

Reductive Polymerization of Halothiophene

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ABSTRACT: The reductive preparation of poly(thiophene) and copolymers from 2,5-dibromothiophene and tetrabromothiophene is described. In this reaction, hydrazine and palladium catalysts were used. Yield of the polymer was 65% when 2,5-dibromothiophene was used as a monomer. Electric conductivity of the polymer was $1 \times 10^{-5} \text{ S cm}^{-1}$ (I_2 20 wt%) and $1 \times 10^{-3} \text{ S cm}^{-1}$ (I_2 50 wt%). The polymer had 1.6 wt% of bromine residue. As the mixing ratio of 2,5-dibromothiophene to tetrabromothiophene decreased, yield of the polymer decreased. A polymer from tetrabromothiophene gave yield of 41%. As for electric conductivity, the polymer prepared from only 2,5-dibromothiophene gave a higher value than copolymers of 2,5-dibromothiophene and tetrabromothiophene. Increasing the a mixing ratio of tetrabromothiophene caused a decrease of the conductivity. The polymer from tetrabromothiophene gave electric conductivity of $\sim 10^{-6}$ — $10^{-7} \text{ S cm}^{-1}$ (I_2 20 wt%).

KEY WORDS Poly(thiophene) / 2,5-Dibromothiophene / Tetrabromothiophene / Palladium / Reductive Polymerization /

The preparations and electric properties of conducting polymers have been investigated from scientific and industrial points of view in recent years. Heterocyclic polymers have been presented in several reports. They were prepared by electrochemical polymerization,¹⁻³ Grignard reaction,⁴⁻⁷ and oxidative condensation.⁸ However chemical reductive condensation is not reported yet. The reductive coupling of organic halide was reported.⁹⁻¹¹ We applied this reductive coupling for polymerization, using hydrazine and a palladium catalyst in solvent of methanol or ethanol. As the reaction proceeds using the solvent or the materials containing water, it is not necessary to employ anhydrous materials. This reaction is also safe with low toxicity because the reaction can be carried out in the solvent of aliphatic alcohol. This will be applied to an industrial production easily. In this paper, the above reaction was applied to the preparation of poly(thiophene). Characteristic properties such as electric conductivity and optical spectra

of these polymers were measured.

EXPERIMENTAL

Materials

The reagents were commercial reagent grade except for those noted below. 2,5-Dibromothiophene was distilled *in vacuo*, subsequently, was recrystallized from hexane. The solvents, MeOH and EtOH were used after distillation.

Preparation: Method A

Monomer, 12.1 g (50 mmol) of 2,5-dibromothiophene was added to a mixture of 12.0 g (300 mmol) of sodium hydroxide, and 1.77 g (10 mmol) of palladium chloride in 200 cm³ of solvent. Subsequently the mixture was stirred at reflux for 30 min. Hydrazine monohydrate was added to the mixture and stirred at reflux for 3 h. The resulting mixture was filtered, and the polymer with a residual Pd metal was washed with MeOH, CHCl_3 , and water. Copo-

lymerizations were carried out analogously.

Preparation: Method B (Run 16)

Monomer, 12.1 g (50 mmol) of 2,5-dibromothiophene was added to a mixture of Pd-plates (geometrical surface area 200 cm^2) and 12.0 g (300 mmol) of NaOH in 200 cm^3 (EtOH) of solvent. Subsequently the mixture stirred at reflux for 30 min. Hydrogen hydrate was added to the mixture and was stirred at reflux for 8 h. The resulting mixture was filtered. Pd-plates and the polymer were washed with MeOH, CHCl_3 , and water. The polymer was collected and dried *in vacuo*.

Purification: Method I

The polymer containing the residual Pd metal was added to a mixture of acetone, HCl (35%), and H_2O_2 (35%) (= 10 : 5 : 1). After 1h of irradiation of ultrasonic, the mixture was permitted to stand overnight at room temperature. The polymer was filtered and washed with MeOH using a Soxhlet extractor for 50 h. After vacuum drying, the weight of polymer was measured.

Purification: Method II (Run 15)

The polymer with the residual Pd metal was added to the solution (acetone:HCl (35%): H_2O_2 (35%)=10:5:1), and refluxed for 2 h. The polymer was filtered and washed with MeOH using a Soxhlet extractor for 50 h. After vacuum drying, the weight of polymer was measured.

