

NOTES

**Synthesis of Poly(3,3'-diphenyl-2,2'-bithienyl-5,5'-diyl)
by Nickel-Catalyzed Coupling Polymerization
of Dichlorodiphenylbithienyl**

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As part of our research program on developing efficient and mild methods for the synthesis of condensation polymers, our group has been studying the nickel-catalyzed coupling polymerization of aryl dichlorides and showed this method is very useful for the synthesis of aromatic poly(ether ketone)s and poly(ether sulfone)s.¹

In the preceding paper,² this method was successfully extended to the synthesis of poly(3-phenyl-2,5-thiophene) with a relatively high molecular weight from 3-phenyl-2,5-dichlorothiophene. However, the microstructure of the polymer obtained was random on regiospecificity.

A completely stereoregular poly(3-substituted-2,5-thiophene) with a head-to-head or tail-to-tail sequence can be obtained by the polymerization of the thiophene dimers with substituents on the 3,3' or 4,4' position. Recently, Wudl *et al.* reported on the synthesis and properties of stereoregular poly(alkylbithienyl)s by the polymerization of 3,3'-dialkyl-2,2'-bithienyls.³

In this work, we describe the synthesis and characterization of 5,5'-dichloro-3,3' (and 4,4')-diphenyl-2,2'-bithienyls and their regio-specific polymerizations to poly(3,3'-diphenyl-

2,2'-bithienyl-5,5'-diyl).

EXPERIMENTAL

Materials

Reagent grade anhydrous NiCl₂ was dried at 220°C under vacuum. Triphenylphosphine (PPh₃) was purified by recrystallization from *n*-hexane. Powdered (400-mesh) zinc was purified by stirring with acetic acid, filtering, washing thoroughly with ethyl ether, and drying under vacuum. *N,N*-Dimethylacetamide (DMAc) was stirred over powdered calcium hydride overnight, distilled under reduced pressure, and stored over 4-Å molecular sieves.

4,4'-Diphenyl-2,2'-bithienyl (**3**). 2-Chloro-4-phenylthiophene (**2**) was prepared by AlCl₃-catalyzed arylation of 2,5-dichlorothiophene (**1**). In a 25 ml two-necked round bottomed flask were placed NiCl₂ (0.259 g, 2.0 mmol), PPh₃ (7.87 g, 30 mmol), bipyridine (bpy) (0.313 g, 2.0 mmol), zinc (4.00 g, 6.1 mmol), and **2** (7.79 g, 40 mmol).³ The flask was evacuated and filled with nitrogen three times. The dry DMAc (25 ml) was added *via* syringe through the serum cap. The mixture was stirred at 90°C for 6 h. The mixture was poured into a HCl-methanol (2:6, 800 ml) solution. The

precipitate was filtered, washed with methanol, and dried. The yield was 6.4 g (100%). Recrystallization from benzene yielded white needles. mp 224–225°C (lit.³ 224–225°C). IR (KBr): 1653, 1597, 1491, 1453, and 826 cm⁻¹ (thiophene ring C–H), 3106, 734, 692 cm⁻¹ (monosubstituted benzene ring). ¹H NMR (CDCl₃): δ = 7.2–7.7 ppm (m, bithienyl, phenyl).

5,5'-Dichloro-4,4'-diphenyl-2,2'-bithienyl (4). In a 500 ml three necked round bottomed flask, fitted with a magnetic stirrer, a pressure-equalizing dropping funnel, and a reflux condenser fitted with a gas outlet tube leading through the alkaline trap, are placed compound **3** (6.0 g, 19 mmol) and benzene (180 ml). The reaction flask was heated at 60°C. To this solution was added dropwise sulfonyl chloride (3.0 ml, 38 mmol) over a 30 min period. After addition was complete, the solution was refluxed for 4 h, and was then poured into ice-water. The mixture was stirred for 6 h. The aqueous phase was extracted with benzene. The combined organic phases were washed successively with 5% aqueous sodium hydrogen carbonate and water, and then dried (MgSO₄). After evaporation of benzene, the product was purified by column chromatography on silica gel, using CHCl₃/Et₂O as eluent. The yield was 7.4 g (60%). Recrystallization from chloroform–ethanol (1:1) produced faint yellow crystals. mp 181–182°C. IR (KBr): 1644, 1489, 1449, and 820 cm⁻¹ (thiophene ring C–H), 3106, 760, 700 cm⁻¹ (monosubstituted benzene ring). ¹H NMR (CDCl₃): δ = 6.92 (2H, s, 3H and 3'-H) and 7.05–7.50 ppm (10H, m, phenyl). MS *m/z* 386 (M⁺). *Anal.* Calcd for C₂₀H₁₂Cl₂S₂: C, 62.02%; H, 3.12%. Found: C, 61.75%; H, 3.12%.

