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Preparation of Poly(*p*-phenylene) via a New Precursor Route

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ABSTRACT: Methyl 2,5-dichlorobenzoate (1) was polymerized in dimethylformamide with a catalyst system comprised of nickel(II) bromide, triphenylphosphine, and zinc to produce poly[2-(methoxycarbonyl)phenylene-1,4-diyl] (2). The GPC measurements indicated that the molecular weight distribution of 2 was monomodal and the degree of polymerization was around 100. The hydrolysis of 2 yielded poly(2-carboxyphenylene-1,4-diyl) (3). Polymer 3 was soluble in quinoline and pyridine as well as aqueous sodium hydroxide. The catalytic decarboxylation of 3 produced poly(*p*-phenylene) (PPP) powder. Copper(II) oxide, basic copper(II) carbonate, and copper(I) oxide were effective catalysts for the decarboxylation. Both these catalysts with quinoline as solvent were necessary to cause the decarboxylation. The IR spectrum indicates that the PPP has a regular structure. The electrical conductivity of a pressed pellet was as high as 18 S/cm after vapor-phase doping with antimony pentafluoride.

Introduction

The conducting polymers have been attracting increased attention due to their potential applications.[1,2] In addition to moderate electrical conductivity, poly(*p*-phenylene) (PPP) shows high thermal stability in its neutral state, and so it is not only a very interesting conducting polymer but also an excellent heat-resistant polymer. PPP was prepared by the chemical coupling of benzene[3-6] or oxidative electrochemical polymerization of benzene.[7-10] PPP has not been well characterized due to its insolubility. Electrochemically prepared PPP was assumed to have a degree of polymerization as low as 20 from the end-group analysis in its IR spectrum. Some of these polymers had structural defects, one of which was indicated as being polynuclear moieties by the IR band at 1600 cm^{-1}. PPP is insoluble and infusible, and therefore intractable.

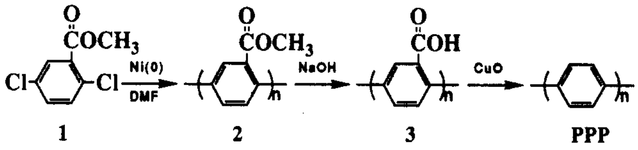
Ballard et al. reported a fundamentally new procedure where PPP films were produced by pyrolysis of soluble and processible precursors, where the degree of polymerization of the precursor polymer was as high as 600–1000 and films or fibers could be made from a precursor solution.[11] However, this PPP contained 15% *o*-phenylene moieties.[12] The starting materials were produced by oxidation of benzene with genetically modified bacteria, *Pseudomonas putida*, implying that this procedure is not easily accessible to polymer chemists. Thus, it is desirable to find a new route to structurally regular PPP via processible precursor polymers.

In this paper, we report a new procedure to prepare structurally regular PPP with a definite molecular weight starting with commercially available materials. In this procedure, methyl 2,5-dichlorobenzoate (1) was polymerizied in the presence of zerovalent nickel generated in situ by the reduction of nickel(II) bromide with triphenylphosphine and zinc powder. Poly[2-(methoxycarbonyl)-phenylene-1,4-diyl] (2) obtained was hydrolyzed to poly-(2-carboxyphenylene-1,4-diyl) (3), followed by catalytic decarboxylation to produce PPP.

Experimental Section

Materials. Methyl 2,5-dichlorobenzoate (1) was obtained from Aldrich Chemical Co., Inc., and recrystallized from its methanol solution. *N,N*-Dimethylformamide (DMF) was dried over calcium hydride and distilled under argon. Nickel(II) bromide, triphenylphosphine, zinc powder, copper(II) oxide, and quinoline were purchased from Wako Pure Chemical Industries Ltd. and used without further purification.

