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Regioregular and Regioirregular Poly(*p*-phenylene)s via Ni(0)-Catalyzed Homocoupling of Arylene Bismesylates

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ABSTRACT: Head-to-head regioregular poly(*p*-phenylene)s (PPPs) were synthesized via Ni(0)-catalyzed polymerization of 2,2′-disubstituted 4,4′-bis[(methylsulfonyl)oxy]biphenyls (**9**). The corresponding regioirregular PPPs were prepared by the Ni(0)-catalyzed homopolymerization of 2-substituted 1,4-bis[(methylsulfonyl)oxy]benzenes (**6**) and by copolymerization of **6** with **9**. The precursors of **6** and **9**, i.e., 2-substituted 1,4-dihydroxybenzene (**5**) and 2,2′-disubstituted 4,4′-dihydroxybiphenyl (**8**), were synthesized by a synthetic method elaborated previously in our laboratory [*J. Org. Chem.* **1995**, *60*, 1066]. Head-to-head regioregular PPPs are crystalline and insoluble (except when the substituent is 4-*tert*-butylbenzoyl) while the corresponding regioirregular polymers are noncrystalline and soluble. The highest molecular weight regioirregular PPP was obtained by copolymerization of a 1:1 ratio of **6** with the corresponding **9**. The influence of the size and the electronic properties of the substituent on the reactivity of monomers **6** and **9** and on the molecular weight of the regioirregular PPP is discussed. The highest molecular weight (M_n = 34 790, corresponding to 176 phenylene groups relative to polystyrene standards) regioirregular PPP was obtained with a 4-fluorobenzoyl substituent. Fluorine both influences the reactivity of the leaving group and acts as more than one substituent since the hydrogen(s) *ortho* to it is (are) acidic.

Introduction

Synthetic procedures for the preparation of substituted and unsubstituted poly(*p*-phenylene)s (PPP) can be classified as *direct* or *indirect* methods.[1−3] The two most efficient *direct* methods for the synthesis of PPP are based on the Suzuki cross-coupling and Ni(0)-catalyzed homocoupling reactions.[1−4] The application of Ni(0)-catalyzed homocoupling reactions to the synthesis of PPP was elaborated in our laboratory.[2,3a] Both substituted 1,4-dihalobenzenes (i.e., dibromo and dichloro)[2a,b,d,e] and bis(sulfonates) of substituted hydroquinones and other dihydroxyarylenes[2a−c,3a] were used as monomers in Ni(0)-catalyzed polymerization reactions. In our first series of experiments, chlorine and bromine groups were used only as models for the sulfonate leaving groups. Even so, the synthesis of PPP by Ni(0)-catalyzed polymerization of various dihalobenzenes has very rapidly received interest in various laboratories.[4] The use of aryl sulfonates in Ni(0)-catalyzed homocoupling reactions is of great synthetic value since it provides a method to generate carbon−carbon bonds from phenolic carbon−oxygen bonds. Since a large number of substituted hydroquinones and bisphenols are available commercially and readily through published procedures, this broadens considerably the scope of this synthetic methodology. However, the extensive application of this methodology to the synthesis of PPP has been slow since the very expensive triflate was the first successful leaving group used.[2a−c]

Recent investigations on less expensive sulfonate groups have demonstrated that aryl mesylates, which were previously considered to be unreactive toward transition metal catalysts, are under suitable reaction conditions very effective leaving groups in both homocoupling and cross-coupling reactions.[5] The homocoupling reaction of bis(methylsulfonyl)oxy derivatives (i.e., bismesylates) of substituted hydroquinones was subsequently applied to the synthesis of functional PPP.[3a] PPPs with number-average molecular weights (relative to polystyrene standards) of up to 20 300 (DP = 101) were obtained.

Although much progress has been made in the development of synthetic methods for the *direct* synthesis of PPP, there has been very little success in the control of their molecular weight and chain ends. In order to obtain high molecular weight PPPs, the coupling reaction needs to proceed with 100% conversion and the resulting polymer should be soluble in the polymerization solution. The solubility of the polymer is determined by its crystallinity and rate of crystallization. The melting temperature and the rate of crystallization of PPP can be decreased by increasing its configurational and conformational entropy.[6] Four common strategies for this are (a) the attachment of flexible lateral substituents which exhibit a large number of conformers,[7,8] (b) increasing the number of constitutional isomers of the aromatic repeat units,[2b,9] (c) generating a linear chain conformation from various *meta* and other phenylenic units,[2e] and (d) decreasing the rate of interconversion between the pseudo-atropisomeric conformers (i.e., replacing a 4,4′-diphenylene with a 4,4′-binaphthylene).[2c,f,10] The most soluble PPP obtained to date contained long alkyl pendant groups.[8a,c−e] Their solubility is due to the high entropy generated by the large number of conformational isomers of the side groups. When small substituents, which have few conformational or configurational isomers, are used, an enhancement of the overall entropy can be obtained only by increasing the number of constitutional isomeric monomeric repeat units.

This paper reports the synthesis of head-to-head (HH) regioregular PPPs by the Ni(0)-catalyzed homopolymerization of 2,2′-disubstituted 4,4′-bis[(methylsulfonyl)oxy]biphenyl. Regioirregular PPP was synthesized by the homopolymerization of 2-substituted 1,4-bis[(methylsulfonyl)oxy]benzene and its copolymerization with 2,2′-disubstituted 4,4′-bis[(methylsulfonyl)oxy]biphenyls. The influence of the PPP's regioregularity on the solubility and molecular weight of these polymers is discussed.