3,3'-Dichloro-4,4'-diphenyl-2,2'-bithienyl (6). 5-Chloro-2-iodo-3-phenylthiophene (**5**) was prepared by the reaction of **1** with potassium iodide and potassium nitrate in acetic acid.⁴

A 25 ml three-necked flask equipped with a magnetic stirring bar, a pressure-equalizing dropping funnel, and a reflux condenser

attached to a nitrogen inlet was charged with magnesium turnings (0.32 g, 13 mmol). Small amounts of a solution of **4** (4.2 g, 13 mmol) in anhydrous diethyl ether (18 ml) was added. The mixture was warmed, and within a few minutes an exothermic reaction began. The remaining ether solution was added dropwise over *ca.* 40 min. After addition was complete, the mixture was refluxed with stirring for 1 h, and then cooled to room temperature. The resulting solution was diluted with benzene (4 ml). To this solution was added a solution of **4** (4.2 g, 13 mmol) and Ni (acac) (30 mg) in benzene (10 ml). The nickel complex reacted immediately with the Grignard reagent, and the resulting clear-tan reaction mixture was refluxed for 5 h. The mixture was cooled to room temperature and poured into an aqueous ammonium chloride solution. The organic layer was separated and the aqueous layer was extracted with benzene. The combined organic layer and extracts were washed with water, dried over anhydrous calcium chloride, and filtered. After evaporation of the solvent the residue was purified by column chromatography on silica gel, using CHCl₃/Et₂O as eluent. Yield was 5.0 g (23%). Recrystallization from chloroform–ethanol (1:1) produced faint gray crystals. mp 174–176°C. IR (KBr): 1676, 1491, 1447, and 845 cm⁻¹ (thiophene ring C–H), 3087, 762, 698 cm⁻¹ (monosubstituted benzene ring). ¹H NMR (CDCl₃): δ = 6.8 (2H, s, 4-H and 4'-H) and 6.85–7.20 ppm (10H, m, phenyl). MS *m/z* 386 (M⁺). *Anal.* Calcd for C₂₀H₁₂Cl₂S₂: C, 62.02%; H, 3.12%. Found: C, 61.77%; H, 3.18%.

Polymer Synthesis

A typical example of the polymerization follows.

Polymer 7 from 4. In a 25 ml two-necked round bottomed flask were placed NiCl₂ (4.5 mg, 0.035 mmol), PPh₃ (184 mg, 0.7 mmol), bpy (5.47 mg, 0.035 mmol), zinc (101 mg, 1.5 mmol), and monomer **4** (194 mg, 0.5 mmol). The flask was evacuated and filled with

nitrogen three times. The dry DMAc (1.0 ml) was added *via* syringe through the serum cap. The mixture was stirred at 100°C for 24 h. The mixture became red-brown in 10 min, and the polymer precipitated in 1 h. The mixture was diluted with DMAc and poured into a large amount of HCl-methanol. The polymer was collected, washed with methanol, and dried *in vacuo* at 100°C for 24 h. The yield was (90%). The inherent viscosity of the polymer in concentrated sulfuric acid was 0.23 dl g⁻¹, measured at a concentration of 0.2 g dl⁻¹ at 30°C. IR (KBr): 3058, 1655, 1489, 831 (thiophene ring), 760, 698 cm⁻¹ (monosubstituted benzene ring). *Anal.* Calcd for (C₂₀H₁₂S₂)_n: C, 75.91%; H, 3.83%. Found C, 75.42%; H, 4.08%.

