Synthesis of Poly(3-phenyl-2,5-thiophene) by Nickel-Catalyzed Coupling Polymerization of 3-Phenyl-2,5-dichlorothiophene

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ABSTRACT: Poly(3-phenyl-2,5-thiophene) was prepared by the nickel-catalyzed coupling polymerization. Polymerizations were conducted in *N,N*-dimethylacetamide (DMAc) in the presence of zinc, triphenylphosphine, and bipyridine and produced polymer 4 with inherent viscosities up to 0.50 dL·g^{-1} under mild conditions. The effects of various factors, such as amount of catalyst and ligand, reaction medium, and reaction temperature, were studied. The microstructure of polymer 4 was investigated by means of ^{13}C NMR spectroscopy, and it has been found that the polymer obtained had the expected structure without mislinkage through the β-position and the random structure on regiospecificity. The polymer was readily soluble in common organic solvents and can be processed into uniform films from their solution. The thermogravimetry of polymer 4 showed 10% weight loss at 550 and 570 °C in air and in nitrogen, respectively.

Introduction

Organic conducting polymers and optical nonlinear active polymers synthesized from thiophene derivatives have attracted increasing interest owing to their enhanced stability in both oxidized and neutral stages and high third-order nonlinear susceptibility.[1,2]

A number of synthetic routes for producing poly(thiophene)s have been described in the literature.[1,3] They can be prepared in two ways, by dehydrogenation polymerization using an electrochemical or a chemical method. High molecular weight polymers have been generally prepared by the former method. However, the electrochemically obtained polymers contain β-coupling.[1,3,4]

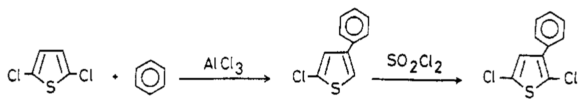
Recently, Hotta et al. reported on the synthesis of well-defined poly(3-alkylthiophene)s with high molecular weights by dehydrohalogenation of 3-alkyl-2-halogenothiophene in the presence of Lewis acid.[4] The stereoregular head-to-head versions of poly(alkylthiophene)s were prepared by the polymerization of 3,3′-dialkyl-2,2′-bithiophenes, and their properties were compared to those of the conventional polymers obtained from polymerization of 3-alkylthiophenes.[3]

In a preceding paper,[5] we showed that nickel-catalyzed coupling polymerization of aryl dichlorides is a very useful method for the synthesis of aromatic poly(ether ketone)s. Quite recently, the synthesis of aromatic poly(ether sulfone)s by nickel coupling of aryl dichlorides was reported.[6] In our continuing investigation of the versatility of this method, we now report the successful synthesis of poly(3-phenyl-2,5-thiophene) by nickel-catalyzed coupling of 3-phenyl-2,5-dichlorothiophene.

Experimental Section

Materials. Reagent grade anhydrous $NiCl_2$ was dried at 220 °C under vacuum. Triphenylphosphine (PPh_3) was purified by recrystallization from *n*-hexane. Powdered (400-mesh) zinc was purified by stirring with acetic acid, filtering, washing throughly with ethyl ether, and drying under vacuum. All solvents such as *N,N*-dimethylacetamide (DMAc), *N,N*-dimethylformamide (DMF), and *N*-methyl-2-pyrrolidone (NMP) were stirred over powdered calcium hydride overnight, then distilled under reduced pressure, and stored over 4-Å molecular sieves.

Scheme I



1 2 3

2,5-Dichloro-3-phenylthiophene (3). This compound was prepared from 2,5-dichlorothiophene (1) in 42% yield in two steps, which involved $AlCl_3$-catalyzed arylation of 1,[7] followed by chlorination of the resulting 2-chloro-4-phenylthiophene (2) with sulfuryl chloride:[8] IR (NaCl) 840 (2,3,5-trisubstituted thiophene ring C–H), 750, 680 cm^{-1} (monosubstituted benzene ring); ^{1}H NMR ($CDCl_3$) δ 7.25–7.50 (m, Ph-*H*, 5 H), 6.85 (s, thiophene-*H*, 1 H).

3,4′-Diphenyl-2,2′-bithienyl (5). This compound was prepared by $AlCl_3$-catalyzed self-condensation of compound 2, followed by catalytic dechlorination of the 5-chloro-3,4′-diphenyl-2,2′-bithienyl with palladium on charcoal.[8]

Polymer Synthesis. A typical example of the polymerization follows.