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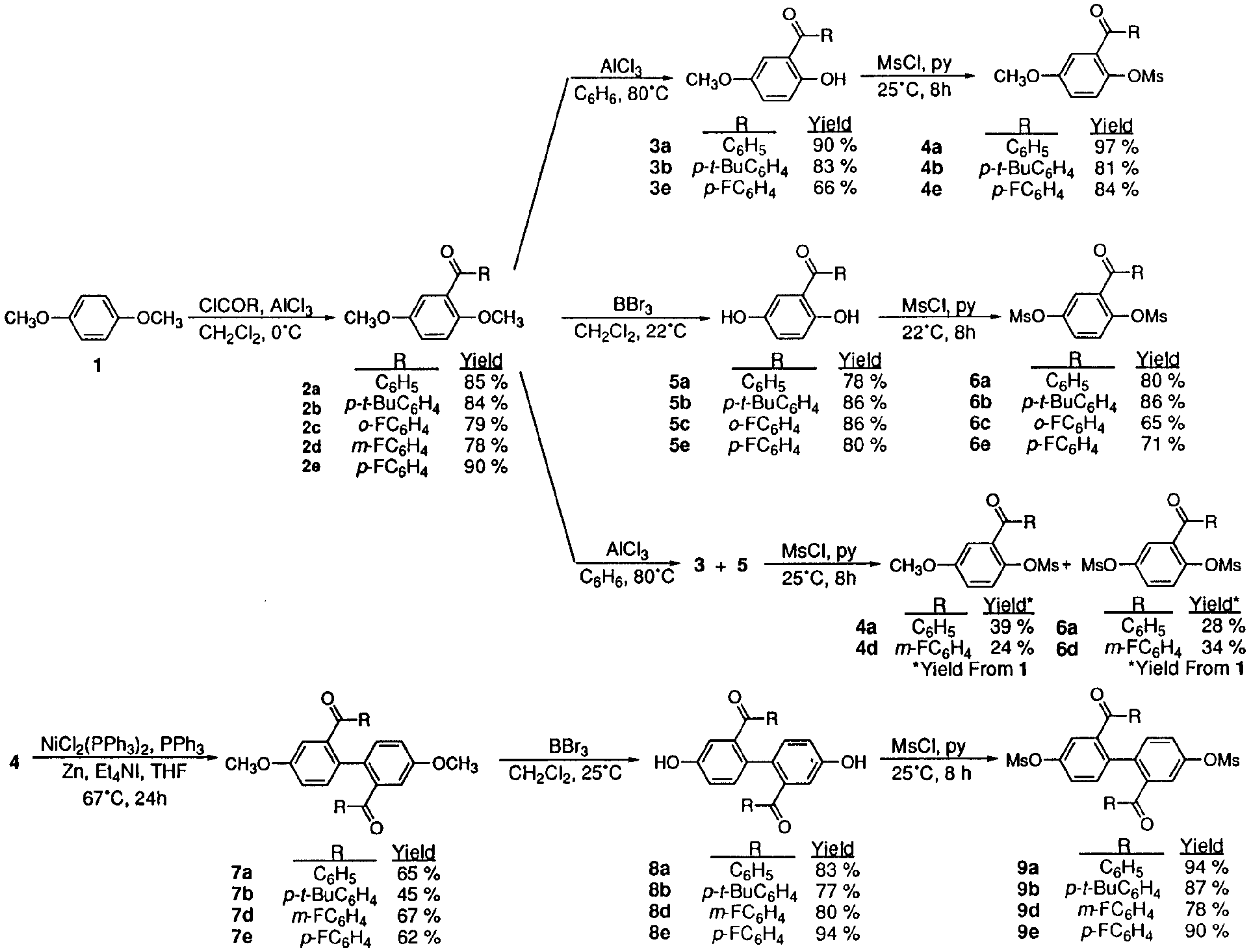
Scheme 1. Synthesis of 2-Aroyl-1,4-bis[(methylsulfonyl)oxy]benzenes 6a–e and 2,2′-Aroyl-4,4′-bis[(methylsulfonyl)oxy]biphenyls 9a,b,d,e



Experimental Section

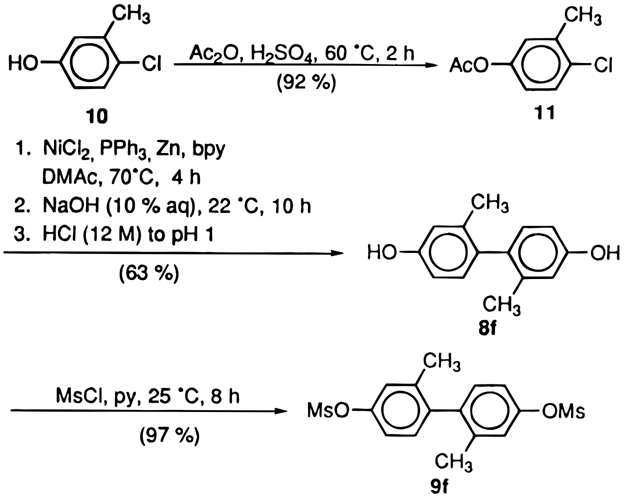
Techniques. Melting points are uncorrected and were determined with a Thomas-Hoover Uni-Melt capillary melting point apparatus. ^{1}H NMR (200 MHz) spectra were recorded on a Varian Gemini-200 spectrometer, in $CDCl_3$ and with TMS as an internal standard except when reported. GC analyses were performed on a Hewlett-Packard 5890 using a flame ionization detector and a 10% SP-2100 column. Thin-layer chromatography (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 Al_2O_3 (Brockmann I, 150 mesh). A Perkin-Elmer DSC-7 differential scanning calorimeter (DSC) 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 Nelson analytical 900 series integrator data station. The measurements were made at 40 °C using the UV detector set at 254 nm with THF as solvent (1 mL/min). A set of Phenomenex Phenogel columns (500 and 5×10^4 Å) and a calibration plot constructed with polystyrene standards was used to determine the molecular weights. Therefore, all molecular weights determined by GPC are relative to polystyrene.

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.[11] Unless otherwise noted, all compounds synthesized were purified until their 200 MHz ^{1}H NMR spectra corresponded to the expected structure and the purity was established by comparison with published melting point or found to be higher than 99.5% by GC or HPLC.

Monomers. The synthesis of 2,2′-disubstituted 4,4′-bis[(methylsulfonyl)oxy]biphenyls and 2-substituted 1,4-bis[(methylsulfonyl)oxy]benzenes is outlined in Schemes 1 and 2.

Aryl Bismesylates. Aryl bismesylates were synthesized by the reaction of methanesulfonyl chloride with the corresponding phenol in pyridine.[12] 2,5-Bis[(methylsulfonyl)oxy]benzophenone (**6a**),[2a] 4′-fluoro-2,5-bis-[(methylsulfonyl)oxy]benzophenone (**6e**),[2a] 2-methyl-1,4-bis[(methylsulfonyl)oxy]benzene (**6f**),[2a] 2,2′-dibenzoyl-4,4′-bis[(methylsulfonyl)oxy]biphenyl (**9a**),[5c] 2,2′-bis(*p*-fluorobenzoyl)-4,4′-bis[(methylsulfonyl)oxy]biphenyl (**9e**),[5c] and 2,2′-bis(*p*-*tert*-butylbenzoyl)-4,4′-bis[(methylsulfo-

Scheme 2. Synthesis of 2,2′-Dimethyl-4,4′-bis[(methylsulfonyl)oxy]biphenyl (9f)



nyl)oxy]biphenyl (**9b**)[5c] were synthesized as reported previously.

2′-Fluoro-2,5-dimethoxybenzophenone (2c). To a stirred solution of 1,4-dimethoxybenzene (9.80 g, 70.9 mmol) in CH_2Cl_2 (100 mL) cooled to 0 °C was added $AlCl_3$ (9.45 g, 70.9 mmol). The reaction mixture was stirred for 10 min, and 2-fluorobenzoyl chloride (11.4 g, 71.9 mmol) was added dropwise. After stirring at 0 °C for 4 h, the reaction mixture was poured into ice water (200 mL) containing 10 mL of concentrated HCl. The organic phase was separated and the solvent was evaporated. The residue was dissolved in Et_2O (100 mL), washed with 10% NaOH (30 mL), dried ($MgSO_4$), evaporated *in vacuo*, and purified by column chromatography (silica gel, Et_2O/EtOAc 10:1) to give 14.6 g (56.1 mmol, 79.1%) of white crystals: mp 51−52 °C (Et_2O/EtOAc 10:1); ^1H NMR ($CDCl_3$) δ 7.67 (t, $J = 1.9$ Hz, 1 H), 7.48 (m, 1 H), 7.27−7.03 (m, 4 H), 6.90 (d, $J = 8.8$ Hz, 1 H), 3.83 (s, 3 H), 3.63 (s, 3 H).

