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Synthesis and Characterization of Regiocontrolled Poly(2,5-di-*n*-butoxy-1,4-phenylene) by Oxovanadium-Catalyzed Oxidative Coupling Polymerization

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ABSTRACT: Poly(2,5-di-*n*-butoxyphenylene) (**4**) was prepared by oxovanadium-catalyzed oxidative coupling polymerization of 1,4-di-*n*-butoxybenzene (**3**). Polymerizations were conducted in 1,2-dichloroethane in the presence of $VO(acac)_2$, CF_3SO_3H, and $(CF_3CO)_2O$ under an oxygen atmosphere at room temperature and produced polymer **4** having number-average molecular weight up to 12 000. $VO(acac)_2$ acted as an oxidative catalyst and the polymerization proceeded in the presence of 7.5% $VO(acac)_2$ (based on the monomer). The structure of polymer was characterized by ^1H- and ^{13}C-NMR spectroscopies and was estimated to consist almost completely of 1,4-linkage. The polymer was readily soluble in common organic solvents and could be processed into uniform films from solution. Thermogravimetric analysis showed 10% weight loss at 385 °C in nitrogen.

Introduction

Poly(*p*-phenylene) (PPP) has been investigated as a candidate for high strength, high temperature, and conducting polymers.[1] A large number of direct preparative methods have been exploited to yield PPPs such as oxidative coupling of benzene, the Wurtz−Fittig reaction of dichlorobenzene,[2] and the coupling of the mono-Grignard reagent of *p*-dihalobenzene in the presence of Ni catalyst.[3] However, these methods generally give low yields and low molecular weights due to the low solubility of PPP in solvents.

To remedy the serious solubility problems, it is effective to introduce flexible side chains on the aromatic rings.[4] A number of recent methods include the nickel-catalyzed coupling of aromatic dihalides in the presence of zinc[5] and bis[[(trifluoromethyl)sulfonyl]oxy] or bis[(methylsulfonyl)oxy] derivatives of substituted hydroquinones,[6] the Pd(0) cross coupling of boronic acids and aryl halides,[7] and the polymerization of in situ generated *p*-lithiobromobenzene.[8] Another approach to prepare PPP is to use a soluble intermediate polymer proposed by Ballard et al.[9] This process involves the radical polymerization of the bis(acetyl) derivative of *cis*-5,6-dihydroxy-1,3-cyclohexadiene, followed by pyrolysis of the resulting polymer to PPP. Recently, the modified method using transition-metal-catalyzed polymerization has been reported.[10]

On the other hand, oxidative polymerization by dehydrogenation coupling is advantageous because of the rapidity and simplicity of the reaction and mild conditions.[11] A typical example of the oxidative polyarylations reported by Kovacic is the reaction of benzene with the $AlCl_3-CuCl_2$ reagent system.[12] However, the direct method generally gives low regiocontrolled and low molecular weight PPPs.

As part of the program on the synthesis of condensation polymers by oxidative coupling polymerization, we reported a facile synthesis of poly(2,5-di-*n*-butoxyphenylene) by oxidative coupling polymerization of 1,4-di-*n*-butoxybenzene using $FeCl_3$ as an oxidant and Lewis acid.[13] In this polymerization, however, excess amounts of $FeCl_3$ were required to obtain the high molecular weights polymers. Quite recently, we have developed a more efficient procedure to prepare poly(naphthylene ether)s by oxidative coupling polymerization of bis(1-naphthoxy) compounds, where a catalytic amount of vanadyl complex with oxygen system was employed in place of $FeCl_3$.[14] In order to expand the preparative utility of this method, we applied this method to the oxidative coupling polymerization of 1,4-di-*n*-butoxybenzene.

This article describes a successful synthesis and characterization of poly(2,5-di-*n*-butoxyphenylene) by

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oxovanadium-catalyzed oxidative coupling polymerization of 1,4-di-*n*-butoxybenzene.

Experimental Section

Materials. Vanadyl acetylacetonate (VO(acac)$_2$) (Kanto Chem. Co.) was recrystallized from acetone, dried *in vacuo* overnight at 70 °C. Reagent grade anhydrous ferric chloride (FeCl$_3$) (Kanto Chem. Co.) was purified by sublimation. 1-Methoxynaphthalene (**1**) was obtained from Tokyo Kasei Co. and distilled under nitrogen (133 °C/9 mmHg). Hydroquinone and 1-bromobutane were used as received. Trifluoromethanesulfonic acid (CF$_3$SO$_3$H) and trifluoroacetic anhydride ((CF$_3$CO)$_2$O) were obtained from Tokyo Kasei Co. (reagent grade) and used without further purification. Nitrobenzene, dichloromethane, and 1,2-dichloroethane were purified by distillation with conventional methods.