Polymer 4 from 3. In a 25-mL two-necked round-bottomed flask were placed $NiCl_2$ (9.0 mg, 0.07 mmol), PPh_3 (367 mg, 1.4 mmol), bipyridine (bpy; 10.9 mg, 0.07 mmol), zinc (283 mg, 4.34 mmol), and monomer 3 (229 mg, 1 mmol). The flask was evacuated and filled with nitrogen three times. Then dry DMAc (0.44 mL) was added via syringe through the serum cap. The mixture was stirred at 90 °C for 3 h. The mixture became red-brown in 10 min, and the polymer precipitated in 1 h. The mixture was diluted with NMP (2 mL) and poured into a large amount of HCl/methanol. The polymer was collected, washed with methanol, and dried in vacuo at 80 °C for 24 h. The yield was 0.159 g (100%). The inherent viscosity of the polymer in NMP was 0.5 dL·g^{-1}, measured at a concentration of 0.5 g·dL^{-1} at 30 °C: IR (film) 840 (2,3,5-trisubstituted thiophene ring CH). Anal. Calcd for $(C_{12}H_6S)_n$: C, 75.91; H, 3.82. Found: C, 76.26; H, 4.15.

Measurements. The infrared spectra were recorded on a Hitachi I-5020 FT-IR spectrometer, the ultraviolet spectra on a Hitachi Model 100-60 UV/vis spectrometer, and the NMR spectra on a Hitachi R-22 (90 MHz) instrument. Viscosity measurements were carried out by using an Ostwald viscometer at 30 °C. Thermal analyses were performed on a Seiko SSS 5000 thermal analyzer at a heating rate 10 °C·min^{-1} for thermogravimetric analysis (TGA) and for differential scanning calorimetry (DSC).

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Table I
Effect of Solvent on Polymerization[a]

	polymer	
solvent	yield, %	η_{inh},[b] $dL{\cdot}g^{-1}$
DMAc	99	0.15
NMP	99	0.13
THF[c]		

[a] Reaction conditions: monomer (1 mmol), $NiCl_2$ (0.05 mmol), PPh_3 (0.6 mmol), Zn (3.1 mmol), bpy (0.05 mmol), solvent (0.44 mL), 90 °C, 6 h. [b] Measured at a concentration of 0.5 $g{\cdot}dL^{-1}$ in NMP at 30 °C. [c] 60 °C.

Table II
Effect of Amount of DMAc on Polymerization[a]

DMAc,	polymer		DMAc,	polymer	
mL	yield, %	η_{inh},[b] $dL{\cdot}g^{-1}$	mL	yield, %	η_{inh},[b] $dL{\cdot}g^{-1}$
0.30	99	0.17	0.90	97	0.10
0.44	95	0.20			

[a] Reaction conditions: monomer (1 mmol), $NiCl_2$ (0.07 mmol), PPh_3 (0.6 mmol), Zn (3.1 mmol), bpy (0.07 mmol), 90 °C, 6 h. [b] Measured at a concentration of 0.5 $g{\cdot}dL^{-}$ in NMP at 30 °C.

Table III
Effect of the Reaction Temperature on Polymerization[a]

temp,	polymer		temp,	polymer	
°C	yield, %	η_{inh},[b] $dL{\cdot}g^{-1}$	°C	yield, %	η_{inh},[b] $dL{\cdot}g^{-1}$
60			90	99	0.30
70	92	0.15	100	99	0.16
80	99	0.15			

[a] Reaction conditions: monomer (1 mmol), $NiCl_2$ (0.05 mmol), PPh_3 (0.6 mmol), Zn (3.1 mmol), bpy (0.05 mmol), DMAc (0.44 mL), 6 h. [b] Measured at a concentration of 0.5 $g{\cdot}dL^{-1}$ in NMP at 30 °C.

Table IV
Effect of Amount of Catalyst on Polymerization[a]

catalyst	polymer		catalyst	polymer	
$NiCl_2$/bpy (1:1), mol %	yield, %	η_{inh},[b] $dL{\cdot}g^{-1}$	$NiCl_2$/bpy (1:1), mol %	yield, %	η_{inh},[b] $dL{\cdot}g^{-1}$
5	97	0.22	8	100	0.49
6	99	0.36	9	98	0.27
7	99	0.50			

[a] Reaction conditions: monomer (1 mmol), $NiCl_2$ (0.05 mmol), PPh_3 (1.4 mmol), Zn (3.1 mmol), DMAc (0.44 mL), 90 °C, 6 h. [b] Measured at a concentration of 0.5 $g{\cdot}dL^{-1}$ in NMP at 30 °C.