Scheme I. Synthetic Route of PPP



Poly[2-(methoxycarbonyl)phenylene-1,4-diyl] (2). A three-necked flask was charged with 0.654 g (3 mmol) of nickel(II) bromide, 5.97 g (23 mmol) of triphenylphosphine, and 6.06 g (93 mmol) of zinc powder. To the flask was added 30 mL of DMF under a strong flow of argon, and this reaction mixture was magnetically stirred at 40–45 °C. After the red catalyst was formed in 15 min, 6.15 g (30 mmol) of 1 in 15 mL of DMF was added to the reaction mixture. The polymerization was conducted at 30–80 °C for a fixed duration of time under a mild flow of argon. After the polymerization was complete, an excess amount of acetone was added and stirred for 0.5 h to remove triphenylphosphine and unreacted monomer. The solid polymer collected on a filter was added to dilute aqueous hydrochloride to remove zinc and other inorganic materials. The polymer was repeatedly washed with distilled water, methanol, and acetone and dried in vacuo at 60 °C for 5 h to yield 2.

Poly(2-carboxyphenylene-1,4-diyl) (3). The hydrolysis of 2 was carried out by refluxing it with 10% sodium hydroxide solution in methanol for 1.5 h. The reaction mixture was poured into diluted hydrochloric acid to recover the solid product. It was washed with distilled water and dried in air overnight. Drying at 60 °C in vacuo for 5 h produced 3 in almost quantitative yield.

Poly(*p*-phenylene) (PPP). The decarboxylation of 3 was performed by heating to reflux 1.5 g in 24 mL of quinoline in the presence of 0.15 g of copper(II) oxide under argon for 3 h. PPP obtained was washed with acetone to remove quinoline and then stirred in aqueous hydrochloric acid to remove residual inorganic compounds. The PPP was repeatedly washed with water and methanol and then dried in vacuo at 60 °C for 5 h. The conversion of 3 to PPP was almost quantitative. Copper powder, basic copper(II) carbonate, and copper(I) oxide were also used for the decarboxylation of 3.

Measurements. Thermogravimetric Analysis (TGA). The TGA measurements were carried out from 25 to 420 °C in air as well as under nitrogen, using 10 mg of each sample in an aluminum sample pan. The heating rate was 10 °C min^{-1}.

Molecular Weight Determination. The molecular weight of 2 was measured in chloroform on a gel permeation chromatography (GPC) apparatus at room temperature using standard polystyrene samples. The concentration of 2 in chloroform was 0.2%.

Absorption Spectrum. The absorption spectra of 2 and 3 were recorded for thin films which were spin-coated on a quartz plate from chloroform or pyridine solutions, respectively.

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Table I. Polymerization of Methyl 2,5-Dichlorobenzoate[a]

entry	temp (°C)	time (h)	yield (%)	mp (°C)[b]	M_n ($\times 10^{-3}$)	M_w/M_n	DP
1	80	24	69	320–324	10	1.6	75
2	60	48	53	327–334	8.6	1.6	64
3	30	48	51	305–307	19	1.3	142
					6.4	1.2	48
4[c]	80	48	73	233–238	12	1.8	90
5	80	48	85	240–245	14	2.1	104
6	80	3	70	235–240	11	1.6	82
7	30	40	22	210–215	7.3	1.4	55
8	80	48	80	235–240	12	1.9	90

[a] Nickel(II) bromide, 1 mmol; triphenylphosphine, 7.6 mmol; zinc, 31 mmol; monomer, 10 mmol; DMF, 15 mL. Entry 8 was performed in 10 times large scale. For entries 1–3, the monomer was used without purification. For entries 4–8, the monomer was recrystallized from methanol. [b] Mp was measured under microscopic observation. [c] Potassium iodide (1 mmol) was added.

Table II. Decarboxylation of Poly(2-carboxyphenylene-1,4-diyl)[a]

catalyst	ratio[b]	time (h)	C–O band[c]	color PPP
CuO	2:1	3	non	green
CuO	7:1	3	non	green
CuO	20:1	3	non	gray
$CuCO_3$[d]	7:1	3	non	green
$CuCO_3$[d]	20:1	3	slight	green
Cu_2O	7:1	3	small	green
Cu_2O	20:1	3	small	green
Cu powder	2:1	5	medium	yellow
Cu powder	7:1	5	medium	yellow
Cu powder	20:1	5	medium	yellow

[a] Refluxing in quinoline. [b] Weight ratio of polymer to catalyst. [c] C–O stretching band at 1225 cm^{-1}. [d] Basic copper(II) carbonate.