1,4-Di-*n*-butoxybenzene (3). Monomer **3** was prepared according to the reported procedure:[13] Yield 80%; mp 43−45 °C (lit.[13] mp 43.5−45.5 °C). IR (KBr) ν 3050 and 2960−2870 (C−H), 1510 and 1480 (C=C), 1230 cm^{-1} (C−O−C). ^{1}H-NMR (CDCl$_3$) δ 0.96 (t, $J = 7.2$ Hz, 6H, CH$_3$), 1.43−1.54 (multiplet, 4H, −CH$_2$−), 1.68−1.79 (multiplet, 4H, −CH$_2$−), 3.90 (t, $J = 6.2$ Hz, 4H, −OCH$_2$−), 6.82 ppm (s, 4H, arom); ^{13}C-NMR (CDCl$_3$) δ 13.9 (q, CH$_3$), 19.3, 31.5, and 68.3 (t, −CH$_2$−), 115.4 (d, arom), 153.2 ppm (s, arom).

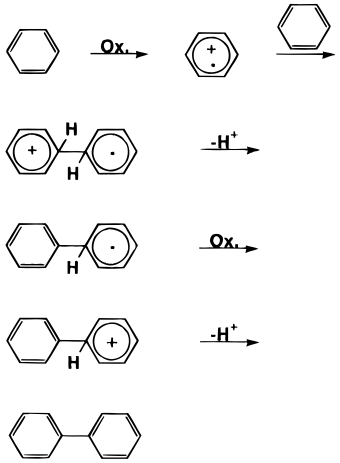
Model Reaction. The coupling reaction of 1-methoxynaphthalene (**1**) was performed as follows. VO(acac)$_2$ (0.066 g, 0.25 mmol) was placed in a 25 mL two-necked flask, equipped with an oxygen inlet and septum cap, constituting a closed system. The atmosphere was flushed with oxygen, followed by the addition of nitrobenzene (2 mL), (CF$_3$CO)$_2$O (1.39 mL, 10.0 mmol), and CF$_3$SO$_3$H (0.044 mL, 0.5 mmol) through the septum cap via syringe, and stirred for 1 h. Then, compound **1** (0.791 g, 5.0 mmol) dissolved in nitrobenzene (3 mL) was added. The reaction mixture was stirred at room temperature for 10 h and poured into methanol (100 mL) containing 5% hydrochloric acid. The precipitate was filtered and gave pure 4,4′-dimethoxy-1,1′-dinaphthyl (**2**). The yield of crude material was 95%. Recrystallization from acetone and methanol produced a light yellow solid: Yield 89%; mp 256 °C (by DTA) (lit.[12] mp 257 °C); IR (KBr) ν 3055 and 2960−2870 (C−H), 1590 and 1510 (C=C), 1240 cm^{-1} (C−O−C); ^{1}H-NMR (CDCl$_3$) δ 4.08 (s, 6H, CH$_3$), 6.91−8.37 ppm (multiplet, 12H, arom).

Polymer Synthesis. A typical example of the polymerization follows.

