Synthesis of Functional Polyphenylenes from Substituted Hydroquinones via Nickel(0)-Catalyzed Polymerization of Their Bismesylates

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ABSTRACT: This paper reports the elaboration of a novel synthetic method for the preparation of polyphenylenes. It consists of the Ni(0)-catalyzed polymerization of bis[(methylsulfonyl)oxy] derivatives (i.e., arylene bismesylates) of substituted hydroquinones. The Ni(0) catalysts used were generated in situ from $NiCl_2(PPh_3)_2$, Zn, Et_4NI in THF, dioxane, or DMAc. The influence of solvent, temperature, additional ligands, and the size and electronic properties of the substituent groups of the monomers on their polymerizability was investigated. Soluble poly(*p*-phenylene)s and poly(*m*-phenylene)s can be obtained by a proper selection of their substituents. Poly(*p*-phenylene)s with number-average molecular weights (relative to polystyrene standards) of up to 20 030 (DP = 101) were obtained.

Introduction

Poly(*p*-phenylene) (PPP) is the simplest aromatic polymer containing only carbon and hydrogen and, therefore, is the aromatic homologue of polyethylene (PE). PE is an excellent model for fundamental investigations on the crystallization and morphology of flexible-chain polymers.[1] Its present status was facilitated by the availability of synthetic methods for the preparation of linear and cyclic oligomers of polyethylene with well-defined size and uniform molecular weight distribution[1c,2] and also by their solubility.

PPP is the simplest rigid-rod-like polymer, and convenient methods for its synthesis would generate a model for rigid-rod-like polymers. Unfortunately, only oligo(*p*-phenylene)s with seven and less than seven phenylenic units are soluble, the largest of them only in low concentration and at elevated temperatures.[3]

Several synthetic strategies are available for the preparation of PPPs. Oxidative polymerization of benzene is the simplest direct method, but the resulting polymers do not contain only para-structural units and their molecular weight is low since it is determined by the limited solubility of the polymer.[4] Higher molecular weights and more regular structures were obtained by indirect methods which involved the synthesis of soluble precursors followed by their chemical transformation into PPP. Anionic polymerization of 1,3-cyclohexadiene followed by bromination and dehydrogenation[5a] and radical polymerization of bis(octyl) or bis(methoxycarbonyl) derivatives of *cis*-5,6-dihydroxy-1,3-cyclohexadiene followed by thermally induced acid elimination[5b−d] yield mixtures of para and other phenylenic structural units and respectively provide cleavage during pyrolysis. The most successful indirect method reported for the synthesis of PPP is based on the polymerization of *cis*-5,6-bis(trimethylsiloxy)-1,3-cyclohexadiene followed by a three-step aromatization reaction to yield PPP with number-average degrees of polymerization of up to 150.[5e−g] However, the utility of the insoluble PPP for physical investigations is very limited.

Soluble PPPs are typically obtained by increasing their configurational entropy.[3a,6a] Alternatively, the presence of groups with favorable ionic interactions with the solvent medium solubilizes PPP. For example, water-soluble PPPs have been synthesized by the attachment of carboxylate or sulfonate groups.[6b,c] An increase in the configurational entropy can be accomplished by attaching functional side groups to the backbone of PPP[3a,4b,c,7] by increasing the number of constitutional and configurational isomers of the repeat units,[8] by increasing the configurational entropy of the main chain through a proper combination of kinked phenylenic units which generate a linear extended-chain conformation,[3a,6a,9] and by combinations of all these techniques.[10] Thus, soluble high molecular weight phenylated poly(*p*-phenylene)s were synthesized by Diels−Alder reaction of bis(tetracyclone)s with *p*- or *m*-diethynylbenzene[8a−c] and of the bibenzynes with bis(tetracyclone)s.[8d] Additional classes of soluble poly(*p*-phenylene)s were obtained by the polymerization of 2,5-dibromo-1,4-di-*n*-alkylbenzenes and 2,5-dibromobiphenyl, respectively, using the Yamamoto reaction,[10a,b] Pd(0)-catalyzed polymerization of 4-bromo-2,5-di-*n*-hexylbenzeneboronic acid (i.e., the Suzuki reaction),[10c,d] anionic polymerization of 2-phenyl-1,3-cyclohexadiene followed by aromatization,[10b] and spontaneous polymerization of 1-bromo-4-lithiobenzene in hexamethylphosphoramide.[10e]

Hyperbranched polyphenylenes were synthesized by cocyclotrimerization of *p*-diethynylbenzene with phenylacetylene,[11] by Pd(0)-catalyzed coupling of (3,5-dibromophenyl)boronic acid,[12a] and by a stepwise variant of it.[12b] The first examples of macrocyclic oligo(*p*-phenylene) with degrees of oligomerization of up to 10 were synthesized by an indirect method.[12c] Both branched and macrocyclic polyphenylenes are soluble.

Soluble polyarylenes containing binaphthylene structural units were synthesized by the cation-radical polymerization of bis(1-naphthyl)biphenyls[13a] and by Ni(0)-catalyzed polymerization of 2,5-bis(4-chloro-1-naphthyl)biphenyl.[13b] The twisted binaphthylene structural unit is responsible for the solubility of the resulting polymers since it generates a large number of conformers along the chain.

In 1991 we reported a novel synthetic method for the preparation of functional PPP and polyarylenes starting from readily available hydroquinones and bisphenols via Ni(0)-catalyzed polymerization of their corresponding triflates and via the Ni(0) polymerization of various

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substituted dichlorobenzene derivatives.[14] This method is readily applicable to the preparation of a large variety of functionally substituted and soluble PPPs.[14b] Synthesis of PPP by Ni(0)-catalyzed polymerization of various dichlorobenzenes has very rapidly received interest in various laboratories.[15] Some of these substituted poly(*p*-phenylene)s can also be transformed into the unsubstituted and insoluble PPP via subsequent chemical modifications.[14b,15a,b] The synthesis of PPP from hydroquinones and bisphenols is limited by the high price of triflic anhydride which is required for the preparation of the corresponding triflates.

We recently ascertained reaction conditions under which a large variety of aryl sulfonates including aryl mesylate undergo Ni(0)-catalyzed homocoupling reactions.[16] The purpose of this paper is to report the use of this reaction to generate a novel method for the synthesis of functional polyphenylenes. Thus, polyphenylenes were synthesized via a Ni(0)-catalyzed homocoupling of functional bis[(methylsulfonyl)oxy] derivatives (i.e., bismesylates) of substituted hydroquinones. This novel synthetic procedure may prove to be one of the most convenient and versatile methods for the synthesis of soluble, well-defined, and functional PPPs with high molecular weight. Therefore, it opens novel and numerous synthetic capabilities in this field, since it uses readily available and/or accessible starting hydroquinones and bisphenols.

Experimental Section

General Considerations. Melting points are uncorrected and were determined with a Thomas Hoover Uni-Melt capillary melting point apparatus. ^{1}H-NMR (200-MHz) and ^{13}C-{^{1}H}-NMR (50-MHz) spectra were recorded on a Gemini-200 spectrometer, in $CDCl_3$ and with TMS as an internal standard except when reported. GC analyses were performed on a Hewlett Packard 5890 gas chromatograph using a flame ionization detector and a 3% SP-2250 column. Yields were determined by GC (diphenyl ether as an internal standard) and, in some cases, by ^{1}H-NMR spectroscopy. TLC analyses were performed on polyester sheets precoated with 0.25-mm-thick silica gel containing a 254-nm indicator (Kodak 13181). Column chromatographic purifications were performed with 32–63-mesh ICN silica gel or activated basic Brockmann I 150-mesh aluminum oxide. A Perkin-Elmer DSC-7 differential scanning calorimeter, equipped with a TAC 7/DX thermal analysis controller, was used to determine the thermal transitions which were reported as the maxima and minima of their endothermic and exothermic peaks, respectively. In all cases, heating and cooling rates were 20 °C/min. Glass transition temperatures (T_g) were read at the middle of the change in the heat capacity. Molecular weights were determined by gel permeation chromatography (GPC) with a Perkin-Elmer series 10 LC instrument equipped with an LC-100 column oven and a Nelson analytical 900 series integrator data station. The measurements were made at 40 °C using the UV detector set at 254 nm. A set of Perkin-Elmer PL gel columns of 10^4 and 500 Å with THF as solvent (1 mL/min) and a calibration plot constructed with polystyrene standards was used to determine the molecular weights. High-pressure liquid chromatography (HPLC) experiments were performed with the same instrument.

