

NOTES

Synthesis of Poly(4-substituted-*m*-phenylene)s by Nickel-Catalyzed Coupling Polymerization of *m*-Dichlorobenzene Derivatives

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Polyphenylene, which is the simplest of the aromatic ring systems has been expected as a candidate for high strength, high temperature, and conducting polymers. A large number of preparative methods have been found to yield polyphenylene.¹ Oxidative coupling of benzene in the presence of Lewis acids and oxidants (Kovacic method), the Wurtz–Fittig reaction between dichlorobenzene and metallic sodium, and polymerization of dibromobenzene in the presence of magnesium using a nickel catalyst (Yamamoto method) as a direct route, and polymerization of 1,3-cyclohexadiene followed by dehydrogenation as an indirect route are typical examples. The direct method generally gives low yields and low molecular weights due to the low solubility of polyphenylene in solvents.

The major drawback like this has been overcome by the polymerization of alkyl-substituted monomers, the resulting polymers being soluble in common organic solvents.

To remedy the serious solubility problem, it is effective to introduce the flexible side chains on the aromatic nuclei. Recently, Wegner *et al.* reported on the synthesis of alkyl-substituted poly(*p*-phenylene)s with a number-average molecular weights of $\bar{M}_n = 21000$ by polymerization of Pd-catalyzed polymerization of bisboronic benzene-oligomers.²

Transition metal catalyzed coupling reactions are an attractive method for the synthesis of aromatic polymers, many of which are inaccessible by other routes, and have consequently attracted increasing interest in recent years.³

In previous articles, we reported a successful synthesis of poly(phenylene ether ketone)s,⁴ poly(phenylene ether sulfone)s,⁵ and poly(3-phenyl-2,5-thiophene)⁶ by the nickel catalyzed coupling polymerization of aromatic dichlorides. Continuing our investigations on the versatility of this method, we now report a successful synthesis of poly(4-substituted-*m*-phenylene) by nickel-catalyzed coupling of 4-substituted-*m*-dichlorobenzenes.

EXPERIMENTAL

Materials

Reagent grade anhydrous NiCl₂ was dried at 220°C under vacuum. Triphenylphosphine (PPh₃) was purified by recrystallization from hexane. Powdered (400 mesh) zinc was purified by stirring with acetic acid, filtering, washing thoroughly with ethyl ether, and drying under vacuum. All solvents such as *N,N*-dimethylacetamide (DMAc), *N*-methyl-2-pyrrolidone (NMP), and *N,N*-dimethylformamide (DMF) were stirred over powdered calcium hydride

overnight, then distilled under reduced pressure, and stored over 4-Å molecular sieves. *m*-Dichlorobenzene (**1a**), 2,4-dichlorotoluene (**1b**) and 2,4-dichloroacetophenone (**1c**) were purified by vacuum distillation. 2,4-Dichlorobenzaldehyde (**1d**) was recrystallized from petroleum ether.

2,4-Dichlorobenzophenone (1e). In a 300 ml three-necked flask equipped with a mechanical stirrer and a reflux condenser with a calcium chloride drying tube were placed 2,4-dichlorobenzoyl chloride (20 g, 0.096 mol) and benzene (100 ml). The flask was immersed in an ice bath, and anhydrous aluminium chloride (15.4 g, 0.1 mol) was added over a period of 30 min. The ice bath was removed after addition of aluminium chloride, and the mixture was stirred for 30 min at room temperature, and then for 3 h at 50°C. The benzene was distilled off under reduced pressure, and the residue was poured into a mixture of ice and 2 M hydrochloric acid. The solution was extracted with ether. The ether solution was washed successively with 5% aqueous sodium hydrogencarbonate, and then with water. After drying (MgSO₄) and evaporation of the ether, the product was crystallized from petroleum ether to give white crystals. The yield was 16.9 g (70%). mp 49–50°C (lit.⁷ 52°C). IR (NaCl): ν 1675 cm⁻¹ (C=O).

2,4-Dichloropropiophenone (1f). This compound was prepared from *m*-dichlorobenzene (7.35 g, 50 mmol) and propionyl chloride (5 ml, 55 mmol) as described above. bp 144–145°C/4–5 mmHg. Yield: 10.1 g (50%). IR (KBr): ν 1700 cm⁻¹ (C=O). ¹H NMR (CDCl₃): δ (ppm) 1.2 (t, methyl, 3H), 2.9 (q, methylene, 2H), 7.1–7.5 (m, phenyl, 3H). *Anal.* Calcd for C₉H₈OCl₂: C, 53.23%; H, 3.97%. Found: C, 52.99%; H, 4.00%.