Regiocontrolled Polymer 4 by Oxovanadium-Catalyzed Polymerization of 3. VO(acac)$_2$ (0.0199 g, 0.075 mmol) was placed in a 25 mL two-necked flask, equipped with an oxygen inlet and septum cap, constituting a closed system. The atmosphere was flushed with oxygen, followed by the addition of 1,2-dichloroethane (0.3 mL), (CF$_3$CO)$_2$O (0.278 mL, 2.0 mmol), and CF$_3$SO$_3$H (0.0066 mL, 0.075 mmol) through the septum cap via syringe, then stirred for 1 h. 1,4-Di-*n*-butoxybenzene (0.222 g, 1.0 mmol) dissolved in 1,2-dichloroethane (0.7 mL) was then added to the mixture. The reaction mixture was stirred at room temperature for 20 h and poured into methanol (30 mL) containing 5% hydrochloric acid. The precipitated product was collected. Purification of the polymer was carried out by Soxhlet extractions with a mixture of methanol and chloroform (v/v = 20/1) for 24 h. The fibrous polymer was dried in vacuo at 80 °C: Yield 84%; IR (film) ν 2960−2870 (C−H), 1490 and 1470 (C=C), 1205 cm^{-1} (C−O−C); ^{1}H-NMR (CDCl$_3$) δ 0.9 (6H, CH$_3$), 1.4 and 1.7 (8H, −CH$_2$−), 3.9 (4H, −OCH$_2$−), 6.9−7.2 ppm (2H, arom); ^{13}C-NMR (CDCl$_3$) δ 13.8 (q, CH$_3$), 19.2, 31.6, and 69.2 (t, −CH$_2$−), 117.3 (d, arom), 127.5 and 150.0 ppm (s, arom). Elemental Anal. Calcd for $(C_{14}H_{20}O_2\cdot{}^1/_{10}H_2O)_n$: C; 75.71, H; 9.17. Found: C; 75.31, H; 8.88. $\bar{M}_n = 12\,000$, $\bar{M}_w = 30\,000$, $\bar{M}_w/\bar{M}_n = 2.6$ [polystyrene (PSt) standard].

Regiorandom Polymer 5 from 3 Using Ferric Chloride. In a 50 mL three-necked round-bottomed flask, fitted with a stirrer, septum cap, nitrogen inlet, and nitrogen outlet leading into a flask containing alkaline solution to neutralize the hydrogen chloride evolved, were placed 1,4-di-*n*-dibutoxybenzene (0.222 g, 1 mmol) and anhydrous FeCl$_3$ (0.649 g, 4 mmol). This operation was performed in a glovebag filled with nitrogen. Then, dry nitrobenzene (4 mL) was added via syringe through the septum cap. The solution was stirred at room temperature under a slow stream of nitrogen. After 6 h, the solidified mixture was dissolved in nitrobenzene and poured into methanol containing 5% hydrochloric acid (100 mL). The precipitated polymer was collected by filtration and refluxed in methanol for 2 h. The fibrous polymer was collected and dried in vacuo at 80 °C: Yield 81%; IR (film) ν 2960−2870 (C−H), 1490 and 1470 (C=C), 1205 cm^{-1} (C−O−C); ^{1}H-NMR (CDCl$_3$) δ 0.9 (6H, CH$_3$), 1.4 and 1.7 (8H, −CH$_2$−), 4.0 and 4.1 (4H, −OCH$_2$−), 7.1 and 7.5−7.6 ppm (2H, arom); ^{13}C-NMR (CDCl$_3$) δ 13.8 (q, CH$_3$), 19.3, 31.8, and 69.6 (t, −CH$_2$−), 117.5 and 117.9 (d, arom), 128.1, 128.2, 150.5, 150.6 and 153.3 ppm (s, arom). Elemental Anal. Calcd for $(C_{14}H_{20}O_2\cdot{}^1/_{10}H_2O)_n$: C; 75.71, H; 9.17. Found: C; 75.92, H; 8.85. $\bar{M}_n = 16\,000$, $\bar{M}_w = 45\,000$, $\bar{M}_w/\bar{M}_n = 2.9$ (PSt standard).

Scheme 1

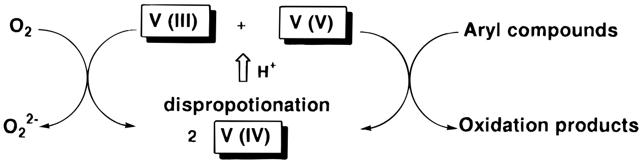


Measurements. The infrared spectra were recorded on a Hitachi I-5020 FT-IR spectrometer, the UV−visible spectra were obtained on a SHIMADZU UV-2200 spectrophotometer, and the NMR spectra on JEOL EX 270 (^{1}H, 270 MHz; ^{13}C, 68.5 MHz) and GX 500 (^{1}H, 500 MHz; ^{13}C, 125 MHz) spectrometers. Thermogravimetric analyses (TGA) were performed on a Seiko SSC/5200 (TG/DTA 220) thermal analyzer at a heating rate of 10 °C/min. The glass transition temperature (T_g) was measured on a Seiko SSC/5200 (DSC 220) instrument at a heating rate of 20 °C/min in nitrogen. Molecular weights were determinated by a gel permeation chromatograph (GPC) using polystyrene as the standard on a JASCO TRIROTAR-III HPLC equipped with a Shodex KF-80M column at 40 °C in THF. Weight-average molecular weights were measured by the light-scattering method with a TOSOH HLC-8120GPC equipped with a TOSOH LS-8000 light-scattering photometer at 40 °C in DMF. The cyclic voltammograms were measured in acetonitrile solution containing 0.1 M tetrabutylammonium perchlorate (TBAPC) and 10 mM monomer with the aid of a Hokuto Denko HA-501 potentiostat/galvanostat; the scanning rate was 50 mV/s. A Pt disk with a diameter of 2 mm was used as a working electrode, and an aqueous SCE as the reference electrode. The ESR spectra were obtained with the aid of a JEOL JES-FR30 ESR spectrometer. $\bar{M}_n{}^{2+}$/MgO and 4-hydroxy-2,2,6,6-tetramethylpiperidinyloxy (4-hydroxy-TEMPO) free radical were used as reference.