Materials. All reagents were purchased from commercial sources (Aldrich or Lancaster) and used without further purification except when reported. Pyridine was dried over CaH_2 and distilled. THF was distilled over sodium/benzophenone. Zinc dust was stirred in acetic acid, washed with water, and dried *in vacuo* at 120 °C. $NiCl_2(PPh_3)_2$ was prepared according to a literature procedure.[17]

2,5-Dihydroxybenzoic acid, 3,5-dihydroxybenzoic acid, phenylhydroquinone, methylhydroquinone, *tert*-butylhydroquinone, 1,4-dimethoxybenzene, 1,4-dichlorobenzoic acid (all from Aldrich), 2,5-dimethoxybenzonitrile, 1,4-dibromobenzoic acid (Lancaster), and diethyl 2,5-dihydroxyterephthalate (Riedel-Dehaen Co.) were used as received.

2,5-Dihydroxybenzophenone was synthesized by a published procedure.[18] 2-Ethylhexyl 2,5-dibromobenzoate and 2-ethylhexyl 2,5-dichlorobenzoate were prepared by acid-catalyzed esterification of 2,5-dibromobenzoic acid and 2,5-dichlorobenzoic acid with 2-ethyl-1-hexanol.[19] Unless otherwise noted, all compounds synthesized in the present chapter were purified until their 200-MHz ^{1}H-NMR spectra corresponded to the expected structure, and the purity was established by comparison with published mp's or found to be higher than 99.5% by GC or HPLC.

Monomer Synthesis. All dihydroxybenzoates were prepared by acid-catalyzed esterification of dihydroxybenzoic acid with the corresponding alcohols.[18]

Methyl 2,5-dihydroxybenzoate: 78%; white crystals (hexanes/EtOAc); mp 84–85 °C; ^{1}H NMR δ 7.28 (d, J = 2.0 Hz, 1H, ortho to $-\mathrm{CO_2CH_3}$), 7.01 (d, J = 8.2 Hz, 1H, para to $-\mathrm{CO_2CH_3}$), 6.87 (d, J = 8.0 Hz, 1H, meta to $-\mathrm{CO_2CH_3}$), 3.87 (s, 3H, $-\mathrm{CO_2C}H_3$).

Methyl 3,5-dihydroxybenzoate: 94%; white crystals (hexanes/EtOAc); mp 163–165 °C; ^{1}H NMR δ 8.60 (br s, 2H, $-\mathrm{O}H$), 6.63 (d, J = 2.2 Hz, 2H, ortho to $-\mathrm{CO_2CH_3}$), 6.20 (d, J = 2.2 Hz, 1H, para to $-\mathrm{CO_2CH_3}$), 3.50 (s, 3H, $-\mathrm{CO_2C}H_3$).

2-Ethylhexyl 2,5-dihydroxybenzoate: 88%; colorless oil; ^{1}H NMR δ 10.53 (s, 1H, $-\mathrm{O}H$), 7.30 (d, J = 2.9 Hz, 1H, ortho to $-\mathrm{CO_2}-$), 7.01 (dd, J = 8.9 and 3.0 Hz, 1H, para to $-\mathrm{CO_2}-$), 6.89 (d, J = 8.9 Hz, 1H, meta to $-\mathrm{CO_2}-$), 5.86 (s, 1H, $-\mathrm{O}H$), 4.24 (d, J = 5.7 Hz, 2H, $-\mathrm{CO_2C}H_2\mathrm{CH}-$), 1.73–1.67 (m, 1H, $-\mathrm{CO_2CH_2C}H\mathrm{(CH_2CH_3)(CH_2)_3CH_3}$), 1.46–1.24 (m, 8H, $-\mathrm{CO_2CH_2CH(C}H_2\mathrm{CH_3)(C}H_2\mathrm{)_3CH_3}$), 0.96–0.84 (m, 6H, $-\mathrm{CO_2CH_2CH(CH_2C}H_3\mathrm{)(CH_2)_3C}H_3$).

Isopropyl 2,5-dihydroxybenzoate: 77%; colorless oil; ^{1}H NMR δ 7.91 (d, J = 3.0 Hz, 1H, ortho to $-\mathrm{CO_2}-$), 7.62 (d, J = 10.0, Hz, 1H, para to $-\mathrm{CO_2}-$), 7.60 (d, J = 9.0 Hz, 1H, meta to $-\mathrm{CO_2}-$), 5.85 (sept, J = 7.0 Hz, 1H, $-\mathrm{CO_2C}H\mathrm{(CH_3)_2}$), 5.70 (br s, 2H, $-\mathrm{O}H$), 1.95 (d, J = 7.0 Hz, 6H, $-\mathrm{CO_2CH(C}H_3\mathrm{)_2}$).

2,5-Dihydroxybenzonitrile was prepared from 2,5-dimethoxybenzonitrile:[20] 88%; white crystals (EtOH); mp 150 °C; ^{1}H NMR δ 9.75 (br s, 2H, $-\mathrm{O}H$), 6.93–6.80 (m, 3H, aromatic protons).

2-Ethylhexyl 2,5-dibromobenzoate: 82%; colorless oil; bp 110–113 °C/0.1 mmHg; ^{1}H NMR δ 7.90 (d, J = 2.3 Hz, 1H, ortho to $-\mathrm{CO_2}-$), 7.50 (d, J = 8.5 Hz, 1H, meta to $-\mathrm{CO_2}-$), 7.46 (dd, J = 8.5 and 2.1 Hz, 1H, para to $-\mathrm{CO_2}-$), 4.28 (d, J = 5.7 Hz, 2H, $-\mathrm{CO_2C}H_2\mathrm{CH}-$), 1.78–1.66 (m, 1H, $-\mathrm{CO_2CH_2C}H\mathrm{(CH_2CH_3)(CH_2)_3CH_3}$), 1.42–1.34 (m, 8H, $-\mathrm{CO_2CH_2CH(C}H_2\mathrm{CH_3)(C}H_2\mathrm{)_3CH_3}$), 0.98–0.90 (m, 6H, $-\mathrm{CO_2CH_2CH(CH_2C}H_3\mathrm{)(CH_2)_3C}H_3$).

2-Ethylhexyl 2,5-dichlorobenzoate: 82%; colorless oil; bp 111–114 °C/0.06 mmHg; ^{1}H NMR δ 7.80 (d, J = 1.5 Hz, 1H, ortho to $-\mathrm{CO_2}-$), 7.39 (s, 2H, meta and para to $-\mathrm{CO_2}-$), 4.28 (d, J = 5.6 Hz, 2H, $-\mathrm{CO_2C}H_2\mathrm{CH}-$), 1.77–1.63 (m, 1H, $-\mathrm{CO_2CH_2C}H\mathrm{(CH_2CH_3)(CH_2)_3CH_3}$), 1.52–1.25 (m, 8H, $-\mathrm{CO_2CH_2CH(C}H_2\mathrm{CH_3)(C}H_2\mathrm{)_3CH_3}$), 0.98–0.89 (m, 6H, $-\mathrm{CO_2CH_2CH(CH_2C}H_3\mathrm{)(CH_2)_3C}H_3$).

Substituted 2,5-dimethoxybenzophenones were obtained by the Friedel–Crafts acylation of 1,4-dimethoxybenzene with the appropriate acid chloride.

2,5-Dimethoxy-4′-fluorobenzophenone. $AlCl_3$ (21 g, 0.158 mol) was slowly added to a solution of 1,4-dimethoxybenzene (20 g, 0.145 mol) in CH_2Cl_2 (140 mL) at 0 °C. 4-Fluorobenzoyl chloride (25.3 g, 0.160 mol) (prepared from 4-fluorobenzoic acid and thionyl chloride) was added dropwise. The reaction mixture was stirred at 0 °C for 8 h and then poured into ice water (100 mL) containing concentrated HCl (10 mL). The organic phase was separated, washed (10% NaOH), dried ($MgSO_4$), and evaporated. Recrystallization (95% EtOH) gave 34 g (90%): mp 51–52 °C (lit.[16b] mp 52 °C); ^{1}H NMR δ 7.88–7.81 (m, 2H, aromatic protons meta to fluorine), 7.13–6.90 (m, 5H, two aromatic protons ortho to fluorine and three aromatic protons ortho, meta, and para to carbonyl), 3.77 (s, 3H, $-\mathrm{OC}H_3$ ortho to carbonyl), 3.65 (s, 3H, $-\mathrm{OC}H_3$ meta to carbonyl).