Measurement

For measurement of the bromine residue, about 5 mg of the polymer were combusted in combustion flask. The combusted gas was bubbled into 10 ml adsorbent solution (0.15% NaOH, H_2O_2 , in water). The solution was quantified to bromo ions by an ion-chromatography (2010i Dionex Co.) after diluting to the mark with water in a 50 cm^3 mess flask.

For measurement of the palladium residue, the polymer was powdered with a mortar and

pestle. The polymer of 100 mg of Powder weighed and 5 cm^3 of acetone were placed in a 50 cm^3 Erlenmeyer flask. After irradiation of ultrasonic, about 20 cm^3 of aqua regio were placed in it. Particles of the polymer in aqua regio were displaced completely. The solution was permitted to stand for at least over night. It was diluted to the mark with 3% of HCl in 10 ml of a mess flask. The palladium concentration in the solution was analyzed by ICP (SPS-400, Seiko Instrument Inc.).

A Takeda Riken R-8651 electrometer was used to measured electric conductivity. IR spectra were recorded on a Perkin-Elmer FT-IR 1600 series. UV-vis spectra were obtained with a Hitachi U-3210 spectrophotometer.

RESULTS AND DISCUSSION

The reaction was carried out using a mixture of halothiophene, sodium hydroxide, hydrazine hydrate, and palladium chloride in solvent (MeOH or EtOH). Palladium chloride reacted with sodium hydroxide to give palladium hydroxide. Palladium hydroxide was reduced by hydrazine *in situ* to metal at the initial reaction and this metal had catalytic activity. This metal was used for reductive polymerization of halothiophene with hydrazine. As shown in Table I, 2,5-dibromothiophene as a monomer was polymerized at reflux to give poly(thiophene) and as shown in Table II, mixtures of 2,5-dibromothiophene and tetrabromothiophene as monomers were polymerized at reflux to give their copolymers. Poly(thiophene) was dark reddish brown but copolymers were dark brown. In the preparation of poly(thiophene) from 2,5-dibromothiophene (Run 1 and Run 2), the solvent (MeOH, EtOH) had no influence on the yield of poly(thiophene). Refluxing temperature was 73°C in the solvent of MeOH and 83°C in the solvent of EtOH. However this depended on amount of the Pd catalyst in Table I. In spite of using of hydrazine monohydrate and sodium

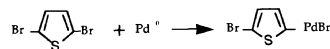
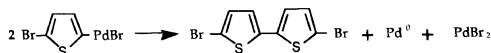
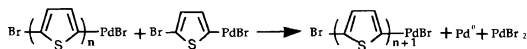
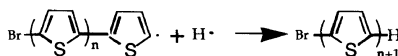
Table I. Preparation of poly(thiophene)^a

Run	Monomer	Catalyst	Solvent	Time	Yield
	mmol	mmol		h	%
1	2,5-Dibromothiophene 50	PdCl ₂ 10	EtOH	3	68
2	2,5-Dibromothiophene 50	PdCl ₂ 10	MeOH	3	68
3	2,5-Dibromothiophene 50	PdCl ₂ 5	EtOH	3	43
4	2,5-Dibromothiophene 50	PdCl ₂ 5	EtOH	6	50
5	2,5-Dibromothiophene 50	PdCl ₂ 20	EtOH	3	80
6	2,5-Dibromothiophene 50	NiCl ₂ 10	MeOH	6	0
7	Tetrabromothiophene 50	PdCl ₂ 10	MeOH	3	17
8	Tetrabromothiophene 50	PdCl ₂ 10	EtOH	3	46
15	2,5-Dibromothiophene 50	PdCl ₂ 10	MeOH	3	66
16	2,5-Dibromothiophene 50	Pd-plates 200 cm ²	EtOH	8	Trace

^a Runs 1–8 were conducted by Method A and Method I. Run 15 was conducted by Method A and Method II. Run 16 was conducted by Method B.

hydroxide in the system, the reaction proceeded and gave a high yield. The reaction did not require anhydrous materials or anhydrous condition.

The mechanism of this reaction is inferred from analogy with reports^{9–11} for halothiophene. A halothiophene and palladium(0) combine by oxidative addition, and the thiophene palladium(II) complex is formed (Scheme 1). Bimolecular decomposition of the thiophene palladium(II) complex gives bihalothiophene, a palladium metal and a Palladium(II) bromide (Scheme 2).