3′-Fluoro-2,5-dimethoxybenzophenone (2d). Following the same procedure as for the synthesis of **2c**, 1,4-dimethoxybenzene (2.00 g, 14.5 mmol) in CH_2Cl_2 (15 mL) was aroylated at 0 °C in the presence of $AlCl_3$ (2.30 g, 17.2 mmol) with 3-fluorobenzoyl chloride (2.50 g, 15.8 mmol). After purification by column chromatography (silica gel, Et_2O/EtOAc 10:1), 2.95 g (11.3 mmol, 77.9%) of colorless crystals was obtained: mp 66−67 °C (Et_2O/EtOAc 10:1); ^1H NMR ($CDCl_3$) δ 7.56−7.18 (m, 4 H), 7.08−6.90 (m, 3H), 3.80 (s, 3 H), 3.67 (s, 3 H).

2′-Fluoro-2,5-dihydroxybenzophenone (5c). To a stirred solution containing CH_2Cl_2 (50 mL) and 50 mL of 1.0 M BBr_3 solution in CH_2Cl_2 cooled to −70 °C, a solution of 2′-fluoro-2,5-dimethoxybenzophenone (**2c**) (6.00 g, 23.1 mmol) in 25 mL of CH_2Cl_2 was added dropwise.[13] The mixture was allowed to warm to 25 °C and was stirred for 24 h. Water (50 mL) was added dropwise and the organic phase was separated, dried ($MgSO_4$), concentrated, purified by column chromatography (silica gel, hexanes/ethyl acetate 4:1), and recrystallized (ethyl acetate) to afford 4.62 g (19.9 mol, 86.1%) of slightly yellow crystals: mp 118−119 °C (EtOAc); ^1H NMR ($CDCl_3$) δ 7.54−7.49 (m, 2 H), 7.31−7.19 (m, 2 H), 7.11−6.83 (m, 3 H).

2′-Fluoro-2,5-bis[(methylsulfonyl)oxy]benzophenone (6c). Methanesulfonyl chloride (19.5 g, 0.17 mol) was added dropwise to a stirred solution of **5c** (12.9 g, 55.6 mmol) in pyridine (60 mL) at 0 °C. The mixture was warmed to 25 °C and stirred for 12 h. The reaction mixture was poured into ice water (100 mL), and the resulting precipitate was collected, washed with water, recrystallized from $CHCl_3$/EtOAc (1:1), purified by column chromatography (silica gel, hexanes/ethyl acetate 4:1), and recrystallized from $CHCl_3$/EtOAc (1:1) to give 14.1 g (36.3 mmol, 65.3%) of white crystals: mp 121−122 °C ($CHCl_3$/EtOAc 1:1); ^1H NMR δ 7.78−7.53 (m, 4 H), 7.34−7.10 (m, 3 H), 3.20 (s, 3 H, OSO_2CH_3 *o* to CO), 2.95 (s, 3 H, OSO_2CH_3 *m* to CO).

“One-Pot” Preparation of 3′-Fluoro-5-methoxy-2-[(methylsulfonyl)oxy]benzophenone (4d) and 3′-Fluoro-2,5-bis[(methylsulfonyl)oxy]benzophenone (6d). A solution of 1,4-dimethoxybenzene (20.0 g, 0.145 mol) in CH_2Cl_2 (150 mL) was cooled to 0 °C, and $AlCl_3$ (23.0 g, 0.173 mol) was added in several portions. After the solution was stirred for 10 min, 3-fluorobenzoyl chloride (25.0 g, 0.158 mol) was added dropwise. The solution was stirred at 0 °C for 5 h. The CH_2Cl_2 was evaporated *in vacuo*, and benzene (100 mL) and $AlCl_3$ (30.0 g, 0.225 mol) were added at 25 °C. The stirring was continued at 80 °C for 10 h. The reaction mixture was cooled to 25 °C and poured into 300 mL of ice water containing 20 mL of concentrated HCl. The resulting mixture was partitioned between Et_2O (150 mL) and H_2O. The organic phase was washed with H_2O (150 mL) and dried ($MgSO_4$). After evaporation of the solvent *in vacuo*, the residue was recrystallized (hexanes/ethyl acetate 1:1) to afford 27.7 g of a 4:6 mixture of 3′-fluoro-2-hydroxy-5-methoxybenzophenone (**3d**) and 3′-fluoro-2,5-dihydroxybenzophenone (**5d**). This mixture was dissolved in pyridine (140 mL). Methanesulfonyl chloride (34.4 g, 0.30 mol) was added dropwise to the stirred solution at 0 °C. The mixture was warmed to 25 °C and stirred for 12 h. The reaction mixture was poured into ice water (100 mL), and the resulting precipitate was collected, washed with water, and recrystallized ($CHCl_3$/EtOAc 1:1). **4d** was more soluble than **6d** in hexanes/ethyl acetate 4:1. The two aryl mesylates were separated from each other by column chromatography (silica gel, hexanes/ethyl acetate 4:1) and recrystallized ($CHCl_3$/EtOAc 1:1). **4d**: 11.2 g (34.5 mmol, 23.7%, $R_f = 0.40$ in hexanes/EtOAc 4:1); white crystals; mp 98−99 °C ($CHCl_3$/EtOAc); ^1H NMR ($CDCl_3$) δ 7.57−7.27 (m, 5 H), 7.11−6.95 (m, 2 H), 3.82 (s, 3 H, OCH_3), 2.94 (s, 3 H, OSO_2CH_3). **6d**: 19.0 g (48.9 mmol, 33.7%, $R_f = 0.14$ in hexanes/EtOAc 4:1); white crystals; mp 124−125 °C ($CHCl_3$/EtOAc); ^1H NMR ($CDCl_3$) δ 7.57−7.26 (m, 7 H), 3.22 (s, 3 H, OSO_2CH_3 *o* to CO), 3.06 (s, 3 H, OSO_2CH_3 *m* to CO).