Table V
Effect of Amount of Triphenylphosphine on Polymerization[a]

PPh_3,	polymer		PPh_3,	polymer	
mol %	yield, %	η_{inh},[b] $dL{\cdot}g^{-1}$	mol %	yield, %	η_{inh},[b] $dL{\cdot}g^{-1}$
60	95	0.20	120	99	0.31
80	99	0.32	140	99	0.50
100	99	0.32	160	99	0.39

[a] Reaction conditions: monomer (1 mmol), $NiCl_2$ (0.07 mmol), bpy (0.07 mmol), Zn (3.1 mmol), DMAc (0.44 mL), 90 °C, 6 h. [b] Measured at a concentration of 0.5 $g{\cdot}dL^{-1}$ in NMP at 30 °C.

Table VI
Effect of Amount of Bipyridine on Polymerization[a]

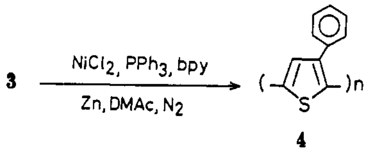
		polymer				polymer	
bpy, mol %	bpy/ $NiCl_2$	yield, %	η_{inh},[b] $dL{\cdot}g^{-1}$	bpy, mol %	bpy/ $NiCl_2$	yield, %	η_{inh},[b] $dL{\cdot}g^{-1}$
3.5	0.5	99	0.25	10.5	1.5	94	0.21
7.0	1.0	99	0.50				

[a] Reaction conditions: monomer (1 mmol), $NiCl_2$ (0.07 mmol), PPh_3 (1.4 mmol), Zn (3.1 mmol), DMAc (0.44 mL), 90 °C, 6 h. [b] Measured at a concentration of 0.5 $g{\cdot}dL^{-1}$ in NMP at 30 °C.

Results and Discussion

Polymer-forming monomer, 2,5-dichloro-3-phenylthoiphene(3) was prepared by the reaction shown in the Scheme I. The $AlCl_3$-catalyzed reaction of 2,5-dichlorothiophene (1) with benzene gave 2-chloro-4-phenylthiophene (2) in 60% yield.[6] Compound 2 was converted to compound 3 in 70% yield by treatment with sulfuryl chloride.[8]

On the basis of previous results on the synthesis of poly(ether ketone)s by nickel-catalyzed coupling polymerization of aromatic dichlorides,[5] the polymerization of monomer 3 was carried out in the presence of $NiCl_2$, zinc, triphenylphosphine (PPh_3), and bipyridine (bpy). To determine optimal conditions for polymerization, the following factors that influence the reaction were studied: solvent, temperature of the polymerization, amount of catalyst and ligand. Table I lists the effect of solvent on the polymerization. The polymerization proceeded with the formation of a red mixture at 90 °C in DMAc or NMP. On the other hand, monomer 3 did not polymerize in THF, probably due to low reaction temperature. Although the polymers were isolated in excellent yields in DMAc and NMP, the molecular weights were low.



Next, the effect of the amount of solvent on the polymerization was studied (Table II). The amount of DMAc found to be appropriate for the reaction on a 1-mmol scale was 0.3–0.4 mL. Then the effect of reaction temperature on the inherent viscosity of the resulting polymer was examined over the temperature range 60–100 °C. The polymerization at 90 °C gave a polymer with an inherent viscosity of 0.30 $dL{\cdot}g^{-1}$. Polymerization did not start at 60 °C and raising the temperature to 100 °C gave inferior results, probably due to transfer of aryl groups from triarylphosphine.[9] These results are summarized in Table III.

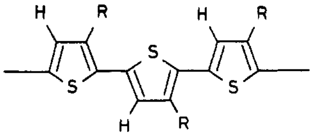
With consideration of the coupling mechanism in which the metathesis of the arylnickel species I is very slow (Scheme II), a minimum amount of Ni catalyst that minimizes the formation of the arylnickel species I, after all of the aryl chloride end group of the polymer is consumed, is preferred to obtain higher molecular weights of polymer.[10] The effect of amount of catalyst on the polymerization is summarized in Table IV. The inherent viscosity of the polymer reached its highest value with 7 mol % of the catalyst based on the monomer.