Conductivity. A pressed pellet made under a pressure of 200 kg cm^{-2} was exposed in vacuo to antimony pentafluoride vapor for doping, and the conductivity of this pellet was measured in situ according to the four-probe arrangement.

Apparatus. ^{1}H NMR spectra were measured in deuterated chloroform on a Jeol GSX 270 spectrometer operating at 270 MHz at room temperature. IR spectra were recorded as a KBr disk on a Perkin-Elmer FT-IR spectrophotometer. UV–vis spectra were recorded on a Hitachi U-3400 absorption spectrophotometer. The melting points were determined on a Yanaco micro melting point apparatus and uncorrected. GPC was measured on a LC-908 gel permeation liquid chromatography (Japan Analytical Industry Co., Ltd.). The TGA curves were recorded on a Rigaku thermal analyzer.

Results

Synthesis. Preparation of **2**, **3**, and PPP was carried out according to the procedure shown in Scheme I.

The dehalogenative polymerization of **1** was effected by zerovalent nickel, which was prepared in situ from nickel(II) bromide in the presence of zinc powder and triphenylphosphine according to Colon's method.[13] This method was useful for dehalogenative polymerization of monomers containing a carbonyl group. The results of the polymerization of **1** are summarized in Table I. Polymer **2** was isolated as a white powder, which was soluble in chloroform at room temperature but insoluble in such common solvents as toluene and tetrahydrofuran. **2** was soluble in refluxing pyridine and DMF. It precipitated from a DMF solution upon cooling but did not from a pyridine solution. Polymer **3** was obtained by the hydrolysis of **2** in quantitative yield and was soluble in pyridine and quinoline as well as aqueous sodium hydroxide.

3 was decarboxylated by heating in quinoline in the presence of copper-based catalysts such as copper(II) oxide,[14] copper powder,[15] basic copper(II) carbonate, or copper(I) oxide.[16] PPP was obtained almost quantitatively. The summary of the decarboxylation is presented in Table II.

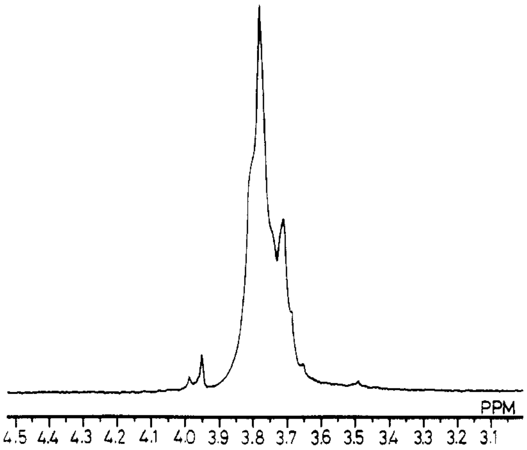

Figure 1. ^{1}H NMR of poly[2-(methoxycarbonyl)phenylene-1,4-diyl].