2,2′-Bis(*m*-fluorobenzoyl)-4,4′-dimethoxybiphenyl (7d). A 200 mL round-bottom flask containing **4d** (17.5 g, 54.0 mmol), $NiCl_2(PPh_3)_2$ (2.20 g, 3.36 mmol), PPh_3 (1.80 g, 6.86 mmol), Zn powder (6.50 g, 99.4 mmol), Et_4NI (4.30 g, 16.7 mmol), and a magnetic stir bar was sealed with a rubber septum and filled with N_2 followed by three evacuation−filling cycles. Freshly distilled THF (15 mL) was added via syringe through the rubber septum. The mixture was stirred at 22 °C for 5 min and during this time the color of the mixture changed from yellow-green to deep red. The reaction was stirred at 70 °C for 24 h. The mixture was cooled to 22 °C and diluted with $CHCl_3$ (50 mL), filtered, dried ($MgSO_4$), and evaporated *in vacuo*. The residue was purified by column chromatography (silica gel, hexanes/ethyl acetate 5:1) to afford 8.31 g (18.1 mmol, 67.0%) of colorless crystals: mp 117−118 °C (hexanes/ethyl acetate 5:1);

^{1}H NMR ($CDCl_3$) δ 7.55−7.38 (m, 4 H), 7.20−7.05 (m, 6 H), 6.96−6.83 (m, 4 H), 3.77 (s, 6 H).

2,2′-Bis(*m*-fluorobenzoyl)-4,4′-dihydroxybiphenyl (8d). A solution of **7d** (8.00 g, 17.5 mmol) in 50 mL of CH_2Cl_2 was added dropwise to the stirred solution of 50 mL of CH_2Cl_2 and 50 mL of 1.0 M BBr_3 solution in CH_2Cl_2 cooled to −70 °C. The mixture was allowed to warm to 25 °C and after 8 h water (40 mL) was added dropwise. The organic phase was separated, dried ($MgSO_4$), and concentrated. Purification by column chromatography (silica gel, hexanes/ethyl acetate 4:1) and recrystallization (ethyl acetate) afforded 6.02 g (14.0 mmol, 80.0%) of slightly yellow crystals: mp 239−241 °C (EtOAc); ^{1}H NMR ($CDCl_3$) δ 9.23 (s, 2 H), 7.54 (d, J = 7.6 Hz, 4 H), 7.43 (d, J = 9.4 Hz, 4 H), 6.98 (d, J = 7.6 Hz, 4 H), 6.87−6.70 (m, 8 H), 6.57−6.49 (m, 8 H).

2,2′-Bis(*m*-fluorobenzoyl)-4,4′-bis[(methylsulfonyl)oxy]biphenyl (9d) was synthesized by the reaction of methanesulfonyl chloride with **8d** in pyridine (78%): white crystals; mp 145−146 °C ($CHCl_3$); ^{1}H NMR δ 7.44−7.15 (m, 14 H, aromatic protons), 3.16 (s, 6 H, OSO_2CH_3).

4-Chloro-3-methylphenyl Acetate (11). 4-Chloro-3-methylphenol (**10**) (43 g, 0.30 mol), acetic anhydride (34 mL, 0.36 mol) and a few drops of H_2SO_4 were stirred at 60 °C for 2 h, cooled to 22 °C, poured into H_2O (200 mL), stirred (1 h), and extracted with Et_2O (200 mL). The organic phase was dried ($MgSO_4$), concentrated, and chromatographed (SiO_2, hexanes/Et_2O 10:1) to give a colorless liquid (51 g, 92%): bp 65−68 °C/0.15 mmHg; ^{1}H NMR δ 7.32 (d, J = 8.5 Hz, 1 H, *o* to chlorine), 6.96 (d, J = 2.5 Hz, 1 H, *o* to CH_3), 6.87 (dd, J = 8.5, 2.5 Hz, 1 H, *p* to CH_3), 2.35 (s, 3 H, $OC(=O)CH_3$), 2.27 (s, 3 H, CH_3).

2,2′-Dimethyl-4,4′-dihydroxybiphenyl (8f). DMAc (116 mL) was added to a 500 mL flask containing $NiCl_2$ (1.56 g, 12.0 mmol), PPh_3 (15.74 g, 60.00 mmol), Zn (22.68 g, 0.346.9 mmol), and 2,2′-bipyridine (1.87 g, 12.0 mmol). The mixture was heated to 65 °C, **11** (42.73 g, 231.4 mmol) was added, and the reaction was stirred at 70 °C for 4 h. The mixture was filtered, poured into a solution of NaOH (50 g/500 mL of H_2O), stirred overnight at 22 °C, washed with Et_2O (300 mL), and acidified with concentrated HCl to pH ~ 1. The resulting precipitate was collected by filtration, washed with water, dried, and recrystallized (hexanes/$CHCl_3$ 10:1) to give brownish crystals (15.5 g, 62.5%): mp 154−155 °C (lit.[14] mp 156 °C); ^{1}H NMR δ 6.92 (d, J = 8.1 Hz, 2 H, *m* to hydroxy and methyl), 6.66 (s, 2 H, O*H*), 6.77−6.70 (m, 4 H, aromatic protons, *o* and *p* to methyl), 1.98 (s, 6 H, CH_3).

2,2′-Dimethyl-4,4′-bis[(methylsulfonyl)oxy]biphenyl (9f) was synthesized by the reaction of methanesulfonyl chloride with **8f** in pyridine and purified by column chromatography (SiO_2, Et_2O) and recrystallization (hexanes/EtOAc 1:1). (97%): pale white crystals; mp 101−102 °C (hexanes/EtOAc); ^{1}H NMR δ 7.22−7.10 (m, 6H, aromatic protons), 3.21 (s, 6 H, OSO_2CH_3), 2.07 (s, 6 H, CH_3).

Polymerizations. The synthesis of regioregular and regioirregular PPPs is presented in Scheme 3 and summarized in Table 1. In a typical polymerization (Table 1, entry 14), a 125 mL Schlenk tube was charged with $NiCl_2(PPh_3)_2$ (0.115 g, 0.175 mmol), PPh_3 (0.275 g, 1.05 mmol), Zn (0.800 g, 12.3 mmol), Et_4NI (0.675 g, 2.63 mmol), **6e** (0.340 g, 0.875 mmol), **9e** (0.513 g, 0.875 mmol), and a magnetic stir bar. The tube was sealed with a rubber septum, evacuated (1×10^{-3} mmHg) for 0.5 h, and placed under an Ar atmosphere by filling with Ar followed by three evacuation−fill cycles. Freshly distilled THF (2.0 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) and 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, dissolved in 2 mL of $CHCl_3$, filtered, and poured into 100 mL of methanol. The precipitate was filtered and dried *in vacuo* (440 mg, 79%). The polymer was purified by reprecipitation into MeOH from $CHCl_3$ solution before being analyzed by GPC. ($M_{\rm n}$ = 34 790, $M_{\rm w}/M_{\rm n}$ = 1.86, DP = 176).

