Macromolecules **1992,** *25,* 5125–5130

Synthesis of Poly(2,5-dialkoxyphenylene)

Mitsuru Ueda,* Tetsuya Abe, and Hiroshi Awano

Department of Materials Science and Engineering, Faculty of Engineering, Yamagata University, Yonezawa, Yamagata 992, Japan

Received March 5, 1992; Revised Manuscript Received May 28, 1992

ABSTRACT: Poly(2,5-dialkoxyphenylene) (4) was prepared by oxidative coupling polymerization of 1,4-dialkoxybenzene. Polymerizations were conducted in nitrobenzene in the presence of $FeCl_3$ at room temperature and produced poly(2,5-dibutoxyphenylene) (**4b**) with inherent viscosities up to 0.92 $dL \cdot g^{-1}$. The effects of various factors, such as amount of solvent and $FeCl_3$ and reaction temperature were studied. The structure of polymer **4b** was characterized in detail by 500-MHz ^1H and 125-MHz ^{13}C NMR spectroscopies and was estimated to consist of almost equal fractions of 1,4- and 1,3-linkages. Polymer **4b** was readily soluble in common organic solvents and could be processed into uniform films from solution. Thermogravimetry of polymer **4b** showed 10% weight loss at 385 °C in both air and nitrogen.

Introduction

The coupling of two aromatic molecules by treatment with a Lewis acid and a protonic acid is called the Scholl reaction. However, yields are low and the synthesis is seldom useful except for the coupling of 1-alkoxynaphthalene in the presence of $AlCl_3$.[1] Feasey et al.[2] studied the reaction and found that the coupling yield is improved in the presence of $FeCl_3$ in nitrobenzene. On the basis of this finding, they prepared high molecular weights of poly(dinaphthyl alkylene ether)s by oxidative coupling of dinaphthyl ethers. Recently, the reaction was successfully applied to the synthesis of aromatic poly(ether sulfone)s and poly(ether ketone)s.[3]

In order to expand the preparative utility of this method, we investigated the new monomer in place of dinaphthyl ethers, and found that 2,5-dimethoxybenzene has a low redox potential (1.27 V) as well as 1-methoxynaphthalene (1.25 V).

This article describes a successful synthesis of poly(2,5-dialkoxyphenylene) by the Scholl reaction of 1,4-dialkoxybenzene.

Experimental Section

Materials. Reagent grade anhydrous $FeCl_3$ was purified by sublimation. Nitrobenzene was purified by washing sequentially with diluted aqueous acid, water, diluted aqueous base, and water followed by drying ($CaCl_2$) and distillation.

1-Methoxynaphthalene (**1a**), anisole (**1b**), and 1,4-dimethoxybenzene (**3a**) were used as received. 1,4-Di-*n*-butoxybenzene (**3b**) was prepared by the reaction of hydroquinone with *n*-butyl bromide in aqueous alkaline solution. Recrystallization from water–methanol gave white plates (yield: 55%), mp 43.5–45.5 °C. Anal. Calcd for $C_{14}H_{22}O_2$: C, 75.63; H, 9.97. Found: C, 75.70; H, 9.71.

Model Compound. 4,4′-Dimethoxy-1,1′-binaphthalene (2a). In a 200-mL three-necked flask equipped with a nitrogen inlet and dropping funnel was placed a solution of anhydrous $FeCl_3$ (2.43 g, 15 mmol) in nitrobenzene (7.5 mL). To the solution was added dropwise 1-methoxynaphthalene (2.37 g, 15 mmol). The solution was stirred at room temperature for 12 h and poured into methanol (100 mL). The product was filtered, washed with methanol, and dried. The yield was 2.20 g (93%). Recrystallization from benzene–acetone produced white powder, mp 255 °C (by DTA) (lit.[4] 251 °C).

Attempted Synthesis of 4,4′-Dimethoxy-1,1′-biphenyl (2b). Coupling reaction of anisole (**1b**) was carried out as described above. The product was a black powder (20%), which might be oligomers of **1b**. The inherent viscosity of the product in concentrated sulfuric acid was 0.03 $dL \cdot g^{-1}$, measured at a concentration of 0.5 $g \cdot dL^{-1}$ at 30 °C.

Polymer Synthesis. A typical example of the polymerization follows.

Polymer 4b from 3b. In a 50-mL three-necked round-bottomed flask fitted with a stirrer, serum 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*-butoxybenzene (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 serum cap. The solution was stirred at room temperature under a slow stream of nitrogen and gradually became dark and viscous with progress of the polymerization. After 24 h, the solidified mixture was dissolved in nitrobenzene (2–4 mL) and poured into methanol (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. The yield was 0.197 g (89%). The inherent viscosity of the polymer in THF was 0.92 $dL \cdot g^{-1}$, measured at a concentration of 0.5 $g \cdot dL^{-1}$ at 30 °C. IR (film): ν 3025, 2870–2960 (C—H), 1480 (C=C), 1205 cm^{-1} (C—O—C). Anal. Calcd for $(C_{14}H_{20}O_2)_n$: C, 76.33; H, 9.15. Found: C, 75.92; H, 8.85.

