Solubilization of Regioregular and Regioirregular Poly(*p*-phenylene)s via CF_3 and OCF_3 Substituents To Generate a Model for Rigid-Rod Polymers

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ABSTRACT: Regioirregular poly(*p*-phenylene)s (PPPs) with OCF_3, CF_3 or OCH_3 substituents (**16a**, **16b**, or **16c**, respectively) were synthesized via Ni(0)-catalyzed polymerization of 2-substituted-1,4-bis-[[(trifluoromethyl)sulfonyl]oxy]benzenes (**5**, **8**, or **10**, respectively). Regioregular *head−to−head* PPPs with OCF_3 or CF_3 substituents (**17a** or **17b**) were prepared from 2,2′-disubstituted-4,4′-bis[[(trifluoromethyl)sulfonyl]oxy]biphenyls **14a**, **14b** and 2,2′-disubstituted-4,4′-bis[methylsulfonyl)oxy]biphenyls **15a**, **15b**. Regioregular *head-to-head* statistical copolymers with combinations of OCF_3 or CF_3 substituents with OCF_3, CF_3, CO(*p*-FC_6H_5), CH_3, or H substituents (**17xy**) were synthesized by the copolymerization of **15a** or **15b** with 2,2′-disubstituted-4,4′-bis[(methylsulfonyl)oxy]biphenyls **15a**−**15e**. Regioirregular and regioregular PPPs with OCF_3 or CF_3 substituents were soluble (THF, $CHCl_3$, dipolar aprotic solvents). The highest molecular weight PPPs were obtained from OCF_3-substituted monomers. Regioirregular PPP (**16a**) with $M_n = 35\,200$ (corresponding to 220 phenylene groups relative to polystyrene standards) was obtained from **5.** Regioregular PPP (**17a**) with $M_n = 54\,500$ (340 phenylene units) was obtained from **14a**. Regioregular PPP copolymers (**17ab**) with $M_n = 55\,200$ (363 phenylene units) were obtained from copolymerization of **15a** and **15b**. The λ_{max} values of OCF_3- and CF_3-substituted PPPs were 302−307 and 273−271, respectively. A 10% weight loss occurs in the range of 550−575 °C for PPPs with OCF_3 substituents and 580−615 °C for those with CF_3 substituents. Polymers **17a**, **17b**, and **17ab** exhibit enantiotropic nematic and lyotropic mesophases. The thermotropic nematic phase of **17a**, **17b**, and **17ab** is stable up to the decomposition temperature. Most probably, **17a** and **17b** also exhibit a second mesophase which is monotropic and becomes enantiotropic in **17ab**. The rigid-rod character of these polymers was demonstrated by the Mark−Houwink coefficient $a = 1.58−1.60$. Phosphorus was not detected (MALDI and ^{31}P NMR) in the structure of these homopolymers and copolymers.

Introduction

Our research group is concerned with the investigation of main-chain liquid crystals (LC) with complex architectures derived from backbones of different flexibilities. The first studies on this topic were initiated by the development of the concept of main-chain liquid crystal polymers (LCPs) based on conformational isomerism.[1] This concept allowed the molecular engineering of main-chain LCPs exhibiting virtual, monotropic and enantiotropic uniaxial nematic,[1a−d] smectic,[1e−i] hexagonal columnar,[1g,j,k] and two uniaxial nematic phases.[1l−o] These LCPs generated a model for the investigation and elucidation of some of the most fundamental problems in the field of linear main-chain LCPs such as chain conformation by 1-D and 2-D ^2H NMR spectroscopy,[2a,b] and SANS,[2c] structure and dynamics of disclinations by electron microscopy,[2d,e] viscoelastic and chain conformation properties by light scattering,[2f−k] and rheology in the nematic and isotropic phases.[2l]

The elaboration of main-chain LCPs with more complex architectures such as macrocyclic,[3] hyperbranched,[4] and dendrimeric[5] was also made possible by using the conformational isomerism concept. The interconversion between virtual, monotropic, and enantiotropic liquid crystalline phases via various molecular, macromolecular, and architectural parameters can be predicted and subsequently engineered by using some thermodynamic schemes elaborated in our laboratory.[6]

Two different approaches are presently used to generate linear chains that have variable diameters and/or flexibility. The first one consists of the use of monodendrons as taper building blocks. These taper building blocks self-assemble via macromolecular or supramolecular backbones in tubular shapes with different diameters and rigidities.[7] The second one consists of the development of a synthetic method for the preparation of soluble poly(*p*-phenylene)s (PPPs) with small substituents. This method should use readily available or accessible starting materials and provide soluble polymers of controllable molecular weight. In addition these polymers should exhibit crystalline thermotropic and lyotropic liquid crystalline phases which can be manipulated via small structural variations such as regioregularity. The state of the art in the field of PPPs including the description of various synthetic methods was reviewed.[8]