2,5-Dimethoxy-4′-chlorobenzophenone was prepared using 4-chlorobenzoyl chloride: 85%; white crystals (benzene);

mp 72–73 °C; ^{1}H NMR δ 7.60 (d, J = 8.6 Hz, 2H, meta to chlorine), 7.40 (d, J = 8.6 Hz, 2H, ortho to chlorine), 7.02–6.90 (m, 3H, ortho, meta, and para to carbonyl), 3.80 (s, 3H, $-\mathrm{OC}H_3$ ortho to carbonyl), 3.67 (s, 3H, $-\mathrm{OC}H_3$ meta to carbonyl).

2,5-Dimethoxy-4′-*tert*-butylbenzophenone: 84%; white crystals (benzene); mp 50 °C (lit.[16b] mp 39–40 °C); ^{1}H NMR δ 7.78 (d, J = 8.4 Hz, 2H, meta to *tert*-butyl), 7.45 (d, J = 8.4 Hz, 2H, ortho to *tert*-butyl), 6.98–6.89 (m, 3H, ortho, meta, and para to carbonyl), 3.78 (s, 3H, $-\mathrm{OC}H_3$ ortho to carbonyl), 3.69 (s, 3H, $-\mathrm{OC}H_3$ meta to carbonyl), 1.34 (s, 9H, $-\mathrm{C(C}H_3)_3$).

Substituted 2,5-dihydroxybenzophenones were synthesized by the BBr_3-induced cleavage of the CH_3–O bonds of the corresponding substituted 2,5-dimethoxybenzophenones.[21]

2,5-Dihydroxy-4′-fluorobenzophenone. 2,5-Dimethoxy-4′-fluorobenzophenone (20 g, 0.077 mol, in 150 mL of CH_2Cl_2) was added dropwise to a solution of 1.0 M BBr_3 in CH_2Cl_2 (195 mL, 0.195 mol) and CH_2Cl_2 (150 mL) at −30 °C, over 30 min. The reaction mixture was allowed to warm to 22 °C, stirred for 5 h, and slowly poured into a mixture of ice water (500 mL) and Et_2O (300 mL). The organic phase was separated, washed (H_2O), and dried ($MgSO_4$). Evaporation and recrystallization (hexane/EtOAc) gave 12.0 g (80%) of yellow crystals: mp 140–141 °C; ^{1}H NMR δ 11.31 (br s, 2H, $-\mathrm{O}H$), 7.74–7.68 (m, 2H, aromatic protons meta to fluorine), 7.19–7.00 (m, 5H, two aromatic protons ortho to fluorine and three aromatic protons ortho, meta, and para to *p*-fluorobenzoyl).

2,5-Dihydroxy-4′-*tert*-butylbenzophenone: 86%; yellow crystals (hexanes/EtOAc); mp 115–116 °C; ^{1}H NMR δ 11.63 (br s, 2H, $-\mathrm{O}H$), 7.62 (d, J = 8.4 Hz, 2H, meta to *tert*-butyl), 7.50 (d, J = 8.4 Hz, 2H, ortho to *tert*-butyl), 7.09–6.97 (m, 3H, aromatic protons ortho, meta, and para to *p*-*tert*-butylbenzoyl), 1.36 (s, 9H, $-\mathrm{C(C}H_3)_3$).

Aryl Bismesylates: Aryl bismesylates were synthesized by the reaction of methanesulfonyl chloride with the corresponding phenol in pyridine.[22]

4′-Fluoro-2,5-bis[(methylsulfonyl)oxy]benzophenone. Methanesulfonyl chloride (16.3 g, 0.142 mol) was added dropwise to a solution of 4′-fluoro-2,5-dihydroxylbenzophenone (11 g, 0.047 mol) in pyridine (80 mL) at 0 °C. The mixture was warmed to 22 °C and stirred for 12 h. The reaction mixture was poured into water (800 mL), and the resulting precipitate was collected, washed (H_2O), and recrystallized twice ($CHCl_3$/EtOAc) to yield white crystals (12.9 g, 71%): mp 141–142 °C; ^{1}H NMR δ 7.73–7.66 (m, 2H, meta to fluorine), 7.40 (br s, 2H, ortho and para to *p*-fluorobenzoyl), 7.28 (br s, 1H, meta to *p*-fluorobenzoyl), 7.08–6.99 (m, 2H, ortho to fluorine), 3.10 (s, 3H, $-\mathrm{OSO_2C}H_3$ ortho to carbonyl), 2.93 (s, 3H, $-\mathrm{OSO_2C}H_3$ meta to carbonyl).

Methyl 2,5-bis[(methylsulfonyl)oxy]benzoate: 81%; white crystals (benzene); mp 70–71 °C; ^{1}H NMR δ 7.90 (s, 1H, ortho to $-CO_2CH_3$), 7.52 (s, 2H, meta and para to $-CO_2CH_3$), 3.95 (s, 3H, $-\mathrm{CO_2C}H_3$), 3.31 (s, 3H, $-\mathrm{OSO_2C}H_3$ ortho to $-CO_2CH_3$), 3.22 (s, 3H, $-\mathrm{OSO_2C}H_3$ meta to $-CO_2CH_3$).

Methyl 3,5-bis[(methylsulfonyl)oxy]benzoate: (84%; white crystals (benzene); mp 96–97 °C; ^{1}H NMR δ 7.92 (d, J = 2.3 Hz, 2H, ortho to $-CO_2CH_3$), 7.47 (d, J = 2.3 Hz, 1H, para to $-CO_2CH_3$), 3.95 (s, 3H, $-\mathrm{CO_2C}H_3$), 3.23 (s, 6H, $-\mathrm{OSO_2C}H_3$).

2-Ethylhexyl 2,5-bis[(methylsulfonyl)oxy]benzoate: 73%; viscous oil; ^{1}H NMR δ 7.85 (br s, 1H, ortho to $-CO_2-$), 7.52 (br s, 2H, meta and para to $-CO_2-$), 4.25 (d, J = 5.6 Hz, 2H, $\mathrm{CO_2C}H_2\mathrm{CH(CH_2CH_3)CH_2}-$), 3.31 (s, 3H, $-\mathrm{OSO_2C}H_3$ ortho to $-CO_2-$), 3.21 (s, 3H, $-\mathrm{OSO_2C}H_3$ meta to $-CO_2-$), 1.73 (m, 1H, $-\mathrm{CO_2CH_2C}H\mathrm{(CH_2CH_3)CH_2}-$), 1.51–1.25 (m, 8H, $-\mathrm{CO_2CH_2CH(C}H_2\mathrm{CH_3)(C}H_2)_3\mathrm{CH_3}$), 0.93–0.83 (m, 6H, $-\mathrm{CO_2CH_2CH(CH_2C}H_3\mathrm{)(CH_2)_3C}H_3$).

Isopropyl 2,5-bis[(methylsulfonyl)oxy]benzoate: 78%; white crystals (benzene); mp 69–70 °C; ^{1}H NMR δ 7.84 (br s, 1H, ortho to $-CO_2-$), 7.50 (br s, 2H, meta and para to $-CO_2-$), 5.26 (sept, J = 6.5 Hz, 1H, $-\mathrm{CO_2C}H\mathrm{(CH_3)_2}$), 3.30 (s, 3H, $-\mathrm{OSO_2C}H_3$ ortho to $-CO_2-$), 3.22 (s, 3H, $\mathrm{-OSO_2C}H_3$ meta to $-CO_2-$), 1.39 (d, J = 6.5 Hz, 6H, $-\mathrm{CO_2CH(C}H_3)_2$).

2,5-Bis[(methylsulfonyl)oxy]benzonitrile: 67%; white crystals ($CHCl_3$/EtOAc); mp 111–112 °C; ^{1}H NMR δ 7.41 (d, J = 2.3 Hz, 1H, ortho to −CN), 7.30–7.27 (m, 2H, meta and para to −CN), 3.07 (s, 3H, $-\mathrm{OSO_2C}H_3$ ortho to −CN), 2.96 (s, 3H, $-\mathrm{OSO_2C}H_3$ meta to −CN).

2,5-Bis[(methylsulfonyl)oxy]benzophenone: 80%; white crystals ($CHCl_3$/EtOAc); mp 118–119 °C; ^{1}H NMR δ 7.85–7.78 (m, 2H, ortho to carbonyl on phenyl), 7.70–7.41 (m, 6H, aromatic protons), 3.21 (s, 3H, $-\mathrm{OSO_2C}H_3$ ortho to benzoyl), 3.01 (s, 3H, $-\mathrm{OSO_2C}H_3$ meta to benzoyl).