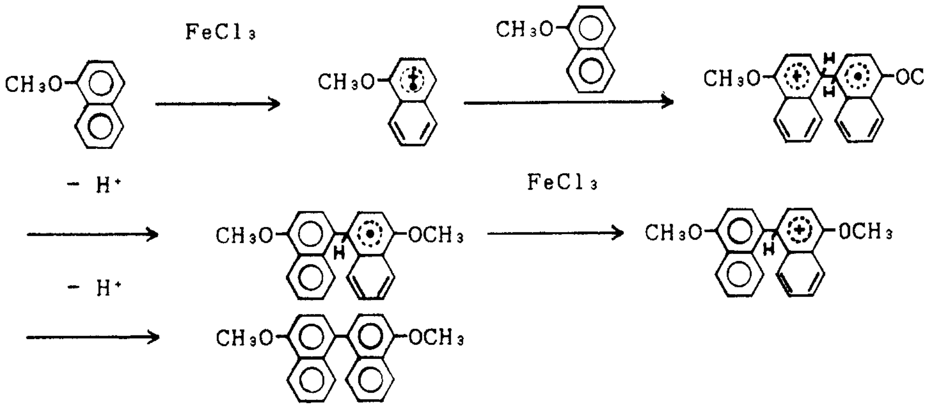
Measurements. The infrared spectra were recorded on a Hitachi I-5020FT-IR spectrometer, the ultraviolet spectra on a Hitachi Model 100-60 UV/vis spectrometer, and the NMR spectra on a Hitachi R-24B (60 MHz) and a JEOL GX 500 (500 MHz) spectrometer. Viscosity measurements were carried out by using an Ostwald visocometer at 30 °C. Thermal analyses were performed on a Seiko SSS 5000 thermal analyzer at a heating rate 10 $°C \cdot min^{-1}$ for thermogravimetric analysis (TGA). The glass transition temperature was measured on a Shimazu TMA-30 instrument at a heating rate of 20 $°C \cdot min^{-1}$ in nitrogen. Molecular weights were determined by a gel permeation chromatograph (GPC) with polystyrene calibration using a JASCO TRIROTAR-III HPLC equipped with Shodex KF-80M column at 25 °C in THF. The cyclic voltammograms were measured in acetonitrile solution containing 0.1 M tetraethylammonium perchlorate and 10 mM monomer with the aid of a Hokuto Denko HA-501 potentiostat/galvanostat. A Pt disk with a diameter of 2 mm was used as a working electrode, and an aqueous SCE as a reference electrode. The ESR spectra were obtained with the aid of a JES-RE1X ESR spectrometer. Mn^{2+}/MgO and 3-carbamoyl-2,2,5,5-tetramethyl-3-pyrrolin-1-yloxy (CTPO) were used as reference.

Results and Discussion

Coupling mechanism of the Scholl reaction is assumed to be as in Scheme I. The first step is a one-electron oxidation of the aromatic nucleus to give a cation radical which attacks the 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 a further oxidation followed by proton loss to give the dimerization product. Therefore, it is very important to select

0024-9297/92/2225-5125$03.00/0

Scheme I



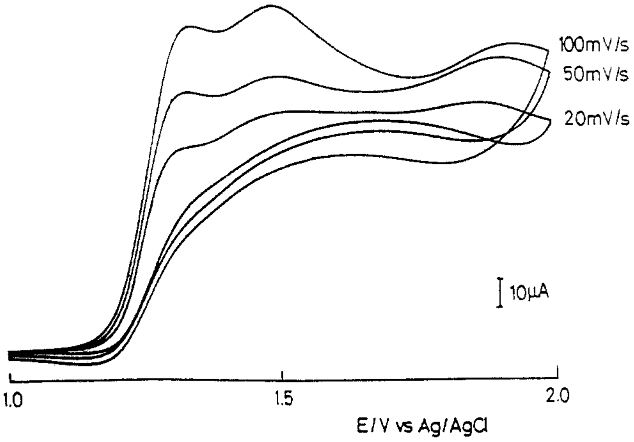


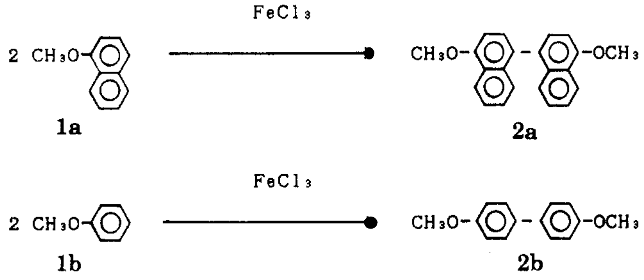
Figure 1. Cyclic voltammograms for **1a** at various scan rates.

