

NOTES

Preparation of Soluble Polypyrrole with $-C\equiv C-p-C_6H_4$ -hexyl Side Chains at the *N*-Position and Its Self-assembling Behavior

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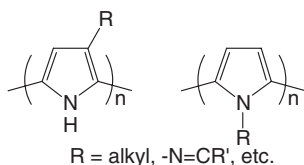
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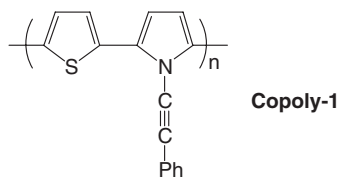
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π -Conjugated polymers are the subject of many papers.^{1–4} Polypyrrole is one of important π -conjugated polymers, and is adopted in industry.^{1–6} Polypyrrole is usually prepared by chemical and electrochemical oxidation of pyrrole. However, well characterization of its molecular structure has been prevented due to its insolubility in solvents. Introduction of substituents at the 3-position and *N*-position of pyrrole sometimes makes polypyrrole soluble in organic solvents, however, introduction of the substituent usually break the π -conjugation system due to steric repulsion between the substituent and the pyrrole ring.^{1–4,6,7}



Copolymers of pyrrole have also been prepared. However, synthesis of well π -conjugated copolymer of pyrrole with a coplanar structure has not received much attention.

Previously we reported a new pyrrole copolymer with an acetylenic $-C\equiv C-Ph$ side group at the *N*-position.⁷ In the copolymer, the $-C\equiv C-Ph$ group did not show the steric repulsion toward the π -conjugated main chain, and the main chain of the copolymer is considered to assume a coplanar structure; powder X-ray diffraction (XRD) pattern of the copolymer supported this notion.



However, the copolymer was not soluble and characterization of the copolymer was limited. By changing the $-C\equiv C-Ph$ side chain to a new $-C\equiv C-Ph-n-C_6H_{13}$ side chain, we have prepared a soluble new polypyrrole and obtained optical, electrochemical, and structural data of the copolymer. Herein we report the results. The obtained data are expected to contribute to better understanding of polypyrroles and related polymers.

Formation of a self-assembled and stacked structure of π -conjugated polymers is attracting recent interest.^{1–3,8} The pyrrole copolymer with the $-C\equiv C-Ph-n-C_6H_{13}$ side chain also shows such a self-assembling behavior, and the results will be also reported.

EXPERIMENTAL

Materials

$Pd(PPh_3)_4$ and 2,5-bis(trimethylstannyl)thiophene were prepared as reported previously.⁷ 2,5-Dibromo-*N*-(4-hexylphenylethynyl)pyrrole (Monomer-1) in Eq. 1 was prepared according to the following procedure.

A mixture of NaH (96 mg, 4.0 mmol) and pyrrole (270 mg, 4.0 mmol) in THF (20 cm³) was stirred in a Schlenk type tube for 2 h at 60 °C under N₂. After cooling to room temperature, 1-chloroethynyl-4-hexylbenzene (800 mg, 3.63 mmol) was added, and the reaction mixture was stirred for 24 h at 60 °C. After cooling to room temperature distilled water was added, and the mixture was stirred for 30 min at room temperature. The product was extracted with hexanes, dried over Na₂SO₄, and purified by column chromatography on SiO₂ (eluent = hexanes). *N*-(4-hexylphenylethynyl)pyrrole was obtained as a colorless oil (0.33 g or 1.3 mmol; 36% yield). ¹H NMR

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(300 MHz, $CDCl_3$) δ : 7.40 (d, 8.1 Hz, 2H), 7.13 (d, 8.1 Hz, 2H), 6.92 (t, 2.1 Hz, 2H), 6.21 (t, 2.1 Hz, 2H), 2.60 (t, 7.7 Hz, 2H), 1.57 (t, 7.7 Hz, 2H), 1.31–1.24 (m, 6H), 0.85 (t, 6.6 Hz, 3H). Anal: Calcd. for $C_{18}H_{21}N$: C, 86.01%; H, 8.42%; N, 5.57%. Found: C, 85.88%; H, 8.70%; N, 5.24%.

