Synthesis of Functional Poly(*p*-phenylene)s from Substituted Hydroquinones via Nickel-Catalyzed Coupling of Their Bistriflates

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ABSTRACT: This paper describes a novel method for the synthesis of soluble polyphenylenes, which consists of the Ni(0)-catalyzed homocoupling reaction of bis[[(trifluoromethyl)sulfonyl]oxy] derivatives of substituted hydroquinones, and compares it with the synthesis of the same polymers by the Ni(0)-catalyzed polymerization of the corresponding benzene derivatives having two bromine or chlorine leaving groups. The following monomers were synthesized and polymerized: 2,5-dichlorobiphenyl (**3**), 2,5-dibromobiphenyl (**4**), 2,5-bis[[(trifluoromethyl)sulfonyl]oxy]biphenyl (**8**), methyl 2,5-dichlorobenzoate (**11**), methyl 2,5-dibromobenzoate (**12**), methyl 2,5-bis[[(trifluoromethyl)sulfonyl]oxy]benzoate (**9**), and 2-*tert*-butyl-1,4-bis[[(trifluoromethyl)sulfonyl]oxy]benzene (**10**). The Ni(0) catalyst was prepared in situ according to two different methods using DMF and THF as solvent, respectively. Soluble substituted polyphenylenes with number-average molecular weights of up to 6300 were obtained.

Introduction

Polyphenylenes represent the simplest aromatic polymers containing only carbon and hydrogen and, therefore, can be considered the aromatic homologue of polyethylene. However, while polyethylene represents the model for fundamental investigations on crystallization and morphology,[1] polyphenylene still is only a synthetic target for polymer chemists. Since the parent poly(*p*-phenylene) is highly crystalline and insoluble, our ability to control its synthesis is very limited.

The improvement of the solubility of poly(*p*-phenylene) has been attempted by attaching lateral substituents.[2] Soluble high molecular weight phenylated poly(*p*-phenylene)s were synthesized by the Diels-Alder reaction of bis(tetracyclone)s with *p*- or *m*-diethynylbenzene[3a-c] and of the bibenzynes with bis(tetracyclone)s.[3d] Additional classes of soluble poly(*p*-phenylene)s were obtained by the polymerization of 2,5-dibromo-1,4-di-*n*-alkylbenzenes[4a] and 2,5-dibromobiphenyl[4b] using the Yamamoto reaction, Pd(0)-catalyzed polymerization of 4-bromo-2,5-di-*n*-hexylbenzeneboronic acid,[4c,d] anionic polymerization of 2-phenyl-1,3-cyclohexadiene followed by aromatization,[4b] and spontaneous polymerization of 1-bromo-4-lithiobenzene in hexamethylphosphoramide.[4e] The polymer resulted from 1-bromo-4-lithiobenzene is soluble because it contains both para and meta linkages.[4e]

Highly branched polyphenylenes can be synthesized by cocyclotrimerization of *p*-diethynylbenzene with phenylacetylene[5] and by Pd(0)-catalyzed homocoupling of (3,5-dibromophenyl)boronic acid and are also soluble.[6]

Soluble polyarylenes containing binaphthylene structural units were recently synthesized by cation-radical polymerization of bis(1-naphthyl)biphenyls.[7] The bulky and twisted binaphthylene structural unit is most likely responsible for the solubility of the resulting polymers.

Recently we have communicated preliminary results which demonstrated a novel synthesis of soluble poly(*p*-phenylene)s by Ni(0)-catalyzed homocoupling reaction of substituted phenylenebistriflates.[8] This novel polymerization reaction provides access to the synthesis of a large variety of substituted polyphenylenes starting from hydroquinones. The goal of this paper is to describe the synthesis and Ni(0)-catalyzed polymerization of 2,5-dichlorobiphenyl (**3**), 2,5-dibromobiphenyl (**4**), 2,5-bis[[(trifluoromethyl)sulfonyl]oxy]biphenyl (**8**), methyl 2,5-dichlorobenzoate (**11**), methyl 2,5-dibromobenzoate (**12**), methyl 2,5-bis[[(trifluoromethyl)sulfonyl]oxy]benzoate (**9**), and 2-*tert*-butyl-1,4-bis[[(trifluoromethyl)sulfonyl]oxy]benzene (**10**). These experiments will compare the polymerizability of monomers containing chloride, bromide, and triflate leaving groups in Ni(0)-catalyzed homocoupling polymerization reactions.

Experimental Section

Materials. 2,5-Dichloroaniline (99%), 2,5-dibromoaniline (98%), 2,5-dihydroxybenzoic acid (99%), trifluoromethanesulfonic anhydride (triflic anhydride), nickel(II) chloride (anhydrous, 99%), triphenylphosphine (99%), 2,2′-dipyridyl (99+%), tetraethylammonium iodide (98%) (all from Aldrich), sodium nitrite (J. T. Baker Chemical, 99.7%), sodium acetate (Matheson Coleman & Bell, 99%), and 2,5-dibromobenzoic acid (Lancaster, 98+%) were used as received. Phenylhydroquinone (Aldrich, 97%) was recrystallized from a mixture of hexanes and toluene (volume ratio = 2/1). *tert*-Butylhydroquinone (Aldrich, 97%) was recrystallized twice from toluene. Pyridine was dried over CaH_2 and distilled. DMF was dried over CaH_2 and vacuum distilled. THF was distilled over sodium benzophenone. Methyl 2,5-dichlorobenzoate (Aldrich, 99%) was purified by column chromatography on silica gel using a mixture of toluene and hexanes (volume ratio = 1/2) as eluent. Purity (HPLC) was >99.9%. Zinc dust (Fluka) was stirred in acetic acid, washed with water, and dried in vacuo at 120 °C. $Ni(Ph_3P)_2Cl_2$ was prepared according to a literature procedure.[9]

Techniques. ^1H NMR (200 MHz) spectra were recorded on a Varian XL-200 spectrometer. All spectra were recorded in $CDCl_3$ with TMS as internal standard. Relative molecular weights were determined by gel permeation chromatography. Gel permeation chromatography (GPC) measurements were performed on a Perkin-Elmer Series 10LC instrument equipped with an LC-100 column oven and a Nelson Analytical 900 Series data station. The measurements were made using a UV detector set at 254 nm, chloroform as solvent (1 mL/min, 40 °C), a set of PL gel columns (500 and 10 000 Å), and a calibration plot constructed with polystyrene standards (Supelco). Purity was similarly determined by high-performance liquid chromatography (HPLC)/GPC using a 100-Å PL gel column. A Perkin-Elmer DSC-4 differential scanning calorimeter equipped with a TADS 3600 data station was used to determine the glass transition temperatures of the polymers at a heating rate of 20 °C/min. The glass transition temperatures were read at the middle of the change in the heat capacity of the second heating scan.