Results and Discussion

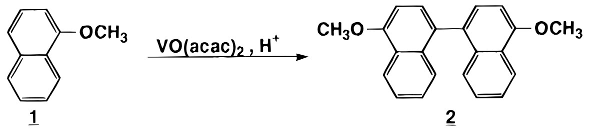
Model Reaction. As described in the Introduction, aryl compounds are polymerized by oxidative coupling reaction in the presence of the oxidants.[12] The mechanism of this coupling reaction is outlined in Scheme 1. The first step is a one-electron oxidation of the

Scheme 2



aromatic nucleus to give a cation radical which attacks an aromatic ring of a second molecule to yield a dihydro radical−cation species. Next, this species releases a proton to form a radical which undergoes further oxidation followed by proton loss to give the dimerization product. Therefore, it is very important to select a monomer having a low redox potential. The oxidation potentials which reflect a one-electron oxidation of the aromatic nucleus were measured by cyclic voltammometry at a platinum electrode in acetonitrile containing TBAPC as the supporting electrolyte. The cyclic voltammogram of **3** was an irreversible cycle; the oxidation peak potential of the first one-electron transfer was 1.27 V vs SCE. On the other hand, the redox potential of vanadyl complex was about 1.5 V in the presence of strong acid. Thus, the oxovanadium−oxygen catalytic system was expected to be suitable for the oxidative coupling polymerization of **3**. The probable mechanism of the oxovanadium−oxygen catalytic system has been proposed as a working model (Scheme 2).[15] The first step is the disproportionation of the VO(acac)$_2$ (vanadium(IV)) to the vanadium(III) and -(V) species by strong acids such as trifluoromethanesulfonic acid and trifluoroacetic acid. The vanadium(V) species oxidizes with aryl compounds to form the active species of the polymerization. The vanadium(III) species is reoxidized with molecular oxygen. At this time, the reduced molecular oxygen reacts with the released proton to generate water, which is trapped by the acid anhydrides such as trifluoroacetic anhydride.

The oxidation peak potential of 1-methoxynaphthalene (**1**) is 1.25 V, which is the same as that of **3**. In the presence of an oxidant, 1-alkoxynaphthalenes are known to produce quantitive yields of 4,4'-dialkoxy-1,1′-dinaphthyls. Therefore, **1** was used as model compound in place of **3**. The dimerization of **1** was studied to determine if this catalytic system gave the desired coupling product, 4,4′-dimethoxy-1,1′-dinaphthyl (**2**). The coupling reaction of **1** was performed in nitrobenzene in the presence of a catalytic amount of VO(acac)$_2$, trifluoromethanesulfonic acid, and trifluoroacetic anhydride under an oxygen atmosphere at room temperature (eq 1). After the reaction was completed, the mixture was poured into methanol containing 5% hydrochloric acid, and the product was collected. The desired product **2** was obtained in excellent yield when more than 5 mol % of oxidant based on the monomer was used. Thus, **3** was expected to be a suitable monomer for oxovanadium-catalyzed oxidative coupling polymerization.