Table I
Oxidation Potentials of Monomers

monomer	E,[a] V vs SCE
anisole	1.75
1-methoxynaphthalene	1.25
1,4-dimethoxybenzene	1.27

[a] Voltammograms run at 100 $mV{\cdot}s^{-1}$.

Scheme II



Scheme III

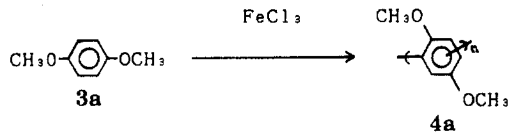


Table II
Effect of Amount of Nitrobenzene on Polymerization[a]

	polymer	
amt of solvent, mL	yield, %	η_{inh},[b] $dL{\cdot}g^{-1}$
1.25	100	0.31
1.5	100	0.28
2.0	91	0.27
2.5	97	0.20
3.0	97	0.21
4.0	94	0.24

[a] Reaction conditions: 1 mmol of monomer, 4 mmol of $FeCl_3$, room temperature, 24 h. [b] Measured at a concentration of 0.5 $g{\cdot}dL^{-1}$ in sulfuric acid at 30 °C.

a monomer having a low redox potential in which the initiation of polymerization occurs easily. As described in the Introduction, dimerization of 1-alkoxynaphthalene easily occurs in the presence of $FeCl_3$ (0.77 V) and high molecular weight linear polymers have been obtained by oxidation of di-1-naphthoxyalkanes.

The introduction of electron-donating groups into the benzene ring generally decreases the redox potential of compounds. Thus, the redox potential of 1-methoxynaphthalene (**1a**), anisole (**1b**), and 1,4-dimethoxybenzene (**3a**) were measured by cyclic voltammetry (CV). The oxidation potentials (E) of these compounds were determined at freshly cleaned Pt surfaces. Figure 1 shows the cyclic voltammograms of **1a** in acetonitrile with various scan rates. The typical irreversible nature of the oxidation can be clearly seen, and the two redox processes, were observed at E values of 1.25 and 1.55 V vs SCE. Since for the Scholl reaction the first redox process at the lower potential is important for initiation, the potentials of the first one-electron transfer from the benzene ring are listed in Table I. The oxidation potential of compound **3a** is 1.27 V, which is comparable to that of **1a**. Thus, compound **3a** was expected to be a suitable monomer for oxidative coupling polymerization.

We first studied the dimerization of **1a** and **1b** in the presence of $FeCl_3$ in nitrobenzene to investigate the difference in the reactivity between the two compounds (Scheme II). The reaction was performed by slowly adding compound 1 into the solution of anhydrous $FeCl_3$ in nitrobenzene and stirring at room temperature. After the reaction was complete, the solution was poured into methanol, and the crude product was recovered by filtration. As expected from the lower oxidation potential of **1a** than **1b**, compound **1a** gave an excellent yield of coupling product **2a**; on the other hand, the coupling reaction of **1b** yielded a small amount of oligomers in place of the desired product **2b**.

Polymer Synthesis. On the basis of these preliminary experiments, the oxidative coupling polymerization of **3a** was carried out in the presence of $FeCl_3$ at room temperature (Scheme III). Mukai et al.[5] attempted to apply the Scholl reaction to the preparation of this polymer by reacting **3a** with $AlCl_3/CuCl_2$ in nitrobenzene, but obtained only a low molecular weight polymer ($\eta_{sp{\cdot}c}^{-1}$ = 0.07 $dL{\cdot}g^{-1}$). Table II lists the effect of amount of solvent on the polymerization. A 1.25-mL quantity of nitrobenzene was found to be appropriate for the reaction on a 1-mmol scale. The polymerization proceeded homogeneously at the

Table III
Effect of Amount of $FeCl_3$ on Polymerization[a]

	polymer	
amt of $FeCl_3$, mmol	yield, %	η_{inh},[b] $dL \cdot g^{-1}$
1	23	
2	44	0.08
3	93	0.17
4	91	0.27
5	97	0.30
8	98	0.34

[a] Reaction conditions: 1 mmol of monomer, 4 mL of nitrobenzene, room temperature, 24 h. [b] Measured at a concentration of 0.5 $g \cdot dL^{-1}$ in sulfuric acid at 30 °C.