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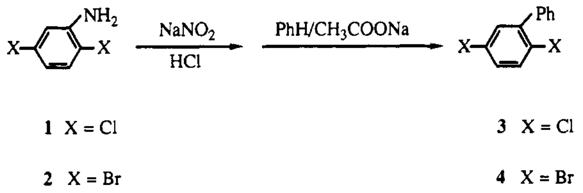
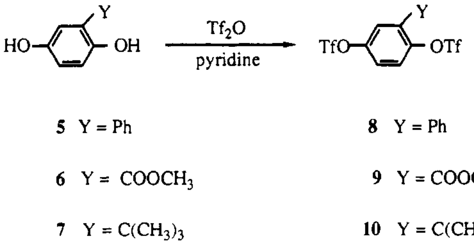
Scheme I
Synthesis of 2,5-Dichlorobiphenyl and 2,5-Dibromobiphenyl



Scheme II
Synthesis of 2,5-Bis[[(trifluoromethyl)sulfonyl]oxy]biphenyl, Methyl 2,5-Bis[[(trifluoromethyl)sulfonyl]oxy]benzoate, and 2-*tert*-Butyl-1,4-bis[[(trifluoromethyl)sulfonyl]oxy]benzene



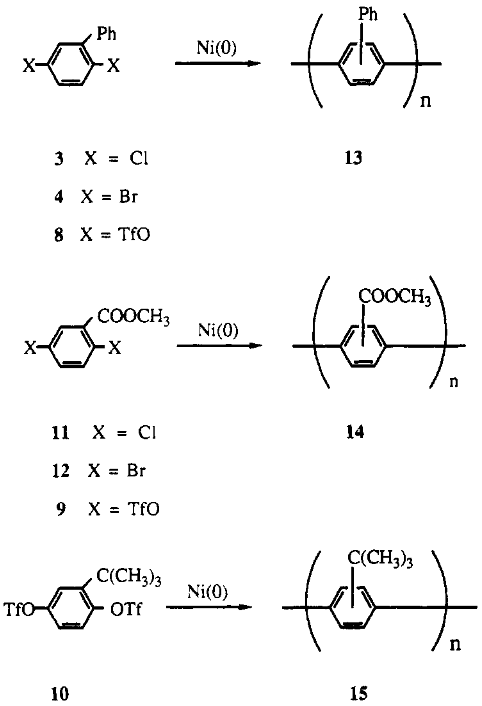
Synthesis of Monomers. The synthesis of monomers is outlined in Schemes I and II. 2,5-Dichlorobiphenyl (**3**) and 2,5-dibromobiphenyl (**4**) were synthesized by phenylation[10] of the diazonium salts derived from 2,5-dichloroaniline and 2,5-dibromoaniline, respectively. 2,5-Bis[[(trifluoromethyl)sulfonyl]oxy]biphenyl (**8**), 2-*tert*-butyl-1,4-bis[[(trifluoromethyl)sulfonyl]oxy]benzene (**10**), and methyl 2,5-bis[[(trifluoromethyl)sulfonyl]oxy]benzoate (**9**) were synthesized by the triflation of the corresponding dihydroxy compounds in pyridine.[11]

(a) 2,5-Dichlorobiphenyl (3). 2,5-Dichloroaniline (**1**) (16.20 g, 0.100 mol) was mixed with water (10 mL) and concentrated HCl (16 mL) and heated at 100 °C with stirring to form its hydrochloride. The mixture was cooled in an ice/water bath. To the cooled mixture was added dropwise in the course of 30 min a cold aqueous solution of $NaNO_2$ (7.40 g, 0.107 mol in 35 mL of water). During this time, the temperature was maintained at 0–5 °C. The resulting yellow suspension was poured into cold benzene (200 mL, about 10 °C), and then the mixture was vigorously stirred. A cold aqueous solution of CH_3COONa (32.0 g, 0.390 mol in 80 mL of water) was slowly added. The mixture was gradually warmed to room temperature without external heating over 2 h, and stirring was continued for 48 h. The mixture was extracted with benzene four times, and the extract was washed with water, twice with 10% HCl, water, twice with 10% KOH aqueous solution, and twice with water and dried over anhydrous $MgSO_4$. The solvent was removed on a rotary evaporator, and the oily residue was purified by flash column chromatography on silica gel using hexanes as eluent. The crude product was vacuum distilled, and a colorless liquid was obtained. The yield was 9.266 g (41.5%): bp 105–109 °C/0.35 mmHg (lit.[12] 95–98 °C/0.01 mmHg); purity (HPLC) 99.0%; ^1H NMR ($CDCl_3$) δ 7.23 (dd, 1 H, J = 8, 2.5 Hz, 4-*H*), 7.31–7.43 (m, 7 H).

(b) 2,5-Dibromobiphenyl (4). 2,5-Dibromobiphenyl (**4**) was synthesized from 2,5-dibromoaniline (**2**) according to the same procedure described for the synthesis of 2,5-dichlorobiphenyl (**3**). The crude product was purified twice by column chromatography on silica gel using hexanes as eluent. Starting from 15.04 g (59.9 mmol) of 2,5-dibromoaniline (**2**), 9.910 g (53.0%) of 2,5-dibromobiphenyl (**4**) was obtained as colorless crystals: mp 38–40 °C (lit.[12] 39 °C); purity (HPLC) >99.9%; ^1H NMR ($CDCl_3$) δ 7.31 (dd, 1 H, J = 8.5, 2 Hz, 4-*H*), 7.34–7.46 (m, 5 H) 7.46 (d, 1 H, J = 2 Hz, 6-*H*), 7.51 (d, 1 H, J = 8.5 Hz, 3-*H*).

(c) Methyl 2,5-Dibromobenzoate (12). 2,5-Dibromobenzoic acid was esterified with methanol using H_2SO_4 as acid catalyst. The ester was purified by column chromatography on silica gel using a mixture of toluene and hexanes (volume ratio = 1/2) as eluent. White crystals were obtained: mp 49–50 °C; purity (HPLC) >99.9%; ^1H NMR ($CDCl_3$) δ 7.44 (dd, 1 H, J = 8.5, 2.5 Hz, 4-*H*), 7.54 (d, 1 H, J = 8.5 Hz, 3-*H*), 7.93 (d, 1 H, J = 2.5 Hz, 6-*H*).