(1)

Table 1. Effect of the Amount of VO(acac)$_2$ and CF$_3$SO$_3$H on Polymerization[a]

entry no.	VO(acac)$_2$ (mol %)	CF$_3$SO$_3$H (mol %)	yield (%)	$\bar{M}_n$[b]	$\bar{M}_w/\bar{M}_n$[b]
1	2.5	5.0	27	4 000	1.9
2	5.0	10	58	10 000	2.2
3	7.5	7.5	68	12 000	2.0
4	7.5	15	63[d]	10 000	1.9
5	10	10	75	14 000	2.0
6	10	20	80[d]	13 000[c]	2.8[c]

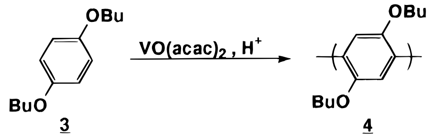
[a] Reaction conditions: 1.0 mmol of monomer, 2.0 mmol of (CF$_3$CO)$_2$O, solvent = 1.0 mL, CH$_2$Cl$_2$, room temperature, O$_2$ atmosphere. [b] Measured by GPC based on the standard PSt. [c] Gel (soluble part). [d] C═O absorption was observed by IR spectroscopy.

Table 2. Preparation of Polymer 4 in Various Solvents[a]

entry no.	solvent	CF$_3$SO$_3$H (mol %)	yield (%)	$\bar{M}_n$[b]	$\bar{M}_w/\bar{M}_n$[b]
7	dichloromethane	7.5	68	12 000	2.0
8		15	63[c]	10 000	1.9
9	nitrobenzene	7.5	71	8 000	2.5
10		15	76	7 000	2.7
11	1,2-dichloroethane	7.5	87	12 000	2.6
12		15	84[c]	15 000	3.7

[a] Reaction condition: 1.0 mmol of monomer, 2.0 mmol of (CF$_3$CO)$_2$O, 0.075 mmol of VO(acac)$_2$, solvent volume = 1.0 mL, room temperature, O$_2$ atmosphere. [b] Measured by GPC based on standard PSt. [c] CdO absorption was observed by IR spectroscopy.

Polymer Synthesis. On the basis of these preliminary experiments, the oxidative coupling polymerization of **3** was carried out. To determine the optimum conditions for polymerization, the polymerization of **3** was studied in detail (eq 2). The polymerization was performed by the same procedure as used in the synthesis of **2**. Table 1 summarizes the effect of the amounts of catalyst and trifluoromethanesulfonic acid on the polymerization. Polymers with high molecular weights were easily obtained when more than 5 mol % of VO(acac)$_2$ and trifluoromethanesulfonic acid based on the monomer were used. The use of excess amounts of trifluoromethanesulfonic acid led to the undesirable side reactions such as scission of ether linkages. This wide range of polymer yields would be due to the extraction of oligomers during workup.



(2)

The effect of solvent on the polymerization was studied, using nitrobenzene, 1,2-dichloroethane, and dichloromethane. The dielectric constants of nitrobenzene, 1,2-dichloroethane, and dichloromethane are 34.8, 10.4, and 9.1 F/m at 20 °C, respectively. These results are listed in Table 2. However, no discernible effect on the molecular weights of polymers was observed among them.

The influence of the amount of solvent and reaction time on the polymerization was also examined. A 1.0 mL quantity of solvent was found to be approprite for a 1.0 mmol scale reaction. The highest molecular weight polymer was obtained in 20 h. Further polymerization gave polymer containing a few percent of trifluoroacetylated or quinone structures and insoluble gel. These behaviors would be explained by the extra oxidation of the polymer, which induces coupling between the polymer molecules.

Polymer Characterization. The characterization of polymer **4** was performed by infrared, UV−visible, and NMR spectroscopies and elemental analysis.