Several years ago, we initiated a program to develop new synthetic methods for the preparation of PPP via Ni(0) homocoupling of substituted dichlorobenzene derivatives[9] and of bis(sulfonate)s derived from substituted hydroquinones and biphenyls.[9a,c,d,10] Since substituted hydroquinones and biphenyls are easily accessible either from commercial sources or by conventional synthetic methods, the preparation of PPP from arylene bis(sulfonate)s is extremely attractive. Originally, tri-

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flate[9a,c,d,10a] was the only leaving group reactive enough for this polymerization reaction. Recent research in our laboratory elaborated reaction conditions under which even the least reactive sulfonates, including mesylate, can be used efficiently in Ni(0)-catalyzed homocoupling and cross-coupling[11] as well as in polymerization[10c,d] reactions. Since we are concerned with PPP containing small substituents, the enhanced entropy[6] required to reduce their crystallinity and subsequently to increase their solubility can be accomplished in this case via the regioirregularity of the repeat units and the strong electron-withdrawing character of the substituent.[10c,d] In a previous paper, we have shown that fluorine is an extremely efficient substituent for the solubilization of PPPs since the vicinal hydrogens become acidic and, therefore, act as additional substituents which enhance the polymer regioirregularity.[10d] These results are in line with the enhanced solubility of other classes of semifluorinated polymers.[12]

Of particular interest to this goal are the CF_3 and OCF_3 groups. They have been exploited previously in the solubilization of other polymers such as polyamides[12c,d] and polyimides.[12a,e] In addition, synthetic methods are available for the preparation of 4,4′-diamino-2,2′-bis(trifluoromethyl)biphenyl,[12d] and 4,4′-diamino-2,2′-bis(trifluoromethoxy)biphenyl,[12e] which are intermediate compounds required for the synthesis of the corresponding substituted PPPs.

The goal of this paper is to report the synthesis of regioregular and regioirregular PPPs containing CF_3 and OCF_3 substituents via the Ni(0)-catalyzed homocoupling of the bis(triflate)s and bis(mesylate)s of the substituted hydroquinone and 4,4′-dihydroxy-2,2′-disubstituted biphenyls. A dramatic solubilization of PPP was obtained with OCF_3 or a combination of CF_3 and OCF_3 substituents, even in regioregular sequences. Preliminary solution and solid state characterization results show that the resulting polymers could be synthesized with the highest molecular weight reported to date and that they exhibit both thermotropic and lyotropic liquid crystalline phases. These results demonstrate that PPPs with these and other combinations of fluorine-containing substituents may provide suitable models for the investigation of rigid−rod polymers both in solution and in melt phase.

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, 300, or 500 MHz), $^{13}C\{^1H\}$ NMR (50, 75, 126 MHz), and $^{19}F\{^1H\}$ NMR (470.5 MHz) spectra were recorded on Varian Gemini-200, GE QE Plus, or GE ES500 spectrometer and referenced to 0 ppm with TMS (^{1}H and ^{13}C NMR) or $CFCl_3$ (^{19}F NMR). 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 aluminum oxide (Brockmann I, 150 mesh). A Perkin−Elmer DSC−7 differential scanning calorimeter, equipped with a TAC 7/DX thermal analysis controller, or a DuPont 912 differential scanning calorimeter 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. Relative 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 and with THF as solvent (1 mL/min). A set of Phenomenex Phenogel columns (5×10^4 and 500 Å) and a calibration plot constructed with polystyrene standards was used to determine the molecular weights. Mark−Houwink coefficients (a) were calculated from $[\eta] = KM_w^a$. The values of M_w, $[\eta]$, and K were determined by GPC equipped with a triple detector: refractometer, viscometer, and laser for light scattering. Thermogravimetry was measured on a DuPont 951 thermogravimetric analyzer. Heating rates of 20 °C/min were used for determination of the decomposition temperature at 10% weight loss under nitrogen. Matrix-assisted laser desorption/ionization (MALDI) spectra were obtained with a Finnigan LASERMAT 2000.

Materials. 3-(Trifluoromethyl)phenol (**6**, Rhône-Poulenc), methoxyhydroquinone (**9**, Aldrich), and all other reagents were purchased from commercial sources (Aldrich, Fisher, Fluka) 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. $NiCl_2(PPh_3)_2$[13] was prepared by a literature procedure. 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 points or found to be higher than 99.5% by GC or HPLC.

