# Synthesis of Semiconducting Polymers through Soluble Precursor Polymers with Thermally Removable Groups and Their Application to Organic Transistors

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Ⓢ *Supporting Information*

ABSTRACT: Novel semiconducting polymers consisting of thiophene and anthracene units without alkyl groups were successfully synthesized through soluble precursor polymers and applied to the organic thin-film transistors (OTFTs). Thermal elimination of leaving groups from the precursor polymers by retro Diels−Alder reaction was proved by thermogravimetric analysis (TGA), FT-IR, and UV−vis spectroscopy. The resulting films of the semiconducting polymers showed good surface morphologies even after thermal elimination, resulting in good semiconducting behavior with mobility of 0.015 $cm^2 V^{-1} s^{-1}$ in the typical top-contact OTFT. In addition, the devices based on these polymers are stable under ambient conditions and maintained good transistor performance even after being stored in air for 2 months.
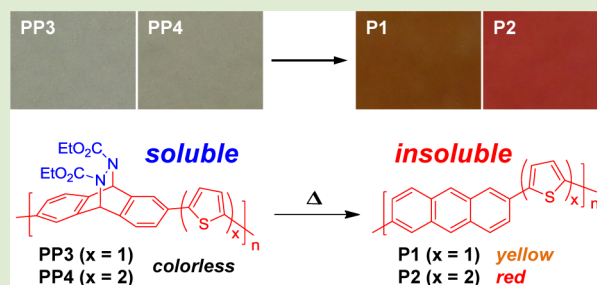
Solution processable organic semiconductors enable large-area, low-temperature, and low-cost production of organic thin-film transistors (OTFTs) by using printing methods. Pentacene is the most common organic semiconductor with its relatively high mobility and large on/off ratio.[1−3] However, vacuum deposition is required to fabricate OTFT devices owing to their low solubility in common organic solvents at room temperature. To achieve a solution process for pentacene, many attempts have been made to synthesize soluble pentacene. One approach is the use of substituted pentacene[4,5] and pentacene-based polymers.[6,7] The other is soluble pentacene precursors using Diels−Alder reactions.[8−13] The advantage of the precursor method is that a precursor film becomes insoluble after the conversion, making it ideal for postprocessing steps such as encapsulation. However, the thin films prepared from precursors of small-molecule materials can show apparent cracks through the elimination of leaving groups.[10] These discontinuous regions might prevent charge transport and decrease the performance and stability of devices. Thus, the mobilities obtained from pentacene using precursor methods are lower than those of vacuum-deposited pentacene. Since semiconducting polymers generally provide uniform thin films, they are suitable for use in solution processes. Nevertheless, polymers that apply precursor methods have been reported in a few cases,[14−16] and to our knowledge, there have been no other examples of polymers using the Diels−Alder reaction for OTFT devices. On the other hand, soluble thiophene polymers such as poly(3-hexylthiophene) (**P3HT**)[17,18] and its derivatives[19−23] exhibit high charge carrier mobilities through an organization of a polymer backbone promoted by alkyl groups. However, such insulating hydrocarbons reduce the density of π-conjugated regions in the film

and may inhibit isotropic charge transport of materials.[24] Therefore, semiconducting polymers excluding alkyl groups and consisting only of a π-conjugated framework are expected to show better reproducibility than alkyl-substituted polymers. To date, poly(2,5-thienylene-vinylene) (PTV) as a semiconducting polymer without alkyl groups has been applied to OTFT devices through a precursor approach.[25] However, the precursor is treated with HCl gas, which may adversely affect the devices. Therefore, new soluble precursor polymers are needed.

Here, we report on a precursor method using the Diels−Alder reaction, which was applied to novel insoluble π-conjugated polymers **P1** and **P2**, alternately consisting of anthracene and thiophene copolymers. Anthracene is suitable for introducing a leaving group and has high stability in air. The compounds of anthracene with thiophene have a nearly flat conformation, which is expected to provide high charge carrier mobility.[26,27] It is assumed that polymers **P1** and **P2** are converted from precursor polymers **PP1−PP3** and **PP4** by using retro Diels−Alder reactions that proceed only through heating. The formation of uniform thin film leading to better performance can be expected by utilizing novel semiconducting polymers.