4′-Chloro-2,5-bis[(methylsulfonyl)oxy]benzophenone: 89%; white crystals ($CHCl_3$/EtOAc); mp 153–154 °C; ^{1}H NMR δ 7.76 (d, J = 8.8 Hz, 2H, meta to chlorine), 7.57–7.42 (m, 5H, aromatic protons), 3.22 (s, 3H, $-\mathrm{OSO_2C}H_3$ ortho to *p*-chlorobenzoyl), 3.06 (s, 3H, $-\mathrm{OSO_2C}H_3$ meta to *p*-chlorobenzoyl).

4′-*tert*-Butyl-2,5-bis[(methylsulfonyl)oxy]benzophenone: 86%; white crystals (hexanes/EtOAc); mp 142–143 °C; ^{1}H NMR δ 7.74 (d, J = 8.4 Hz, 2H, meta to *tert*-butyl), 7.56–7.48 (m, 5H, aromatic protons), 3.20 (s, 3H, $-\mathrm{OSO_2C}H_3$ ortho to *p*-*tert*-butylbenzoyl), 3.02 (s, 3H, $-\mathrm{OSO_2C}H_3$ meta to *p*-*tert*-butylbenzoyl), 1.34 (s, 9H, $-\mathrm{C(C}H_3)_3$).

Diethyl 2,5-Bis[(methylsulfonyl)oxy]terephthalate: 81%; white crystals ($CHCl_3$/EtOAc); mp 134–135 °C; ^{1}H NMR δ 7.98 (s, 2H, aromatic protons), 4.42 (q, J = 7.1 Hz, 4H, $-\mathrm{CO_2C}H_2\mathrm{CH_3}$), 3.33 (s, 6H, $-\mathrm{OSO_2C}H_3$), 1.42 (t, J = 7.1 Hz, 6H, $-\mathrm{CO_2CH_2C}H_3$).

2-*tert*-Butyl-1,4-bis[(methylsulfonyl)oxy]benzene: 76%; white crystals ($CHCl_3$); mp 106–107 °C; ^{1}H NMR δ 7.60 (d, J = 9.1 Hz, 1H, meta to *tert*-butyl), 7.34 (d, J = 3.0 Hz, 1H, ortho to *tert*-butyl), 7.18 (dd, J = 9.1 and 3.0 Hz, 1H, para to *tert*-butyl), 3.29 (s, 3H, $-\mathrm{OSO_2C}H_3$ meta to *tert*-butyl), 3.16 (s, 3H, $-\mathrm{OSO_2C}H_3$ ortho to *tert*-butyl), 1.40 (s, 9H, $-\mathrm{C(C}H_3)_3$).

1,4-Bis[(methylsulfonyl)oxy]benzene: 90%; white crystals; mp 167–168 °C; ^{1}H NMR δ 7.36 (s, 4H, ortho to oxygen), 3.19 (s, 6H, $-\mathrm{OSO_2C}H_3$).

2-Methyl-1,4-bis[(methylsulfonyl)oxy]benzene: 92%; white crystals ($CHCl_3$/EtOAc); mp 87–88 °C; ^{1}H NMR δ 7.35 (d, J = 8.7 Hz, 1H, meta to methyl), 7.24–7.13 (m, 2H, ortho and para to methyl), 3.23 (s, 3H, $-\mathrm{OSO_2C}H_3$ meta to methyl), 3.16 (s, 3H, $-\mathrm{OSO_2C}H_3$ ortho to methyl), 2.34 (s, 3H, $-\mathrm{C}H_3$).

2,5-Bis[(methylsulfonyl)oxy]biphenyl: 84%; white crystals ($CHCl_3$); mp 118–119 °C; ^{1}H NMR δ 7.52 (m, 8H, aromatic protons), 3.20 (s, 3H, $-\mathrm{OSO_2C}H_3$ meta to phenyl), 2.56 (s, 3H, $-\mathrm{OSO_2C}H_3$ ortho to phenyl).

Aryl Bistriflates and Aryl Bis(*p*-fluorobenzenesulfonate)s. Aryl bistriflates[23] were synthesized by the reaction of triflic anhydride with the appropriate phenol in pyridine, and aryl bis(*p*-fluorobenzenesulfonate)s were synthesized by the reaction of the *p*-fluorobenzenesulfonyl chloride with the corresponding phenol in pyridine.

2-Ethylhexyl 2,5-bis[[(4-fluorophenyl)sulfonyl]oxy]benzoate: 69%; pale yellowish oil; ^{1}H NMR δ 7.95–7.84 (m, 4H, meta to fluorine), 7.43 (d, J = 2.7 Hz, 1H, ortho to $-CO_2-$), 7.29–7.12 (m, 6H, four aromatic protons ortho to fluorine on *p*-fluorophenyl and two aromatic protons meta and para to $-CO_2-$), 4.12 (d, J = 6.5 Hz, 2H, $-\mathrm{CO_2C}H_2\mathrm{CH(CH_2CH_3)CH_2}-$), 1.77–1.61 (m, 1H, $-\mathrm{CO_2CH_2C}H\mathrm{(CH_2CH_3)CH_2}-$), 1.43–1.29 (m, 8H, $-\mathrm{CO_2CH_2CH(C}H_2\mathrm{CH_3)(C}H_2)_3\mathrm{CH_3}$), 0.94–0.86 (m, 6H, $-\mathrm{CO_2CH_2CH(CH_2C}H_3\mathrm{)(CH_2)_3C}H_3$).

2-Ethylhexyl 2,5-bis(trifluoromethylsulfonyloxy)benzoate: 78%; colorless oil; bp 117–120 °C/0.1 mmHg; ^{1}H NMR δ 7.95 (d, J = 3.1 Hz, 1H, ortho to $-CO_2-$), 7.54 (dd, J = 9.0 and 3.1 Hz, 1H, para to $-CO_2-$), 7.45 (d, J = 9.0 Hz, 1H, meta to $-CO_2-$), 4.31 (d, J = 5.1 Hz, 2H, $-\mathrm{CO_2C}H_2\mathrm{CH(CH_2CH_3)CH_2}-$), 1.85–1.67 (m, 1H, $-\mathrm{CO_2CH_2C}H\mathrm{(CH_2CH_3)CH_2}-$), 1.41–1.33 (m, 8H, $-\mathrm{CO_2CH_2CH(C}H_2\mathrm{CH_3)(C}H_2)_3\mathrm{CH_3}$), 0.99–0.90 (m, 6H, $-\mathrm{CO_2CH_2CH(CH_2C}H_3\mathrm{)(CH_2)_3C}H_3$).

Polymerizations. Method A. In a typical polymerization (Table 1, entry 1), a 125-mL Schlenk tube was charged with $NiCl_2(PPh_3)_2$ (115 mg, 0.175 mmol), Zn (800 mg, 12.3 mmol), Et_4NI (675 mg, 2.63 mmol), and a magnetic stirring bar. The tube was sealed with a rubber septum and the contents were dried at 22 °C under vacuum (1×10^{-6} mmHg) for 24 h. After placing the contents under an Ar atmosphere, dry THF (1.0 mL) was added via a syringe through the rubber septum. The mixture was stirred at 22 °C for 5 min (the color of the mixture gradually changed to deep red–brown). Methyl 2,5-bis[(methylsulfonyl)oxy]benzoate (568 mg, 1.75 mmol) in THF (0.5

Table 1. Ni(0)-Catalyzed Polymerization of Methyl 2,5-Bis[(methylsulfonyl)oxy]benzoate

	reaction conditions[a]				polymer				
entry	Ni(0) (mol %)	solvent	temp (°C)	time (h)	yield (%)	M_n	M_w/M_n	DP	T_g (°C)
1	10	THF	67	10	75	3950	2.24	29	
2	7	THF	67	10	50	2379	1.60	18	
3	5	THF	67	10	33	2109	1.34	16	
4	3	THF	67	1	5	2116	1.34	16	
5	1.5	THF	67	0.1[b]		oligomers			
6[c]	10	THF	67	24	71	3006	1.91	22	
7	10	dioxane	80	10	85	4260	2.00	32	
8	10	dioxane	80	24	80	4544	1.94	34	101
9[d]	10	dioxane	80	24	88	3832	2.08	29	
10	15	dioxane	80	24	94	4160	1.86	32	
11	10	DMAc	80	24	62	3033	1.40	23	
12[e]	10	DMAc	80	24	84	3083	2.15	23	
13[f]	10	DMAc	80	24	54	2594	1.30	19	
14[g]	10	DMAc	80	0.1[b]		oligomers			
15[h]	10	DMac	80	0.1[b]		oligomers			
16[i]	10	DMAc	80	0.1[b]		oligomers			