2,4-Dichlorovalerophenone (1g). This compound was prepared from *m*-dichlorobenzene (8.8 g, 60 mmol) and valeroyl chloride (3.6 g, 30 mmol) in the presence of FeCl₃ (8.0 g, 60 mmol) at 80°C for 12 h. bp 118–120°C/4–5

mmHg. Yield: 3.1 g (45%). IR (NaCl): ν 1700 cm⁻¹ (C=O). ¹H NMR (CDCl₃): δ (ppm) 0.9 (t, methyl, 3H), 1.4 (m, methylene, 2H), 1.7 (m, methylene, 2H), 2.9 (t, methylene, 2H), 7.3–7.5 (m, phenyl, 3H). *Anal.* Calcd for C₁₁H₁₂OCl₂: C, 57.17%; H, 5.23%. Found: C, 57.61%; H, 5.44%.

Polymer Synthesis. A typical example of the polymerization is as follows.

Polymer (2c) from (1c). In a 25 ml two-necked round bottomed flask were placed NiCl₂ (9.14 mg, 0.071 mmol), PPh₃ (0.221 g, 0.85 mmol), bipyridine (bpy) (11 mg, 0.071 mmol), and zinc (0.286 g, 4.37 mmol). The flask was evacuated and filled with nitrogen three times. Then, dry DMAc (0.8 ml) was added *via* syringe through the serum cap. The mixture was stirred at 85°C. After the red-brown catalyst had formed, monomer **1c** (0.2 ml, 1.4 mmol) was added *via* syringe to the reaction mixture. The reaction was conducted at 85°C for 3 h. The resulting viscous mixture was diluted with NMP (2 ml) and poured into a large amount of HCl-methanol (1:9). The polymer was collected, washed with methanol and dried *in vacuo* at 80°C for 24 h. The yield was 0.165 g (100%). The inherent viscosity of the polymer in NMP was 0.56 dl g⁻¹, measured at a concentration of 0.5 g dl⁻¹ at 30°C. IR (film): 1690 cm⁻¹. *Anal.* Calcd for (C₈H₆O)_n: C, 81.34%; H, 5.12%. Found: C, 81.28%; H, 5.04%.

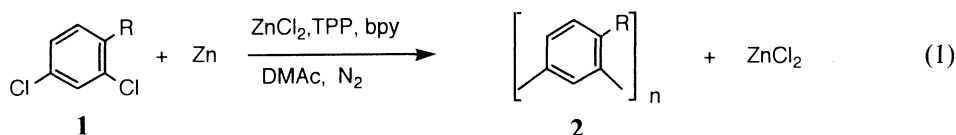
Measurement

The infrared spectra were recorded on a Hitachi I-5020 FT-IR spectrometer, and the NMR spectra on a Hitach R-22 (90 MHz), and a JEOL GX 500 (500 MHz) spectrometers. 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 of 10°C min⁻¹ for thermogravimetry (TGA). The glass transition temperature was measured on a Seiko SSS 5000 differential scanning calorimetry (DSC) at a heating rate of

10°C 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 40°C in tetrahydrofuran (THF).

RESULTS AND DISCUSSION

Based on the results on the successful



R: nil (**1a**), CH₃ (**1b**), CH₃CO (**1c**)
CHO (**1d**), C₆H₅CO (**1e**)

The polycondensation of these monomers was carried out with 1 mmol of monomer in DMAc in the presence of zinc, triphenylphosphine (TPP), and bipyridine (bpy) at 90°C for 2.5 h. The results are shown in Table I. The polymerizations proceeded smoothly and gave the corresponding poly(*m*-phenylene) (**2**) in excellent yields. However, poly(*m*-phenylene) (**2a**) and poly(4-formyl-*m*-phenylene) (**2d**) were insoluble in all solvents including sulfuric acid and methansulfonic acid. Among them polymerization of **1c** gave relatively good results. To determine optimum conditions for polymerization, the following factors that influence on the polymerization of **1c** were studied: amount of catalyst, ligand and zinc, and reaction temperature.