Scheme II

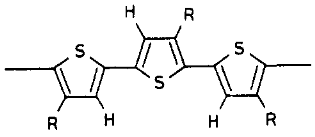
$$\underset{\text{I}}{2\text{ArNi}^{\text{I}}\text{L}_3} \xrightarrow[\text{slow}]{-\text{L}} \text{Ar}_2\text{Ni}^{\text{II}}\text{L}_2 + \text{Ni}^0\text{L}_3 \xrightarrow[\text{fast}]{+\text{L}} \text{ArAr} + \text{Ni}^0\text{L}_3$$

One of the main side reactions in the nickel-catalyzed coupling of aryl chlorides is the transfer of aryl groups from triphenylphosphine to metal, which reaction is suppressed by using bipyridine and excess amounts of triphenylphosphine to $NiCl_2$ (Scheme III). The effect of amount of PPh_3 on the polymerization is shown in Table V. A large excess of PPh_3 was required to obtain higher molecular weights of polymer. These results are quite different from that for the synthesis of poly(ether-ketone)s, where 7 times the molar quantity of triphenylphosphine

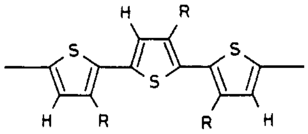
Chart I



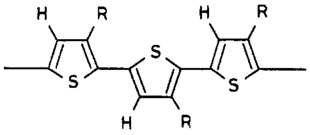
two head-to-head or tail-to-tail linkage



one head-to-head and one head-to-tail linkage

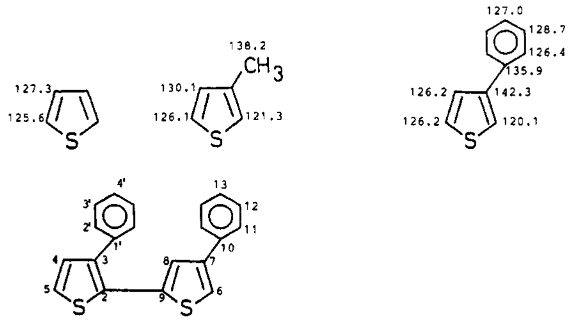


one head-to-head and one head-to-tail linkage



two head-to-tail linkage

Chart II[a]



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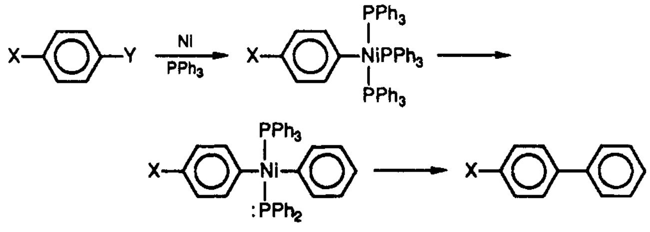
2: 128.8. 3: 139.1. (*4, 5, 11, 2′*): 127.3, 127.1, 126.1. 6: 120. 5: 142.0. 8: 123.9. (*9, 10, 1′*): 135.4, 136.0, 136.6. (*12, 3′*): 129.2, 130.4. (*13, 4′*): 128.2, 128.6.

Scheme III



to $NiCl_2$ was enough to obtain high molecular weights of polymer. The probable explanation is that an aryl chloride with electron-donating substituents is susceptible to phenyl transfer from triarylphosphine.

The influence of the amount of bipyridine on the polymerization is shown in Table VI. An equimolar amount of bipyridine to $NiCl_2$ turned out to be effective. Upon addition of an excess of bipyridine to $NiCl_2$ the inherent viscosity of the polymer decreased because of the formation of a stable Ni^0–bipyridine complex, which retarded the oxidative addition of aryl chloride.