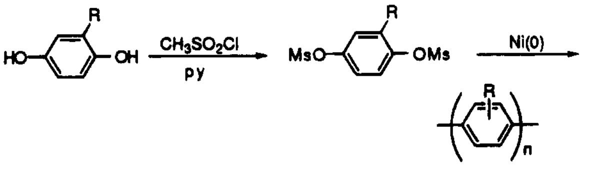
[a] Method A: $NiCl_2(PPh_3)_2/Et_4Ni/Zn$ (see the Experimental Section). [b] The catalyst decomposed immediately. [c] Additional PPh_3 (20 mol %). [d] Additional PPh_3 (10 mol %). [e] $NiCl_2$ (10%)/PPh_3 (77%)/Zn (310%) [f] $NiCl_2$ (10%)/PPh_3 (150%)/bpy (10%)/Zn (310%). [g] $NiCl_2$ (10%)/$AsPh_3$ (77%)/Zn (310%). [h] $NiCl_2$ (10%)/P(o-tolyl)$_3$ (77%)/Zn (310%). [i] $NiCl_2$ (10%)/PCy_3 (77%)/Zn (310%) were used respectively in the indicated amounts instead of $NiCl_2(PPh_3)_2/Et_4NI/Zn$.

mL) was added, and the mixture was heated at 67 °C for 10 h. After cooling to 22 °C, the reaction mixture was poured into 100 mL of methanol acidified with 25 mL of concentrated HCl. The resulting precipitate was collected by filtration and dissolved in 2 mL of $CHCl_3$. The solution was filtered and poured into 100 mL of methanol. The precipitate was collected by filtration and dried *in vacuo* (75 mg, 75%). The polymer was purified by reprecipitation into MeOH from a $CHCl_3$ solution before being analyzed by GPC (M_n = 3950, M_w/M_n = 2.24, DP = 29).

Method B. In a typical polymerization (Table 5, entry 5), a 125-mL Schlenk tube was charged with $NiCl_2(PPh_3)_2$ (115 mg, 0.175 mmol), Zn (800 mg, 12.25 mmol), Et_4NI (675 mg, 2.625 mmol), PPh_3 (275 mg, 1.048 mmol), 2,5-bis[(methylsulfonyl)oxy]biphenyl (599 mg, 1.75 mmol), and a magnetic stirring bar. The tube was sealed with a rubber septum, and the contents were dried at 22 °C under vacuum (1×10^{-6} mmHg) for 2 h. After the reactants were placed under an Ar atmosphere, 1.5 mL of dry THF was added via a syringe through the rubber septum. The mixture was stirred at 22 °C for 20 min (the color of the mixture gradually changed to deep red–brown) and heated at 67 °C for 24 h. After cooling to 22 °C, the reaction mixture was poured into 100 mL of methanol acidified with 25 mL of concentrated HCl. The resulting precipitate was collected by filtration and dissolved in 2 mL of $CHCl_3$. The solution was filtered and poured into 100 mL of methanol. The resulting precipitate was collected by filtration and vacuum dried (218 mg, 82%). The polymer was purified by reprecipitation into methanol from a $CHCl_3$ solution before being analyzed by GPC (M_n = 1310, M_w/M_n = 1.3, DP = 9).

Results and Discussion

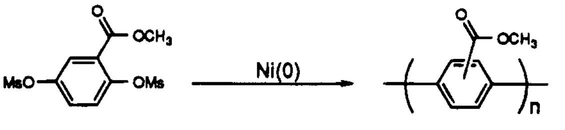
The general procedure for the preparation of functional poly(*p*-phenylene)s utilized the Ni(0)-catalyzed homocoupling reaction of aryl bismesylates derived from substituted hydroquinones (eq 1).



(1)

Two general methods for the *in situ* preparation of Ni(0) catalysts from air-stable precursors were used.[16a] These methods were previously developed as effective catalytic systems in Ni(0)-mediated coupling reactions of aryl halides and aryl triflates.[16,24a–e] The first method (method A) involved the generation of the Ni(0) catalyst upon the addition of solvent (usually THF) to a mixture of $NiCl_2(PPh_3)_2$, Zn, and Et_4NI under an inert atmosphere.[24a] After stirring the mixture for 5 min, the formation of Ni(0) was indicated by a red–brown solution color. Then a solution containing monomer was added to the mixture via syringe. The second method (method B) involved the generation of the Ni(0) catalyst upon the addition of solvent (usually THF) to a mixture of $NiCl_2(PPh_3)_2$, Zn, Et_4NI, and PPh_3 under an inert atmosphere in the presence of the monomer. This method was developed for dipolar aprotic solvents such as DMF and DMAc.[24c–e] The Ni(0) catalysts prepared by either method had a deep red–brown color. The color provided a visual indication of Ni(0) catalyst formation and decomposition. Et_4NI has been proposed to function as a bridging agent between Ni and Zn, thus facilitating electron transfer in the reduction of Ni(II) to Ni(0) and Ni(III) to Ni(I).[24a,b]

The initial polymerization reactions utilized methyl 2,5-bis[(methylsulfonyl)oxy]benzoate as the monomer (eq 2).



1 2 (2)

This monomer was chosen for the initial polymerization reactions because electron-withdrawing substituent groups (including *p*-alkoxycarbonyl) have been demonstrated to activate aryl halides,[24e] triflates,[14b,16a] and mesylates[16] in Ni(0)-mediated homocoupling reactions. The results obtained for the polymerization of methyl 2,5-bis[(methylsulfonyl)oxy]benzoate are summarized in Table 1. In THF, optimum results (75% yield, M_n = 3950) were obtained using 10% nickel catalyst (Table 1, entry 1). Reaction yields dropped dramatically when lesser amounts of catalyst were used (Table 1, entries 2–5). The addition of PPh_3 to Ni(0) catalysts is known to stabilize the Ni(0) catalyst, resulting in less premature catalyst decomposition as well as reducing side products formed by phenyl group transfer from PPh_3.[16a,24b,25] The addition of 20 mol % PPh_3 resulted in an increased reaction time (10 h to 24 h) and a slight decrease in molecular weight (cf. Table 1, entries 1 and 6). Slightly increased yields and molecular weight were obtained in dioxane at higher temperatures (cf. Table 1, entries 1 and 7) which enhance the solubility. The addition of PPh_3 to the reaction solution did not result in improved molecular weight (cf. Table 1, entries 8 and 9). Also, molecular weight was not increased by an increase to 15% Ni catalyst (cf. Table 1, entries 8 and 10). Decreased yields and molecular weights were obtained when the polymerization was performed in DMAc using method A (cf. Table 1, entries 1, 8, and 11). There was no significant change in molecular weight when the catalyst was generated from $NiCl_2$ and excess PPh_3 instead of $NiCl_2(PPh_3)_2$ and Et_4NI (Table 1, entry 12). Phenyl group transfer is often a side reaction in Ni(0)-catalyzed reactions.[26] The occurrence of this side reaction in the polymerization reaction would result in

Table 2. Ni(0)-Catalyzed Polymerization of 2-Ethylhexyl 2,5-Bis[(methylsulfonyl)oxy]benzoate

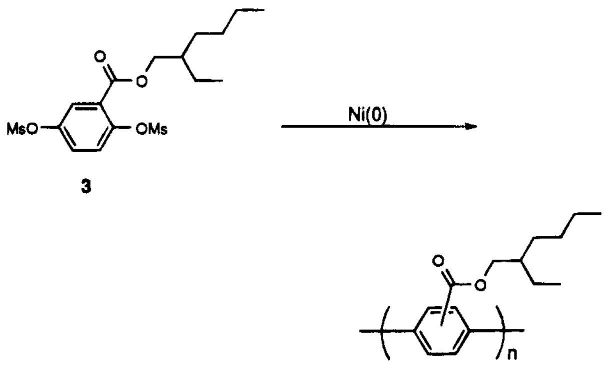
	reaction conditions[a]					polymer				
entry	additional PPh_3 (equiv)[b]	Zn (equiv)[b]	solvent	temp (°C)	time (h)	yield (%)	M_n	M_w/M_n	DP	T_g
1	none	1.7	THF	67	10	16	1852	1.24	8	
2	none	5	THF	67	10	45	1870	1.28	8	
3	none	7	THF	67	10	66	2443	1.63	11	
4	0.1	7	THF	67	24	89	1670	1.52	7	
5	0.2	7	THF	67	24	90	2351	1.82	10	
6	0.4	7	THF	67	24	97	4960	2.47	21	
7	0.6	7	THF	67	24	96	7230	2.60	31	−3[d]
8	none[c]	7	THF	67	24	63	2211	1.72	10	
9	none	7	dioxane	80	10	18	2064	1.35	9	

[a] Method A: $NiCl_2(PPh_3)_2/Et_4NI/Zn$. [b] Equivalents relative to monomer. [c] 0.1 equiv of 2,2′-dipyridyl was added. [d] T_{n-i} = 59 °C (1st heating scan).

a reduction of molecular weight. 2,2′-Dipyridyl has been effective in some Ni(0)-catalyzed reactions in suppressing a phenyl group transfer.[24e] The addition of 2,2′-dipyridyl resulted in a decreased yield and molecular weight (Table 1, entries 12 and 13). The substitution of the PPh_3 ligand with $AsPh_3$, P(*p*-tolyl)$_3$, or P(cy)$_3$ resulted in rapid catalyst decomposition and the concomitant formation of oligomers (Table 1, entries 14–16). The highest molecular weight obtained with methyl 2,5-bis[(methylsulfonyl)oxy]benzoate was 4544 (Table 1, entry 8).