Results and Discussion

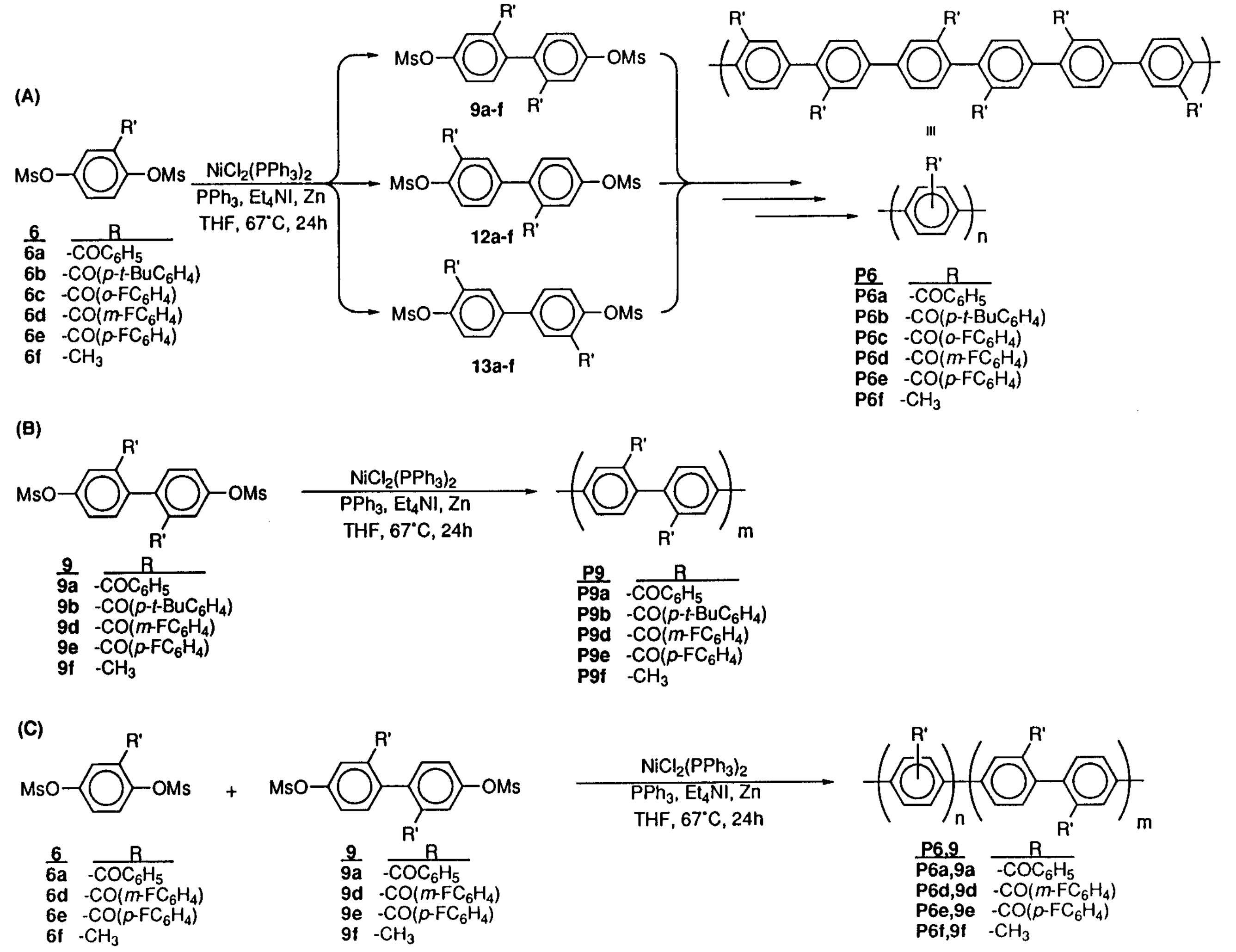
Synthesis of Monomers. Monomers 2-aroyl-1,4-bis-[(methylsulfonyl)oxy]benzene[3a] (**6a**−**e**) and 2,2′-aroyl-4,4′-bis[(methylsulfonyl)oxy]biphenyl[5c] (**9a**,**b**,**d**,**e**) were prepared from 1,4-dimethoxybenzene by a previously reported method or by a one-pot procedure which produced **4** (a precursor to **9**) and **6** as an easily separable mixture (Scheme 1). Column chromatography (hexanes/EtOAc 4:1) was used to separate **4d** (R_f = 0.40) from **6d** (R_f = 0.14). **4d** is more soluble than **6d** in hexanes/EtOAc 4:1, and in principle these compounds could also be separated by fractional crystallization.

2-Aroyl-1,4-dimethoxybenzenes (**2a**−**e**) were prepared by the high-yield (78−90%) $AlCl_3$-catalyzed Friedel−Crafts aroylation of **1** with benzoyl chloride derivatives in CH_2Cl_2 at 0 °C.[5c] 2-Aroyl-1,4-bis[(methylsulfonyl)-oxy]benzenes (**6a**−**c**,**e**) were prepared from **2a**−**c**,**e** by demethylation with BBr_3[13] in CH_2Cl_2 at 22 °C to give the corresponding 2-substituted hydroquinones **5a**−**c**,**e** (78−86%) which were reacted with methanesulfonyl chloride in pyridine at 22 °C for 8 h (65−86%).

The 2,2′-aroyl-4,4′-bis[(methylsulfonyl)oxy]biphenyl (**9**) monomers were prepared from **2** by a series of reactions beginning with the regioselective demethylation of the 1-position of **2** with $AlCl_3$ in benzene at 80 °C to give the monomethyl ethers **3a**,**b**,**e** (66−90%) which were converted to mesylates **4a**,**b**,**e** by reaction with methanesulfonyl chloride in pyridine (81−97%).[5c] Mesylate **4d** was obtained by an alternative method described below. The Ni(0)-catalyzed homocoupling reactions of **4a**,**b**,**d**,**e** (45−67%) followed by cleavage of the CH_3−O bonds with BBr_3[13] gave the 2,2′-disubstituted 4,4′-dihydroxybiphenyls **8a**,**b**,**d**,**e** (77−94%) which were reacted with methanesulfonyl chloride to produce 2,2′-aroyl-4,4′-bis[(methylsulfonyl)oxy]biphenyls (**9a**,**b**,**d**,**e**) (78−94%).[5c]

Monomers **6a,d** and **9a,d** were also synthesized from **1** by an alternative “one-pot” procedure which produced a mixture of **4** and **6**, which were easily separable by column chromatography. The $AlCl_3$-catalyzed Friedel−Crafts reaction of **1** with a benzoyl chloride derivative in CH_2Cl_2 at 0 °C for 5 h gave **2**. After the CH_2Cl_2 was evaporated, benzene and $AlCl_3$ were added. The reaction mixture was stirred at 80 °C until **2** was consumed and the desired ratio of **3** to **5** (determined by TLC or GC) was obtained (typically 10 h). The mixture of **3** and **5** obtained from this reaction was converted to the corresponding mesylates **4** and **6** prior to separation by column chromatography. The mesylates were more stable and more easily separated than the corresponding

Scheme 3. Synthesis of Regioirregular and Regioregular PPPs via the Ni(0)-Catalyzed Homopolymerization of 6 and 9 and the Copolymerization of 6 and 9: (A) Generation of Constitutional Isomeric Structural Units during the Polymerization of 6 To Give Regioirregular P6; (B) Polymerization of 9 To Give Regioregular P9; (C) Copolymerization of 6 and 9 To Give Regioirregular P6,9