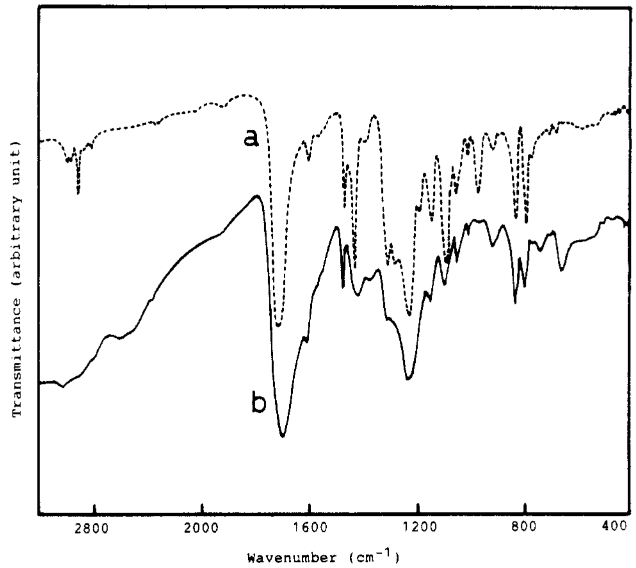

Figure 2. FT-IR spectra: (a) poly[2-(methoxycarbonyl)phenylene-1,4-diyl]; (b) poly(2-carboxyphenylene-1,4-diyl).

Characterization of 2. The ^{1}H NMR spectrum of **2** is essentially identical to that of poly[2-(methoxycarbonyl)phenylene-1,4-diyl], prepared from methyl 2,5-bis[[(trifluoromethyl)sulfonyl]oxy]benzoate.[17] The methyl part of the spectrum is presented in Figure 1. The main peak occurred at 3.78 ppm and the second peak at 3.71 ppm. The small peaks were located at 3.65, 3.69, 3.95, and 3.99 ppm and a shoulder on each slope of the main peak. These complex features can be attributed to the combination of head-to-tail and head-to-head bondings and the flipping of phenylene rings. The integral of the peak at 3.95 ppm was found to be inversely proportional to the degree of polymerization. The integral ratio of the peak to the sum of the other peaks was 50 in Figure 1, corresponding to a degree of polymerization of 104 determined by GPC. The

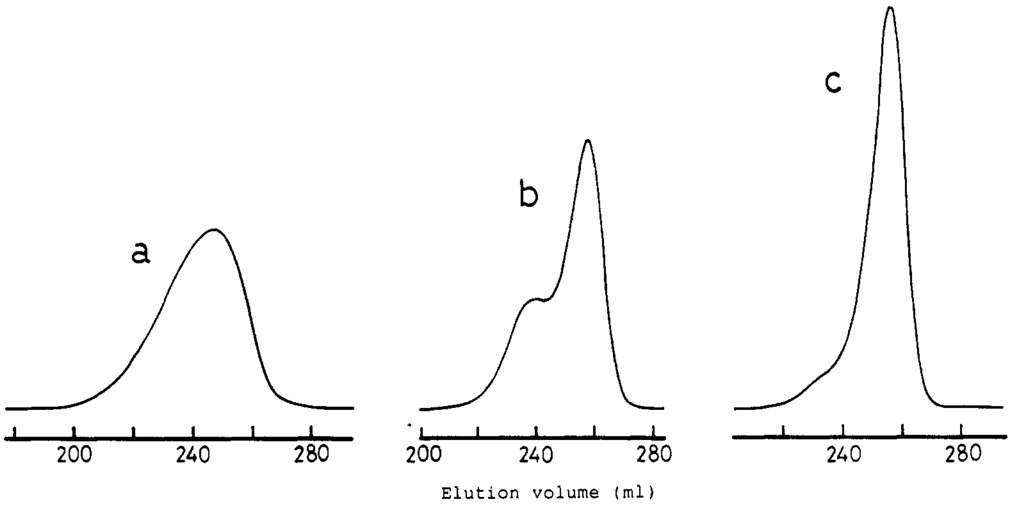

Figure 3. GPC traces of poly[2-(methoxycarbonyl)phenylene-1,4-diyl]: (a) polymerization temperature 80 °C, from recrystallized monomer (entry 8 in Table I); (b) polymerization temperature 30 °C, from as-received monomer (entry 3); (c) polymerization temperature 30 °C, from recrystallized monomer (entry 7).

ratio for polymers with a degree of polymerization of 55 was 22. This peak is due to the phenyl group termini.