Scheme IV

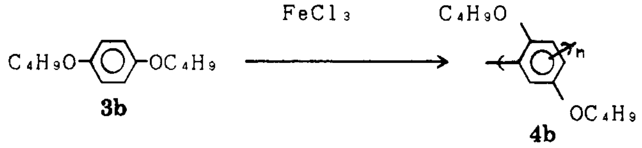


Table IV
Effect of Amount of Nitrobenzene on Polymerization[a]

	polymer	
amt of solvent, mL	yield, %	η_{inh},[b] $dL \cdot g^{-1}$
1	85	gel
2	80	gel
3	89	1.15[c]
4	89	0.92
5	78	0.61

[a] Reaction conditions: 1 mmol of monomer, 4 mmol of $FeCl_3$, room temperature, 24 h. [b] Measured at a concentration of 0.5 $g \cdot dL^{-1}$ in THF at 30 °C. [c] Soluble part.

initial stage and then heterogeneously. Therefore, the effect of the ammount of $FeCl_3$ on the polymerization was studied in 4 mL of nitrobenzene to keep a homogeneous solution as long as possible. The results are shown in Table III. This polymerization requires theoretically at least 2 molar equiv. of $FeCl_3$, based on monomer. However, a large excess amount of $FeCl_3$ was required to obtain polymers with inherent viscosities up to 0.34 $dL \cdot g^{-1}$. These results are quite different from those expected for the synthesis of poly(dinaphthyl alkylene ether)s, where a small excess of $FeCl_3$ was enough to obtain high molecular weights of polymer. The probable explanation is that the polymerization proceeded heterogeneously.

To improve the solubility of polymers, 1,4-di-*n*-butoxybenzene (**3b**) was prepared by the reaction of hydroquinone and *n*-butyl bromide. The polymerization of **3b**, which gave soluble polymer in nitrobenzene, was studied in detail (Scheme IV). The effect of the amount of solvent on the polymerization is shown in Table IV. The amount of solvent found to be appropriate for the reaction on a 1-mmol scale was 4 mL. The polymerization in 3 mL of nitrobenzene produced a higher molecular weight of polymer which contained a few percent of insoluble gel. The effect of the amount of $FeCl_3$ on the polymerization is shown in Table V. The inherent viscosity of the polymer reached its highest value with 4 mmol of $FeCl_3$, based on 1 mmol of **3b**. Upon addition of a large excess of $FeCl_3$ to monomer, a gel polymer formed because of the extra oxidation of the polymer, which induced coupling between the polymers.

Table V
Effect of Amount of $FeCl_3$ on Polymerization[a]

	polymer	
amt of $FeCl_3$, mmol	yield, %	η_{inh},[b] $dL \cdot g^{-1}$
1	20	0.11
2	66	0.19
3	73	0.40
4	89	0.92
5	75	gel

[a] Reaction conditions: 1 mmol of monomer, 4 mL of nitrobenzene, room temperature, 24 h. [b] Measured at a concentration of 0.5 $g \cdot dL^{-1}$ in THF at 30 °C.

Table VI
Effect of Reaction Temperature on Polymerization[a]

	polymer	
temp, °C	yield, %	η_{inh},[b] $dL \cdot g^{-1}$
0	74	0.14
10	77	0.30
room	89	0.92
40		gel

[a] Reaction conditions: 1 mmol of monomer, 4 mL of nitrobenzene, 24 h. [b] Measured at a concentration of 0.5 $g \cdot dL^{-1}$ in THF at 30 °C.

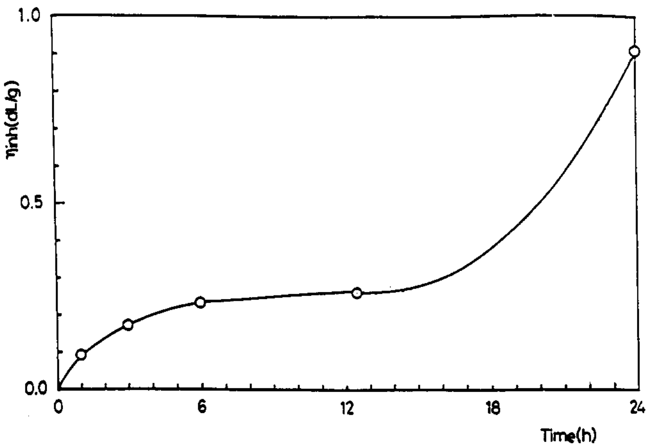


Figure 2. Course of the polymerization in terms of inherent viscosity of the resulting polymer.

Next, the influence of reaction temperature on the inherent viscosity of the resulting polymer was examined between 0 and 40 °C. The polymerization was found to be highly dependent on temperature, and the highest viscosity was attained at 20 °C. At a lower temperature of 0 °C, the reaction rate was so slow that polymer **4b** only attained a low molecular weight. Raising the temperature to 40 °C gave a gel polymer. These results are summarized in Table VI.

