective reflection of the cholesteric liquid crystal in the reaction flask was reconfirmed, indicating that the cholesteric liquid crystal phase had been maintained. The dark orange polymer film obtained was then washed with acetone, water, methanol, and tetrahydrofuran in order to completely remove residual precursor and cholesteric liquid crystal. The resultant polymer was then dried under vacuum. The molecular weight of the polymer could not be measured because the polymer is insoluble and infusible. Here, molecular weight of the polymer after conversion may be lower than that of the precursor due to occurrence of partial scission reaction during the conversion process. We can conclude that the resultant polymer consists of PPV skeleton.³⁷

Figure 1

RESULTS AND DISCUSSION

Thermal properties

The TG-DTA results for the PPV precursor at normal atmospheric pressure are shown in Figure 2. The measurement was carried out at 1 atm. The sample displays inflection points of weight loss at 123 °C, 140 °C, and 182 °C on heating in TG. Simultaneously, an exothermic peak at 140 °C was observed in DTA. The transition at 140 °C on heating is due to elimination of the side-chain, which contains sulfur, from the main-chain and reconstruction of the precursor backbone into the PPV skeleton. The DTA results suggests that the conversion occurs at 140 °C, however the transformation also occur at 110 °C in the conversion process with compound **3** in long reaction time under vacuum conditions. Visible color change of the film and spectral results (IR and UV/Vis absorption spectrum) indicates the conversion was successfully performed. During the conversion process at 100 °C under vacuum, H₂S gas was detected with gas chromatography. The H₂S amount in the vessel was increased with annealing time due to the conversion progressed and molecular fraction containing sulfur atom was eliminated and decomposed (Figure 3).

Figure 2.

Figure 3.

Infrared absorption spectroscopy

Figure 4 shows the infrared absorption spectra for the precursor and PPV. Both polymers display an absorption band at around 2950 cm⁻¹ due to νCH or νCH₃. After heat treatment, the polymer film exhibited a peak at 962 cm⁻¹ assignable to out-of-plane bending of the *trans*-vinylene C–H bond. This result indicates that the configuration of the polymer chain was mainly *trans*. Although the PPV precursor displays an absorption at 1039 cm⁻¹ due to S=O stretching vibration,^{33,38} the PPV used in the present synthesis exhibited no such absorption band due to the elimination of the S=O group in the conversion to the polymer structure. The spectrum also lacked the characteristic absorption band at around 1700 cm⁻¹ due to C=O of the cholesteric liquid crystal **1**. This result

indicates that the PPV after the conversion was well washed and contained no traces of compound **1**.

Figure 4.

Optical properties

Figure 5 shows the ultraviolet-visible absorption spectra for the precursor polymer and the converted PPV. The PPV precursor displays an absorption maximum in the ultraviolet region (310 nm), while the converted PPV exhibits an absorption band at 402 nm due to the π - π^* transition of the PPV conjugated main-chain. It should be noted that the polymer displays a weak Cotton effect in circular dichroism measurements. The weakness of the effect is due to conversion of only the top surface of the PPV precursor to the ordered PPV structure.

Figure 4.

Optical texture

Cholesterics show various optical textures such as fingerprint texture, fan-shaped texture, and oily streaks texture depends on anchoring condition to substrate. Figure 6 (top) shows a POM image of compound **1**, revealing an oily streak texture typical of a cholesteric phase.⁴⁶ The circular differential interference microscopy (C-DIM) image and PCM images of the PPV film also display a streaky texture resembling that of the cholesteric liquid crystal (Figure 6, middle and bottom). This result shows that the conversion of the precursor to PPV involves reconstruction of the macroscopic structure at the interface with the cholesteric liquid crystal. The cholesteric compound **1** may play the role of a “molecular imprinter” from the molecular level to the macroscopic level during conversion of the PPV precursor. That is, the conversion proceeds at the interface mechanically rather than chemically. However, the ordered structure was not imparted on the entire PPV film. This result suggests that the cholesteric liquid crystal “stamp” did not penetrate the PPV precursor fully, likely due to the high viscosity of the precursor despite heating at 105–110 °C to lower the viscosity. As the present cholesteric liquid crystal has relatively low viscosity, high-viscosity chiral liquid crystals such as compounds showing chiral smectic phases (SmC*,

SmG*, SmI*, or SmB*) may provide more effective chiral transcription to the PPV precursor. The mechanism of the conversion in the present study may be related to “polymer mediated growth” method. Here, dramatic changes occurs in the structure and morphology of a guest material dispersed in a polymer matrix.⁴⁷

Figure 6.

To confirm this conversion process, conversion of the precursor was also performed using cholesteric liquid crystal in the isotropic phase at 160 °C. The synthesized PPV did not exhibit any ordered optical texture under PCM observation, although the characteristic absorption band at 402 nm was observed in the ultraviolet-visible spectrum.

Conclusions

PPV film displaying in part a fingerprint texture was prepared using a cholesteric liquid crystal reaction medium without chemical reaction between the chiral molecules and the cholesteric liquid crystal interface. The cholesteric liquid crystal in this application functions as a soft stamp, representing a type of interfacial conversion method. Use of cholesteric polymer liquid crystals with higher viscosity may provide more complete conversion results. Further study on the development of this interfacial conversion method is currently in progress.

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