Figure 2a shows the IR spectrum of 2. In the spectrum of 2, the aromatic and aliphatic C–H stretching bands occur at 3041 and 3091 cm^{-1} and 2876 and 2990 cm^{-1}, respectively. The intense band at 1727 cm^{-1} is assigned to the carbonyl group of the ester. The band of the asymmetrical and symmetrical C–O stretching vibrations occurred at 1225 cm^{-1}. The band at 825 cm^{-1} is due to the isolated hydrogen at the 3-position. The bands at 787 and 762 cm^{-1} are due to the out-of-plane deformation vibrations of the neighboring hydrogens at the 5- and 6-positions. A new peak which was absent in 1 appeared at 1003 cm^{-1} and is due to the corresponding in-plane deformation. The band at 1130 cm^{-1} due to C–Cl stretching disappeared upon polymerization, indicating that the interphenylene bondings are formed at the 1- and 4-positions of the benzene rings.[18] The band at 1470 cm^{-1} is assigned to the C–C stretching of the benzene ring.

The molecular weight of 2 was determined by GPC analysis. Figure 3 shows GPC traces of polymers from recrystallized and as-received monomers. The degree of polymerization was as high as 10^2. When polymerization was carried out at 80 °C using recrystallized monomer, the degree of polymerization was 90 (Figure 3a). When the as-received monomer was polymerized at low temperature (30 °C), the resulting polymer had a bimodal molecular weight distribution as previously reported (Figure 3b).[17] When the recrystallized monomer was used, the molecular weight distribution was monomodal even at the lower temperature (Figure 3c). Comparing Figure 3c with Figure 3a, the molecular weight was lower but the molecular weight distribution was narrower at a lower temperature (30 °C) than at a higher temperature (80 °C). The molecular weight and yield increased with the increase in polymerization time. The addition of potassium iodide increased neither yield nor molecular weight.

The UV–vis absorption spectrum of 2 is presented in Figure 4a. A film on a quartz plate showed two peaks at 220 and 322 nm.

TGA indicates that 2 is highly stable. It showed no weight loss up to 420 °C under air and nitrogen.

Properties of 3. The IR spectrum of 3 is presented in Figure 2b. The aliphatic bands at 2800–3000 cm^{-1} disappeared upon hydrolysis. The carbonyl and C–O bands remained at almost the same positions as before the hydrolysis.

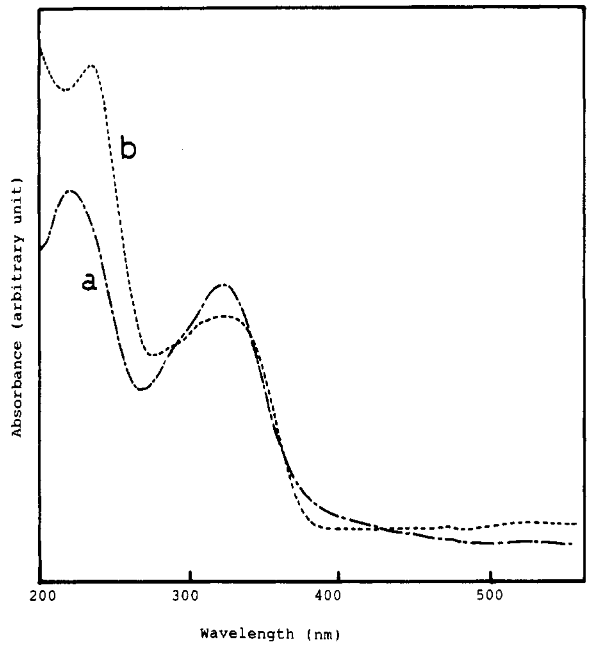

Figure 4. UV–visible spectra: (a) poly[2-(methoxycarbonyl)-phenylene-1,4-diyl]; (b) poly(2-carboxyphenylene-1,4-diyl).

While 3 was insoluble in hydrocarbon solvents, it is soluble in aqueous sodium hydroxide as well as such basic solvents as pyridine and quinoline. Thus, a film could be cast from a solution in these solvents.

A film of 3 was made by casting its pyridine solution on a quartz plate. Its UV–vis absorption spectrum is presented in Figure 4b. The film showed two peaks at 233 and 322 nm.