It is noted again that the reported molecular weights were determined by GPC relative to polystyrene standards. This allows facile comparison with molecular weights previously reported in the literature by many research groups. However, these reported apparent molecular weights versus polystyrene are expected to be overestimates of the actual M_n's of the PPPs synthesized in this paper.

A larger and branched substituent, [(2-ethylhexyl)oxy]carbonyl, was used in an effort to increase the molecular weight of the resulting polymer (eq 3).



3

4

(3)

Through increased configurational entropy, this group was expected to make the resulting polymer more soluble, consequently increasing the number of repeat units allowed in the polymer chain before precipitation occurred. Even though the resulting polymer was very soluble, there was no improvement in molecular weight (Table 2). This result is consistent with a retardation of the coupling reaction due to the large size of this group. Although the use of this group did not result in the desired increase in molecular weight, some noteworthy observations can be made from the results obtained with this series of reactions.

Relatively large amounts of Zn were necessary for the polymerization of sterically hindered monomers. Increases in both molecular weight and yield occurred as the relative amount of Zn increased (Table 2, entries 1–3). Thus, an additive effect was evidenced in regard to the amount of Zn required for polymerizations. This has precedent, as a Zn additive effect has, to a certain limit, been reported in Ni(0)-mediated reactions.[24e,27] The highest molecular weight polymers obtained from the sterically hindered monomer **3** were obtained with 7 equiv of Zn relative to monomer. In contrast, only 1.7 equiv of Zn (relative to the aryl mesylate) was necessary to obtain high conversions to symmetrical biaryls in the Ni(0)-mediated homocoupling reaction of aryl mesylates.[16] Thus, a larger amount of Zn was required for polymerizations. Finally, the Ni(0) coupling reaction employed is truly heterogeneous, as Zn is not soluble in THF.

Increasing the amount of PPh_3 decreases the reaction rate by forming a more stable (and hence less reactive) Ni species.[25] Although a longer reaction time was required, a higher molecular weight was obtained with an increased amount of PPh_3 (Table 2, entries 4–7). A change in solvent to dioxane allowed an increase in reaction temperature. This was expected to increase the reactivity of the Ni catalyst toward the aryl bismesylates. However, the increase in temperature resulted in a lower molecular weight and yield (Table 2, entry 9). Contributing factors, to this, may be faster catalyst decomposition as well as the increased proportion of side reactions that often accompany a temperature increase.[28] As with **3**, the addition of 2,2′-dipyridyl did not result in an increase in molecular weight (Table 2, entries 3 and 8).

Attachment of the bulky and noncrystallizable substituent [(2-ethylhexyl)oxy]carbonyl to the backbone of the poly(*p*-phenylene) resulted in highly enhanced solubility of the polymer. However, the molecular weight of the polymer may be limited by the increased number of side reactions associated with sterically hindered substrates. To investigate this, four other aryl monomers with the [(2-ethylhexyl)oxy]carbonyl substituent but different leaving groups (Br, Cl, $OSO_2C_6H_4$-*p*-F, OSO_2CF_3) were polymerized. The results of polymerization of five monomers under the identical conditions are summarized in Table 3. In THF, the molecular weight and polymer yield increase in the order of OSO_2CH_3 < Br < $OSO_2C_6H_4$-*p*-F < OSO_2CF_3 < Cl (Table 3, entries 1–5). Using dioxane as the solvent at an elevated reaction temperature, the less reactive[16a] bismesylate and bis(*p*-fluorobenzenesulfonate) gave slight changes in molecular weight. In comparison, the more reactive dichloro and bistriflate[14] were sensitive to the increase in temperature, resulting in a significant decrease in molecular weight (Table 3, entries 8 and 9). This is consistent with the more reactive groups becoming much less selective under more vigorous reaction conditions, which is in agree-

Table 3. Ni(0)-Catalyzed Polymerization of [(2-Ethylhexyl)oxy]carbonyl-Substituted Benzene Derivatives Containing Bromine, Chlorine, Trifluoromethanesulfonate, 4-Fluorobenzenesulfonate, and Methanesulfonate Leaving Groups

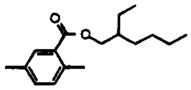
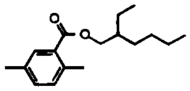
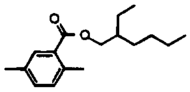
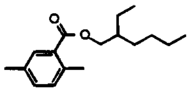
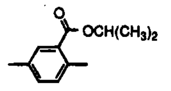
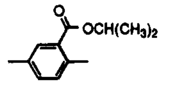
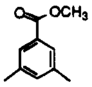
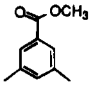
	reaction conditions[a]			polymer			
entry	leaving group	solvent	temp (°C)	yield (%)	M_n	M_w/M_n	DP
1	OSO_2CH_3	THF	67	66	2443	1.63	11
2	OSO_2PhF	THF	67	80	6467	1.70	28
3	OSO_2CF_3	THF	67	81	8471	2.60	36
4	Cl	THF	67	87	12905	2.88	56
5	Br	THF	67	81	2729	1.55	12
6	OSO_2CH_3	dioxane	80	48	2064	1.35	9
7	OSO_2PhF	dioxane	80	94	6805	2.60	29
8	OSO_2CF_3	dioxane	80	83	4223	1.97	18
9	Cl	dioxane	80	82	5068	2.89	22
10	Br	dioxane	80	84	1924	1.82	8

[a] Polymerization using method A: $NiCl_2(PPh_3)_2/Et_4NI/Zn$.

ment with the reactivity–selectivity principle.[24f] However, this lessening of selectivity was less pronounced with less reactive bismesylate and bis(*p*-fluorobenzenesulfonate). Side reactions compete more effectively with homocoupling as steric hindrance increases. The dichloride, which is usually the least reactive leaving group (ArCl < ArBr < ArI) among aryl halides in most other Ni(0) homocoupling reactions,[24a–e] produces higher molecular weight polymers than bistriflate (Table 3, entries 3 and 4). However, at higher reaction temperature, the selectivity is less than *p*-fluorobenzenesulfonate (Table 3, entries 7 and 9). The dibromo monomers which contain a usually more reactive leaving group than the chloro group gave poor results in both THF and dioxane (Table 3, entries 5 and 10). This was again consistent with the more reactive substrates possessing less selectivity when a large sterically hindering group was present ortho to the carbon which could participate in the coupling reaction. To summarize the results of Table 3, four monomers (i.e., Br, Cl, $OSO_2C_6H_4$-*p*-F, OSO_2CF_3), which are expected to be more reactive than bismesylate monomers, did not give the high molecular weight polymers. This indicated that high molecular weights would not be obtained through the homopolymerization of a 1,4-bismesylate monomer containing the sterically bulky [(2-ethylhexyl)oxy]carbonyl group, under the reaction conditions employed.