Scheme III
Polymerization of 2,5-Dichlorobiphenyl, 2,5-Dibromobiphenyl, 2,5-Bis[[(trifluoromethyl)sulfonyl]oxy]biphenyl, Methyl 2,5-Dichlorobenzoate, Methyl 2,5-Dibromobenzoate, Methyl 2,5-Bis[[(trifluoromethyl)sulfonyl]oxy]benzoate, and 2-*tert*-Butyl-1,4-bis[[(trifluoromethyl)sulfonyl]oxy]benzene

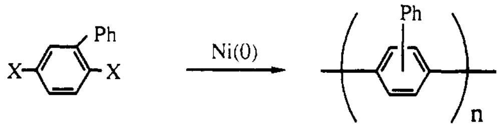


(d) Methyl 2,5-Bis[[(trifluoromethyl)sulfonyl]oxy]benzoate (9). Methyl 2,5-dihydroxybenzoate (**6**) (purity 99.5%, 2.240 g, 13.32 mmol) was dissolved in dry pyridine (50 mL) at 0 °C under N_2. To this solution was added dropwise trifluoromethanesulfonic anhydride (6.0 mL, 10.06 g, 35.66 mmol). The resulting red solution was stirred at 0 °C for 10 min and allowed to warm to room temperature. Stirring was continued for 40 h at room temperature, and then the reaction mixture was poured into water. The mixture was extracted three times with diethyl ether, and the extract was washed with water, twice with 10% hydrochloric acid, water, and twice with saturated sodium chloride solution. The extract was dried over anhydrous $MgSO_4$ and the solvent removed on a rotary evaporator. The crude oily product was purified by silica gel column chromatography using hexanes as eluent. A colorless oil was obtained. The yield was 4.69 g (81.5%): purity (HPLC) 96.3%; ^1H NMR ($CDCl_3$) δ 3.96 (s, 3 H, $COOCH_3$), 7.41 (d, 1 H, J = 8.5 Hz, 3-*H*), 7.55 (dd, 1 H, J = 8.5, 2.5 Hz, 4-*H*), 8.00 (d, 1 H, J = 2.5 Hz, 6-*H*).

(e) 2,5-Bis[[(trifluoromethyl)sulfonyl]oxy]biphenyl (8). 2,5-Bis[[(trifluoromethyl)sulfonyl]oxy]biphenyl (**8**) was synthesized from phenylhydroquinone (**5**) according to the same procedure described for the synthesis of methyl 2,5-bis[[(trifluoromethyl)sulfonyl]oxy]benzoate (**9**). The crude product was purified by silica gel column chromatography using a mixture of hexanes and benzene (volume ratio = 5/1) to yield a colorless oil: yield 92.4%; purity (HPLC) >99.9%; ^1H NMR ($CDCl_3$) δ 7.34 (dd, 1 H, J = 2.5, 9 Hz, 4-*H*), 7.40 (d, 1 H, J = 2.5 Hz, 6-*H*), 7.43–7.54 (m, 6 H).

(f) 2-*tert*-Butyl-1,4-bis[[(trifluoromethyl)sulfonyl]oxy]benzene (10). 2-*tert*-Butyl-1,4-bis[[(trifluoromethyl)sulfonyl]oxy]benzene (**10**) was synthesized from *tert*-butylhydroquinone (**7**) according to the same procedure as that described for the synthesis of methyl 2,5-bis[[(trifluoromethyl)sulfonyl]oxy]benzoate (**9**). The crude product was purified by silica gel column chromatography using hexanes as eluent to yield a colorless oil: yield 83.0%; purity (HPLC) >99.9%; ^1H NMR ($CDCl_3$) δ 1.39 (s, 9 H, $C(CH_3)_3$), 7.23 (dd, 1 H, J = 9, 2.5 Hz, 5-*H*), 7.37 (d, 1 H, J = 2.5 Hz, 3-*H*), 7.47 (d, 1 H, J = 9 Hz, 6-*H*).

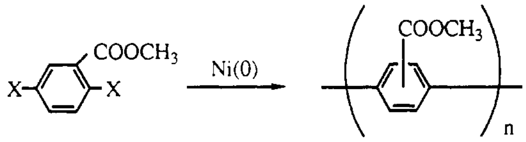
Table I
Polymerization of 2,5-Dichlorobiphenyl, 2,5-Dibromobiphenyl, and 2,5-Bis[[(trifluoromethyl)sulfonyl]oxy]biphenyl



	reaction conditions							polymer				
	monomer											
entry	X	mmol	Ni(0), mol %	method[a]	solvent, mL	temp, °C	time, h	yield, %	M_n	M_w/M_n	DP	T_g, °C
1	Cl	5.09	3.5	A[b]	5.0	70	1.0		1000	1.1	6	
2	Cl	5.09	3.5	A[b]	5.0	70	5.0		1000	1.2	6	
3	Cl	5.09	3.5	A[b]	5.0	70	20.0		900	1.2	6	124
4	Cl	2.50	7.0	A[c]	1.0	70	20.0	9.0	700	1.1	5	
5	Cl	2.55	7.1	A[c]	1.0	90	1.0	56.7	800	1.3	5	
6	Cl	5.02	3.4	B[b]	5.0	67	20.0	0.3	800	1.2	5	
7	Cl	2.58	7.4	B[b]	1.0	67	20.0	41.6	900	1.3	6	127
8	Cl	2.60	7.1	B[b]	1.0	67	50.0	37.7	900	1.3	6	123
9	Cl	2.54	12.8	B[b]	1.5	67	1.0	53.6	700	1.2	5	
10	Br	2.53	7.0	A[c]	1.0	90	1.0	14.7	700	1.2	5	
11	Br	2.52	8.0	B[b]	1.0	67	20.0	40.1	1300	1.6	9	
12	Br	2.50	8.4	B[c]	1.0	67	20.0	38.9	1100	1.3	9	
13	Br	2.54	12.9	B[b]	1.5	67	1.0	78.7	900	1.3	6	
14	TfO	2.53	7.1	A[c]	1.0	90	1.0	8.0	500	1.2	5	
15	TfO	2.54	3.4	B[b]	1.5	67	1.0	6.3	1700	1.2	11	
16	TfO	2.49	7.6	B[b]	1.0	67	20.0	41.1	1800	1.5	12	
17	TfO	2.57	12.8	B[b]	2.0	67	1.0		2100	1.6	14	
18	TfO	2.57	12.8	B[b]	2.0	67	2.5		2300	1.6	15	
19	TfO	2.57	12.8	B[b]	2.0	67	24.0		2100	1.6	14	163
20	TfO	2.62	12.5	B[b]	1.5	67	1.0	48.8	2000	1.4	13	

[a] Method A: $NiCl_2/Ph_3P/Zn/2,2'$-dipyridyl/DMF. Method B: $NiCl_2(Ph_3P)_2/Zn/Et_4NI/THF$. [b] Monomer solution was added to the preformed catalyst solution. [c] All of the reagents including monomer were mixed, and the polymerization was started by adding solvent.

Table II
Polymerization of Methyl 2,5-Dichlorobenzoate, Methyl 2,5-Dibromobenzoate, and Methyl 2,5-Bis[[(trifluoromethyl)sulfonyl]oxy]benzoate



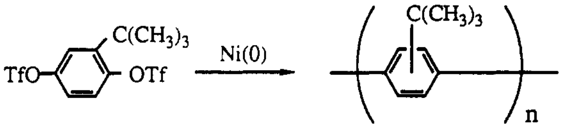
	reaction conditions							polymer				
	monomer											
entry	X	mmol	Ni(0), mol %	method[a]	solvent, mL	temp, °C	time, h	yield, %	M_n	M_w/M_n	DP	T_g, °C
1	Cl	2.50	6.9	A[b]	1.0	90	1.0	72.4	3500	1.7	26	
2	Br	2.51	6.7	A[b]	1.0	90	1.0	21.0	4500[e]	18.7[e]	36	
3	TfO	2.50	6.8	A[b]	1.0	90	1.0	76.4	4000	1.5	30	
4	Cl	2.51	13.0	B[b]	1.0	67	0.1[d]	88.1	3600	2.1	27	
5	Br	2.49	13.1	B[b]	1.0	67	1.0	49.8	2400	1.3	18	
6	TfO	2.52	13.0	B[b]	1.0	67	1.0	64.8	3900	2.0	26	
7	TfO	2.02	12.9	B[c]	2.0	67	3.0	16.0	6300	2.1	47	115, 178[f]

[a] Method A: $NiCl_2/Ph_3P/Zn/2,2'$-dipyridyl/DMF. Method B: $NiCl_2(Ph_3P)_2/Zn/Et_4NI/THF$. [b] All of the reagents including monomer were mixed, and the polymerization was started by adding solvent. [c] Monomer solution was added to the preformed catalyst solution. [d] The reaction mixture became very thick, and stirring was impossible. [e] Bimodal molecular weight distribution (M_n 2200, M_w/M_n 1.2; M_n 34 200, M_w/M_n 3.4). [f] At first heating scan, an exothermic peak was observed at 266 °C, which was not observed at second heating scan.