First, the effect of reaction temperature on the inherent viscosity of the resulting polymer was examined between 70 and 95°C. The polymerization was found to be highly dependent on temperature and the highest viscosity was attained at 85°C. Polymerization did not start at 70°C and raising temperature to 95°C gave a gel polymer. This phenomenon would be explained by the Aldol condensation

synthesis of poly(phenylene ether ketone)s by the nickel-catalyzed coupling of aromatic dichlorides,⁴ preliminary experiments using five derivatives of *m*-dichlorobenzenes, such as *m*-dichlorobenzene (**1a**), 2,4-dichlorotoluene (**1b**), 2,4-dichloroacetophenone (**1c**), 2,4-dichlorobenzaldehyde (**1d**), and 2,4-dichlorobenzophenone (**1e**), were performed to determine which monomers were suitable for polymer-formation (eq 1).

Table I. Preparation of poly(4-substituted-*m*-phenylene)^a

Monomer	Polymer	
	Yield/%	$\eta_{\text{inh}}^{\text{b}}/\text{dl g}^{-1}$
1a	94	— ^c
1b	91	0.06
1c	100	0.14
1d	77	— ^c
1e	100	0.09

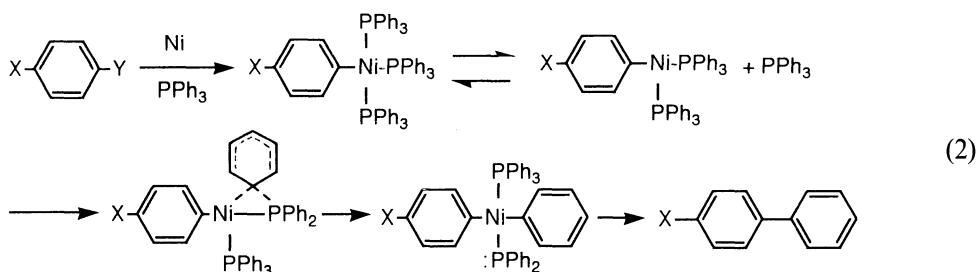
^a Reaction conditions: monomer (1.0 mmol), NiCl₂ (0.05 mmol), TPP (0.3 mmol), Zn (3.1 mmol), bpy (0.05 mmol), DMAc (0.8 ml), 90°C, 2.5 h.

^b Measured at a concentration of 0.5 g dl⁻¹ in NMP at 30°C.

^c Insoluble in all organic solvents.

between two acetyl groups in the presence of zinc chloride formed. These results are summarized in Table II.

One of the main side reactions in the nickel-catalyzed coupling of aryl chlorides is the transfer of aryl groups from triphenylphosphine to metal (eq 2).⁸ This side reaction is suppressed by using bipyridine and excess amounts of triphenylphosphine to NiCl₂.⁹

**Table II.** Effect of reaction temperature on polymerization of **1c**^a

Temperature (°C)	Polymer	
	Yield/%	η_{inh}^b /dl g ⁻¹
70	—	—
80	100	0.22
85	100	0.56
90	100	0.43
95	100	— ^c

^a Reaction conditions: monomer (1.4 mmol), NiCl₂ (0.071 mmol), TPP (0.85 mmol), Zn (4.3 mmol), bpy (0.071 mmol), DMAc (0.8 ml), 3 h.

^b Measured at a concentration of 0.5 g dl⁻¹ in NMP at 30°C.

^c A gel polymer.

Table III. Effect of amount of triphenylphosphine on polymerization of **1c**^a

Reaction conditions	Polymer	
	Yield/%	η_{inh}^b /dl g ⁻¹
Molar ratio of TPP/NiCl ₂		
4	100	— ^c
8	100	— ^c
12	100	0.56
16	100	0.21
20	100	0.19
28	100	0.12

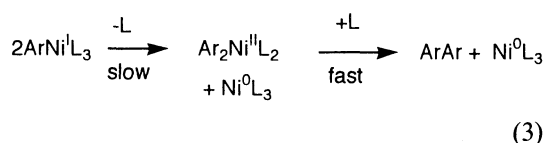
^a Reaction conditions: monomer (1.4 mmol), NiCl₂ (0.071 mmol), Zn (4.3 mmol), bpy (0.071 mmol), DMAc (0.8 ml), 85°C, 3 h.

^b Measured at a concentration of 0.5 g dl⁻¹ in NMP at 30°C.

^c A gel polymer.