N-Bromosuccinimide (890 mg, 5.02 mmol) was added to a DMF (60 cm³) solution of *N*-(4-hexylethynyl)pyrrole (600 mg, 2.39 mmol) under N_2 at 0 °C. The mixture was warmed to room temperature and stirred at room temperature for 16 h. After addition of distilled water, the product was extracted with hexanes, dried over Na_2SO_4 , and purified by column chromatography on SiO_2 (eluent = hexanes). The Monomer-1 was obtained as a colorless oil (540 mg, 1.33 mmol; 56% yield). ¹H NMR (300 MHz, $CDCl_3$) δ : 7.46 (d, 8.4 Hz, 2H), 7.16 (d, 8.4 Hz, 2H), 6.21 (s, 2H), 2.61 (t, 7.7 Hz, 2H), 1.58 (t, 7.7 Hz, 2H), 1.30–1.23 (m, 6H), 0.87 (t, 6.9 Hz).

Measurements

¹H NMR and IR spectra were recorded on a JEOL EX-400 spectrometer and JASCO IR 810 spectrophotometer, respectively. CP-MAS ¹³C NMR spectra were recorded on a JEOL GSX-270 spectrometer equipped with a CP/MAS probe. UV-vis and photoluminescence spectra were measured with Shimadzu UV-3100 and Hitachi F-4010 spectrophotometers, respectively. Powder X-ray diffraction (XRD) patterns were obtained using Rigaku RINT-2100 with $Cu-K\alpha$ (1.54 Å) radiation. Thermal analysis was performed with a Shimadzu TA-50 WS thermal analyzer equipped with a Shimadzu DSC-50 differential scanning calorimeter and a Shimadzu TGA-50 thermogravimetric analyzer. GPC curves were obtained with a Tosoh

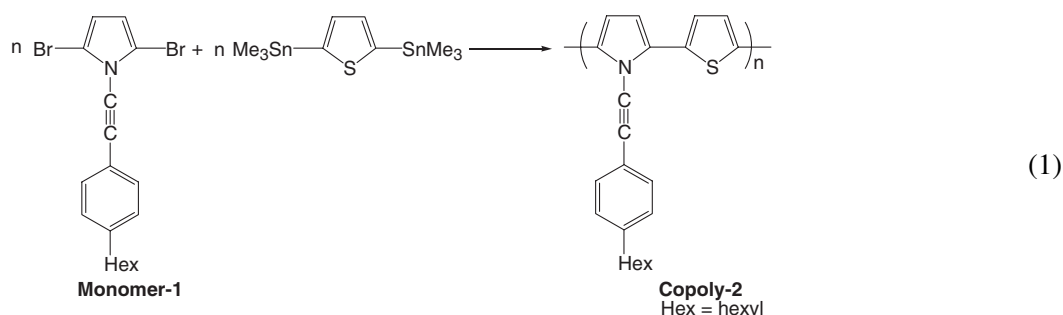
HLC-8120 GPC system using Tosoh TSKgel G5000H columns (eluent = DMF, vs. polystyrene standards). Density of **Copoly-2** was measured by a sink and float method using chloroform and methanol.

Preparation of Copolymer-2

To a dry DMF (20 mL) solution containing Monomer-1 (0.60 g, 1.47 mmol) and 2,5-bis(trimethylstannyl)thiophene (0.60 g, 1.47 mmol), $[Pd(PPh_3)_4]$ (0.085 g, 0.074 mmol) was added. After the mixture was stirred at 70 °C for 48 h, it was poured into an aqueous KF solution. The solution was stirred for 24 h at room temperature. The precipitate was collected by filtration, washed by HCl aq., NH_3 aq., distilled water, and MeOH successively, and dried *in vacuo*. Yield: 0.33 g (1.00 mmol, 68%). Anal. Calcd for $(C_{22}H_{21}NS \cdot 2H_2O)_n$: C, 71.90%; H, 6.86%; N, 3.81%; S, 8.73%; Br, 0%. Found: C, 71.42%; H, 5.26%; N, 3.39%; S, 9.38%; Br, 0%. IR (KBr, cm^{-1}): 3099, 2953, 2924, 2852, 2251, 1495, 1465, 1422, 1362, 1260, 1184, 1148, 1018, 823, 793, 758, 691, 532. ¹H NMR (400 MHz, $CDCl_3$): δ 7.50 (br, 2H, Ph-H), 7.41 (br, 2H, Ph-H), 7.13 (br, 2H, Th-H), 6.46 (br, 2H, Pyr-H), 2.59 (br, 2H, αCH_2), 1.59 (br, 2H, βCH_2), 1.28 (br, 6H, CH_2), 0.85 (br, 3H, CH_3). CP/MAS Solid-¹³C NMR (100 MHz): δ 139.82, 131.62, 128.10, 122.09, 111.04, 85.61, 73.60, 37.56, 32.28, 24.23, 14.70.