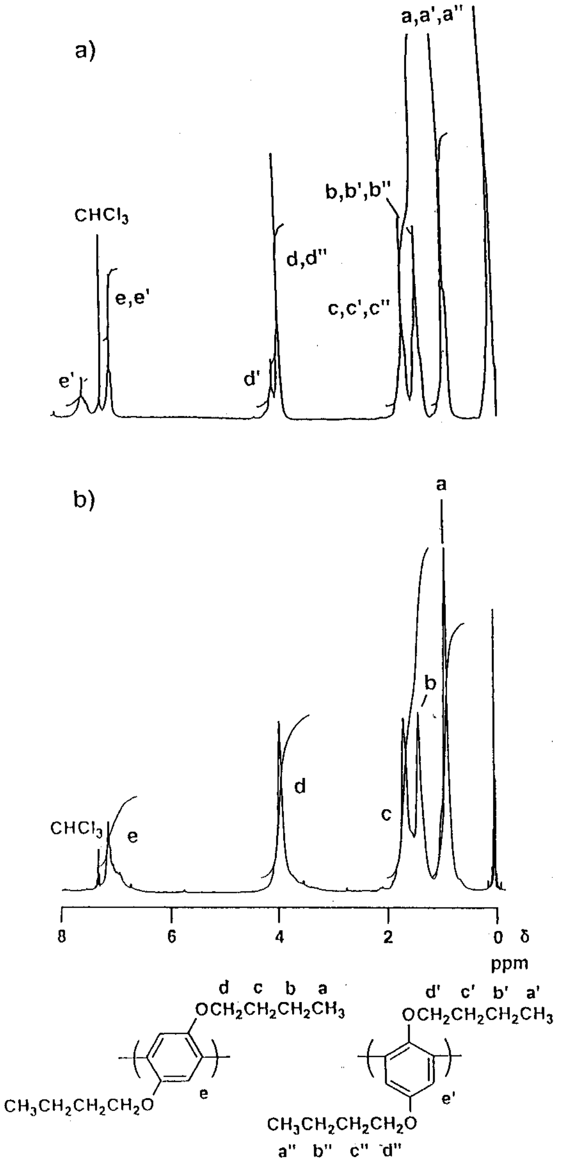


Figure 1. ^{1}H NMR spectra of regiorandom polymer **5** (a) and regioregular polymer **4** (b) in $CDCl_3$.

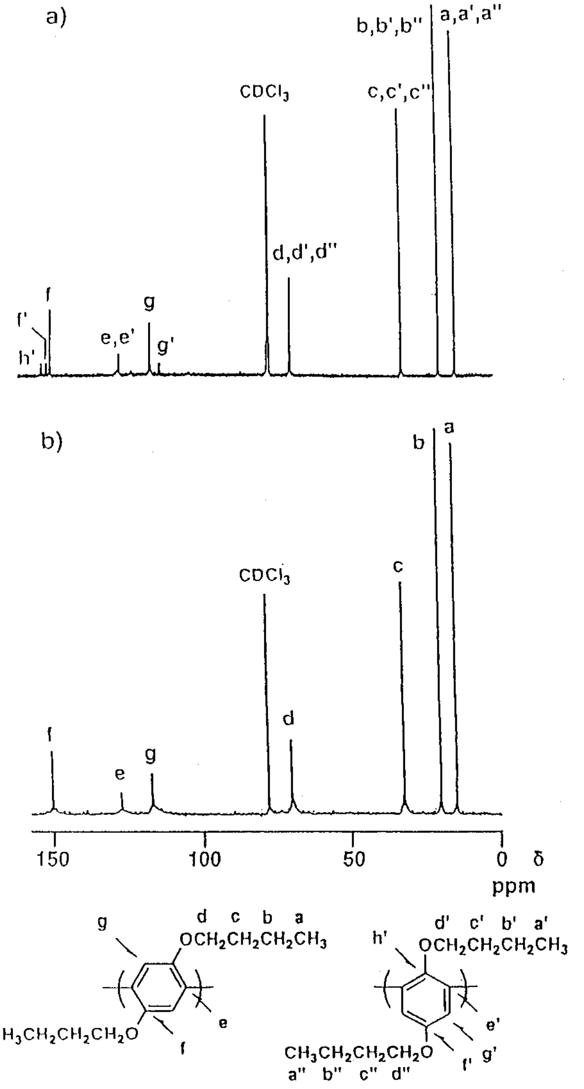


Figure 2. ^{13}C NMR spectra of regiorandom polymer **5** (a) and regioregular polymer **4** (b) in $CDCl_3$.

Infrared Spectroscopy. The IR spectrum of polymer **4** exhibited characteristic absorptions at 2960–2870, 1490, and 1205 cm^{-1} due to the C–H, C=C, and C–O–C stretching, respectively. The absorption at 865 cm^{-1} attributed to the C–H out-of-plane vibration of tetrasubstituted benzene and the absorptions derived from di- and trisubstituted benzene were not obtained. Furthermore, no absorption ascribed to the C=O stretching derived from the cleavage of ether linkage was detected.

The elemental analysis also supported the formation of the expected polymer.