Furthermore, the coupling rate of arylchloride increases when the PPh₃ to NiCl₂ ratio is increased from 3 to 6 but levels off rapidly at higher ratios.⁹ The effect of amount of PPh₃ on the polymerization of **1c** is shown in Table III. A gel polymer was obtained in the presence of a little excess amounts of PPh₃. The reason for the gelation is not clear. The 12-fold molar quantity was required to obtain higher molecular weights of polymer. These results are quite similar to those for the synthesis of poly(ether-sulfone)s and poly(thiophene).

With consideration of the coupling mechanism in which the disproportionation of the arylnickel species I is very slow (eq 3),⁹ a minimum ratio of Ni catalyst and monomer that minimizes the formation of the arylnickel species I, is preferable to obtain higher molecular weights of polymer (eq 3).



The effect of amount of catalyst on the polymerization of **1c** is summarized in Table IV. The inherent viscosity of the polymer reached its highest value with 5 mol% of catalyst based on the monomer.

As the rate-determining step was reported to be a reduction process involving nickel and zinc metal in the presence of excess aryl chloride,⁹ the effect of the ratio of zinc to nickel catalyst on the polymerization was investigated. As shown in Table V, a large excess of zinc was required to obtain higher molecular weights of polymer.

Table IV. Effect of amount of catalyst on polymerization of **1c**^a

Reaction conditions	Polymer	
	Yield/%	η_{inh}^b /dl g ⁻¹
Cat. (NiCl ₂ /bpy = 1) mol%		
3	100	0.32
4	100	0.48
5	100	0.56
6	100	0.33
7	97	0.30

^a Reaction conditions: monomer (1.4 mmol), TPP (0.85 mmol), Zn (4.3 mmol), DMAc (0.8 ml), 85°C, 3 h.

^b Measured at a concentration of 0.5 g dl⁻¹ in NMP at 30°C.

Table V. Effect of amount of zinc on polymerization of **1c**^a

Reaction conditions	Polymer	
	Yield/%	η_{inh}^b /dl g ⁻¹
Molar ratio of Zinc/NiCl ₂		
40	100	0.17
62	100	0.56
80	100	0.38

^a Reaction conditions: monomer (1.4 mmol), NiCl₂ (0.071 mmol), TPP (0.85 mmol), bpy (0.071 mmol), Zn (0.43 mmol), DMAc (0.8 ml), 85°C, 3 h.

^b Measured at a concentration of 0.5 g dl⁻¹ in NMP at 30°C.

Based on these results, various poly(4-acyl-*m*-phenylene)s were prepared from monomers **1** under optimum reaction conditions. The results from the various studies are summarized in Table VI. Poly(*m*-phenylene)s **2** with inherent viscosities up to 0.56 dl g⁻¹ could be obtained. Bulky ortho substituents seem to prevent the formation of polymer with high molecular weights.

Polymer Characterization

Polymers were defined as the corresponding poly(*m*-phenylene)s by means of infrared spectroscopy and elemental analysis. The IR spectra exhibited characteristic absorptions at around 1690 and 1595 cm⁻¹ due to the C=O and C=C stretching, respectively. Elemental

Table VI. Preparation of poly(4-substituted-*m*-phenylene) **2**^a

Monomer	Polymer		
	Type	Yield/%	η_{inh}^b /dl g ⁻¹
1b	2b	99	0.19
1c	2c	100	0.56
1e	2e	100	0.13
1f	2f	100	0.10
1g	2g	100	0.09

^a Reaction conditions: monomer (1.4 mmol), NiCl₂ (0.071 mmol), TPP (0.85 mmol), bpy (0.071 mmol), DMAc (0.8 ml), 85°C, 3 h.

^b Measured at a concentration of 0.5 g dl⁻¹ in NMR at 30°C.

analyses also supported the formation of the expected polymers.

The microstructure of the polymers was revealed by ¹³C NMR. The ¹³C NMR spectrum of polymer **2b** is shown in Figure 1 together with assignments of the observed resonances. Considering triads of monomer units, illustrated in Chart 1, polymerization of non-symmetric monomer **1b** will be expected to give the four regio-selective polymers listed. Therefore, if a random polymer is obtained, 24 peaks in the aromatic region would be expected to appear for the polymer **2b**. Indeed, 22 well-resolved peaks can be observed. It can be assumed that the difference in the chemical shifts in the aromatic region is so small that two sets of peaks are overlapped.