RESULTS AND DISCUSSION

The following Pd-catalyzed organometallic polycondensation based on Stille coupling⁹ give the following copolymer, **Copoly-2**.



GPC analysis of **Copoly-2** indicated a number average molecular weight (M_n) of 4300 (or n of about 13 in Eq. 1) with an M_w/M_n of 1.3. Although the degree of the polymerization is not high, **Copoly-2** is considered to give basic information about optical and electrochemical properties of such a type of polymer; optical and redox properties of π -conjugated molecules are usually saturated below about 10 aromatic units.^{1–4,10}

Copoly-2 was soluble in organic solvents such as DMF, THF, and chloroform, and gave cast film suited for optical and electrochemical measurements. ¹H NMR data of **Copoly-2** agree with the structure of the copolymer. IR spectrum of **Copoly-2** indicated $\nu(C\equiv C)$ peak at 2251 cm^{-1} . The thermo-gravimetric analysis of **Copoly-2** showed a 5% weight-loss temperature at 399 °C.

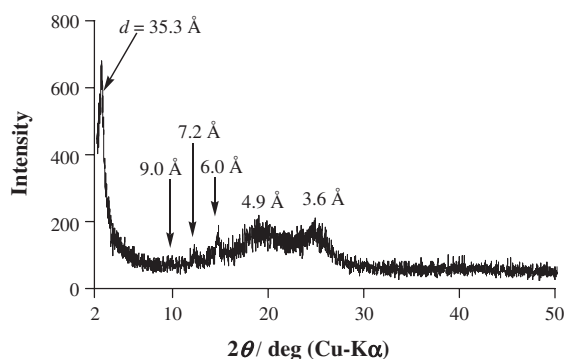


Figure 1. Powder XRD pattern of **Copoly-2**.

XRD Pattern and Packing Structure

Figure 1 shows the XRD pattern of **Copoly-2**. The XRD pattern of **Copoly-2** resembles that of the previously reported **Copoly-1**.⁷ For **Copoly-1** a double-running packing structure has been proposed based on its XRD pattern,⁷ and resemblance of the XRD pattern of **Copoly-2** with that of **Copoly-1** suggests the following similar double-running packing structure of **Copoly-2**.

As shown in Figure 1, **Copoly-2** gives peaks at about $d = 35/n$ Å ($n = 1, 4, 5, 6$).¹¹ The $d_1 = 35$ Å distance is considered to correspond to the distance between the doubly-running polymer main chains, as shown in Chart 1, and the distance agrees with the molecular packing model. The polymer main chain is considered to be essentially coplanar, similar to **Copoly-1**,⁷ because there is no steric repulsion between the $-\text{C}\equiv\text{C}-\text{Ph}-n-\text{C}_6\text{H}_{13}$ side chain and the main chain as judged by a CPK molecular model.

The $d_2 = 3.6$ Å distance is reasonable for a π -stacking distance between π -conjugated polymers, and somewhat shorter than that (3.8 Å)⁸ observed with head-to-tail type poly(3-alkylthiophene-2,5-diyl), HT-P3RTh. In the case of HT-P3RTh, all the repeating heterocyclic units contain large sulfur, and this seems to be the reason for the longer d_2 distance in HT-P3RTh than in **Copoly-2**. The repeating length (7.54 Å) of **Copoly-2** is considered to be the same as that proposed for **Copoly-1**.⁷ This repeating length and tilting of the hexyl chain by 50° give a hexyl chain-hexyl chain distance of 4.7 Å which roughly agrees with an effective diameter (about 4.5 Å) of linear alkyl chain.¹² The observed density of 1.23 g cm⁻³ roughly agrees with the calculated density of 1.28 g cm⁻³.¹³

Optical Data and Solvatochromism

Figure 2 exhibits UV-vis spectra of **Copoly-2** in chloroform and in solid. As exhibited in Figure 2, **Copoly-2** gives the π - π^* absorption peak at 456 nm in CHCl₃, which is near the π - π^* absorption peak

