

NOTE

Effects of solvent and temperature on regioregularity of poly(3-hexylthiophene-2,5-diyl) prepared by chemical oxidative polymerization

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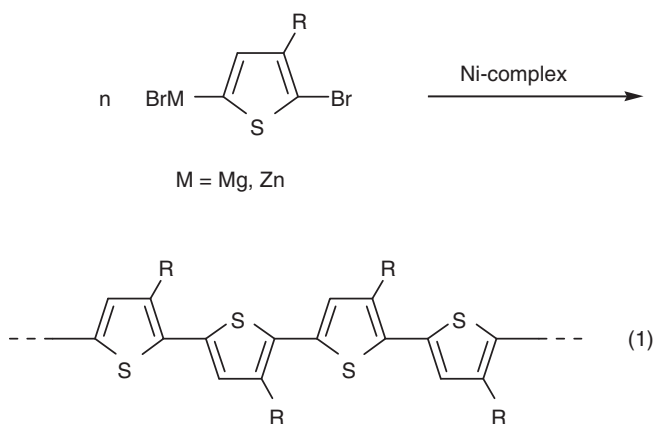
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Keywords: chemical oxidative polymerization; π -conjugated polymer; poly(3-hexylthiophene-2,5-diyl); regioregularity; solvent effect; stacking

INTRODUCTION

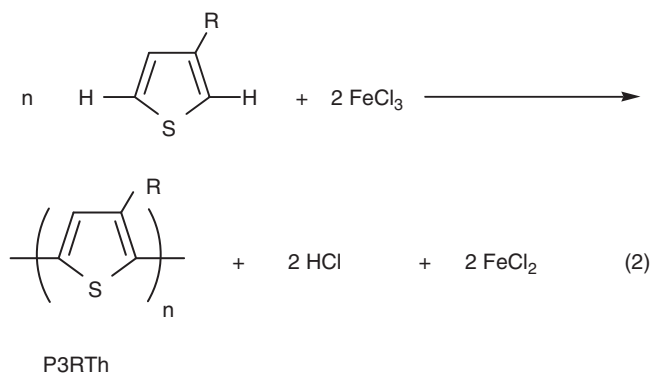
π -Conjugated polymers bearing electronic and optical functionalities are the subject of many papers. Control of regioregularity of π -conjugated polymers is important to improve their electronic and optical properties.^{1–4} For example, regioregular head-to-tail poly(3-alkylthiophene-2,5-diyl), HT-P3RTh, shows a higher electrical conductivity than the corresponding regio-random poly(3-alkylthiophene-2,5-diyl), rand-P3RTh.⁵

Regioregular π -conjugated polymers are usually obtained by organometallic polycondensation^{5–7} (OMP) (for example, equation (1)), and OMP gives HT-P3RTh with a HT content higher than 98%.^{5,6}



On the other hand, chemical oxidative polymerization^{8–10} (COP) of 3-alkylthiophene proceeds in a simpler reaction system, using more common reagents such as FeCl_3 .

Typical COP using FeCl_3 has been carried out mostly in halogenated solvents, such as CHCl_3 at room temperature (equation (2)).



Effects of reaction conditions of COP have been studied, and Ueda *et al.*^{11–13} have revealed that the HT content of P3RTh can be increased when polymerization is carried out in CHCl_3 at low temperature, for example, at -45°C .¹¹ They optimized reaction conditions, such as monomer concentration and reaction time, and obtained P3RTh with an HT content of 88%. However, solvent effect on the regioregularity of P3RTh was not revealed. Revealing effects of regioregularity of the COP-prepared P3RTh on its physical and chemical properties is considered to be interesting; physical and chemical properties of P3RTh have mainly been studied with OMP-prepared P3RTh.

Here we report solvent and temperature effects on regioregularity and polydispersity (PDI) of the COP-prepared P3HexTh (R in P3RTh = hexyl) as well as effects of the regioregularity of the COP-prepared P3HexTh on its physical and chemical properties.

EXPERIMENTAL PROCEDURE

Measurements

NMR spectra and IR spectra were recorded on a JEOL EX-300 and JASCO IR-800 spectrometers, respectively. UV-vis spectra of a polymer solution and film were measured with a Shimadzu (Kyoto, Japan) UV-3100PC and UV-2500PC spectrometers. Gel-permeation chromatography was carried out with a Shimadzu SIL-20A liquid chromatograph using chloroform as the eluent (polystyrene standards). Powder X-ray diffraction (XRD) patterns were obtained by using a Rigaku (Tokyo, Japan) RINT2100 powder X-ray diffractometer with CuK α (1.54 Å) radiation. Electrical conductivity of the p-doped polymer film was measured with a LORESTA-IP MCP-T250 resistometry by a four-probe method.