The copolymerization of two monomers was the next method investigated in the effort to obtain soluble high molecular weight polymers by increasing the configurational entropy of the main chain. Methyl 2,5-bis[(methylsulfonyl)oxy]benzoate had limited solubility which resulted in premature precipitation of the polymer from the reaction solution. This gave low molecular weight polymer (Table 1). In order to increase the solubility of the polymer, methyl 2,5-bis[(methylsulfonyl)oxy]benzoate was copolymerized with 2-ethylhexyl 2,5-bis[(methylsulfonyl)oxy]benzoate in different molar ratios under the same reaction conditions (Table 4, entries 1–4). Highest M_n and yield were obtained with 50 mol % 2-ethylhexyl 2,5-bis[(methylsulfonyl)oxy]benzoate (Table 4, entry 4). A slightly higher degree of polymerization was obtained when 25 mol % of this comonomer was used (Table 4, entry 3). All the polymers from these copolymerizations are soluble. When using isopropyl 2,5-bis[(methylsulfonyl)oxy]benzoate as comonomer, a large mole percent was required to increase the solubility and molecular weight (Table 4, entries 5 and 6) since it has a smaller branched substituent group than 2-ethylhexyl 2,5-bi[s(methylsulfonyl)oxy]benzoate. However, when methyl 3,5-bis[(methylsulfonyl)oxy]benzoate was the comonomer, 10 mol % comonomer ratio was enough to give soluble and relatively high molecular weight polymers (Table 4, entries 7 and 8). This is because kinked phenylenic units are generated in the main chain from this unit.

Table 4. Ni(0)-Catalyzed Copolymerization of Methyl 2,5-Bis[(methylsulfonyl)oxy]benzoate with Various Comonomers MsOArOMs[a]

entry	Ar of comonomer	mol % Ar	yield (%)	M_n	M_w/M_n	DP	T_g, °C
1		5	82	4390	1.6	32	98
2		10	89	7760	3.1	54	80
3		25	90	8860	2.3	56	54
4		50	99	9400	2.2	51	30
5		10	82	4880	1.7	36	106
6		50	88	7250	2.3	49	90
7		10	85	6140	2.4	46	123
8		50	98	4450	3.0	33	181

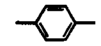
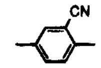
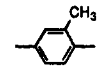
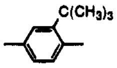
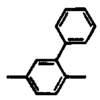
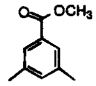
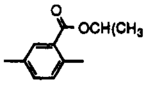
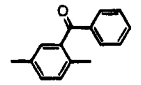
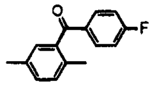
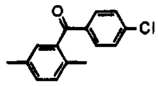
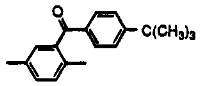
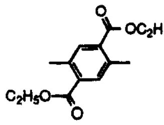
[a] Polymerization using method B: $NiCl_2(PPh_3)_2/PPh_3/Et_4NI/Zn/THF$.

A wide variety of aryl bismesylates was polymerized (Table 5). Insoluble products were obtained in the homopolymerization of 1,4-bis[(methylsulfonyl)oxy]benzene and 2-cyano-1,4-bis[(methylsulfonyl)oxy]benzene (Table 5, entries 1 and 2). The attachment of a methyl substituent to 1,4-bis[(methylsulfonyl)oxy]benzene resulted in a large increase in solubility ($M_n = 2150$, entry 3 in Table 5). In comparison with unsubstituted PPP, the attachment of *tert*-butyl or phenyl substituents also resulted in improved solubility (Table 5, entries 4 and 5). However, in regard to increasing the molecular weight of the resulting polymers they were not as effective as the methyl group. Substituents ortho to the mesylate group are known to retard the reaction.[16] The larger size of these groups inhibited the coupling reaction. Thus, the steric bulk of the *tert*-butyl group is sufficient enough to hinder the coupling reaction.

The attachment of an alkoxycarbonyl substituent to 1,4-bis[(methylsulfonyl)oxy]benzene results in much higher molecular weights (up to $M_n = 7230$; Table 2, entry 7). This group has several positive effects on the polymerization reaction. For example, the polymer is more soluble than unsubstituted poly(*p*-phenylene), so higher molecular weights are attainable. In addition, the alkoxycarbonyl group activates the aryl mesylate toward reaction with the Ni(0) catalyst. An important

Table 5. Ni(0)-Catalyzed Homocoupling Polymerization of Various Aryl Bismesylates MsOArOMs[a]

$$\mathrm{MsOArOMs} \xrightarrow{\mathrm{Ni(0)}} -(\mathrm{Ar})-_n$$

entry	Ar of MsOArOMs	yield (%)	M_n	M_w/M_n	DP	Tg, °C
1		50		insoluble		
2		68		insoluble		163
3		87	2150	1.4	24	62
4		85	690	1.1	6	54
5		82	1410	1.4	9	126
6		85	1150	1.2	9	136
7		88	4920	2.0	30	85
8		95	7370	3.3	41	162
9		68	20030	2.2	101	168
10		98		insoluble		
11		82	7170	2.9	30	180
12		81	2630	3.1	12	

[a] Polymerization using method B: $\mathrm{NiCl_2(PPh_3)_2/PPh_3/Et_4NI/Zn/THF}$.

factor in this increased reactivity is its electron-withdrawing ability via resonance.[16] When the group was in a position where it could not interact through resonance with the carbon undergoing substitution, there was no improvement of molecular weight (cf. Table 5, entry 6 and Table 1, entry 1). Some of this apparent effect may be the result of the more flexible polymer structure obtained from the meta-substituted monomer.

The benzoyl group is also an activating group through electron-withdrawing by resonance. The benzoyl group gave a molecular weight 7370 which corresponds to a DP 41 (Table 5, entry 8). The group can be made even more electron-withdrawing by substitution with a *p*-fluoro group. The highest molecular weight obtained in the homocoupling reaction was realized with this monomer (M_n = 20030, DP = 101; Table 5, entry 9). In addition, the *p*-fluoro group makes the polymer more soluble. The *p*-chlorobenzoyl-substituted monomer gave an insoluble gel (Table 5, entry 10). This was due to the participation of the chloro group in the polymerization reaction which yields a highly cross-linked polymer.

An increase in the molecular weight and solubility of poly(*p*-phenylene) polymers was realized by two general strategies. In the first, high molecular weight poly(*p*-phenylene)s were obtained by the homopolymerization of monomers containing strongly activating groups that were bulky enough to solubilize the corresponding polymers but not so bulky that they inhibited the coupling reaction in a deleterious manner. In an example, an aryl mesylate monomer containing the *p*-fluorobenzoyl group was polymerized to give high molecular weight substituted poly(*p*-phenylene) (M_n = 20 030; Table 5, entry 9). The alternative strategy which resulted in high molecular weight substituted poly(*p*-phenylene)s was the copolymerization of appropriately selected monomers (Table 4, entries 3 and 6).

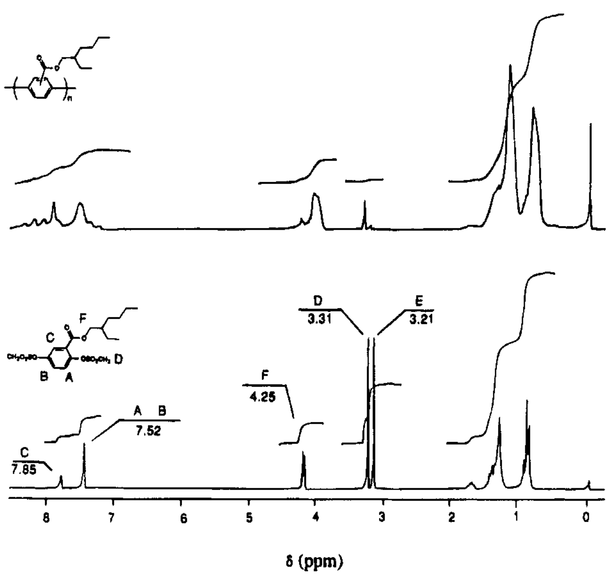
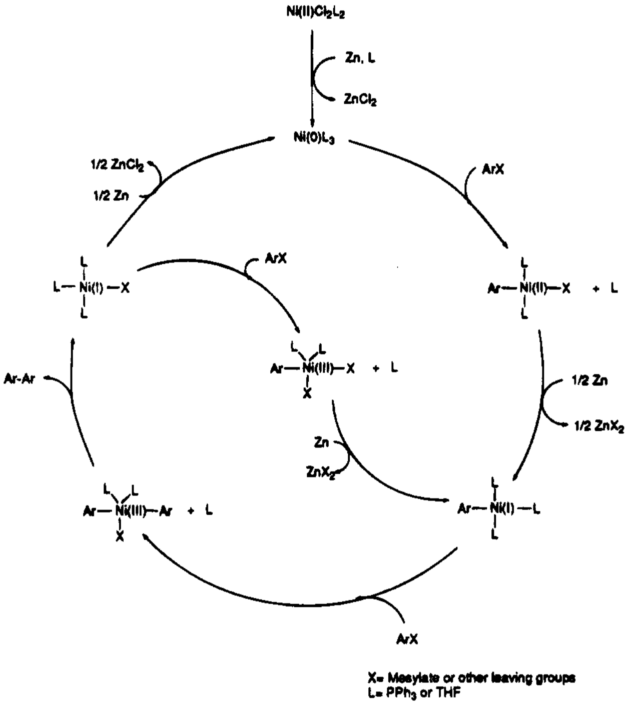


Figure 1. ^{1}H NMR spectra of (a) 2-ethylhexyl 2,5-bis[(methylsulfonyl)oxy]benzoate and (b) its oligomer.