The synthesis of precursor polymers **PP1−PP4** is outlined in Scheme 1. The Diels−Alder reaction of 2,6-dibromoanthracene (**4**) and leaving groups (LGs) such as N-phenylmaleimide, N-n-hexylmaleimide, and diethyl azodicarboxylate gave **5**, **6**, and **7** with good yields. The LGs were selected to be commercially

Scheme 1. Synthesis of Precursor Polymers PP1−PP4[a]
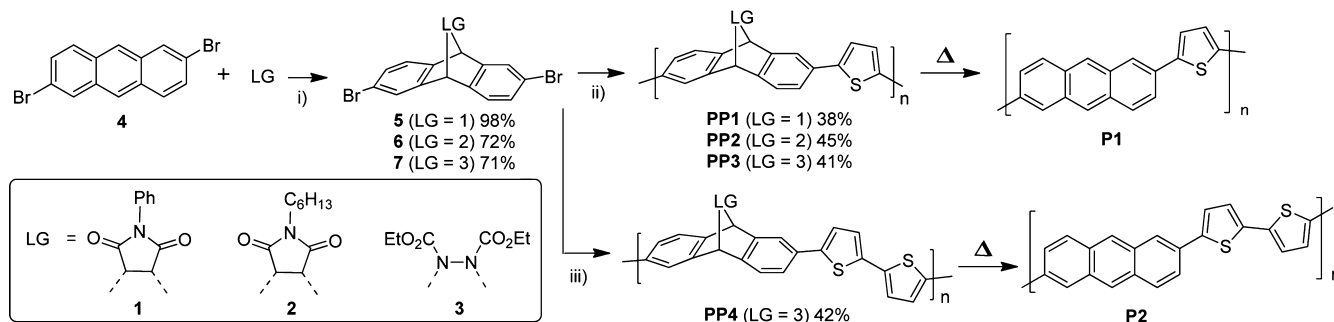
[a]Reagents and conditions: (i) toluene reflux; (ii) 2,5-bis(trimethylstannyl)thiophene, Pd(PPh$_3$)$_4$, DMF, 110−130 °C; (iii) 5,5′-bis(trimethylstannyl)-2,2′-bithiophene, Pd(PPh$_3$)$_4$, DMF, 110 °C.

available or easy to synthesize, further contributing to enhancement of the polymer solubility. The precursor polymers **PP1−PP3** were synthesized via Stille copolymerization of **5**, **6**, and **7** with 2,5-bis(trimethylstannyl)thiophene in DMF at 130 °C for **PP1** and **PP2** and 110 °C for **PP3**. The **PP4** was synthesized from **7** with 5,5′-bis(trimethylstannyl)-2,2′-bithiophene at 110 °C. During the reaction, the higher molecular weight components of **PP1** and **PP2** were precipitated due to their low solubility. The reaction for **PP3** and **PP4** at higher temperatures partially resulted in the retro Diels−Alder reactions. In addition, molecular weights did not increase with longer reaction times. The crude polymers were then purified using Soxhlet extraction, and the chloroform fractions were collected. Only in the case of **PP1**, a large amount of insoluble components remained after extraction. The higher molecular weight components of **PP1** may be due to the lower solubility of **PP1** than that of other polymers. **PP1−PP4** were obtained as light yellow solids by the precipitation into methanol. The chemical structures for the polymers were identified by ^{1}H NMR, FT-IR spectra, and elemental analysis. The weight-average molecular weight (M_w) and polydispersity index (PDI) of polymers were estimated to be 13 300 and 1.66 for **PP1**, 26 000 and 2.03 for **PP2**, 13 800 and 1.41 for **PP3**, and 11 600 and 1.36 for **PP4**, respectively, by gel permeation chromatography (GPC) with polystyrene standards in chloroform as an eluent, as shown in Table 1. These precursor polymers are highly soluble in common organic solvents and very stable in air.