Materials

3-Hexylthiophene was purchased from Tokyo Chemical Industry Co., Ltd. (Tokyo, Japan) Anhydrous organic solvents were purchased from Kanto Chemical Co., Inc. (Tokyo, Japan) and stored under N₂ before use.

Preparation of P3HexTh

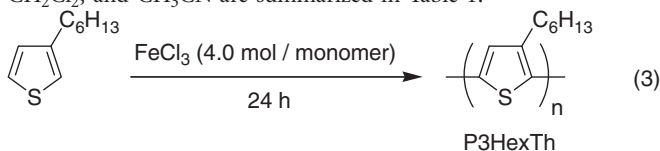
A typical example of the preparation of P3HexTh: 3-Hexylthiophene (0.50 g, 3.0 mmol) and FeCl₃ (1.94 g, 12.0 mmol) were added to anhydrous chloroform (50 ml) at -60 °C in a Schlenk tube under N₂.⁸ After stirring at the temperature for 24 h under N₂, the reaction mixture was poured into methanol, and the precipitate was collected by filtration. The crude product dissolved in chloroform was de-doped by treatment with an aqueous solution of hydrazine. The organic layer was separated and the solvent was removed by evaporation to give P3HexTh as a green film. The polymer was extracted with a Soxhlet extractor with chloroform and the chloroform solution was added to methanol to recover purified P3HexTh. Purified P3HexTh was collected by filtration and dried under reduced pressure to give a green solid (Run 6 in Table 1) (0.37 g, 74% yield). ¹H NMR (CDCl₃): δ = 6.98 (s, 1H, H at the thiophene ring), 2.80 (t, 1.74 H, α -CH₂, HT unit), 2.55 (t, 0.26 H, α -CH₂, HH unit), 1.77 (quintet, 2H, β -CH₂), 1.50–1.30 (m, 6H, -(CH₂)₃-), 0.92 (t, 3H, -CH₃). IR (KBr): 2952, 2905, 2851, 1750, 1643, 1524, 1452, 1393, 1363, 1226, 1143, 1071, 923, 845, 821, 762, 679, 655, 619 cm⁻¹. Anal. calcd for (C₁₀H₁₄S)_n: C, 72.23; H, 8.49; S, 19.28%. Found: C, 71.19; H, 8.64; S, 19.21%. Elemental analytical data of P3HexTh have been discussed.¹⁴

Other polymers were prepared analogously. As described later, CH₃CN as the solvent gave P3HexThs with relatively small PDI. Obtained polymers did not seem to contain the polymerization solvent because the content of nitrogen was negligible (within an experimental error): for example, analytical data of Run 14 P3HexTh in Table 1: Found: C, 71.65; H, 8.72; N, 0.09 (negligible, within experimental error); S, 18.62%.

The HT content was estimated from α -CH₂ proton peaks observed at δ 2.80 (HT unit) and δ 2.55 (HH unit). HT content = (peak area of the peak at δ 2.80)/(peak area of the peak at δ 2.80 + peak area of the peak at δ 2.55).⁶

RESULTS AND DISCUSSION

Preparation of P3HexTh was carried out under conditions shown in equation (3) and the results of the polymerization in hexane, CHCl₃, CH₂Cl₂, and CH₃CN are summarized in Table 1.



Hexane gave P3HexTh with low HT contents of 62% and 69% at room temperature and -20 °C, respectively (Runs 1 and 2). Results of COP in CHCl₃ (Runs 3–6) basically agreed with those reported previously.¹¹ 3-Hexylthiophene was also smoothly polymerized in CH₂Cl₂ and CH₃CN to afford P3HexTh with high HT contents of

Table 1 Chemical oxidation polymerization of 3-hexylthiophene

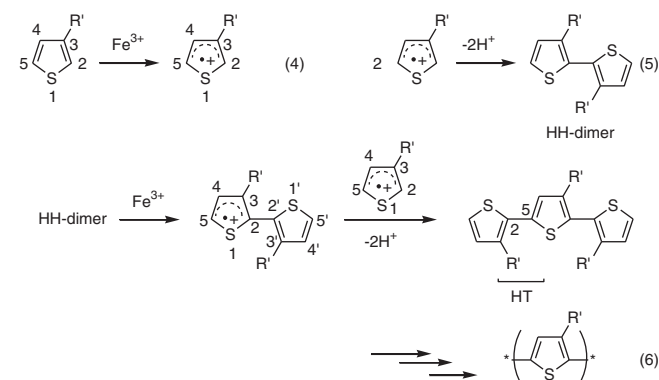
Run	Solvent	Temperature (°C)	Yield (%)	M _n ^a × 10 ⁻³	PDI ^b	HT ^c (%)	HT/HH ^c ratio
1	hexane	rt ^d	65	18	3.3	62	1.6
2	hexane	-20	50	28	4.6	69	2.2
3	CHCl ₃	rt	70	22	5.7	67	2.0
(P1)							
4	CHCl ₃	-20	70	19	2.8	81	4.3
(P2)							
5	CHCl ₃	-40	80	19	2.7	87	6.7
(P3)							
6	CHCl ₃	-60	74	19	2.6	87	6.7
7	CH ₂ Cl ₂	rt	67	34	4.0	78	3.4
8	CH ₂ Cl ₂	-20	55	31	4.1	83	4.9
9	CH ₂ Cl ₂	-40	50	46	5.0	87	6.7
10	CH ₂ Cl ₂	-60	45	46	4.3	87	6.7
11	CH ₃ CN	rt	70	34	1.5	75	3.0
12	CH ₃ CN	0	65	41	1.7	77	3.3
13	CH ₃ CN	-20	54	45	1.7	83	4.9
14	CH ₃ CN	-40	50	42	1.6	83	4.9