Figure 2 shows the course of the polymerization in terms of inherent viscosity of the resulting polymer. Rapid polymerization occurred in 3 h, followed by a constant viscosity and then by another increase in inherent viscosity. Further polymerization (more than 30 h) gave polymer that contained a few percent of insoluble gel. This polymerization behavior seems to support that the oxidative coupling polymerization of 1,4-alkoxybenzene in the presence of $FeCl_3$ follows a reactive intermediate polycondensation mechanism proposed by Heitz.[6]

Polymer Characterization. Polymer 4 was confirmed to be the corresponding poly(2,5-dialkoxyphenylene) by means of infrared and NMR spectroscopies and elemental analysis. The IR spectra exhibited characteristic absorptions at 2870–2960, 1480, and 1205 cm^{-1} due to the C—H, C═C, and C—O—C stretching, respectively. Elemental analyses also supported the formation of the expected polymers. The poly(phenylene) (PP) from $FeCl_3$ treatment of benzene contains more chlorine than that from $AlCl_3/CuCl_2$.[7] Thus, the chlorine analysis was carried out. The weight percentage of chlorine in the polymer was only

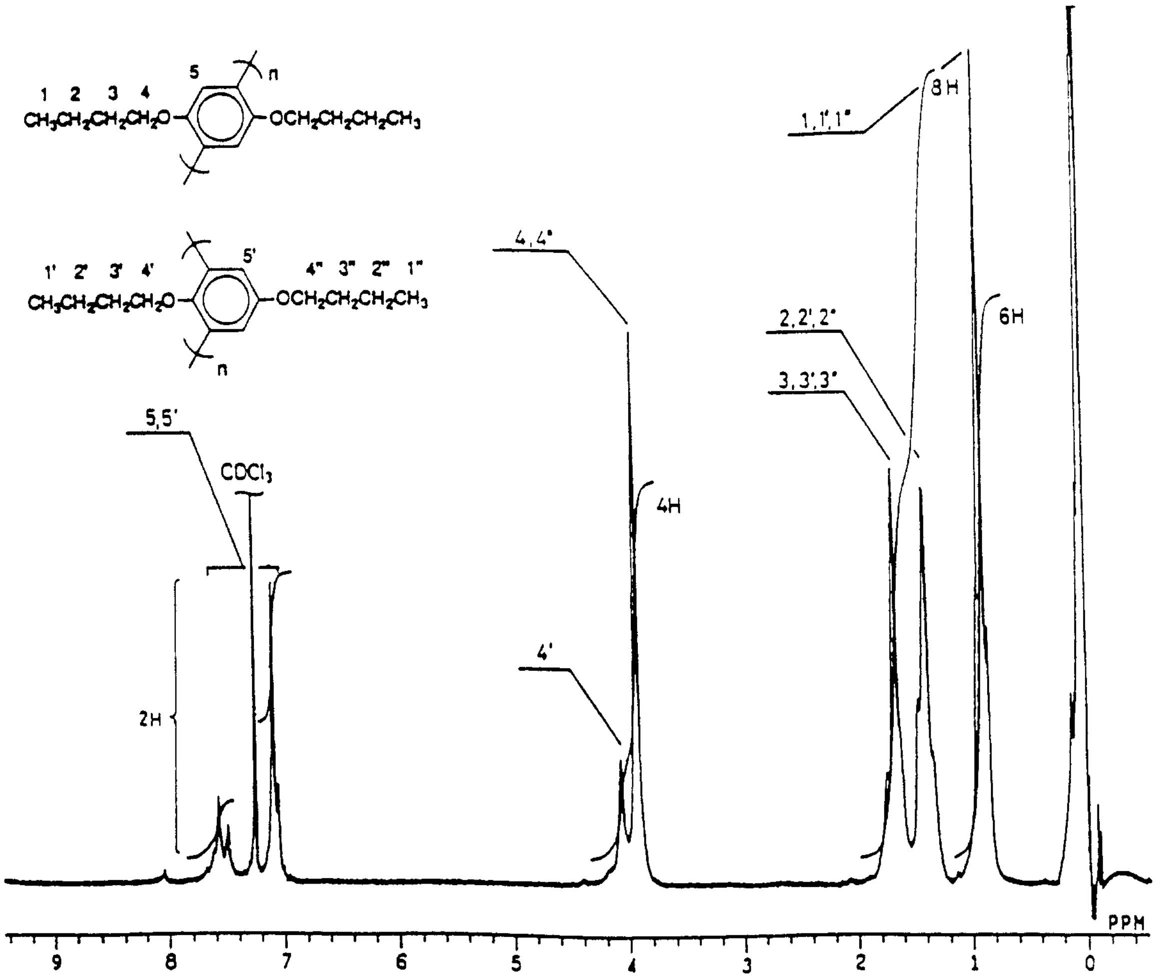


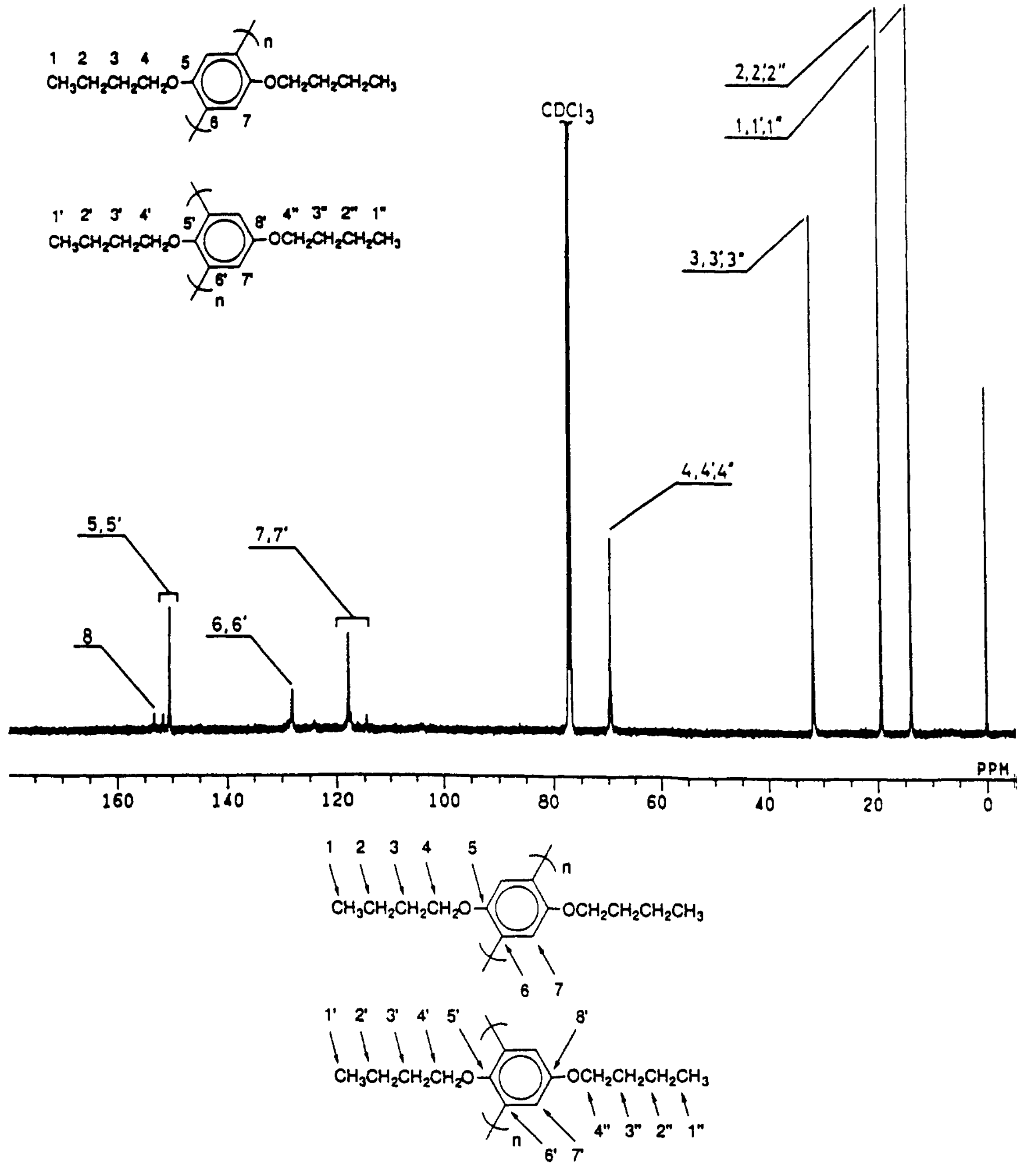
Figure 3. 500-MHz ^{1}H NMR spectrum of polymer **4b** in $CDCl_3$ at 50 °C.

0.16, which corresponds to about 1 unit containing chlorine per 100 repeating units.