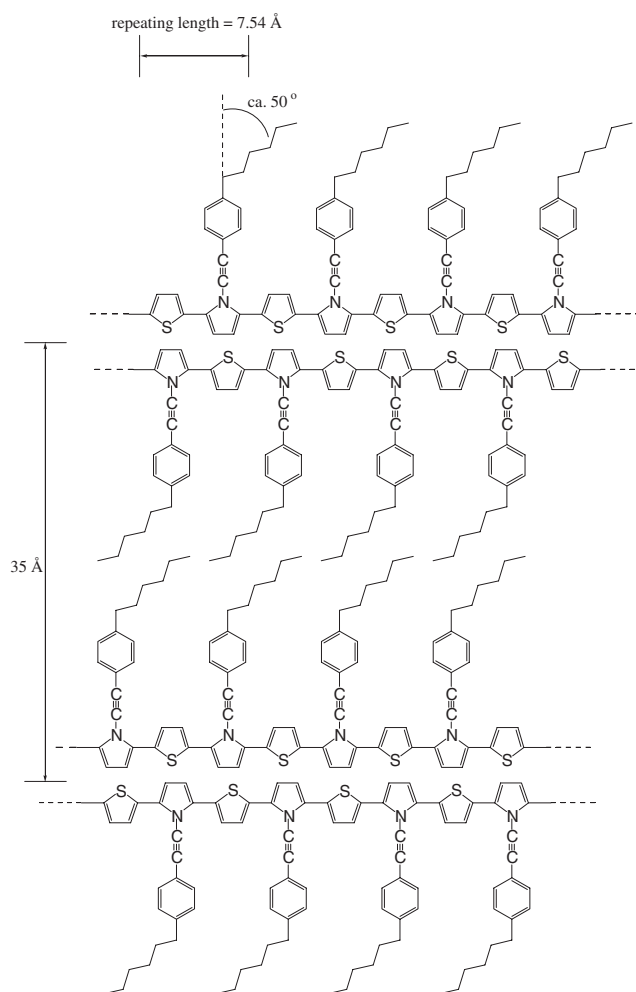


Chart 1. Doubly-running packing structure of **Copoly-2** in the solid state. The repeating length (7.54 Å) of **Copoly-2** is considered to be the same as that proposed for **Copoly-1**.⁷ Only one sheet is shown. Sheets are considered to form a stacked structure with the d_2 space of 3.6 Å.

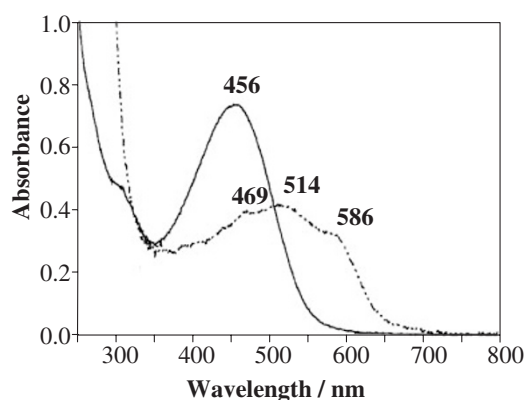


Figure 2. UV-vis spectra of **Copoly-2** in CHCl₃ (solid line) and in cast film (broken line).

($\lambda_{\text{max}} =$ about 450 nm) of HT-P3RTh having a similar π -conjugated system composed of five-membered rings. However, the UV-vis peak position locates at a shorter wavelength than that ($\lambda_{\text{max}} =$ about

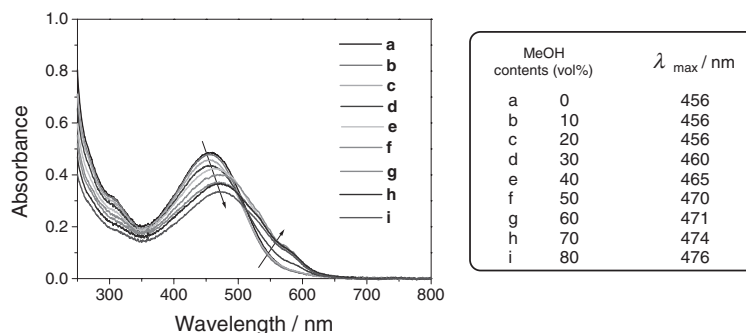


Figure 3. Changes of UV-vis spectrum of **Copoly-2** on addition of methanol to the CHCl_3 solution of **Copoly-2**.