Table 1. Characteristics of Precursor Polymers and Semiconducting Polymers

	before heating				after heating	
polymer	M_w (g/mol)	PDI	T_{d5} (°C)	λ_{max} (nm)	λ_{max} (nm)	IP (eV)
PP1	13300	1.66	295	340	360, 487, 517	5.40
PP2	26000	2.03	275	345	358, 488, 518	5.40
PP3	13800	1.41	203	350	360, 488, 518	5.42
PP4	11600	1.36	198	390	380, 500, 535	5.37

Thermogravimetric analysis (TGA) showed that precursor polymers undergo the retro Diels−Alder reactions starting around 265 °C for **PP1**, 255 °C for **PP2**, 185 °C for **PP3**, and 180 °C for **PP4** (Figure S1a, Supporting Information). The 5% weight loss temperatures (T_{d5}) are 295 °C for **PP1**, 275 °C for **PP2**, 203 °C for **PP3**, and 198 °C for **PP4**. The semiconducting polymers used in the latter experiments were

converted at temperatures higher than T_{d5}. The leaving groups such as maleimide required much higher temperature than the azo group. The T_{d5} (203 and 198 °C) of **PP3** and **PP4** was slightly lower than T_{d5} (218 °C) of the corresponding monomer dibromide **7**, although **PP1** and **PP2** showed slightly higher T_{d5} than **5** and **6**, respectively. The lower conversion temperatures of **PP3** and **PP4** are advantageous for device fabrication. The final weight losses of 40% for **PP1**, 41% for **PP2**, 40% for **PP3**, and 34% for **PP4** were in accordance with the theoretical weight losses due to the elimination of maleimide and the azo moiety from the precursor polymers. These results validate the thermal conversion of precursor polymers **PP1−PP3** and **PP4** into the semiconducting polymers **P1** and **P2**. Moreover, **PP1−PP4** are not subject to decomposition even at the higher temperatures in nitrogen.

Additional data on the thermal conversion were detected with FT-IR (Figure 1) and UV−vis spectroscopy (Figure S2,
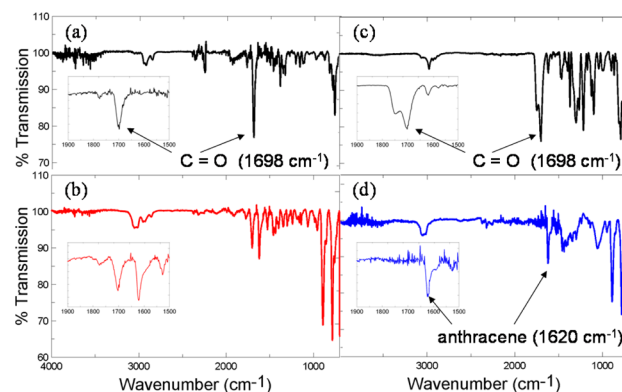

Figure 1. FT-IR spectra of films for (a) as-coated **PP2**, (b) **PP2** heated at 350 °C for 5 h, (c) as-coated **PP3**, and (d) **PP3** heated at 250 °C for 2 h.

Supporting Information). Both spectra for the thin films were obtained before and after heating at a temperature higher than T_{d5} in nitrogen ambient. During heating, the precursor polymer films changed from being almost colorless to a dark yellow.

The UV−vis spectra of precursor polymers **PP1−PP3** have a strong peak around 350 nm with no absorbance above 500 nm, and the heating leads the peak to shift 360 nm and to a new absorption band of anthracene moiety around 400−550 nm (Figure S2, Supporting Information). The absorption maxima (λ_{max}) are summarized in Table 1. These spectra after heating converged to the same absorbance. This result indicated that

the elimination of leaving groups for **PP1**−**PP3** progressed, leading to the same polymer **P1**. The 390 nm peak of **PP4** shifted to 380 nm, and an absorption band that had a λ_{max} of 500 and 535 nm appeared. Comparing λ_{max} of **PP3** and **PP4** after heating, the π-conjugation length of **P2** is assumed to be longer than that of **P1** due to the effect of improved flatness, which may contribute to the higher mobility.

Photoelectron spectroscopy in air was carried out to evaluate the ionization potential (IP), that is, the HOMO level (E_{HOMO}) of the polymers in the thin films. As listed in Table 1, the IPs for heated **PP1**−**PP4** were 5.37−5.42 eV. These values are close to the HOMO level (5.27 eV) of a similar anthracene-alkylthiophene copolymer, poly[2,6-bis(3′-dodecythiophene-2′-yl)anthracene] (**PDTAn**).[28] The HOMO levels for **P1** and **P2** films from precursor polymers were found to be low, meaning that they are stable against oxidation.