^aDetermined by gel-permeation chromatography (polystyrene standards, eluent = chloroform).

^bPolydispersity. PDI = M_w/M_n.

^cHT = content of the head-to-tail unit. ⁶HH = content of the head-to-head unit.

^drt = room temperature (ca. 25 °C).

Scheme 1 Suggested mechanism for COP of 3-substituted thiophene.¹²

87% (Runs 9 and 10) and 83% (Runs 13 and 14), respectively. Results shown in Table 1 indicate that COP in CH₂Cl₂ and CH₃CN gave P3HexTh with larger M_n than COP in CHCl₃, and M_n became larger than 40 000 at lower temperatures. In the case of CH₃CN, P3HexTh had relatively narrow PDIs (PDI = M_w/M_n) of 1.5–1.7.

Barbarella *et al.*¹² suggested the mechanism shown in Scheme 1 (R' in Scheme 1 = -SR in their paper) for COP of 3-substituted thiophene. First, two oxidized thiophene monomers (equation (4)) are thought to couple together at the 2-position to give head-to-head type bithiophene (HH-dimer) (equation (5)).^{11,12} As shown in equation (6), the 5-position of the oxidized HH-dimer is considered to couple with the 2-position of the oxidized monomer to form a new HT bond in the trimer; the coupling reaction is accompanied by liberation of two H⁺. Repetition of such reaction is thought to finally give P3RTh with a high HT content.

As shown in Table 1, the HT content of P3HexTh increases by lowering polymerization temperature, revealing that formation of the HT unit is energetically advantageous than that of the HH unit. By

lowering temperature from room temperature (ca. 25 °C) to -40 °C, the HT/HH ratio becomes about double, which corresponds to Arrhenius' activation energy difference of about 6 kJ mol⁻¹ between the HT-forming reaction and HH-forming reaction. Regio-controlled HT-P3HexTh forms aggregates by self-assembly especially at low temperatures,³ and formation of stable aggregates of regio-controlled P3HexTh is thought to contribute to increase the HT content at low temperatures.

As shown in Table 1, choice of CH₃CN gives HT-type P3HexTh with a relatively narrow molecular weight distribution (PDI = 1.5–1.7), although P3HexTh prepared by COP and OMP usually had a wider molecular weight distribution (PDI = ca. 2–4). Because of the narrower molecular weight distribution, the HT-type P3HexTh obtained in CH₃CN may be used without fractionation.¹⁵

Effects of the HT content on physical and chemical properties of COP-prepared P3HexTh have been examined using **P1**–**P3**. **P3** has a relatively high HT content and may show tendency to self-assemble similar to the case of OMP-prepared P3RTh,^{1–6} whereas **P1** will show different physical and chemical properties from those of **P3** because of its lower HT content. Table 2 summarizes UV-vis data and electrical conductivities of the polymers.

Figure 1 shows UV-vis spectra of **P1**–**P3** films before doping and after p-doping. In CHCl₃, the three polymers show only a UV-vis peak originated from single P3HexTh molecules, giving rise to a peak in a range of 430–444 nm (cf. Table 2).³ In film, the UV-vis peak shifts to a longer wavelength, reflecting molecular assembly of the polymer in the solid state. The main peak of **P1** in CHCl₃ at 430 nm shifts to 477 nm in film (shift (Δ) = 477 – 430 = 47 nm), and **P2** and **P3** films give rise to main UV-vis peaks at 511 nm and 520 nm with larger Δ s of 69 nm and 76 nm, respectively. The larger shift of UV-vis peak of **P2** and **P3** by going from solution to film is thought to arise from π -stacking^{1–6} of **P2** and **P3** with larger HT content. The powder XRD data of **P1**–**P3** shown in Figure 2 support this view, and **P3** gives rise to distinct XRD peaks at $d_1 = 15.9$ Å, $d_1/2 = 8.0$ Å, $d_1/3 = 5.3$ Å and $d_2 = 3.8$ Å.