520 nm) of coplanar head-to-head type poly(3-alkynylthiophene-2,5-diyl), HH-P3($C\equiv CR$)Th.¹⁴

In the cast film, the UV-vis peak of **Copoly-2** is shifted to a longer wavelength, and a main peak is observed at 514 nm with a substructure peaks at 469 nm and 586 nm; such a substructure is often observed with films of π -conjugated polymers which forms a stacked structure.⁸ The shift to a longer wavelength in going from the solution to film is considered to arise from intermolecular electronic interaction between the polymer molecules and is characteristic of π -stacking of π -conjugated polymers.^{1,2,8,10} The degree of the shift (about 60 nm from 456 nm to 514 nm; *cf.*, Figure 2) of the main peak is somewhat smaller than that (about 80 nm) observed with HT-P3RTh.^{8,10}

As shown in Figure 3, addition of methanol (poor solvent) to the CHCl_3 (good solvent) solution of **Copoly-2** causes appearance of new absorption band in a range of 550 through 600 nm where the UV-vis absorption band of the film of **Copoly-2** is observed. Similar behavior has been reported when methanol (poor solvent) is added to CHCl_3 (good solvent) solutions of HT-P3RTh and related π -conjugated polymers,^{8e,15} and the phenomenon has been explained by formation of colloidal π -stacked particles of the polymers. The data shown in Figure 3 are also explained by formation of π -stacked colloidal particles of **Copoly-2** on addition of methanol to the chloroform solution of **Copoly-2**.

Figure 4 shows photoluminescence (PL) spectrum of **Copoly-2** in CHCl_3 . As shown in Figure 4, the emission peak appears near the onset position of the UV-vis absorption band at about 560 nm (*cf.*, Figure 2), similar to photoluminescence of π -conjugated molecules and polymers.^{1-3,10} The excitation spectrum normally agrees with the UV-vis spectrum of **Copoly-2**. Photoluminescence of **Copoly-2** gave a quantum yield of 21% in CHCl_3 (*vs.* quinine sulfate standard having a quantum yield of 54.6%¹⁶). The cast film of **Copoly-2**, however, did not show PL. Such negligible or very weak PL is sometimes observed when π -

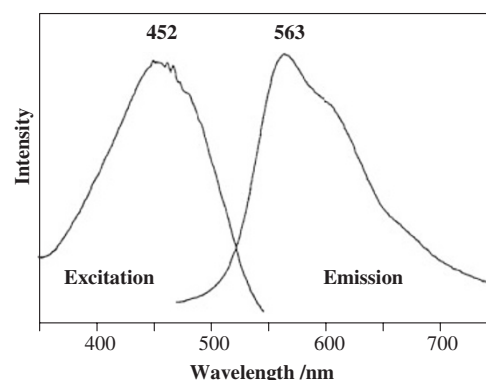


Figure 4. Photoluminescence spectra of **Copoly-2** in CHCl_3 . Excitation and emission spectra are shown.

conjugated polymers have a strong intermolecular electronic interaction. In that case, the photo-activated polymer is considered to form an excimer-like adduct with the polymer in the ground state. The PL results obtained with the cast film of **Copoly-2** are also accounted for by the stabilization of the photo-activated polymer molecule by forming such an excimer-like adduct before emission of the captured photo-energy.

As described above, the XRD, UV-vis, and PL data agree with π -stacking of **Copoly-2**. Such π -stacking has been examined with various polythiophenes with long side chains.^{1-4,8,10} However, study of π -stacking behavior of polypyrrole by using soluble polypyrrole has no precedent to our knowledge.

The cast film of **Copoly-2** was electrochemically active, and showed oxidation (or p-doping) peaks at 0.29 V and 1.08 V *vs.* Ag^+/Ag . The first oxidation potential locates between the oxidation potential of polypyrrole (about -0.3 V *vs.* Ag^+/Ag)¹⁷ and polythiophene (about 0.6 V *vs.* Ag^+/Ag).¹⁷

CONCLUSION

Introduction of hexyl group to the previously reported **Copoly-1** gives soluble **Copoly-2**. The soluble **Copoly-2** has made investigation of optical and elec-

trochemical behavior of the polymer possible. XRD and optical data of **Copoly-2** indicate a tendency of the polymer to form the π -stacked structure. The data are expected to give bases for better understanding of polypyrroles.

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13. If **Copoly-2** contains hydration water as described in the Experimental part, the molecular weight of the repeating unit is 367.5. Consequently the density of **Copoly-2** having the packing mode shown in Chart 1 gives the following calculated density $\rho_{\text{calcd}} = (367.5 \times 2)/(35 \times 3.6 \times 7.54 \times 0.5023) = 1.28 \text{ g cm}^{-3}$.
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