Considering the coupling mechanism, polymerization of **3b** will be expected to give 1,3- and 1,4-linkages. Figure 3 shows the 500-MHz ^{1}H NMR spectrum of polymer **4b** which exhibited five intense absorptions at 0.89, 1.39, 1.66, 4.01, and 7.09 ppm due to the methyl, γ-methylene, β-methylene, and α-methylene protons of the alkoxy group and aromatic protons, respectively. Furthermore, extra weak but well-defined signals were observed at 4.05, 7.49, 7.57, and 7.62 ppm. α-Methylene protons (4′) of the alkoxy group in 1,3-enchained sequences would be more deshielded by the ring current of the two neighboring phenyl rings than those of the alkoxy group in the 1,4-enchained sequences. Thus, the 4.05 ppm resonance may be assigned to the α-methylene protons (4′) of the alkoxy group. Considering triads of monomeric units, polymerization of **4b** will be expected to give the six monomer linkages, p-*p*-p, p-*p*-m, m-*p*-m, p-*m*-p, p-*m*-m, m-*m*-m, where p and m represent the 1,4- and 1,3-linkage, respectively. The structural asymmetry would create slightly different environments for the protons in the central phenyl rings. Therefore, the resonances around 7.0–7.5 ppm arise from the phenyl protons involved in mixed connectivities, but their unambiguous assignments are difficult without further information on the chemical shifts of the model compounds. From the relative integration of signals with respect to the intensity of absorptions for α-methylene protons, we estimate that the percentage of 1,3-linkage in polymer **4b** is ca. 50%. The other spectral evidence for the proposed poly(2,5-di-*n*-butoxyphenylene) structure was provided by 125-MHz ^{13}C NMR spectroscopy. A typical ^{13}C NMR spectrum of polymer **4b** is shown in Figure 4 together with assignments of the observed resonances. The observed chemical shifts are in good agreement with the calculated values except for the C atoms (7 and 7′) of the phenyl rings. The downfield shifts that are found on these C atoms would be explained as an electric field effect by the neighboring phenyl ring. However, the assignments are tentative and further investigation on the structure of the polymer **4b** is under way.

Table VII shows the UV absorption maximum of the polymers in CCl_4 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 polyphenylene backbone, which results in the longer wavelength shift of the absorption band.

As comparable spin densities have been observed for PPP prepared from various methods, the ESR signals of polymer **4b** were examined. Results of the ESR analysis of polymer **4b** in the solid-state are as follows: g value, 2.005; line width, 5.0 G; spin concentration, 2.0×10^{16} spins/g (1.4×10^5 monomer units/spin). For PP, Lerner[8] obtained an ESR signal, whose g value was 2.0032 and line width ranged from 4.4 to 5.3 G. It should be noted that these values are near to those obtained for polymer **4b**. Hsing et al.[9] have summarized the spin concentration of PP obtained by a variety of authors, ranging from 3×10^{16} to 7×10^{18} spins/g. The spin concentration intensely depends upon preparation procedures and specimens. Therefore, it is not surprising that our result is as small as 2.0×10^{16} spins/g for polymer **4b**. The poly(2,5-dialkoxyphenylene)s were brown solids. Polymer **4a** was soluble only in concentrated sulfuric acid. In contrast,



	1	2	3	4	5	6	7
Calcd.	14.6	20.3	33.1	71.2	151.5	127.1	114.4
Found	13.8	19.3	31.8	69.6	150.5	128.1	117.9

	1'	2'	3'	4'	5'	6'	7'	8'
Calcd.	14.6	20.3	33.1	71.2	150.0	128.6	112.9	153.0
Found	13.7	19.2	31.7	69.4	150.6	128.2	117.5	153.3

	1"	2"	3"	4"
Calcd.	14.6	20.3	33.1	71.2
Found	13.8	19.3	31.8	69.6

Figure 4. 125-MHz ^{13}C NMR spectrum of polymer **4b** in $CDCl_3$ at 30 °C.

polymer **4b** was soluble even in THF and CCl_4 at room temperature. A brown transparent film was cast from the solution of polymer **4b** in THF.

The molecular weight of polymer **4b** having an inherent viscosity of 0.92 dL·g^{-1} was determined by means of GPC. A typical chromatogram is shown in Figure 5 in which the monomodal weight distribution was observed. The chromatogram indicated that the M_n and M_w values were 50 000 and 280 000, respectively, for standard polystyrene, and the ratio of M_w/M_n was 5.5.

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

η_{inh},[b] dL·g^{-1}	λ_{max}, nm	η_{inh},[b] dL·g^{-1}	λ_{max}, nm
monomer	286	0.56	333
0.35	328	0.92	343

[a] In CCl_4. [b] Measured at a concentration of 0.5 g·dL^{-1} in THF at 30 °C.