NMR Spectroscopy. Considering the coupling mechanism, polymerization of **3** will be expected to give 1,3- and 1,4-linkages. On the triads of monomeric units, six monomer linkages, *p*–*p*–*p*, *p*–*p*–*m*, *m*–*p*–*m*, *p*–*m*–*p*, *p*–*m*–*m*, *m*–*m*–*m*, will be contained in the polymer main chain, where *m* and *p* represent the 1,3- and 1,4-linkages, respectively. In a preceding paper, we demonstrated a successful oxidative coupling polymerization of **3** using $FeCl_3$ (polymer **5**).[13] The microstructure of polymer **5** was characterized by ^{1}H- and ^{13}C-NMR spectroscopies. Figure 1a shows the 500 MHz ^{1}H-NMR spectrum of polymer **5**, which exhibited five intense absorptions at 0.9, 1.4, 1.7, 4.0, and 7.1 ppm due to the methyl, γ, β, α-methylenes protons of the side chain and aromatic protons, respectively. These peaks should be ascribed to the formation of 1,4-linkage. Furthermore, extra weak signals derived from 1,3-linkage were observed at 4.1, 7.5, and 7.6 ppm. From the relative integration of signals with respect to the intensity of absorptions of α-methylene protons, polymer **5** was estimated to consist of almost equal fractions of 1,3- and 1,4-linkages (regiorandom polymer **5**). More spectral evidence for the proposed structure of polymer **5** was provided by 125 MHz ^{13}C-NMR spectroscopy. A typical ^{13}C-NMR spectrum of polymer **5** is shown in Figure 2a together with assignments of the observed resonances. Figure 1b shows the 500 MHz ^{1}H-NMR spectrum of polymer **4** which was obtained by oxovanadium-catalyzed oxidative coupling polymerization; resonances were observed at 0.9, 1.4, 1.7, 3.9, and 6.9–7.2 ppm due to the methyl, γ, β, α-methylenes protons of the side chain and aromatic protons, respectively. The ratio of aliphatic/aromatic proton was in good agreement with the expected value (18/2). The 125 MHz ^{13}C-NMR spectrum and assignment of polymer **4** is presented in Figure 2b. There are seven intense absorptions due to four aliphatic carbons and three aromatic carbons of benzene ring. In the aromatic region, three absorptions at 117.3, 127.5, and 150.0 ppm were observed. Fur-

Table 3. UV Absorption Maximum of Monomer 3 and Polymer 4[a]

compd	$\bar{M}_n$[b]	$\bar{M}_w$[b]	λ_{max} (nm)
3			286
4	11 000	30 000	331
4	12 000	24 000	333
4[c]	15 000	55 000	325
5[d]	16 000	45 000	328

[a] In chloroform. [b] Measured by GPC based on standard PSt. [c] C=O absorption was observed by IR spectroscopy. [d] Obtained by the reaction of monomer **3** with $FeCl_3$.

Table 4. The ESR Signals of Polymers 4 and 5[a]

polymer	*g* value	line width (G)	spin concentration[b] (spins/g)
4	2.003	5.1	1.5×10^{13}
5	2.005	5.0	2.0×10^{16}

[a] In carbon tetrachloride. [b] 4-Hydroxy-TEMPO free radical as reference.

Table 5. Thermal Properties of Polymers 4 and 5

polymer	T_g[a] (°C)	T_{10}[b] (°C)
4	37	385
5	16	385

[a] Measured by DSC at a heating rate 20 °C/min. [b] Temperature at which a 10% weight loss was recorded by TG at a heating rate of 10 °C/min.

thermore, no extra peaks based on the 1,3-linkage were found. These findings clearly indicate that the coupling took place selectively at the para position and gave an almost completely regiocontrolled polymer having the 1,4-linkage.

UV–Visible Spectroscopy. Table 3 presents the UV absorption maximum of the polymers having different molecular weights in chloroform solution. The position of the absorption is shifted to longer wavelength with increasing number-average molecular weights. The absorptions maximum wavelengths (λ_{max}) of regioregular polymer **4** were relatively higher than that of regiorandom polymer **5** which was synthesized by the reaction **3** with $FeCl_3$. This is equivalent to the presence of a better extended π-conjugation system along the polyphenylene backbone, which results in the longer wavelength shifts of the absorption band.