Ni(0)-Catalyzed Polymerizations. The polymerization reactions are described in Scheme III. They were performed either in DMF (method A)[13] or in THF (method B).[14] The polymerization conditions are summarized in Tables I–III. Typical polymerization examples (entry 5, Table I, and entry 20, Table I) are provided below.

Method A. $NiCl_2$ (23.3 mg, 0.18 mmol), Ph_3P (0.700 g, 2.67 mmol), Zn powder (0.934 g, 14.29 mmol), 2,2′-dipyridyl (22.0 mg, 0.14 mmol), and 2,5-dichlorobiphenyl (0.568 g, 2.546 mmol) were placed in a 50-mL round-bottom flask equipped with a condenser and a stopcock. The flask was evacuated under vacuum for 6 h and filled with N_2. Then, the evacuation and filling with N_2 was repeated four times; 1.0 mL of dry DMF was added via a syringe through the rubber septum on the top of the condenser. The mixture was stirred at room temperature for 5 min, and during this time the color of the mixture gradually changed to deep red brown. The mixture was heated at 90 °C for 1 h. The reaction mixture was cooled to room temperature, and the content was poured into 100 mL of methanol acidified with HCl. The precipitate containing Zn powder was collected by filtration and dissolved in 10 mL of $CHCl_3$. The solution was filtered to remove the unreacted Zn powder, and the filtrate was concentrated and poured into methanol acidified with HCl. The precipitate was collected by filtration and vacuum dried. The yield was 0.220 g (56.7%). The polymer was purified by washing the $CHCl_3$ solution with water and reprecipitation into methanol before being analyzed by GPC. M_n (GPC) = 800; M_w/M_n = 1.3. In some experiments, the monomer solution was added to the preformed catalyst. In other cases (entries 1–3, Table I), the progress of the polymerization was monitored by withdrawing an aliquot of the polymerization mixture, precipitating it into methanol, and purifying it in a manner similar to that described above. The

Table III
Polymerization of 2-*tert*-Butyl-1,4-bis[[(trifluoromethyl)sulfonyl]oxy]benzene



	reaction conditions						polymer				
entry	monomer, mmol	Ni(0), mol %	method[a]	solvent, mL	temp, °C	time, h	yield, %	M_n	M_w/M_n	DP	T_g, °C
1	5.00	7.3	A[b]	1.0	90	1.0	0				
2	1.16	13.8	B[c]	0.8	67	3.0	15.0	1500	1.2	11	122
3	5.06	13.0	B[c]	4.0	67	4.0	5.0	1700	1.2	13	
4	1.15	13.9	B[c]	1.0	67	12.0	17.0	1800	1.2	14	
5	2.27	7.1	B[c]	0.5	67	1.0	16.0	1000	1.2	8	

[a] Method A: NiCl$_2$/Ph$_3$P/Zn/2,2′-dipyridyl/DMF. Method B: NiCl$_2$(Ph$_3$P)$_2$/Zn/Et$_4$NI/THF. [b] All of the reagents including monomer were mixed, and the polymerization was started by adding solvent. [c] Monomer solution was added to the preformed catalyst solution.

obtained samples were analyzed by GPC.

Method B. Ni(Ph$_3$P)$_2$Cl$_2$ (0.215 g, 0.33 mmol), Zn powder (1.688 g, 25.82 mmol), and Et$_4$NI (0.791 g, 3.07 mmol) were placed in a 50-mL round-bottom flask equipped with a condenser and a stopcock. The flask was evacuated under vacuum for 6 h and filled with N$_2$. Then, the evacuation and filling with N$_2$ was repeated four times; 1.0 mL of freshly distilled THF was added via a syringe through the rubber septum on the top of the condenser. The mixture was stirred at room temperature for 5 min, and during this time the color of the mixture gradually changed to deep red brown. 2,5-Bis[[(trifluoromethyl)sulfonyl]oxy]biphenyl (1.177 g, 2.615 mmol) was dissolved in 0.5 mL of freshly distilled THF and added to the catalyst mixture via a syringe through the rubber septum. The reaction mixture was heated to the reflux temperature and stirred at this temperature for 1 h. The reaction mixture was then cooled to room temperature, and its content was poured into 100 mL of methanol acidified with HCl. The precipitate containing Zn powder was collected by filtration and dissolved in 10 mL of CHCl$_3$. The solution was filtered to remove Zn powder, and the filtrate was concentrated and poured into methanol acidified with HCl. The precipitate was collected by filtration and vacuum dried. The yield was 0.194 g (48.8%). The polymer was purified by washing with CHCl$_3$ solution with water and reprecipitation into methanol before being analyzed by GPC. M_n (GPC) = 2000; M_w/M_n = 1.4. In some experiments, the monomer was mixed with the catalyst mixture and evacuated, and the polymerization was started by adding THF. In other cases (entries 17–19, Table I), the progress of the polymerization was monitored by withdrawing an aliquot of the polymerization mixture, precipitating it into methanol, and purifying it in a manner similar to that described above. The obtained samples were analyzed by GPC.

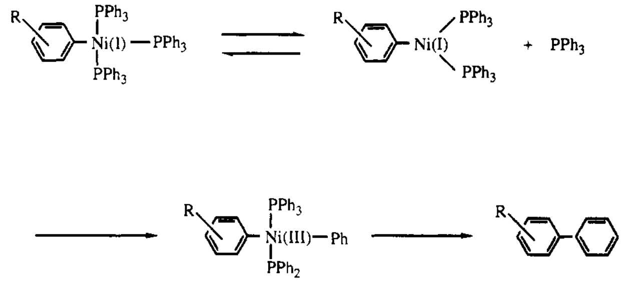
Results and Discussion

The synthesis of monomers is described in Schemes I and II. The polymerization reactions are described in Scheme III. 2,5-Dichlorobiphenyl (3) and 2,5-dibromobiphenyl (4) were synthesized by phenylation[10] of the diazonium salts derived from the corresponding aniline derivatives 1 and 2. 2,5-Bis[[(trifluoromethyl)sulfonyl]oxy]biphenyl (8), methyl 2,5-bis[[(trifluoromethyl)sulfonyl]oxy]benzoate (9), and 2-*tert*-butyl-1,4-bis[[(trifluoromethyl)sulfonyl]oxy]benzene (10) were synthesized by triflation of corresponding dihydroxy compounds 5, 6, and 7.[11] Methyl 2,5-dichlorobenzoate (11) was commercially available and was purified by column chromatography. Methyl 2,5-dibromobenzoate (12) was prepared by esterification of 2,5-dibromobenzoic acid, which is commercially available.