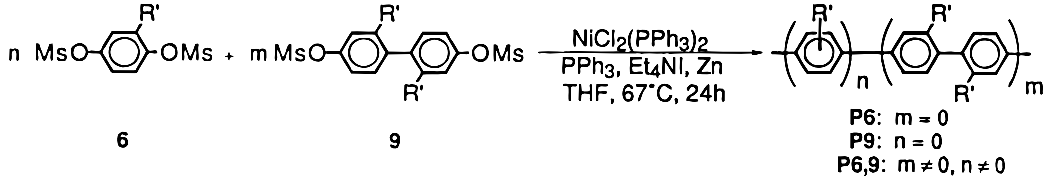
phenol and hydroquinone. The R_f values (hexanes/EtOAc 4:1) for **4d** (0.40) and **6d** (0.14) are indicative of the ease of separation. Mesylates **4a**,**d** and **6a**,**d** were prepared by this method. The yield of **4a** (39%) and **6a** (28%) obtained by this method (combined yield 67%) compares favorably to the yields obtained in the separate synthesis of **4a** (74%)[3a] and **6a** (53%)[5c] from **1** by the earlier routes.

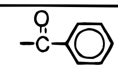
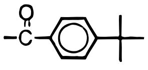
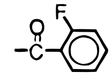
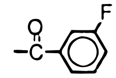
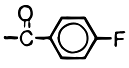
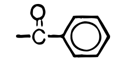
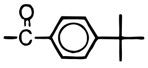
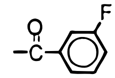
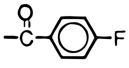
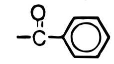
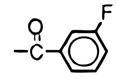
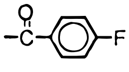
2,2′-Dimethyl-4,4′-bis[(methylsulfonyl)oxy]biphenyl (**9f**) was prepared from 4-chloro-3-methylphenol (**10**) by the sequence of reactions outlined in Scheme 2. The phenol group of **10** was protected as acetate by esterification with Ac_2O at 60 °C for 2 h in the presence of H_2SO_4 catalyst to yield **11** (92%). **11** was dimerized by Ni(0)-catalyzed homocoupling followed by cleavage of the acetate groups to produce **8f** (63%). **8f** was esterified with methanesulfonyl chloride in pyridine to bismesylate **9f** (97%).

Synthesis and Characterization of Regioregular and Regioirregular PPPs. The general procedure for the preparation of regioirregular substituted poly(*p*-phenylene)s utilized the Ni(0)-catalyzed homocoupling reaction of aryl bismesylates derived from substituted hydroquinones (Scheme 3).[3a,5a] The Ni(0) catalyst was generated *in situ* from $NiCl_2(PPh_3)_2$, PPh_3, Zn, and Et_4NI in THF as previously reported.[3a,5] Polymerization results of monomers **6** are reported in Table 1. The reaction solvent has a large influence on the homocoupling reaction.[5a] While we could generate reaction conditions under which the homocoupling reaction yields more than 99% conversion in THF, this is not the case for dipolar aprotic solvents, which produced much lower yields.[5a] The application of these THF-optimized reaction conditions to polymerization reactions performed in dipolar aprotic solvents is ineffective due to the formation of substantial amounts of side products.[5a]

In order to obtain high molecular weight PPP by this method, the coupling reaction must proceed with about 100% conversion and the resulting polymer must be soluble in the reaction medium. The effect of a substituent on the reactivity of the adjacent (i.e., *ortho*) mesylate needs to be considered. Yields in the homocoupling reaction of aryl mesylates decreased to varying extents in the presence of an *ortho* substituent group.[5a] In these cases, side reactions such as reduction and transarylation occur to a greater extent.[5a] Evidence of the inhibitory effect of *ortho* substituents to the mesylate was previously found in the reaction of 2-ethylhexyl 2,5-bis[(methylsulfonyl)oxy]benzoate.[3a] The mesylate group *ortho* to a substituent group was shown to be less reactive toward the coupling reaction and more susceptible to participation in side reactions. The participation of these side reactions in the Ni(0)-catalyzed polymer-

Table 1. Ni(0)-Catalyzed Homo- and Copolymerization of 2-Substituted 1,4-Bis[(methylsulfonyl)oxy]benzene (6) and 2,2′-Disubstituted 4,4′-Bis[(methylsulfonyl)oxy]biphenyl (9)



entry	monomer(s)[a]	R′	polymer (yield, %)	M_n[b]	M_w/M_n[b]	(2m+n)[b]	T_g, °C	T_m, °C
1	**6a**		**P6a** (95)	7370	3.33	41	162	-
2	**6b**		**P6b** (82)	7170	2.88	30	184	-
3	**6c**		**P6c** (77)	-	insoluble		-	329
4	**6d**		**P6d** (69)	3490	2.42	18	122	328
5	**6e**		**P6e** (68)	20030	2.16	101	168	-
6	**6f**	-CH3	**P6f** (87)	2150	1.38	24	62	-
7	**9a**		**P9a** (92)	-	insoluble		-	355
8	**9b**		**P9b** (68)	11120	3.73	47	197	-
9	**9d**		**P9d** (82)	-	insoluble		-	304
10	**9e**		**P9e** (95)	-	insoluble		-	378
11	**9f**	-CH3	**P9f** (66)	-	insoluble		-	255
12	**6a, 9a**		**P6a,9a** (94)	11090	1.97	62	170	-
13	**6d, 9d**		**P6d,9d** (74)	2540	1.64	13	117	327
14	**6e, 9e**		**P6e,9e** (79)	34790	1.86	176	191	-
15	**6f, 9f**	-CH3	**P6f,9f** (76)	3580	1.48	40	75	-

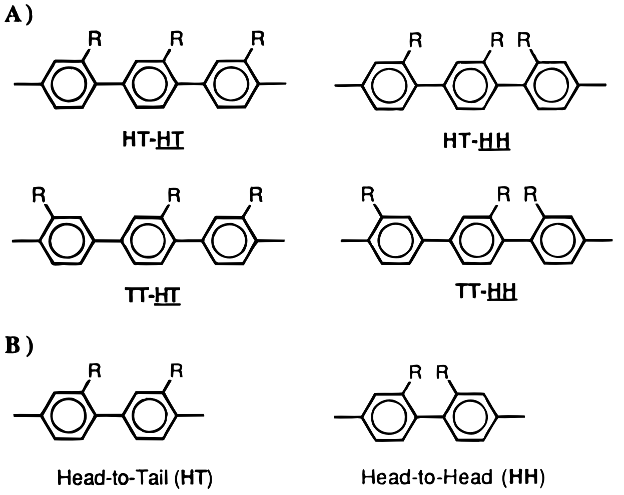
[a] Mole ratio of monomers is 1:1 when comonomers are listed. [b] Determined by GPC versus polystyrene standards.

ization reaction of aryl bismesylates would terminate the polymer chain growth.