On the other hand, the ¹³C NMR spectrum of polymer **2c** is shown in Figure 2 together with assignments of the observed resonances. The 8 major peaks of polymer **2c** can be assigned in accordance with the calculated chemical shifts for polymer **2c**. However, additional minor peaks can be also detected in the aromatic, carbonyl and methyl regions. Therefore, we have to consider additional irregularity of the structure. However, the intensity of these additional peaks is so small that we consider the polymer to consist of head-to-head and tail-to tail coupling as a

Peaks	a	b	c	d	e	f	g
Observed value	134.6	141.8	129.3	139.3	127.0	131.7	20.2
	134.1	141.2	128.6	139.1	126.9	130.5	
	133.7	141.0	128.2	138.2	126.7	130.0	
			127.7	138.0	125.4	129.6	
Calculated value	135.1	142.7	126.2	139.1	126.1	130.0	

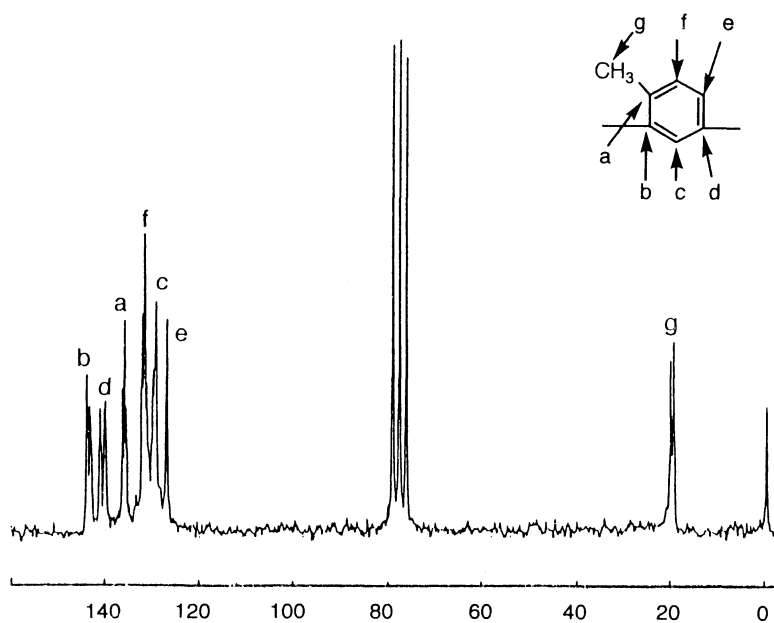


Figure 1. ^{13}C NMR spectrum of polymer **2b** in CDCl_3 .

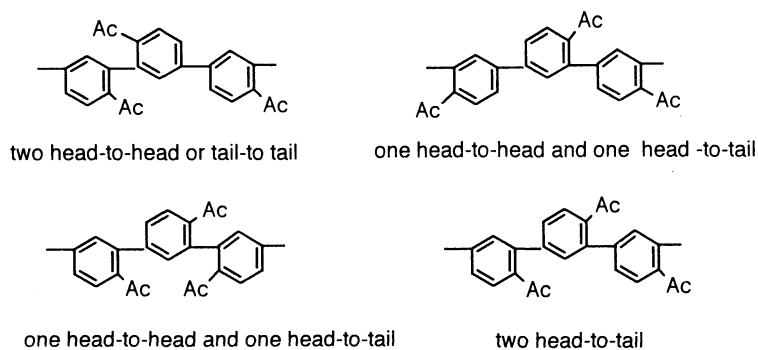


Chart 1.

Poly(*m*-phenylene)

Peaks	a	b	c	d	e	f	g	h
Observed value	139.2	139.5	128.5	143.4	128.9	130.9	202.7	30.4
Calculated value	135.2	142.2	126.2	146.5	126.2	129.5	195.7	25.0