All substituted poly(*p*-phenylene)s synthesized and reported in this paper are soluble in dipolar aprotic solvents, tetrahydrofuran, chloroform, etc.

The polymerizations of 2,5-dichlorobiphenyl (3), 2,5-dibromobiphenyl (4), and 2,5-bis[[(trifluoromethyl)sulfonyl]oxy]biphenyl (8) are summarized in Table I. Two methods for the preparation in situ of the Ni(0) catalyst have been reported so far. In the first one, Ni(0) catalyst is prepared from NiCl$_2$, Ph$_3$P, and Zn in a polar solvent such as DMF or DMAc.[13] 2,2′-Dipyridyl can be added to suppress the phenylation caused by the reaction between Ni(0) species and Ph$_3$P[13] (Scheme IV). In the second one, the Ni(0) catalyst is prepared from Ni(Ph$_3$P)$_2$Cl$_2$, Zn, and Et$_4$NI in a less polar solvent such as THF.[14] Although the role of Et$_4$NI has not been clarified, it is believed to play the role of a bridging agent between Ni and Zn, which facilitates the reduction of Ni(II) to Ni(0).[13] The Ni(0) catalysts prepared by both methods have the same deep red brown color, which can be used as an indication for the formation of the catalysts. We applied both methods to our polymerizations.

Scheme IV
Mechanism of Phenyl Transfer from Triphenylphosphine



Entries 1–5 from Table I show the results of the polymerizations of 2,5-dichlorobiphenyl (3) in DMF. In entries 1–3, the polymerization was performed at 70 °C, and the progress of the polymerization was monitored up to 20 h. However, the molecular weight of the polymer did not change (M_n = 1000, M_w/M_n = 1.1). In entry 4, the amount of catalyst was increased to 7 mol % vs the amount of monomer, but both the yield and the molecular weight were very low (yield = 9.0%, M_n = 700). In entry 5, the polymerization temperature was raised to 90 °C, and the yield increased dramatically (yield = 56.7%). However, the molecular weight was still low (M_n = 800, M_w/M_n = 1.3). Entries 6–9 show the results of the polymerizations of 2,5-dichlorobiphenyl (3) in THF. The amount of catalyst was changed from 3 to 13 mol %, and apparently the polymer yield increased as the amount of catalyst increased (yield = 53.6% with 12.8 mol % of the catalyst). However, the molecular weight did not increase (M_n = 700–900, M_w/M_n = 1.2–1.3).

Entries 10–13 from Table I show the results of the polymerizations of 2,5-dibromobiphenyl (4). Entry 10 shows the result of the polymerization in DMF. Both the

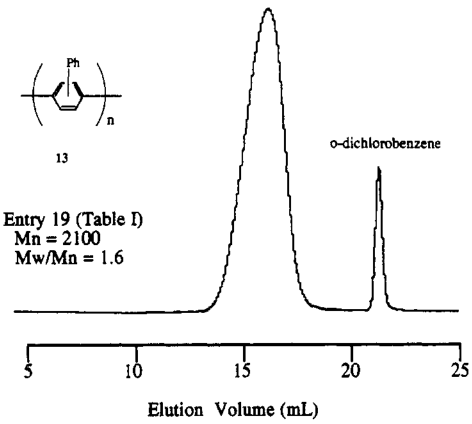


Figure 1. GPC trace of the polymer obtained from 2,5-bis[[(trifluoromethyl)sulfonyl]oxy]biphenyl (**13**, sample from entry 19, Table I).

yield and the molecular weight were low (yield = 14.7%, M_n = 700). In THF, the polymer yield increased up to 78.7% by increasing the amount of the catalyst to 12.9 mol %. A slightly higher molecular weight was obtained with 8.0 mol % catalyst (entry 11, M_n = 1300, M_w/M_n = 1.6).

Entries 14–20 from Table I show the results of the polymerizations of 2,5-bis[[(trifluoromethyl)sulfonyl]oxy]biphenyl (**8**). Entry 14 shows the result of the polymerization in DMF. Both the yield and the molecular weight were very low (yield = 8.0%, M_n = 500). Entries 15–20 show the results of the polymerizations of 2,5-bis[[(trifluoromethyl)sulfonyl]oxy]biphenyl (**8**) in THF. The results of entries 15, 16, and 20 show that as the amount of catalyst increased from 3.4 to 12.5 mol %, the yield increased from 6.3 to 48.8%. At the same time, the molecular weight increased only slightly, i.e., from 1700 to 2000. In entries 17–19, the progress of the polymerization was monitored up to 20 h. However, the molecular weight did not change (M_n = 2100–2300, M_w/M_n = 1.6). A representative GPC trace of the polymer **13** (entry 19 in Table I) is presented in Figure 1. It shows a very clean monomodal molecular weight distribution. The 200-MHz ^{1}H NMR spectra of 2,5-bis[[(trifluoromethyl)sulfonyl]oxy]biphenyl (**8**) and of a representative poly(2,5-biphenylene) (**13**) (entry 18 in Table I) are presented as spectra A and B in Figure 2. Although the proton assignment of the monomer was given, that of the polymer was not given because of the complexity of the peaks, which is probably due to the presence of various constitutional isomeric structural units. The glass transition temperature of the polymer from entry 19 is 163 °C.

The polymerizations of methyl 2,5-dichlorobenzoate (**11**), methyl 2,5-dibromobenzoate (**12**), and methyl 2,5-bis[[(trifluoromethyl)sulfonyl]oxy]benzoate (**9**) are summarized in Table II. Entries 1–3 show the results of the polymerizations of these three monomers in DMF. Methyl 2,5-dichlorobenzoate (**11**) and methyl 2,5-bis[[(trifluoromethyl)sulfonyl]oxy]benzoate (**9**) gave high yields (72.4 and 76.4%, respectively). However, methyl 2,5-dibromobenzoate (**12**) gave a lower yield (21.0%). The molecular weights of these polymers were in the range 3500–4500, which corresponds to a degree of polymerization (DP) ranging from 26 to 36. In the case of methyl 2,5-dibromobenzoate (**12**), as shown in Figure 3, the molecular weight distribution showed a clear bimodal curve. The higher molecular weight portion represents 55 wt %, and its number-average molecular weight is 34 200 (entry 2). Entries 4–6 show the results of the polymerizations of these three monomers in THF. Methyl 2,5-dichlorobenzoate (**11**) gave the highest polymer yield (88.1%), and, again, methyl 2,5-dibromobenzoate (**12**) gave a much lower yield (49.8%). In the case of methyl 2,5-dichlorobenzoate (**11**) (entry 4), the reaction mixture became very viscous during the first 5 min of reaction and stirring became impossible. The molecular weights of the resulted polymers were in the range 2400–3600. These values correspond to degrees of polymerization from 18 to 31. In entry 7, the monomer solution was added to the preformed catalyst solution and the polymerization was performed under more dilute conditions. The polymer yield was lower, but a slightly higher molecular weight polymer was obtained (yield = 16.0%, M_n = 6300, DP = 47, M_w/M_n = 2.1). A representative GPC trace of polymer **14** (entry 7 in Table II) is presented in Figure 4. Although it contains a very small amount of a high molecular weight portion, it shows a clear monomodal molecular weight distribution for the lower molecular weight polymer fraction. The 200-MHz ^{1}H NMR spectra of methyl 2,5-bis[[(trifluoromethyl)sulfonyl]oxy]benzoate (**9**) and of a representative poly(2,5-diphenylene) (**14**) (entry 7 in Table II) are