It is helpful to consider the first reaction that takes place in the polymerization sequence (Scheme 3). The polymerization begins with the dimerization of 2-substituted 1,4-bis[(methylsulfonyl)oxy]benzene, **6**, resulting in the formation of a disubstituted 4,4′-bis[(methylsulfonyl)oxy]biphenyl. There are three isomeric products expected: **9**, **12**, and **13**. Reaction of **6** at the 4-position would be favored. Thus the relative amount of the dimers formed would be expected to follow the order **13** > **12** > **9**. There are sterically hindered reactive positions on both ends of **13**. The reactivity of the dimeric molecule **13** is expected to be lower than that of **12** and **9** and therefore, the polymerization reaction is retarded. Side reactions such as reduction and transarylation become more competitive with the polymerization reaction, resulting in lower molecular weights. In order to avoid these side reactions, monomers with the dimeric structure of **9** were synthesized.

The syntheses of regioregular PPP (**P9**) by the Ni(0)-catalyzed polymerization of monomers **9** and of regioirregular PPP (**P6,9**) by the copolymerization of **6** with **9** are shown in Scheme 3. The nature of the substituents used in monomers **6** and **9** and of polymers **P6** and **P9** are included in Table 1. There is no substituent *ortho* to the mesylate in monomer **9**. Except for **9b** (entry 8, Table 1), homopolymerization of all these bismesylates gave crystalline insoluble polymers (entries 7 and 9–11) with T_m ranging from 255 to 355 °C. Their insolubility is due to their HH–TT regioregular microstructure, which enhances their rate of crystallization. Amorphous (**P6a,9a**; **P6e,9e**; **P6f,9f**) and crystalline PPPs (**P6d,9d**) were obtained by the copolymerization of a 1:1 ratio of **6** and **9**. T_g of these polymers (**P6,9**) ranged from 75 °C (R′ = CH_3, M_n =

Scheme 4. Possible Triads (A) and Diads (B) of Phenylene Units in Regioirregular PPP



3580) to 191 °C (R′ = p-FC$_6$H$_4$CO, M_n = 34 790). These polymers were very soluble and sizable increases in molecular weights over that obtained by the homopolymerization of **6** or **9** (Table 1, entries 12–15) were observed. The highest molecular weight was obtained with the p-fluorobenzoyl substituent (Table 1, entry 14). In this case, the number of phenylene repeat units was 176. This copolymerization strategy which employed 2,2′-disubstituted 4,4′-bismesylbiphenyls which have no steric hindrance on the reacting site and substituted hydroquinone comonomers also increased the molecular weight significantly even for the hydroquinone monomer with a nonactivating substituent such as methyl (Table 1, entry 15). Other examples of HH PPP were reported in the literature however, their goal is not complementary to the investigations reported here.[15]

Some preliminary ^{1}H NMR analyses were performed to obtain information concerning the regioregularity of PPP. The structural arrangement of any triad of phenylene units can be described as HT–HT, HT–HH, TT–HT, or TT–HH (Scheme 4A). The head of the central phenylene unit in each triad is connected to the adjacent phenylene group in either a head-to-tail (HT) or head-to-head (HH) manner (Scheme 4B). This is emphasized in Scheme 4A by underlining either HT or HH. The degree of regioregularity can be determined by quantifying the relative amount of each of these units in the polymer backbone. The regioregularity of low molecular weight poly(methyl-1,4-phenylene)s prepared via the polymerization of **6f**, the copolymerization of **6f** and **9f** (1:1 mole ratio), and the polymerization of **9f** were analyzed by ^{1}H NMR spectroscopy (Figure 1, spectra A, B, and C, respectively). The resonance characteristic of the central methyl group in the TT–HH triad was identified by a resonance at 2.23 ppm in the spectrum (Figure 1C) of the regioregular polymer formed from the polymerization of **9f**. End units containing HH methyl groups were identified by detection of a resonance at 2.15 ppm. A resonance due to unreacted mesylate was detected at 3.21 ppm.

The polymer obtained from **9f** allowed the assignment of the chemical shift of the resonance of the central methyl group of the TT–HH triad. Exact assignment of the resonances of the methyl groups of the other three triads (Scheme 4) necessitates the preparation of model compounds. The synthesis of model compounds and a quantitative analysis of the sequence distribution are in progress and will be reported in due time. Nevertheless, qualitative information was deduced concerning the regioregularity of the polymers and copolymers obtained from monomers **6f** and **9f**.

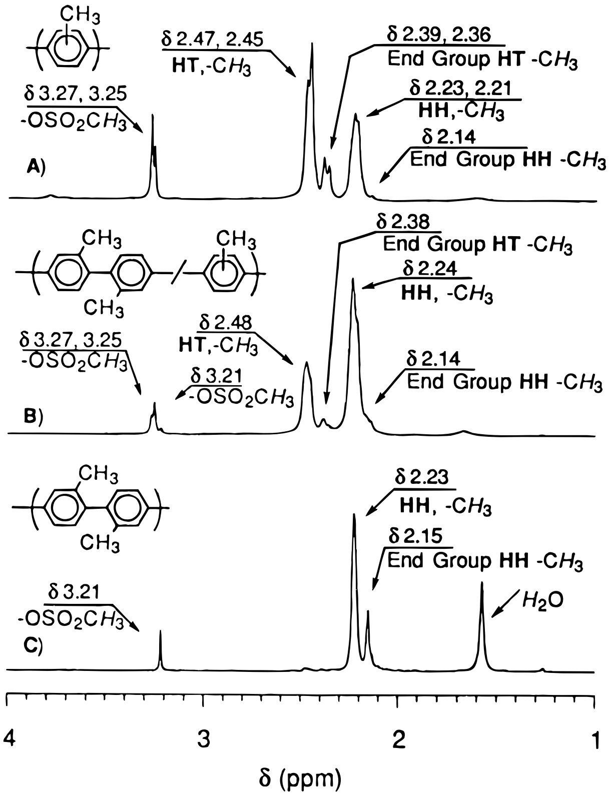


Figure 1. ^{1}H NMR spectra of the polymers obtained from (A) polymerization of 2-methyl-1,4-bis[(methylsulfonyl)oxy]benzene (**6f**), (B) copolymerization (1:1 ratio) of 2-methyl-1,4-bis[(methylsulfonyl)oxy]benzene (**6f**) and 2,2′-dimethyl-4,4′-bis[(methylsulfonyl)oxy]biphenyl (**9f**), and (C) polymerization of 2,2′-dimethyl-4,4′-bis[(methylsulfonyl)oxy]biphenyl (**9f**).