RESULTS AND DISCUSSION

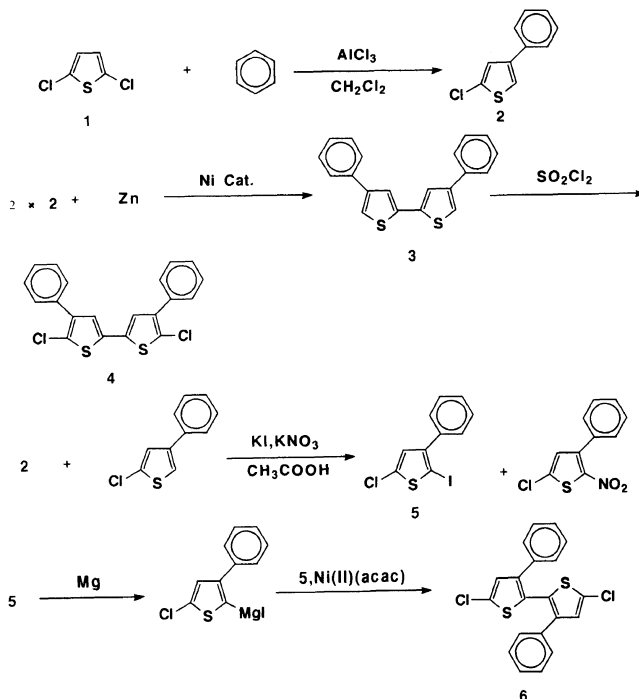
Synthesis of Monomers

As polymer-forming bithienyl monomers, two bithienyl chlorides, 5,5'-dichloro-4,4'-diphenyl-2,2'-bithienyl (**4**) and 5,5'-dichloro-

3,3'-diphenyl-2,2'-bithienyl (**6**) were prepared by the reaction outlined in Scheme 1. In the first step, Friedel-Crafts reaction of 2,5-dichlorothiophene (**1**) with benzene provided 2-chloro-4-phenyl-thiophene (**2**). Then, the coupling reaction of **2** using NiCl₂ in the presence of zinc, triphenylphosphine (PPh₃), and bipyridine (bpy) yielded 4,4'-diphenyl-2,2'-bithienyl (**3**), which was converted to dichloro compound **4** in 60% yield by treatment with sulfuryl chloride. On the other hand, compound **6** was prepared by two steps from **2** as a starting compound. Iodination of **2** by potassium iodide and potassium nitrate in acetic acid yielded 5-chloro-2-iodo-3-phenylthiophene (**5**). The nucleophilic substitution of **5** with its magnesium iodide afforded monomer **6**.

Polymer Synthesis

First, the nickel-catalyzed coupling polymerization of **4** was carried out in DMAc in the presence of zinc, PPh₃, and bpy under



Scheme 1.

various reaction conditions (eq 1).

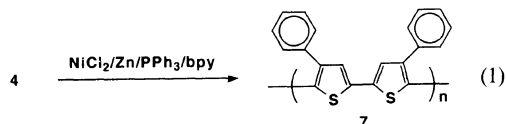
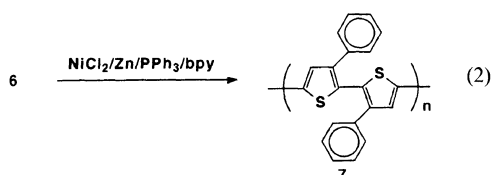


Table I lists the influence of the reaction temperature on the inherent viscosity of the resulting polymer. At lower temperature of 90°C, the polymerization did not initiate. Raising the temperature to 110°C gave inferior results probably due to transfer of aryl group from triphenylphosphine. The highest viscosity was attained at 100°C. The polymerization proceeded rapidly at 110°C, however, the polymer precipitation was observed. To keep the polymer in homogeneous state as long as possible, then, the effect of the amount of DMAc on the polymerization was studied (Table II). Even increasing the amount of solvent from 1.0 ml to 1.5 ml, polymerizations proceeded heterogeneously and the inherent viscosity decreased from 0.23 dl g⁻¹ to 0.08 dl g⁻¹.