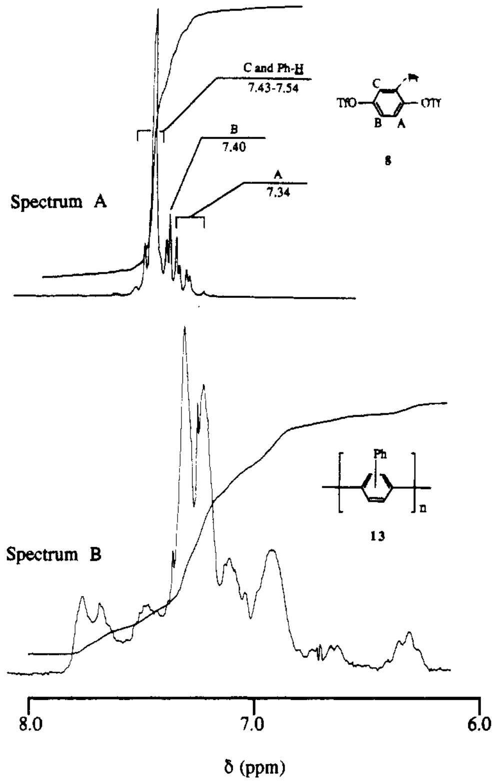


Figure 2. 200-MHz ^{1}H NMR spectra (CDCl$_3$, TMS) of 2,5-bis[[(trifluoromethyl)sulfonyl]oxy]biphenyl (**8**, spectrum A) and the polymer obtained from 2,5-bis[[(trifluoromethyl)sulfonyl]oxy]biphenyl (**13**, spectrum B, sample from entry 18, Table I).

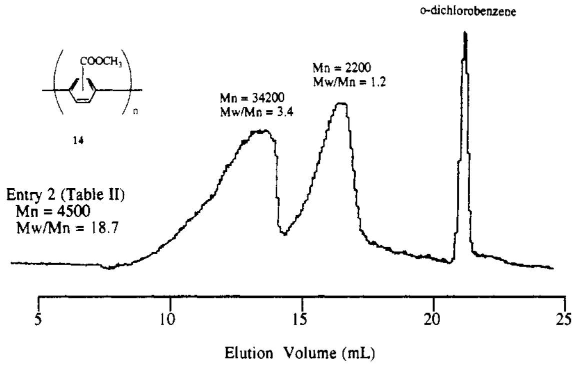


Figure 3. GPC trace of the polymer obtained from methyl 2,5-dibromobenzoate (**14**, sample from entry 2, Table II).

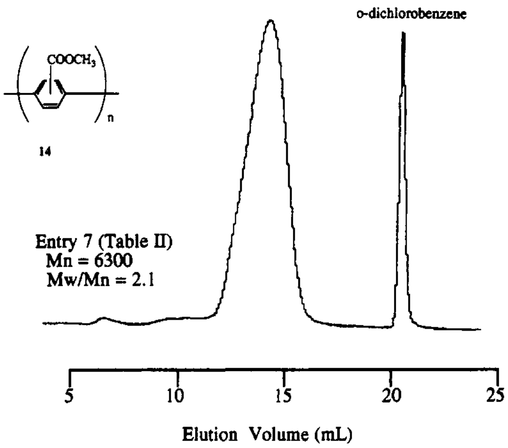


Figure 4. GPC trace of the polymer obtained from methyl 2,5-bis[[(trifluoromethyl)sulfonyl]oxy]benzoate (**14**, sample from entry 7, Table II).

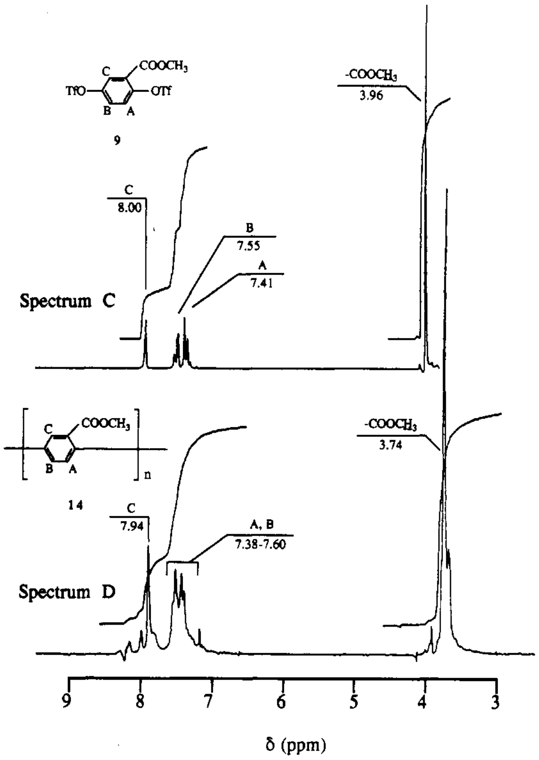


Figure 5. 200-MHz ^{1}H NMR spectra (CDCl$_3$, TMS) of methyl 2,5-bis[[(trifluoromethyl)sulfonyl]oxy]benzoate (**9**, spectrum C) and the polymer obtained from methyl 2,5-bis[[(trifluoromethyl)sulfonyl]oxy]benzoate (**14**, spectrum D, sample from entry 7, Table II).

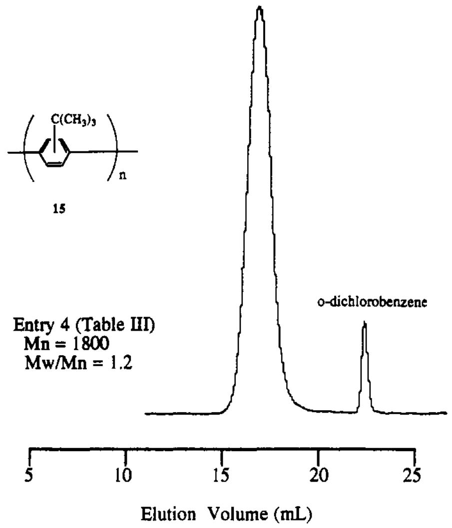


Figure 6. GPC trace of the polymer obtained from 2-*tert*-butyl-1,4-bis[[(trifluoromethyl)sulfonyl]oxy]benzene (**15**, sample from entry 4, Table III).