ESR Spectroscopy. Comparable spin densities have been observed for PPP prepared from various methods. The spin concentration intensely depends upon preparation procedures and specimens. Hsing et al. have summarized the spin concentration of polyphenylene obtained by a variety of authors, ranging from 3×10^{16} to 7×10^{18} spins/g.[16] The ESR signals of polymers **4** and **5** were examined, and the results of the ESR analysis in carbon tetrachloride solution are listed in Table 4. The *g* value of polymer **4** ($g = 2.003$) is smaller than that of polymer **5** ($g = 2.005$). This means that the radicals in polymer **4** are much more delocalized due to a better extended π-conjugation system along the polyphenylene backbone. The spin concentration of polymer **4** (1.5×10^{13} spins/g) is also much lower than that of polymer **5** (2.0×10^{16} spins/g). This presents that there are very few radicals in polymer **4**. This should be due to the influence of the amount of oxidants on the polymerization. The ideal coupling reaction would be accomplished in the oxovanadium-catalyzed oxidative polymerization.

Molecular Weight Chromatography. The molecular weight of the polymers was determined (relative polystylene standard) by GPC in THF. The polymers were purified by Soxhlet extractions with a mixture of methanol and chloroform for 24 h. The chromatograms had monomodal distribution and indicated that $\bar{M}_n$ and $\bar{M}_w$ values were up to 12 000 and 30 000, respectively. The ratio of $\bar{M}_w/\bar{M}_n$ was 2.6. As the polyphenylene are considerably more rigid than polystyrene, weight-average molecular weights were also measured by the lightscattering method. As a typical example on this method, the weight average molecular weight of the polymer (entry number 11, $\bar{M}_n = 12\,000$, $\bar{M}_w = 30\,000$) was measured and indicated that the $\bar{M}_w$ value was 16 000.

Polymer **4** was a brown solid. The polymer was soluble in a wide range of organic solvents, such as chloroform, pyridine, and tetrahydrofuran. A brown transparent film was cast from a chloroform solution of the polymer.

Thermal Properties. The thermal properties of polymers **4** and **5** were examined by TGA and differential scanning calorimetry (DSC). These results are summarized in Table 5. The typical traces for polymer **4** are shown in Figure 3. At first, the decomposition of

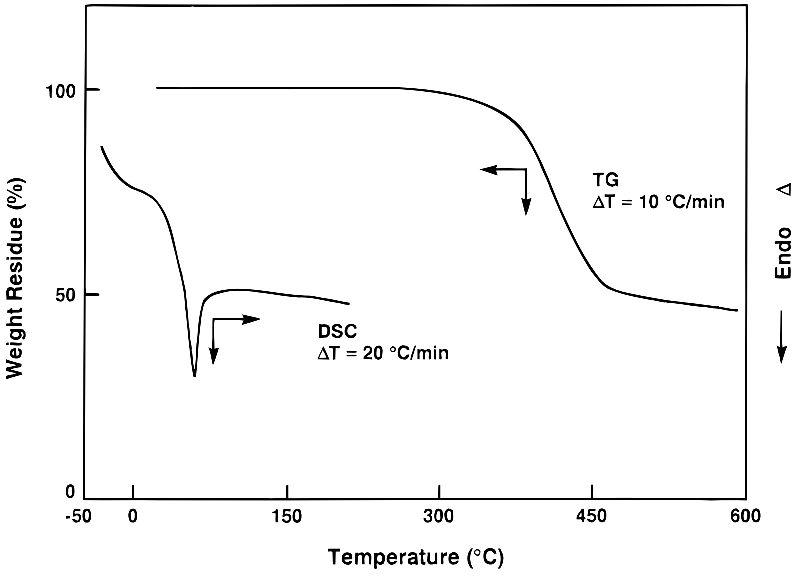


Figure 3. TG and DSC traces of polymer **4** under nitrogen.

alkoxy side chain is found until around 450 °C in nitrogen. Polymer **4** exhibits thermal resistant above 450 °C. The chair yield is 45%, which is good agreement with the expected value (48%). Polymer **4** showed a 10% weight loss at 385 °C in nitrogen as well as polymer **5**. No large differences between polymers **4** and **5** were observed in thermal stability. The T_g of polymers **4** and **5** were observed at 37 and 16 °C, respectively. This behavior would be derived from their regioregularities.

In summary, our studies indicate that poly(2,5-di-*n*-butoxyphenylene) (**4**) with high molecular weight can be readily prepared by oxovanadium-catalyzed oxidative coupling polymerization of 1,4-di-*n*-butoxybenzene (**3**). The structure of polymer was characterized by NMR spectroscopies and estimated to consist almost completely of 1,4-linkage. This catalytic system will be useful to synthesize poly(phenylene)s and polybiaryls from a wide range of monomers with an oxidation potential of around 1.3 V.

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References and Notes

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