Then, we tried to obtain higher molecular weight polymer 7 from monomer 6 (eq 2). Because in the 3,3'-substituted bithienyl the polymerization sites are not subjected to steric hindrance.



The results are shown in Table III. Even in this polymerization, the molecular weight remained low due to the insolubility of the resulting polymer in the polymerization media.

Polymer Characterization

The polymer 7 was brown solid, and only soluble in strong acid, sulfuric acid and methansulfonic acid.

Polymer 7 was defined as poly(3,3'-diphenyl-2,2'-bithienyl-5,5'-diyl) by comparing its IR

Table I. Effect of the reaction temperature on polymerization of monomer 4^a

| Temperature °C | Polymer | |
|-------------------|---------|----------------------------|
| | Yield/% | $\eta_{inh}/dl\ g^{-1\ b}$ |
| 80 | 0 | — |
| 90 | 0 | — |
| 95 | 90 | 0.21 |
| 100 | 90 | 0.23 |
| 110 | 95 | 0.10 |

^a Reaction conditions: monomer 4 (0.5 mmol), TPP (0.7 mmol), Zn (1.55 mmol), bpy (0.035 mmol), DMAc (1.0 ml), 24 h.

^b Measured at a concentration of 0.2 g dl⁻¹ in concd H₂SO₄ at 30°C.

Table II. Effect of the amount of solvent on polymerization of monomer 4^a

| Amount of solvent ml | Polymer | |
|-------------------------|---------|----------------------------|
| | Yield/% | $\eta_{inh}/dl\ g^{-1\ b}$ |
| 0.7 | 100 | 0.17 |
| 1.0 | 95 | 0.23 |
| 1.3 | 100 | 0.13 |
| 1.5 | 97 | 0.08 |

^a Reaction conditions: monomer 4 (0.5 mmol), TPP (0.7 mmol), Zn (1.55 mmol), bpy (0.035 mmol), 100°C, 24 h.

^b Measured at a concentration of 0.2 g dl⁻¹ in concd H₂SO₄ at 30°C.

Table III. Effect of the reaction temperature on polymerization of monomer 6^a

| Temperature °C | Polymer | |
|-------------------|---------|----------------------------|
| | Yield/% | $\eta_{inh}/dl\ g^{-1\ b}$ |
| 80 | 0 | — |
| 90 | 95 | 0.22 |
| 95 | 96 | 0.25 |
| 100 | 98 | 0.25 |

^a Reaction conditions: monomer 6 (0.5 mmol), TPP (0.7 mmol), Zn (1.55 mmol), bpy (0.035 mmol), DMAc (1.0 ml), 24 h.

^b Measured at a concentration of 0.2 g dl⁻¹ in concd H₂SO₄ at 30°C.

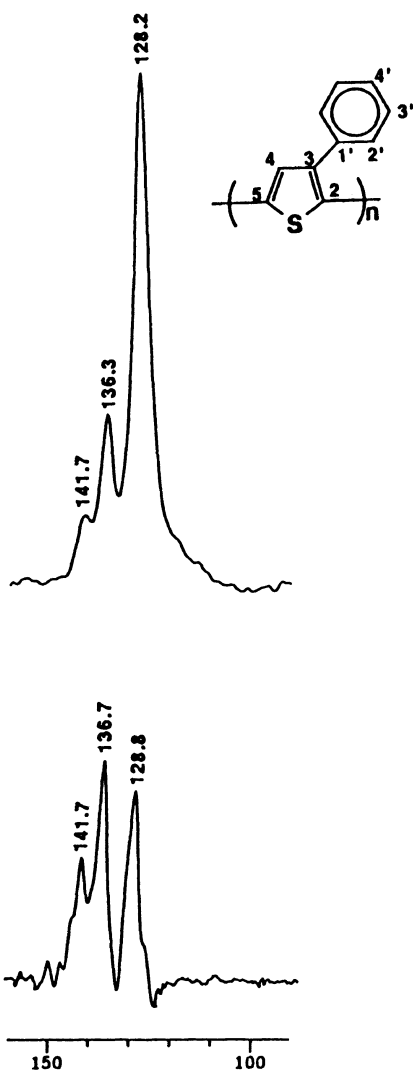


Figure 1. (a, Top) 67.8 MHz ^{13}C CPMAS NMR spectrum of polymer 7 (b, Bottom) ^{13}C DDP spectrum of polymer 7.

spectrum with that of model compounds. The IR spectrum exhibited characteristic absorption at 831 cm^{-1} due to the 2,3,5-trisubstituted thiophene ring C–H out of plane bend and two strong absorptions at 760 and 696 cm^{-1} , which are assigned to the monosubstituted benzene ring bending modes. Elemental analysis also supported the formation of the expected polymer.