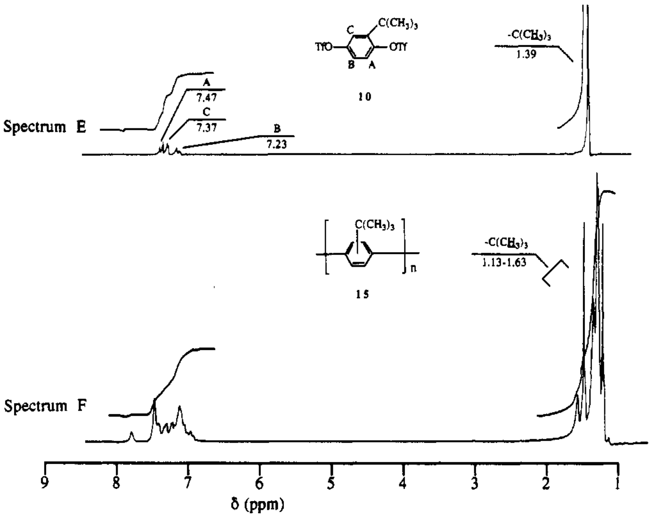


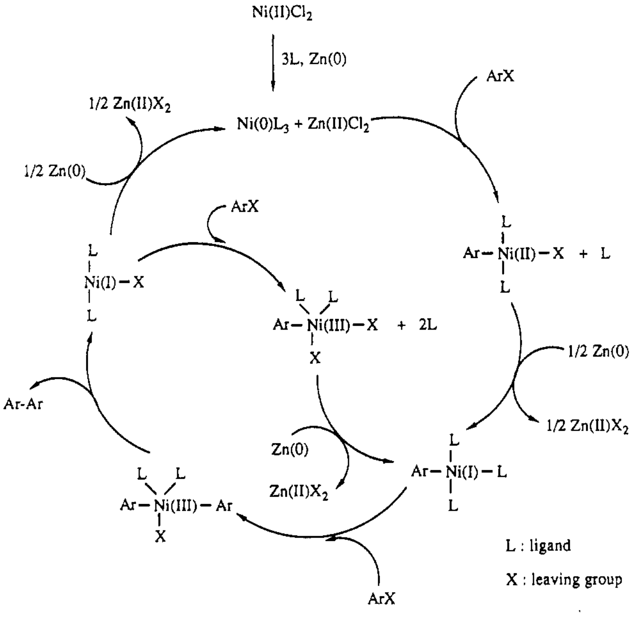
Figure 7. 200-MHz ^{1}H NMR spectra (CDCl$_3$, TMS) of 2-*tert*-butyl-1,4-bis[[(trifluoromethyl)sulfonyl]oxy]benzene (**10**, spectrum E) and the polymer obtained from 2-*tert*-1,4-bis[[(trifluoromethyl)sulfonyl]oxy]benzene (**15**, spectrum F, sample from entry 4, Table III).

presented as spectra C and D in Figure 5 together with their proton assignment. On the first heating scan of the DSC measurement of the polymer from entry 7, an exothermic peak was observed at 266 °C. This peak might be related to the anhydrization of the pendant ester groups. Two small transitions were observed at 115 and 178 °C on the second heating scan.

The polymerizations of 2-*tert*-butyl-1,4-bis[[(trifluoromethyl)sulfonyl]oxy]benzene (**10**) are summarized in Table III. In entry 1, the polymerization was performed in DMF, but no polymer was obtained. In entries 2–4, the polymerizations were performed in THF, and polymers with number-average molecular weights of 1500–1800 were obtained with 13.0–13.9 mol % of catalyst. However, the polymer yields were low (5.0–17.0%). In entry 5, a lower amount of catalyst was used and a lower molecular weight polymer was obtained (M_n = 1000). A representative GPC trace of polymer **15** (entry 4 in Table III) is presented in Figure 6. It shows a clear monomodal molecular weight distribution. The 200-MHz ^{1}H NMR spectra of 2-*tert*-butyl-1,4-bis[[(trifluoromethyl)sulfonyl]oxy]benzene (**10**) and of a representative poly(2,5-biphenylene) (**15**) (entry 4 in Table III) are presented as spectra E and F in Figure 7 together with their proton assignment. The 200-MHz ^{1}H NMR spectrum of the polymer shows a complex multiplet in the aliphatic region. These peaks are likely the singlet peaks of *tert*-butyl groups of various constitutional isomeric structural units. The glass transition temperature of the polymer from entry 2 was 122 °C.

Several mechanisms have been suggested for the Ni(0)-catalyzed homocoupling reaction of arylhalides. Although they are still controversial,[13a–15] the most plausible sequence of reactions[13a,16b] is presented in Scheme V. The first step of this mechanism involves reduction of Ni(II) salt to Ni(0) by Zn. The oxidative addition of aryl triflate or aryl halide to Ni(0) and Ni(I) species and the reductive elimination of biaryl units from the diaryl–Ni(II) complex are considered to be fast reactions.[13a,16b] Under our experimental reaction conditions (i.e., excess of Zn as reducing agent) the rate-determining step is the reduction

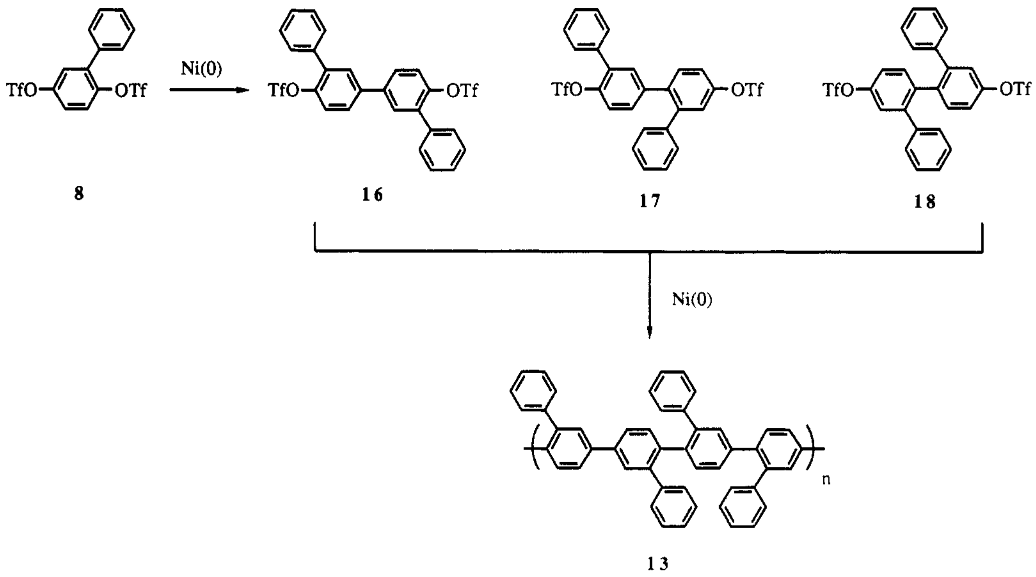
Scheme V
Mechanism of Ni(0)-Catalyzed Homocoupling Reaction



of unreactive aryl–Ni(II) species to reactive aryl–Ni(I) species and, therefore, the overall rate of reaction is influenced by any additive or change in the reaction conditions that would facilitate the single electron transfer in this reaction step.[13c,16b] The presence of the iodide ion in the reaction mixture enhances this rate by bridging between Ni and Zn species in the single electron transfer reduction process[13a,14,17] and, therefore, this result is in agreement with the mechanism outlined in Scheme V. Even if the structure of the leaving group is changed from halide to triflate, the mechanism seems to be basically the same. However, the rate of each step can be influenced by any change such as leaving group or reaction conditions, and the overall rate will be determined by the result of all integrated influences. Therefore, at the present time it is difficult to discuss the dependence of the reactivity on the structure of the leaving group and reaction conditions.