**Scheme 1.****Scheme 2.****Scheme 3.****Scheme 4.**

By continuing the reaction as show in Scheme 3, the polymer is produced. A palladium(II) complex is reduced by hydrazine which changes to a palladium metal. The palladium metal again causes the reaction of Scheme 1.

Bromine Residue in Polymers

Figure 1 shows bromine residues contained in the polymer of 2,5-dibromothiophene as a monomer and the copolymer of 2,5-dibromothiophene and tetrabromothiophene as monomers. The polymer of 2,5-dibromothiophene had 1.6 wt% of bromine residue. This value is lower than that by Grignard reaction method.⁷ However compared with the synthesized polymer by the Grignard method, both polymers showed the same ratio of CHCl₃-soluble fraction. This means that the molecular weight distributions of these are similar. Therefore, low bromine residue in the polymer does not indicate that by the formation of a high molecular weight of the polymer. Hydrogen generated by self-decomposition of hydrazine changes to active hydrogen by Pd-catalyst. This suggests that bromine of end-group in the polymer can be substituted by the hydrogen at a high proportion (Scheme 4). The bromine residue increased in proportion to the rate of tetrabromothiophene as seen

in Table II. This suggests also lower reactivity of bromine of 3,4-positions in the thiophene ring.

Palladium Residue in Polymers

PdCl_2 was reduced by hydrazine and changed to Pd-black (Pd-metal) as mentioned above. The poly(thiophene) contains Pd-black after the reaction. It is necessary to remove Pd-black from the polymer. In general, Pd-metal is an active metal in platinum group. It can be dissolved in HCl with an oxidizing agent. Methods for removing Pd-metal (Pd-black) without damaging polymer units were investigated. In this experiment, the method of removing the Pd-black was under mild

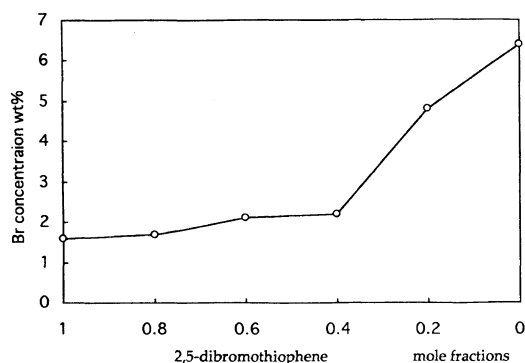


Figure 1. Br residual concentration in polymers. The polymers were obtained in Run 1 and Runs 9–13 in Table II.

conditions. Acetone was used as a solvent to improve the wetting properties of the polymer. Pd-metal (Pd-black) was dissolved in HCl with hydrogen peroxide. Palladium residues (Pd-black) in the polymers were no remarkable difference in the prepared polymers using Method A. Palladium residues were between 1 wt% and 3 wt% in the polymers. It was difficult to remove Pd-black completely and Pd-black still remained in the polymer after the purification. The palladium residue depended on the method of purification.

Content as Preparation Method B (Run 16), plates of metallic palladium were used as the catalyst instead of PdCl_2 . In this case, the polymer adhered to the Pd plates surface after the reaction. The polymer was collected, and washed by solvents (MeOH and CHCl_3). Contamination of the polymer caused by dissolution of the Pd-plate could be ignored, since the weight of the Pd-plates did not change after the above reaction. However the yield of the polymer was a low value because the reaction area of the Pd-plate was smaller than that of Pd-black.

Cross-Linked Poly(thiophene)

Cross-linked poly(thiophene) was investigated for electric conductivity and electronic spectra.

Table II also shows the solubility of

Table II. Copolymerization of 2,5-dibromothiophene and tetrabromothiophene^a

Run	Monomer ratio		Solvent	Yield %	Fraction	
	2,5-Dibromothiophene	Tetrabromothiophene			CHCl ₃ -soluble fraction	CHCl ₃ -insoluble fraction
	mmol	mmol			%	
1	50	0	EtOH	68	46	
9	40	10	EtOH	63	40	
10	30	20	EtOH	50	35	
11	20	30	EtOH	46	35	
12	10	40	EtOH	45	30	
13	0	50	EtOH	41	26	
14	0	50	MeOH	17	9	

^a Runs 1 and 9–14 were carried out by Method A and Method I.

polymers in CHCl_3 at room temperature. When copolymers were prepared from mixtures of 2,5-dibromothiophene and tetrabromothiophene as monomers, the solubility of copolymers in CHCl_3 increased in proportion to the ratio of 2,5-dibromothiophene in the monomers. When the copolymer was prepared from tetrabromothiophene as an additional monomer, solubility in CHCl_3 was low and Br residual content was high. Thus, the reaction may occur on 3,4-positions bromine in thiophene ring to cause crosslinking of the thiophene chain.