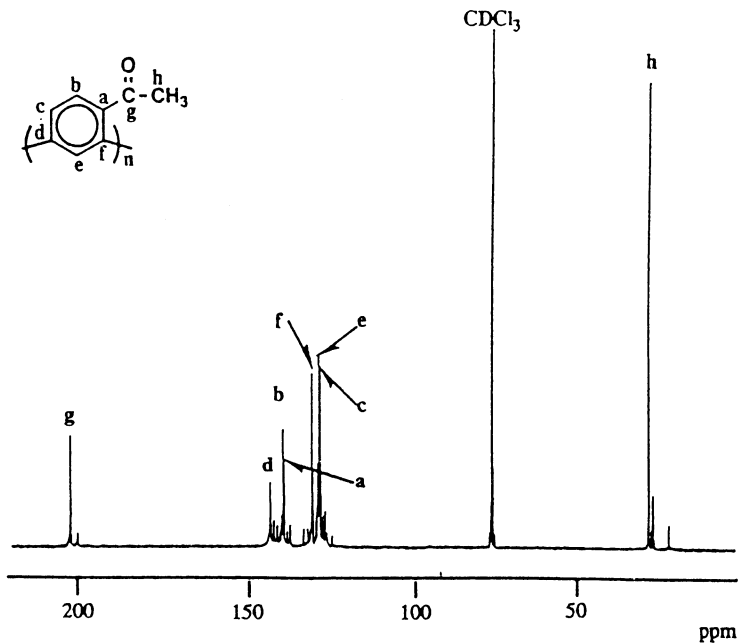


Figure 2. ^{13}C NMR spectrum of polymer **2c** in CDCl_3 .

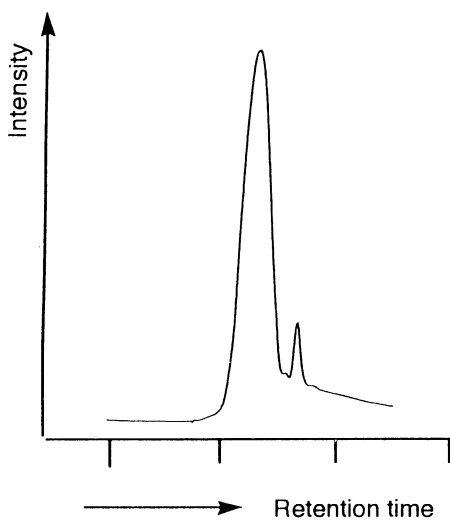


Figure 3. Gel permeation chromatogram of polymer **2c** ($\eta = 0.52 \text{ dl g}^{-1}$).

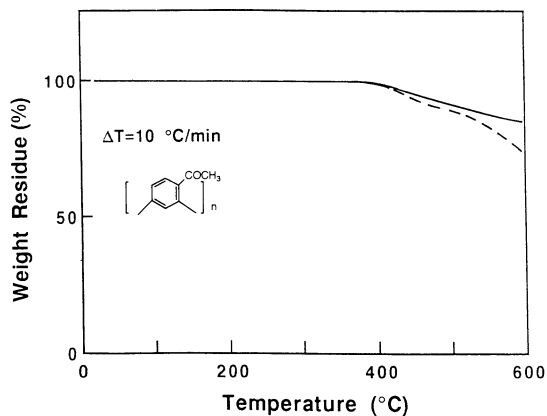


Figure 4. TG curves of polymer **2c** in air (---) and in nitrogen (—).

major structure because of steric hindrance.

The poly(*m*-phenylene)s were white solids, soluble in dipolar aprotic solvents, such as NMP, DMAc, DMF, DMSO, and THF. A film, cast from the solution of polymer **2c** in THF, shows a high degree of toughness.

The molecular weight of polymer **2c** having inherent viscosity of 0.56 dl g⁻¹ was determined by GPC. A typical chromatogram is shown in Figure 3. A bimodal molecular weight distribution was observed. The minor peak 2 is oligomer. The major peak 1 indicated that relative \bar{M}_n and \bar{M}_w values were 25000 and 56000, respectively, for standard polystyrene, and \bar{M}_w/\bar{M}_n was 2.2.

The thermal stability of the polymer was examined by thermogravimetry (TG). A typical trace for polymer **2c** is shown in Figure 4. The polymer showed a 10% weight loss at 480°C in air and at 490°C in nitrogen. Differential scanning calorimetry on powder showed clear endotherms at 215°C, which reflected the glass transition temperature. A melting point for **2c** was not observed, in agreement with X-ray diffraction pattern of **2c**, which showed very little crystalline structure.

In summary, our studies indicate that poly(4-substituted-*m*-phenylene)s with relatively high molecular weights can be prepared by nickel-catalyzed coupling polymerization of 4-substituted-*m*-dichlorobenzenes. The structure of the polymers obtained seems to involve

random linkages.

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