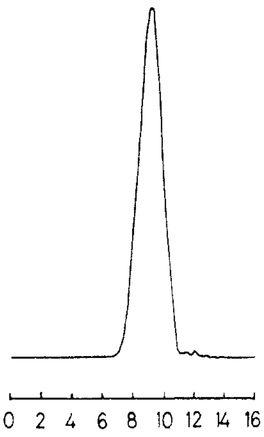


Figure 5. Gel permeation chromatogram of **4b** (η_{inh} = 0.92 dL·g^{-1}).

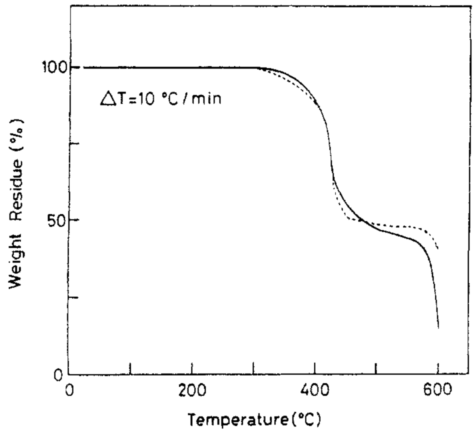


Figure 6. TG curves of polymer **4b**: (—) in air; (- - -) in nitrogen.

Table VIII
Thermal Properties of Polymer 4

		decomp temp, °C[a]	
polymer	T_g, °C	in air	in nitrogen
4a		380	385
4b	79	385	385

[a] Temperature at which a 10% weight loss was recorded by TG at a heating rate at 10 °C·min^{-1}.

The thermal stability of polymer 4 was examined by thermogravimetry (TG). A typical trace for polymer **4b** is shown in Figure 6. The polymer showed a 10% weight loss at 385 °C in both air and nitrogen. The glass transition temperature (T_g) of polymer **4b** determined by thermomechanical analysis (TMA) was 79 °C. A melting point for **4b** was not observed, in agreement with the X-ray diffraction pattern of **4b**, which showed very little crystalline structure. These data are presented in Table VIII.

In summary, our studies indicate that poly(2,5-dialkoxyphenylene) with high molecular weights can readily be prepared by oxidative coupling polymerization of 1,4-dialkoxybenzene. The structure of the polymer obtained seems to involve an almost 1:1 ratio of 1,3- and 1,4-linkages. This method will be applied to the synthesis of poly(phenylene) from the monomers having an oxidation potential of around 1.2 V.

Acknowledgment. We are indebted to Prof. Toshikazu Takada (Tokyo Institute of Technology) for NMR measurements, Sadao Kato for the technical assistance, and Takeyoshi Takahashi for performing the elemental analyses.

References and Notes

(1) Balaban, A. T.; Nenitzescu, C. D. In *Friedel-Crafts and Related Reactions*; Olah, G. A., Ed.; Interscience: New York, 1964; Vol. 2, Part 2, p 979.
(2) Feasey, G. A.; Turner-Jones, A.; Daffurn, P. C.; Freeman, J. L. *Polymer* **1973**, *14*, 241.
(3) (a) Percec, V.; Nava, H. *J. Polym. Sci., Part A: Polym. Chem.* **1988**, *26*, 783. (b) Percec, V.; Wang, J. H.; Oishi, Y. *J. Polym. Sci., Part A: Polym. Chem.* **1991**, *29*, 949. (c) Percec, V.; Wang, J. H.; Oishi, Y.; Feiring, A. E. *J. Polym. Sci., Part A: Polym. Chem.* **1991**, *29*, 965.
(4) Ostermaye, E.; Rosenhek, J. *Ber. Dtsch. Chem. Ges.* **1884**, *17*, 2454.
(5) Mukai, K.; Teshirogi, T.; Kuramoto, N.; Kitamura, T. *J. Polym. Sci., Polym. Chem. Ed.* **1985**, *23*, 1259.
(6) Koch, W.; Risse, W.; Heitz, W. *Makromol. Chem. Suppl.* **1985**, *12*, 105.
(7) Kovacic, P.; Jones, M. R. *Chem. Rev.* **1987**, *87*, 357.
(8) Lerner, N. R. *J. Polym. Sci., Polym. Chem. Ed.* **1974**, *12*, 2477.
(9) Hsing, C.-F.; Khoury, I.; Benzoari, M. D.; Kovacic, P. *J. Polym. Sci., Polym. Chem. Ed.* **1982**, *20*, 3313.

Registry No. 1a, 2216-69-5; **1b**, 100-66-3; **1b** (homopolymer), 36862-96-1; **2a**, 19817-09-5; **3a** (homopolymer), 42500-66-3; **3b**, 104-36-9; **3b** (homopolymer), 87211-17-4; **4a** (SRU), 142978-91-4; **4b** (SRU), 142978-92-5; hydroquinone, 123-31-9; *n*-butyl bromide, 109-65-9.