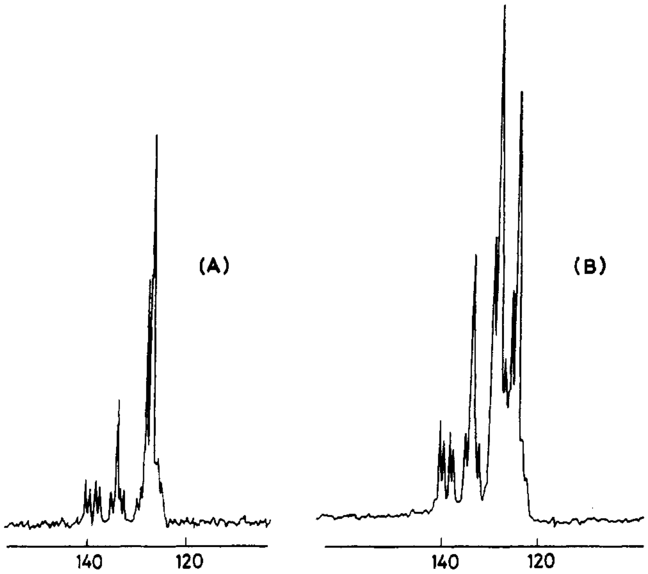


Figure 1. ^{13}C NMR spectrum of polymer 4 (A) and its off-resonance decoupled spectrum (B).

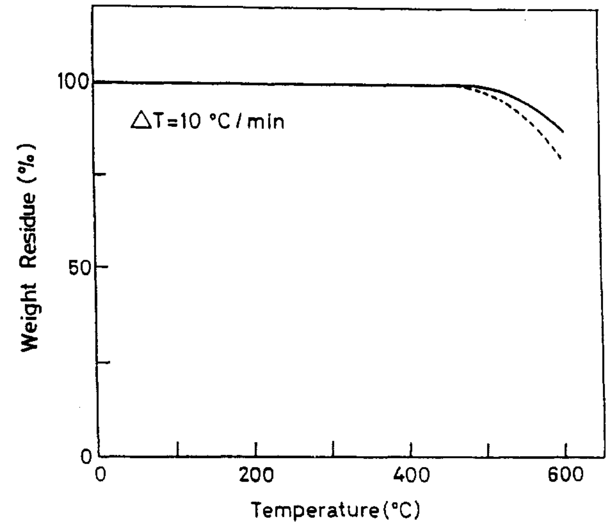


Figure 2. TGA curves of polymer 4: (—) in air, (- - -) in nitrogen.

Numerous organometallic reactions are accelerated by ultrasound.[11] Therefore, the polymerization of 3 was carried out with sonication but with no discernible effect on the inherent viscosity of the polymer.

Polymerization Characterization. Polymer 4 was defined as poly(3-phenyl-2,5-thiophene) by comparing its IR spectrum with those of model compounds. The IR spectrum exhibited characteristic absorption at 840 cm^{-1} due to the 2,3,5-trisubstituted thiophene ring C–H out-of-plane bend and two strong absorptions at 760 and 700 cm^{-1}, which are assigned to the monosubstituted benzene ring bending modes. Polymer 4 prepared by nickel-catalyzed coupling polymerization of monomer 3 has an infrared spectrum that is almost the same as that of the polymer obtained by electrochemical polymerization of 3-phenylthiophene.[12] Elemental analysis also supported the formation of the expected polymer.

Quite recently, the microstructure of polymers obtained by the electrochemical and chemical coupling of 3-alkylthiophene was determined by means of ^{1}H and ^{13}C NMR spectroscopy.[3,13] Considering triads of monomer units, illustrated in Chart I, polymerization of nonsymmetric monomer, 3-substituted thiophene will be expected to give the four regioselective polymers listed.[3] From the analysis of the ^{1}H and ^{13}C NMR spectra of poly(3,3′-dihexyl-2,2′-bithiophene) and poly(3-hexylthiophene), Wudl et al.[3] deduced that the percentage of head-to-head coupling both

Chart III

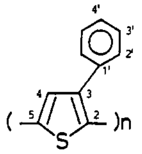


Table VII
UV Absorption Maximum of Polymer 4[a]

η_{inh},[b] dL·g^{-1}	λ_{max}, nm	η_{inh},[b] dL·g^{-1}	λ_{max}, nm
0.1	425	0.3	435
0.2	432	0.5	438

[a] In $CHCl_3$. [b] Measured at a concentration of 0.5 g·dL^{-1} in NMP at 30 °C.