In TGA analysis, 3 showed a 22% weight loss up to 420 °C instead of 36.66% for complete decarboxylation, indicating that heating alone is insufficient to produce PPP.

Preparation of PPP. The conversion of 3 into PPP was effected by copper catalysts such as copper(II) oxide, copper(I) oxide, basic copper(II) carbonate, and copper powder. Figure 5d shows the IR spectrum of PPP prepared by copper(II) oxide. The weight ratio of polymer 3 to copper(II) oxide was 7:1. A very strong peak occurred at 800 cm^{-1}, due to the C–H out-of-plane deformation of 1,4-disubstituted benzene. The peak at 1033 cm^{-1} is due to the corresponding in-plane deformation. The peaks at 1478 and 1403 cm^{-1} are due to the ring stretching. The

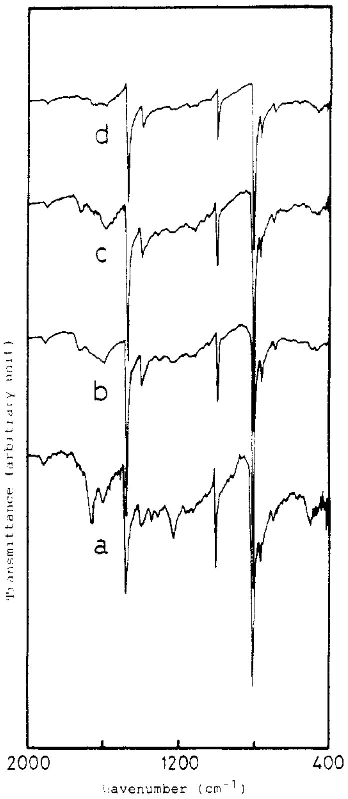

Figure 5. FT-IR spectra of PPP. Catalyst: (a) copper powder, (b) Cu_2O, (c) basic $CuCO_3$, (d) CuO. Ratio = 7:1.

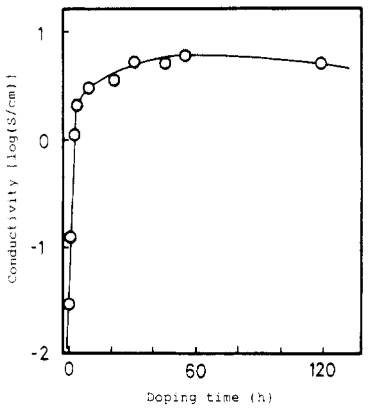

Figure 6. Change in conductivity of a PPP pellet during doping. PPP was prepared in the presence of CuO. Dopant, SbF_5.

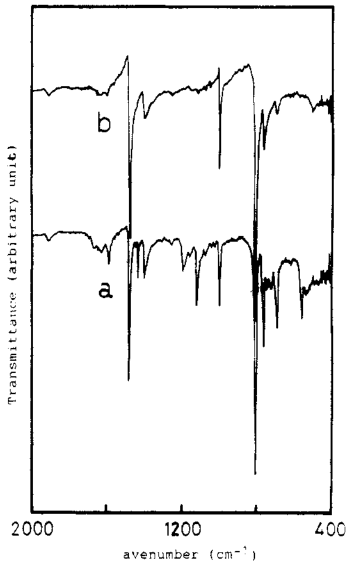

Figure 7. FT-IR spectra of PPP prepared by other methods: (a) PPP prepared by the direct coupling of dibromobenzene in the present procedure; (b) PPP prepared by Kovacic's method.

Table III. Comparison of IR Spectra of Poly(*p*-phenylene)s

PPP	ratio A/B^a	PPP	ratio A/B^a
present	6.43	Grignard	1.92–3.85
Kovacic	4.55		

[a] A = intensity at 800 cm^{-1} for the *p*-phenylene unit. B = (intensity at 770 cm^{-1} + intensity at 690 cm^{-1}) for monosubstituted benzene termini.

peaks at 774 and 690 cm^{-1} are due to the monosubstituted phenyl ring termini. No other IR peaks are apparent. No apparent carbonyl peaks occurred between 1600 and 1650 cm^{-1}. No peak due to C–O stretching was found at 1225 cm^{-1}. The peak at 825 cm^{-1} due to the isolated hydrogen atom at the 3-position which was observed in the IR spectrum of Figure 2b disappeared with decarboxylation. These findings indicate that the present PPP has a highly regular structure.