The XRD pattern of **P3** essentially agrees with that of OMP-prepared P3HexTh with a HT content of 98.5%,^{3,6} and d_1 is assigned to a distance between P3HexTh main chains separated by the hexyl side groups.^{3,6} d_2 is thought to correspond to a π -stacking distance between the P3HexTh molecules. In contrast, **P1** shows only a weak XRD peak at $d_1 = 16.1$ Å, indicating that **P1** does not form a well-packed solid structure.

As shown in Table 2, **P3** shows a higher electrical conductivity than **P1** and **P2** after oxidation (p-doping) with NOBF₄. NOBF₄ is a useful p-doping (oxidizing) reagent for π -conjugated molecules and polymers.^{16,17} The polymer films cast on a Pt plate was dipped in a CH₃CN solution of NOBF₄ (0.1 M) for 15 min at room temperature. The NOBF₄-doped film was peeled off from the plate, and electrical conductivity of the p-doped polymer film was measured with a resistometry by a four-probe method. All the NOBF₄-oxidized^{16,17} polymer films show new peaks at about 700–800 nm and 1600–2000 nm (cf. Figure 1b), which are assigned to a polaron and/or bipolaron band. By increasing the HT content, the new bands shift to a longer wavelength. **P1** shows the new peaks at approximately 700 nm and 1600 nm, whereas **P2** and **P3** give rise to the new peaks at approximately 800 nm and 2000 nm (Figure 1b). The difference is thought to essentially reflect the difference in the UV-vis peaks between original non-doped **P1** and **P2**–**P3**, and p-doped **P2** and **P3** may have a longer effective π -conjugation length and/or stronger intermolecular electronic interaction in solid than p-doped **P1**.

Table 2 UV-vis data and electrical conductivities of **P1**–**P3**

Polymer	UV-vis, λ_{\max} (nm)		σ^c (S cm ⁻¹)
	Solution ^a	Film ^b	
P1	430	477 ^m , 596 ^{sh}	0.1
P2	442	511 ^m , 556 ^{sh} , 596 ^{sh}	1.0
P3	444	520 ^m , 554 ^m , 600 ^{sh}	3.0

^a In CHCl₃.

^b Cast film on a quartz plate. m = main peak. sh = shoulder peak.

^c Electrical conductivity of NOBF₄-oxidized polymer film.¹⁶

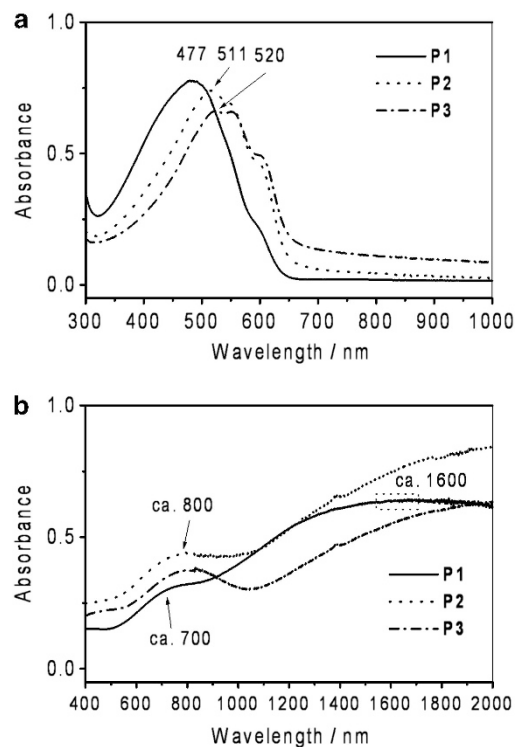


Figure 1 UV-vis spectra of **P1**–**P3**. (a) Non-doped and (b) NOBF₄-oxidized films.

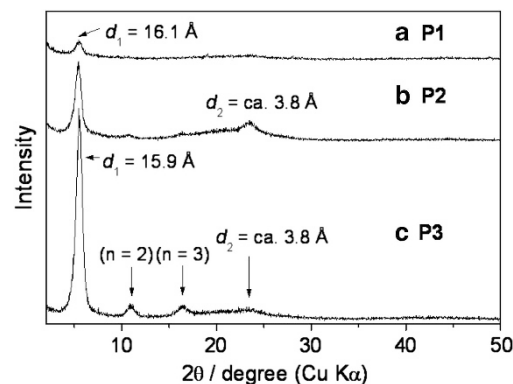


Figure 2 Powder XRD patterns of (a) **P1**, (b) **P2** and (c) **P3**.

CONCLUSIONS

Solvent and temperature effects of COP for the P3HexTh preparation have been revealed, and effects of the HT content of the COP-prepared P3HexTh on its physical and chemical properties are reported. Acetonitrile gave P3HexTh with a high molecular weight, a large HT content and a narrower PDI.

ACKNOWLEDGEMENTS

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