Figure 2 shows the electronic spectra of the CHCl_3 -soluble fraction of polymers. The polymer of Run 1 showed a large bathochromic shift of the π - π^* adsorption peak at 450 nm. However, adding tetrabromothiophene shifts that of peaks to UV-region.

Conductivity and IR

The no doped polymer (Run 1) has electric conductivity of $\sim 10^{-11} \text{ S cm}^{-1}$ at room temperature. The polymer powder exposed to iodine vapor was molded into pressed pellets, and the electric conductivity was $1 \times 10^{-5} \text{ S cm}^{-1}$ (I_2 20 wt%) and $1 \times 10^{-3} \text{ S cm}^{-1}$ (I_2 50 wt%) by the four-point method. Copolymers of 2,5-dibromothiophene and tetrabromothiophene had electric conductivities of $\sim 10^{-6}$ – $10^{-7} \text{ S cm}^{-1}$ (I_2 20 wt%). On the whole, electric conductivity of copolymers was low. Figure 3 shows the IR spectra of polymers prepared in Run 1, 15, and 16 in Table I. The IR spectrum of Run 16 showed one sharp peak at 790 cm^{-1} , an out of plane $\delta_{\text{C-H}}$ vibration band characteristic of 2,5-disubstituted thiophene. The IR spectrum of Run 15 does not show a peak at 790 cm^{-1} , and a sharp peak at 1327 cm^{-1} appeared. That is an asymmetric stretching ν_{as} ($>\text{SO}_2$) vibration band. Poly(thiophene) of Run 16 was prepared with a Pd-plate (geometrical surface area 200 cm^2) as catalyst instead of PdCl_2 . This method makes the process of removing Pd-black unnecessary. The comparison of IR spectra of Run 15 and

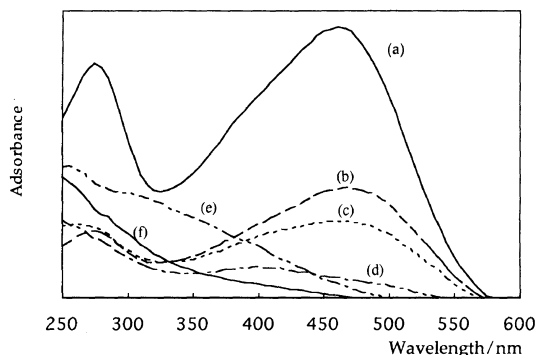


Figure 2. Electronic adsorption spectra of CHCl_3 -soluble fraction. (a) poly(2,5-thiophene); (b) Run 9 in Table II; (c) Run 10 in Table II; (d) Run 11 in Table II; (e) Run 12 in Table II; (f) Run 13 in Table II.



Figure 3. Infrared spectrum of poly(thiophene) (a) obtained from Run 1 in Table I, (b) obtained from Run 15 in Table I, and (c) obtained from Run 16 in Table I.

Run 16 revealed that the polymer units are distracted partly. The reason for this is that the IR spectrum of Run 15 did not show a peak at 790 cm^{-1} . When the Pd-catalyst in the polymer was removed by oxidation with H_2O_2 , thiophene units were partly oxidized.

CONCLUSIONS

A new chemical polymerization method to

produce poly(thiophene) was investigated using 2,5-dibromothiophene as a monomer, palladium chloride as a catalyst and hydrazine hydrate as a reductant. The followings were clarified:

(1) Poly(thiophene) is produced by a reaction system that uses 2,5-dibromothiophene as the monomer, palladium chloride as the catalyst and hydrazine hydrate as the reductant.

(2) Adding tetrabromothiophene to the reaction system decreases polymer production.

(3) The polymer of (2) shows low solubility in CHCl_3 . It seems that 3,4-position bromine in thiophene ring reacts, causing cross-links of thiophene chains.

(4) Bromine arising from the monomer shows a low value of bromine residual concentration in the polymer.

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