Figure 5a shows the IR spectrum of PPP prepared by using copper powder in a 7:1 ratio. The two medium peaks occurred at 1600 and 1650 cm^{-1} due to the carbonyl group and a medium peak occurred at 1225 cm^{-1} due to the C–O stretching, indicating that partial decarboxylation took place. Two small additional peaks also occurred at 1308 and 1340 cm^{-1}.

Figure 5c shows that the decarboxylation by basic copper(II) carbonate is almost complete. The peaks around 1600 cm^{-1} can be attributed to the overtone vibration of water in a potassium bromide disk. The slight peak at 1225 cm^{-1} in Figure 5b indicates that a trace amount of C–O bonding remained after decarboxylation by copper(I) oxide.

The decarboxylation of **3** in quinoline did not take place using other catalysts such as silver(I) oxide and carbonate. An attempt at decarboxylation with copper(II) oxide was unsuccessful in pyridine, triethylamine, trioctylamine, dimethylaniline, piperidine, and 2-phenylquinoline.

Figure 6 shows the change of the electrical conductivity of PPP during doping with antimony pentafluoride vapor. The conductivity increased to 6 S cm^{-1} at 1 h. When the temperature was raised to 70 °C after 2 h, the conductivity increased to 18 S cm^{-1}. The conductivity of PPP is strongly dependent on dopants, and so this value should be compared with the previously reported conductivity of antimony pentafluoride-doped PPP. The conductivities of an electrochemically prepared PPP film and chemically prepared PPP pellet are 6×10^{-4} and 4×10^{-2} S cm^{-1}, respectively.[6,10] Taking these facts into account, the present polymer is highly conducting, consistent with it having a regular structure.

Discussion

Figure 7 shows IR spectra of PPP's prepared by Kovacic's method and by the direct coupling of dibromobenzene in the present procedure. The PPP prepared by Kovacic's method possessed an IR spectrum almost identical to the spectrum in Figure 5d, consistent with it having a regular structure. However, several extra peaks apparently occurred at 724, 756, 1130, 1212, 1428, and 1612 cm^{-1} in Figure 7a, indicating that the direct coupling of dihalobenzene gives a structurally irregular PPP, probably due to the formation of meta-linkage and polynuclear defects. The ratio of peaks at 800 cm^{-1} to peaks at 700 and 690 cm^{-1} was shown to be a measure of the molecular weight of PPP.[4] The ratio for a few polymers is summarized in Table III. The ratio for the present PPP is higher than that for the PPP by Kovacic's method and Grignard coupling. These findings indicate that the introduction of the methoxycarbonyl group into the monomer leads to high quality of the eventual PPP. This effect can be attributed to activation of the halogen atoms on the benzene ring and to the enhanced solubility of the polymer produced.

Pyrolytic decarboxylation was not possible for the decarboxylation of 3 as shown from TGA measurement. Pyrolysis of PPP containing two neighboring carboxyl groups gave the corresponding anhydride.[19] Thus, a copper catalyst is inevitable for the decarboxylation of 3. Quinoline is also necessary as a solvent for the decarboxylation. In spite of these limitations, the present procedure is applicable to the preparation of a variety of substituted polymers.

During the current investigation, a modified precursor procedure has been published.[20,21] In this procedure, the dihydrocatecol ester was polymerized with a transition-metal catalyst instead of a radical initiator.[12] The catalyst gave exclusively the 1,4-addition polymerization product which leads to a highly regular PPP. Its degree of polymerization was as high as 150. However, the starting material is prepared by biooxidation of benzene with genetically modified bacteria.

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