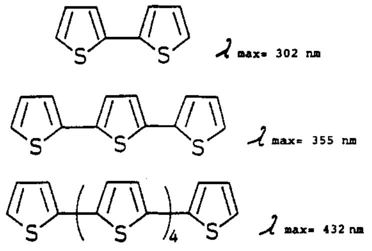
in the electrochemically and in the chemically synthesized poly(3-hexylthiophene) was at least 20%. On the other hand, Wegner et al.[13] reported that poly(3-alkylthiophene) obtained by electrochemical polymerization of 3-alkylthiophene contained a more irregular structure (2,4'-coupling and -branching) compared to that prepared by chemical oxidation polymerization, based on the results of the NMR spectroscopy and X-ray diffraction analyses.

To help clarify the structure of polymer 4, ^{13}C chemical shifts for model compounds are shown in Chart II. The ^{13}C NMR spectrum of polymer 4 (A) and its off-resonance decoupled spectrum (B) in $CDCl_3$ are presented in Figure 1. The peaks in the off-resonance decoupled spectrum in the range between 133.8 and 142.0 ppm remain unchanged, and therefore, they belong to quaternary carbons.

On the basis of above results, we assigned the four peaks at 142.0, 141.2, 139.9, and 139.2 ppm to the carbon atoms (C-3) of the thiophene rings (Chart III) involved in all coupling linkages, as shown in Scheme III. The approximately 1:1:1:1 area ratio of the peak patterns of the polymer indicates that the polymer synthesized by nickel-catalyzed polymerization is almost a random polymer. The resonances with chemical shifts of 136.7, 135.5, 135.3, 134.8, and 133.8 ppm are assigned to C atoms (1') of the benzene rings and quaternary ones (5) of the thiophene ring involved in unordered linkages. Other peaks around 125–130 ppm, which were detected in spectrum A, comprise the phenyl portions (except for C-1') and thiophene (C-2 around 127 ppm and C-4 around 125 ppm). Furthermore, no signals due to the unsubstituted carbon (C-2) of the thiophene ring were observed around 120 ppm. These findings indicate that the C-2 and C-5 carbons are involved completely in the coupling reaction.

Table VII shows the UV absorption maxima of the polymers in chloroform solution, having different inherent viscosities. The position of the absorption is shifted to longer wavelength with increasing inherent viscosities. This is equivalent to the presence of a better extended π-conjugation system along the polythiophene backbone, which results in the longer wavelength shift of the absorption band. In fact, λ_{max} values of thiophene oligomers increase in a manner similar to polymer 4, as shown in Chart IV. The $CHCl_3$-soluble poly(2,5-thiophene), prepared by nickel-catalyzed Grignard coupling of 2,5-dihalothiophenes, showed a λ_{max} at 418 nm in chloroform.[15] On the other hand, the λ_{max} of oligomer 6 of thiophene is at 432 nm. The π–π* transition of polymer 4 occurs at 430–438 nm and is comparable to those of compound 6 and poly(3-hexylthiophene) (λ = 439 nm in chloroform).[3] These results suggest that the pendant phenyl groups are conjugated with the thiophene ring to some extent and steric hindrance due to the phenyl groups seems to influence coplanarity of the polymer backbone and thus overlap of π-electrons.

Chart IV



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The poly(3-phenyl-2,5-thiophene) was a red solid, soluble in dipolar aprotic solvents, such as NMP, DMAc, DMF, DMSO, tetrahydrofuran, chloroform, and toluene. A red and transparent film was cast from the solution of polymer 4 in chloroform or NMP.

The thermal stability of the polymer was examined by thermogravimetric analysis. A typical trace for polymer 4 is shown in Figure 2. The polymer showed a 10% weight loss at 550 and 570 °C in air and in nitrogen, respectively. Differential scanning calorimetry on powder showed a clear endotherm at 177 °C, which reflected the glass transition temperature.

The studies on measurements of the oxidation–reduction potential by cyclic voltammetry and the conductivity of polymer 4 are now in progress.

In summary, our studies indicate that poly(3-phenyl-2,5-thiophene) with relatively high molecular weights can be readily prepared by nickel-catalyzed coupling polymerization of 2,5-dichloro-3-phenylthiophene. This method is advantageous for the formation of poly(3-substituted thiophene) because of no irregular coupling (2,4'-coupling and -branching) compared to conventional electrochemical and chemical methods.

Acknowledgment. We are indebted to Sadao Kato for the technical assistance and to Takeyoshi Takahashi for performing the elemental analyses.

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Registry No. 3 (homopolymer), 132981-60-3; bpy, 37275-48-2; PPh_3, 603-35-0; Zn, 7440-66-6; $NiCl_2$, 7718-54-9.