The FT-IR spectra of precursor polymers **PP2** and **PP3** before heating (Figure 1a and 1c) showed a strong carbonyl stretching peak at ca. 1700 cm^{-1}. During heating of **PP3**, the spectrum showed no carbonyl peak, and new peaks around 1620 cm^{-1} appeared, which is characteristic of anthracene (Figure 1d). On the other hand, the films from **PP2** (Figure 1b) contained carbonyl even after heating at 350 °C for 5 h, which must be high enough to complete the retro Diels−Alder reaction of maleimide. These results suggest the capture of a free maleimide compound in the film. **PP1** and **PP4** showed similar changes to **PP2** and **PP3**, respectively (Figure S3, Supporting Information).

Thus, the FT-IR and UV−vis spectra demonstrate that leaving groups were completely removed from **PP3** and **PP4** films after converting to semiconducting polymers **P1** and **P2** upon heating at moderate temperature; however, the leaving groups were not completely removed after conversion for **PP1** and **PP2**. These findings will be useful for molecular design of the leaving groups for the precursor polymer method.

We observed the quality of the film morphologies using AFM after heating, which was a problem with small-molecule materials. Figure 2 shows AFM images before and after heating. The film for **PP3** exhibited a uniform and smooth
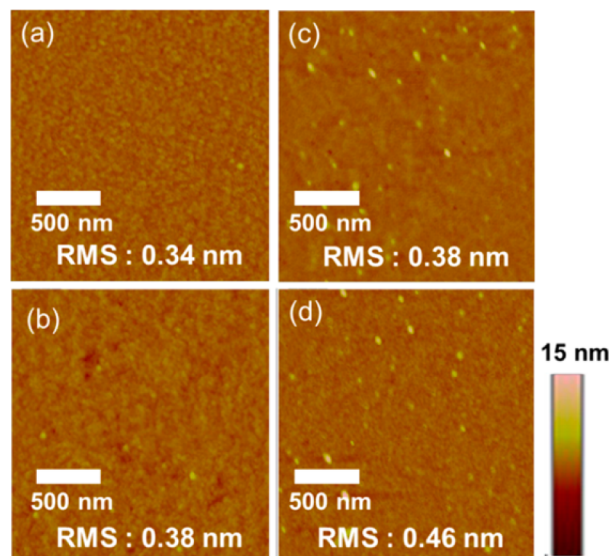

Figure 2. AFM images of (a) before and (b) after heating for **PP2** and (c) before and (d) after heating for **PP3**.

surface that had an RMS roughness of 0.46 nm even after heating, although the film thickness of **PP3** decreased to 28 nm from 45 nm as it was reduced in weight. This film's uniformity is one of the great advantages of polymers, and better performance can be expected in thin films without defects.

The charge transport properties of the semiconducting polymers **P1** and **P2** from precursor polymers **PP1**−**PP3** and **PP4** were investigated using top-contact OTFT devices. Si/SiO$_2$ substrates were treated with hexamethyldisilazane (HMDS). Precursor polymers were spin-coated from the chloroform solution, followed by thermal heating in a nitrogen atmosphere to convert them into semiconducting polymers. The transfer characteristics of the OTFT devices are illustrated in Figure 3. While the devices of unheated precursor polymers
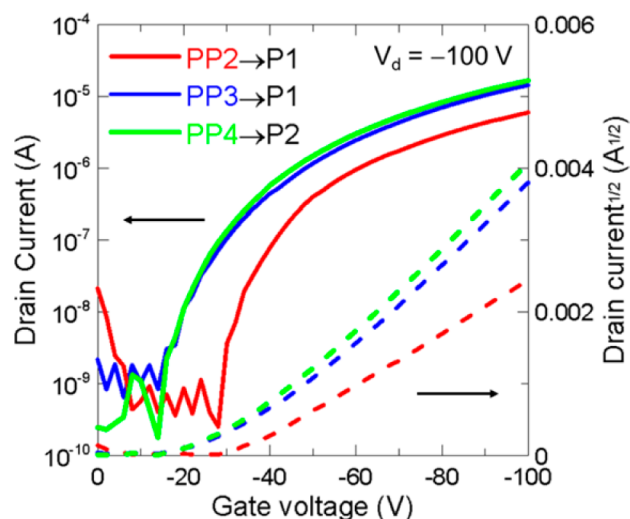