However, we can point out some features of this polymerization from the results summarized in Table I. For the method using DMF, the polymerization temperature was crucial for the polymer yield (entries 4 and 5 in Table I). When the temperature was raised from 70 to 90 °C, the polymer yield increased dramatically. However, the molecular weight did not change. Entries 4, 10, and 14 from Table I were performed under the same reaction conditions using DMF as solvent, and the polymer yield and the molecular weights increased in the order TfO < Br < Cl. This might mean that under these reaction conditions the rate of the oxidative addition of Ni(0) and Ni(I) to the substrate is dominated by the electronegativity of the leaving group. On the other hand, for the method using THF, it seems that the influence of the leaving group is working in an opposite way. Experiments from entries 7, 11, and 16 in Table I were performed under the same conditions using THF as solvent, and the molecular weights increased in the order Cl < Br < TfO. This might mean that under these reaction conditions the rate of the oxidative addition to Ni(0) and Ni(I) is dominated by the dissociation of the leaving group. The other feature of the method using THF is that the polymer yield increased dramatically when the amount of catalyst was increased (entries 15 and 20 in Table I). However, the molecular weight of the polymer did not change. The highest molecular weight of poly(2,5-biphenylene) (**13**) was 2300. The low polymerizability of 2,5-dichlorobiphenyl (**3**), 2,5-dibromobiphenyl (**4**), and 2,5-bis[[(trifluoromethyl)sulfonyl]oxy]biphenyl (**8**) is probably due to the steric hindrance of the phenyl group as substituent as outlined in Scheme VI. It is likely that in the first step most of the monomer molecules would react at the 5-position to form dimeric molecules **16** containing much more hindered reactive positions on both ends. Dimers **17** and **18** are also formed but in a much lower concentration. The reactivity of the dimeric molecule **16** is probably much lower than that of **8** and **17** and, therefore, the polymerization reaction would be significantly retarded. The solubility of polymer **13** is most probably determined by the large number of constitutional isomeric structural units present in its chain (Scheme VI). This increases its configurational entropy and decreases its crystallization ability. Recently, the polymerization of 2,4-dichloro-3-phenylthiophene by Ni(0) catalyst has been reported.[13d] In this case, a high molecular weight polymer was reported. Although the reason for the difference of reactivity between

Scheme VI
Generation of Constitutional Isomeric Structural Units during the Polymerization of 8–13



the present monomers and 2,5-dichloro-3-phenylthiophene is not clear, one possible reason for the higher reactivity of 2,5-dichloro-3-phenylthiophene might be that the 2-position is less hindered compared to the 2-position of 2,5-biphenylene monomers. Recently, the polymer with the structure **13** was synthesized from 2,5-dibromobiphenyl according to the Kumata reaction,[4b] which consists of the condensation reaction of its mono-Grignard reagent in the presence of a Ni catalyst. The molecular weight of $CHCl_3$-soluble fractions ranges from 900 to 2000. These values are comparable to our results A polymer fraction of higher molecular weight which is insoluble in chloroform and soluble in diphenyl ether was also obtained.[4b] The insolubility of this fraction is most probably due to the regioregular structure of the polymer obtained by this method[4b] vs the regioirregular structure of the polymer obtained by our present method.

In the case of polymerization of methoxycarbonyl derivatives summarized in Table II, much higher polymer yields and molecular weights were obtained. This is probably because the steric hindrance of the methoxycarbonyl group is much less than that of the phenyl group and also because the electron-withdrawing character of methoxycarbonyl suppresses the phenyl transfer from triphenylphosphine to Ni (Scheme IV).[13] Entries 1–6 in Table II were performed under the same reaction conditions for both methods using DMF and THF as solvent. The reason that methyl 2,5-dibromobenzoate (**12**) gave lower yields in both methods is not clear. However, the molecular weights were almost in the same level and the comparison of the polymerizability is difficult. In entry 2 from Table II, a clear bimodal molecular weight distribution was observed and the higher molecular weight was 34 200. The reason for the bimodal molecular weight distribution was not yet clarified. In entry 7 from Table II, the monomer solution was added to the preformed catalyst and the polymerization was performed with a slightly lower monomer concentration. This experiment produced the highest molecular weight polymer, i.e., $M_n = 6300$. This value corresponds to a degree of polymerization of 47.

Polymers from 2-*tert*-butyl-1,4-bis[[(trifluoromethyl)sulfonyl]oxy]benzene (**10**) were obtained only under reaction conditions using THF as solvent, but with low yields (entries 2–5 in Table III). No polymer was obtained by the method using DMF as solvent (entry 1 in Table III). The reason for the low yields seems to be the steric hindrance provided by the *tert*-butyl group, which is probably more severe than that of the phenyl group. No polymerization occurred under reaction conditions using DMF, because the TfO group is less favored than Cl and Br under these reaction conditions.

As we can observe from the results summarized in Tables I–III, arylene dichloride, arylene dibromide, and arylene bis(triflate) can be polymerized by the Ni(0) catalyst prepared both in DMF and in THF. In particular, arylene bis(triflate)s are more favored under reaction conditions using THF. According to the reaction mechanism outlined in Scheme V, previous results on similar homocoupling reactions,[13,18] and the results on the spectroscopic characterization of the polymers reported in this paper, this polymerization reaction proceeds by homocoupling only at the positions carrying the leaving group. Therefore, the polymers described in this paper are poly(*p*-phenylene)s. Considering the easier accessibility of arylene bis(triflate)s from corresponding bisphenols and hydroquinones, this polymerization reaction represents a promising novel synthetic avenue to various types of functional and nonfunctional polyarylenes. For example, the ester group of polymers **14** can be hydrolyzed, and the resulting polymers are soluble in basic water. At the same time, the ipso electrophilic cleavage of isobutylene from **15** leads to unsubstituted poly(phenylene)s. Only a few results on the homocoupling of aryl triflates by Ni(0) catalysts are available, and these data claim that the reaction proceeds only under ultrasonication.[18] Therefore, further research on the mechanism and scope of this polymerization and organic reactions is necessary. This research is in progress and will be reported in due time.

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