Identification of the resonances characteristic of TT–HH triads in regioregular poly(methyl-1,4-phenylene) [i.e., poly(2,2′-dimethyl-4,4′-biphenylene)] facilitated the analysis of the degree of regioregularity of poly(methyl-1,4-phenylene) prepared from **6f**. Resonances due to methyl groups attached to main chain phenylene units were detected at 2.47, 2.45 (overlapping singlets), 2.23 and 2.21 (overlapping singlets) ppm (Figure 1A). These methyl resonances were assigned to nonterminal main chain methyl groups on the basis of their chemical shift and integrals in reference to the M_n(GPC) of the polymer. The half-height line widths of the pairs of singlets centered at 2.46 and 2.22 were 8.2 and 10.6 Hz, respectively. The detection of these four methyl resonances indicates that the polymer contains structural units derived from all four triads. Overlap of signals did not permit accurate integration of the relative intensities of each of the four triads. However, the overlapping resonances centered at 2.46 and 2.22 ppm have a 1.4:1.0 integral ratio. Resonances due to methyls which were substituents on end-group phenylene units were detected at 2.39, 2.36 (overlapping singlets) and 2.14 (singlet) ppm. The head of the central phenylene unit is attached to the head of the adjacent phenylene unit (HH) in two of the triads and to its tail (HT) in the other two triads. This difference is expected to have the greatest influence on the chemical shift of the central methyl group. This is expected for several reasons. There is steric repulsion between methyl groups in a HH arrangement which is not present in the HT arrangement. This influences the degree of planarity of the polymer chain and increases the torsional energy of the C−C bond between phenylene units. The HH methyl groups are closest to each other through space and through the number of bonds. Therefore the two pairs of overlapping singlets are probably differentiated from each other by the arrangement of the phenylene group attached to the head of the central phenylene unit. The two triads in which the head of the central phenylene was HH with the adjacent group were HT−HH and TT−HH. The resonance at 2.23 ppm was assigned to the TT−HH triad by comparison with spectrum C (Figure 1) and the 2.21 ppm resonance was assigned to the HT−HH triad. The two triads in which the head of the central phenylene was HT with the adjacent group were HT−HT and TT−HT. The methyl groups of the central phenylene units of these triads exhibit overlapping ^{1}H NMR singlets centered at 2.46 ppm. The degree of regioregularity (not including end groups) as defined in reference to the head of the phenylene units consisted of a 1.4:1.0 ratio of HT:HH. The resonances due to methyls which were substituents on end-group phenylene units were assigned as 2.39 and 2.36 HT and 2.14 HH. The degree of regioregularity (including end groups) as defined in reference to the head of phenylene units consisted of a 1.7:1.0 ratio of HT:HH. Two resonances characteristic of mesylate end groups were detected (3.27 and 3.25 ppm). No resonance characteristic of mesylate end group on the TT−HH triad was detected at 3.21 ppm.

The ^{1}H NMR spectrum of the polymer obtained by copolymerization of **6f** with **9f** (1:1 mole ratio) had broad singlets at 2.48 and 2.24 ppm in a 1.0:2.3 ratio indicative of the ratio of HT and HH units. However, the integral of the resonance at 2.24 ppm included a slight shoulder at approximately 2.14 ppm which was due to the methyl substituent of a HH end group. A broad resonances at 2.38 ppm indicative of HT methyl substituents in end groups was also detected. When the integrals of resonances from all HT methyl groups (including end groups) were compared to the integral of the resonance from HH methyl groups a 1.0:2.0 ratio of HT to HH units was obtained. Three resonances characteristic of mesylate end groups were detected (3.27, 3.25, and 3.21 ppm).

In summary, the ^{1}H NMR of the polymers and copolymers obtained from monomers **6f** and **9f** indicates that the regioregularity of the resulting polymers increases as the relative amount of units derived from **9f** increases.

The highest molecular weight was obtained when the monomer contained a *p*-fluorobenzoyl substituent. Lower molecular weights were obtained when the fluoro group was in the *meta* and *ortho* positions. It is important to note that the fluorobenzoyl substituent is *meta* to the mesylate group in monomer **9** and *ortho* and *meta* to mesylate groups in monomer **6**. When the fluoro group is in the *ortho* and *para* positions of the benzoyl group, the benzoyl group becomes more strongly electron-withdrawing (by the electron-withdrawing inductive effect of the fluoro group).[5a,c] Thus the reactivity of **6** is increased. Also, the acidity of protons *ortho* to the fluoro group is increased. The ability of these protons to form hydrogen bonds with the solvent (THF) increases with the increase in acidity and the solubility of the polymer is correspondingly increased. Two protons have increased acidity in the case of the *m*-fluorobenzoyl and *p*-fluorobenzoyl groups. However, only one proton has increased acidity in the *o*-fluorobenzoyl substituent. These acidic protons act as additional functional groups and influence the solubility of PPP accordingly. Therefore, the *p*-fluorobenzoyl substituent increases both the reactivity of the monomer and the solubility of the resulting polymer. Unrelated examples of enhanced polymer solubility generated via semifluorination are available in the literature,[16] and the use of this concept in the molecular design of other PPPs will be reported in subsequent publications from our laboratory.

Conclusions

Functional PPPs with a HH−TT regioregular microstructure (**P9**) were synthesized by the Ni(0)-catalyzed homopolymerization 2,2′-disubstituted 4,4′-bis[(methylsulfonyl)oxy]biphenyl (**9**). **9** has no *ortho* substituents and is expected to participate in the Ni(0)-catalyzed homocoupling reaction more rapidly and with fewer side reactions than the corresponding polymerization of **6**. The regioregular microstructure of **P9** resulted in crystalline insoluble PPPs (except for amorphous **P9b** with the 4-*tert*-butylbenzoyl substituent). Only when the regioregular PPP was amorphous and soluble (i.e., **P9b**) did the polymerization of **9** result in a higher M_n than that resulted from the polymerization of **6**. This indicates that the Ni(0)-catalyzed homocoupling of **9** is more efficient (than **6**), but the solubility of the resulting regioregular PPP controls the M_n.

The copolymerization of **6** with **9** increases the configurational and conformational entropy of PPP (versus that of the homopolymer obtained from **9**). Soluble amorphous (**P6a,9a**; **P6e,9e**; **P6f,9f**) and crystalline (**P6d,9d**) PPPs were obtained when PPPs with regioirregular microstructures were prepared by the copolymerization of **9** and **6**. The M_n of the amorphous (**P6a,9a**; **P6e,9e**; **P6f,9f**) PPP obtained by the copolymerization of these two types of monomer was significantly higher than that obtained from the homopolymerization of **6** or **9**. The highest M_n of the crystalline PPPs was obtained from **6d**. These results are consistent with two opposing trends: (a) the efficiency of the coupling reaction increases as the number of coupling reactions involving *ortho* substituents is decreased and (b) increased regioregularity can decrease the configurational and conformational entropy to such a degree that insoluble crystalline PPP forms before all mesylates participate in homocoupling reactions. Thus the highest M_n was obtained for amorphous PPP with a 1:1 ratio of **6** and **9** because the number of reactions involving *ortho* substituents was reduced while the solubility of the PPP was maintained. The effect generated by the presence of fluorine on various parts of the molecule is extremely rewarding, since it both influences the reactivity of the leaving group and introduces extra substituents by the enhanced acidity of its ortho hydrogens. These results provide the basis for the elaboration of novel synthetic schemes for the preparation of soluble, well-defined and functional PPPs with high molecular weight and small substituents.

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