Another factor which may affect the molecular weight is the effect of the substituent on the reactivity of the adjacent (i.e., ortho) mesylate. Yields in the homocoupling reaction of aryl mesylates are decreased to varying extents by the presence of an ortho substituent group.[16] In these cases, side reactions such as reduction and transarylation become more important.[16] In the Ni(0)-catalyzed polymerization reaction of aryl bismesylates, these side reactions would terminate polymer chain growth by end-capping the polymer. Furthermore, results from the polymerization of **3** indicate that the polymerization reaction is inhibited by bulky substituent groups ortho to the mesylate group. Additional evidence of the inhibitory effect of a substituent ortho to the mesylate can be found in the reaction of 2-ethylhexyl 2,5-bis[(methylsulfonyl)oxy]benzoate. The ^{1}H NMR spectrum (Figure 1) of the oligomer resulting from 2-ethylhexyl 2,5-bis[(methylsulfonyl)oxy]benzoate shows an important result. The 5-mesylate substituent was consumed to a greater degree than the 2-mesylate substituent. This implies that the 2-mesylate group was less reactive due to steric hindrance. If it was assumed that no side reactions occurred, the molecular weight can be calculated from the integration of the ^{1}H NMR spectrum of the oligomer. However, its molecular weight is much higher than the one obtained from GPC using a polystyrene standard. This implies that the other side reactions also consume the mesylate group. Since the oligomer shows a complicated ^{1}H NMR spectrum probably due to the presence of various constitutional isomeric structural units, the chain ends (except the mesylate end) were not fully characterized. In conclusion, the mesylate group ortho to a substituent

Scheme 1. Plausible Mechanism of Ni(0)-Catalyzed Homocoupling of Aryl Mesylate in the Presence of Excess Zn



group is less reactive toward the coupling reaction and is more susceptible to participation in side reactions.

The participation of side reactions involving the incorporation of phosphorus from triphenylphosphine into the polymer was considered. Two side reactions involving triphenylphosphine were recently shown to result in the incorporation of phosphorus into PPP.[26d–f] An aryl exchange reaction resulted in the formation of phenyl end caps or the incorporation of triarylphosphine groups that can serve as branch points or cross-links. The reaction of the chain ends of PPP with triphenylphosphine resulted in phosphonium ion end caps.[26d–f] The polymer obtained upon polymerization of 4′-fluoro-2,5-bis[(methylsulfonyl)oxy]benzophenone was examined by $^{31}P\{^{1}H\}$ NMR. No phosphorus was detected in this polymer.

Several different reaction mechanisms have been suggested for Ni(0)-catalyzed homocoupling reactions of aryl halides.[16a,24e,27,29] The primary mechanistic pathway followed is highly dependent on the reaction conditions. Under the conditions utilized for the coupling of aryl mesylates, the most plausible mechanism is shown in Scheme 1.[24e,27]

The first step of the mechanism involves the reduction of Ni(II) to Ni(0) by Zn. This is followed by the oxidative addition of ArX (X = mesylate or other sulfonate leaving group) to the Ni(0) species. The resulting Ni(II) species then undergoes an one-electron reduction to form $ArNi^{I}L_3$. ArX oxidatively adds to this species to give a diaryl nickel(III) complex which undergoes rapid reductive elimination, resulting in the formation of the biaryl product and the generation of $Ni^{I}XL_3$. There are two productive reaction pathways available to this Ni species. $Ni^{I}XL_3$ can be reduced by Zn to regenerate $Ni^{0}L_3$, which can then repeat the catalytic cycle. Alternatively, ArX can undergo direct oxidative addition to $Ni^{I}XL_3$ followed by reduction by Zn to form the $ArNi^{I}L_3$ species once again.

The oxidative addition of aryl triflate or aryl halide to Ni(0) and Ni(I) species and the reductive elimination of aryl groups from the bisarylnickel(III) complex are considered to be fast reactions. The rate-determining step in the homocoupling reaction of aryl halides under similar reaction conditions is the reduction of the unreactive arylnickel(II) species to the reactive arylnickel(I) species. The mechanism outlined in Scheme 1 is favored by excess amounts of Zn as well as the presence of iodide ion which enhances the reaction rate by bridging between Ni and Zn species in the single-electron-transfer reduction process.[16a,24e] At high conversion of ArX the rate-determining step becomes addition of ArX to the Ni(I) species.

The mechanism shown in Scheme 1 cannot be operative at high conversions when 10% Ni(0) catalyst is used. As the polymerization approaches completion, all of the aryl mesylate is consumed, but there is still arylnickel species present that have not reacted to give the coupled product. At this point, one possibility is that the polymerization reaction is completed following a mechanism similar to the one proposed by Tsou and Kochi, a double-chain mechanism involving the reaction of $ArNi^{III}X_2$ and $ArNi^{II}X$ to form $Ar_2Ni^{III}X$ in the key step.[29] However, the bimolecular step involves Ni species expected to be present in trace quantities when excess Zn is present. Thus, this mechanism is not expected to be favored when large amounts of Zn are present. Another possibility is that the final coupled product is formed as the result of a metathesis reaction proposed by Colon et al.[24e]

THF was the best solvent in reference to the rate and selectivity of the homocoupling reaction. Typical dipolar aprotic solvents for Ni(0) homocoupling such as DMF and DMAc, which can increase the nucleophilicity of Ni(0) and also act as donor ligands, gave poor results under our reaction conditions. When these solvents were utilized, deposition of a significant amount of nickel-black occurred within minutes of reaction initiation. Early catalyst decomposition was avoided by increasing the amount of PPh_3 present. However, this resulted in a substantial retardation of the reaction rate. Consequently, longer reaction times were required when additional PPh_3 was added. However, when using THF, no additional PPh_3 was required, except with sterically hindered substrates. It is likely that *in situ* generated $Ni^{0}(PPh_3)_2$ complexes were unstable in the more polar and strongly dissociating solvents such as DMF, producing Ni colloidal metal relatively fast before the completion of the reaction. In THF (less polar and slightly dissociating) the complexes are substantially less prone to decomposition. The effectiveness of $NiCl_2(PPh_3)_2$ catalyst without additional PPh_3 in less polar solvents such as THF especially in the presence of iodide source for Ni homocoupling also has been reported.[24e] Although it has been reported that $Ni^{0}PPh_3$ complexes exist in solution entirely as the tris complex (i.e., $Ni^{0}(PPh_3)_3$ due to the bulky PPh_3,[24b] our catalyst system generates $Ni^{0}(PPh_3)_2$ in the absence of added PPh_3. This highly coordinatively unsaturated reactive Ni complex might be stabilized by partial iodide coordination at the reaction temperature (67 °C). It is well-known that side reactions occur during the slow reaction and decrease the yield. Furthermore, at extended reaction times, deactivation of the catalyst would limit the yield. Therefore, the $NiCl_2(PPh_3)_2$, Zn, Et_4NI, and THF system was employed in order to avoid the side reaction and shorten the reaction time by *in situ* generating the reactive $Ni^{0}(PPh_3)_2$ species which would realize selective homocoupling almost free from side reactions. The selection of reaction temperature is another important factor in Ni-catalyzed homocoupling reactions. At higher temperatures side reactions occur to a greater extent.

Thus, it is advantageous to perform the reaction at as low of a temperature as possible. Consequently, the temperature was kept at 67 °C in most reactions.

Conclusions

Functional regioirregular substituted poly(*p*-phenylene)s have been synthesized by the Ni(0)-catalyzed homocoupling of functional bismesylates of substituted hydroquinones. This novel synthetic approach provides a convenient and versatile method for the synthesis of soluble, well-defined, and functional PPPs with high molecular weight. These functional PPPs are suitable starting materials for the synthesis of segmented copolymers and other polymers with more complex architectures.

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