Figure 3. Transfer characteristics of OTFTs using **P1** films from **PP2** and **PP3** and **P2** film from **PP4**.

did not show the anticipated semiconducting properties, the OTFTs for **P1** and **P2** films from **PP1**−**PP4** exhibited typical p-type FET characteristics. The field-effect mobility of **P1** film from **PP3** was calculated to be 0.014 cm^2 V^{-1} s^{-1} in the saturation regime. However, the mobilities of **P1** films from **PP1** and **PP2** were half as low as that for the **PP3** device. This indicated that leaving groups for **PP1** and **PP2** remained as contaminants in the thin films, as indicated in the FT-IR measurements, resulting in lower electrical performance due to the formation of carrier traps. The field-effect mobility of **P2** film from **PP4** was 0.015 cm^2 V^{-1} s^{-1}. The **P2** with one more thiophene than **P1** showed a similar mobility to **P1**, although the results of UV−vis spectra indicated **P2** had a slightly longer conjugation length than **P1**. The reported mobility of the polymer corresponding to **PDTAn**[28] with alkyl groups in **P2** was 1.1×10^{-4} cm^2 V^{-1} s^{-1}. The **P2** device excluding alkyl groups was better than the **PDTAn** device that had alkyl groups. It was concluded that **PDTAn** was distorted slightly, owing to repulsion between the alkyl groups and hydrogen atoms on one and five positions of anthracene. In this system, the alkyl groups may disturb charge transport. Therefore, the strategy of using the precursor polymer method to form polymer films excluding the alkyl groups is very effective. Moreover, the OTFT devices using 2,6-dithienylanthracene (**DTAn**)[26,27] as a monomer unit of polymer **P2** have been reported with a mobility of 4.5×10^{-3} cm^2 V^{-1} s^{-1}. That is, the corresponding polymer **P2** was better, in spite of the fact that

the mobility of polymers generally tends to be lower than that for similar small-molecule materials. X-ray (XRD) patterns of **DTAn**, **P1**, and **P2** thin films did not show any reflection peaks, suggesting that these films are amorphous. These XRD patterns may be specific features of anthracene and thiophene compounds. Nevertheless, the **P2** film showed superior performance to **DTAn**. Thus, we assume that our precursor polymer method can realize the inherent performance of semiconducting polymer backbones. The uniform film quality of the polymer devices may further contribute to better electrical performance.

In addition, anthracene and thiophene derivatives have been reported as p-type organic semiconductors to show better environmental stability than pentacene.[26] We also evaluated the stability of these devices. These polymers can be expected to have atmospheric stability from the deep HOMO level estimated by photoelectron spectroscopy. The devices with these polymers maintained good performance even after the devices had been stored in air for 2 months (Figure S6, Supporting Information).

In conclusion, we have successfully fabricated novel solution processable precursor polymers **PP1**–**PP3** and **PP4** that were converted into the semiconducting polymers **P1** and **P2** in thin films through heating alone. Thermal elimination of leaving groups from **PP1**–**PP4** was investigated. The leaving group of azodicarboxylate was relatively easy to remove upon heating, whereas the leaving group of maleimide after conversion remained in the films and may have degraded device performance. We found that polymers from the precursor method exhibited uniform and smooth surfaces even after the conversion. OTFT devices prepared by the **P2** film from **PP4** exhibited typical p-channel behavior with the mobility of 0.015 $cm^2 V^{-1} s^{-1}$. These results showed that the **P2** device excluding alkyl groups is better than the devices based on alkyl-substituted polymers and a monomer unit. The strategy of using a precursor polymer method to form uniform **P1** and **P2** films without alkyl groups is very effective. Currently, structural optimization is being carried out to further improve the crystallinity.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Detailed synthetic procedures and characterizations of polymer, device fabrication, TGA, FT-IR, and UV−vis spectroscopy. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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