Owing to the insolubility of polymer 7, only

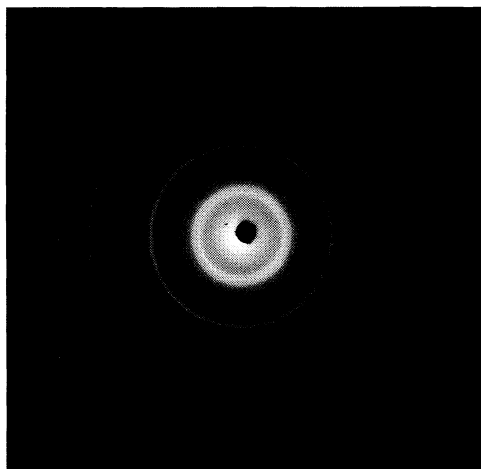


Figure 2. X-Ray powder diffraction pattern of polymer 7.

Table IV. Observed X-ray d -spacings of polymer 7

| d/nm | Intensity ^a |
|---------------|------------------------|
| 1.31 | VS |
| 0.660 | S |
| 0.532 | W |
| 0.470 | W |
| 0.407 | M |
| 0.365 | VW |

^a VW, very weak; W, weak; M, medium; S, strong; VS, very strong.

spectroscopic study in the solid state was possible. Figure 1 shows the solid-state ^{13}C CPMAS NMR spectrum of the polymer and its DDP spectrum. The ^{13}C DDP spectrum clearly demonstrates the peaks at 141.7, 136.7, and 128.8 ppm belong to quaternary carbons.

On the basis of these findings and assignments for model compounds and poly-(thiophene),² was assigned the three peaks at 141.7 ppm, 136.3, and 128.2 ppm to the carbon atoms C-3 of the thiophene ring, C-1' of benzene ring and quaternary ones (5) of the thiophene ring, and other carbon atoms which include the phenyl portions (except for C-1'), thiophene (C-2 at 128.8 ppm and C-4), respectively.

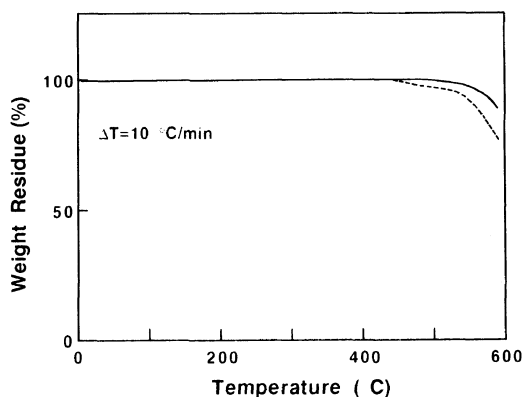


Figure 3. TG curves of polymer 7 in nitrogen (—) and in air (-----).

The formation of stereoregular polymer was also supported by the fact that X-ray diffraction pattern of polymer 7 using nickel-filtered Cu- K_{α} radiation showed a high degree of crystallinity. Six well-defined sharp rings were observed on the polymer (Figure 2). The observed d -spacings of the polymer are also shown in Table IV.

The thermal stability of polymer was examined by thermogravimetry (TG). A typical trace for polymer 7 is shown in Figure 3. The

polymer showed a 10% weight loss at 550 and 560°C in air and under nitrogen, respectively.

In summary, our studies indicate that the stereoregular poly(3,3'-diphenyl-2,2'-bithienyl-5,5'-diyl) can be obtained by the nickel-catalyzed coupling polymerization of bithienyl chlorides. The polymer obtained showed a high degree of crystallinity.

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