Synthesis of Monomers. (a) 3-(Trifluoromethoxy)aniline (2). A 1.4-L Hastelloy pressure vessel was charged with 3-aminophenol (109 g, 1.00 mol) and CCl_4 (432 g, 2.81 mol). The vessel was closed, cooled in dry ice, evacuated, and charged with anhydrous HF (400 g) and anhydrous BF_3 (10.0 g, 0.147 mol).[14] The vessel was heated at 140 °C for 1 h and at 150 °C for 8 h with vigorous agitation in an autoclave. The autoclave was cooled to room temperature and vented to atmospheric pressure. The contents of the vessel were transferred to a polyethylene bottle, diluted with CH_2Cl_2, and made basic with an excess of 10 M KOH solution. After filtration, the aqueous phase was extracted with CH_2Cl_2. The reaction was repeated batchwise (3×). The organic phases of the four reactions were combined, dried ($MgSO_4$), and concentrated to a dark oil. Spinning band distillation gave 287 g (1.62 mol, 40.5%) of colorless liquid: bp 92 °C (32 mmHg) (lit.[14b] bp 70 °C (7 mmHg)); ^{19}F NMR ($CDCl_3$) δ −57.80.

(b) 3-(Trifluoromethoxy)phenol (3). A 2-L three-neck round-bottom flask with a mechanical stirrer, a thermometer, and a dropping funnel was charged with water (405 mL) and concentrated H_2SO_4 (485 mL). The solution was cooled to 90 °C, **2** (100 g, 0.565 mol) was added, and the mixture was cooled to 0 °C. A solution of $NaNO_2$ (44.4 g, 0.643 mol) in water (240 mL) was added to the vigorously stirred mixture while the temperature was maintained at 0−5 °C. After the mixture was stirred for 15 min, excess nitrous acid was destroyed by addition of urea. The aqueous solution was added slowly to a mixture of water (1 L), H_2SO_4 (25 mL), and $CuSO_4$ (100 g). The resulting greenish-red emulsion was heated at the reflux temperature for 20 min, cooled to room temperature, and extracted with CH_2Cl_2. The organic phase was dried ($MgSO_4$) and concentrated. Distillation (95 °C (2 mm)) gave an orange liquid. Spinning band distillation gave 63.2 g (0.355 mol, 62.8%) of colorless compound: bp 95 °C (2 mmHg) (lit.[14b] bp 69.5 °C (12 mmHg)); ^{19}F NMR ($CDCl_3$) δ −58.03.

(c) (Trifluoromethoxy)hydroquinone (4). (75.0 g, 0.420 mol) was added to a solution of NaOH (84.4 g, 2.11 mol) in water (1.05 L) at 0 °C. $K_2S_2O_8$ (114 g, 0.422 mol) was added in small portions to the vigorously stirred solution.[15] The reaction mixture was allowed to warm to 22 °C, stirred for 18 h, acidified with concentrated HCl (165 mL), and extracted with Et_2O (2×1 L). The combined ether phases were dried ($MgSO_4$) and concentrated. Distillation gave 24.9 g (0.14 mol, 33.3%) of **3**. The remaining aqueous reaction solution was treated with an additional 470 mL of concentrated HCl and boiled for 0.5 h. The cooled solution was extracted with CH_2Cl_2; the organic phase was dried ($MgSO_4$), evaporated, and recrystallized (hexanes) to afford 15.7 g (81.0 mmol, 19.3%) of crude solid. Purification by flash chromatography (hexane/acetone 4:1) of 10.3 g (52.9 mmol) of crude solid **4** afforded 9.36 g (48.2 mmol) of pure **4**: mp 102 °C; ^{1}H NMR (DMSO-d_6) δ 9.28 (s, 1H), 9.17 (s, 1H), 6.82 (d, 1H), 6.68−6.55 (m, 2H);

^{13}C{^{1}H} NMR (DMSO-d_6) δ 149.89 (s), 142.01 (s), 135.92 (s), 120.42 (q, J = 255.7 Hz), 118.06 (s), 114.93 (s), 109.51 (s); ^{19}F NMR (CDCl$_3$) δ −56.94.

(d) (Trifluoromethyl)hydroquinone (7) was synthesized[15] from 3-(trifluoromethyl)phenol (**6**) by the same procedure as **4**: Yield 16%; mp 118 °C (lit.[15] mp 107−107 °C); ^{1}H NMR (DMSO-d_6) δ 9.20 (s, 1H), 9.69 (s, 1H), 6.85 (m, 3H); ^{13}C{^{1}H} NMR (DMSO-d_6) δ 149.39 (s), 148.11 (s), 123.99 (q, J = 272.1 Hz), 120.45 (s), 118.09 (s), 115.55 (q, J = 29.8 Hz), 112.27 (q, J = 5.0 Hz); ^{19}F NMR (CDCl$_3$) δ −60.48.

General Procedure for the Synthesis of Triflates. A solution of substituted hydroquinone or 4,4′-dihydroxybiphenyl (12.99 mmol) was dissolved in anhydrous pyridine (50 mL) and cooled to −10 °C; Tf$_2$O (5.1 mL, 30 mmol) was slowly added with a syringe. The solution turned dark red and was allowed to warm to room temperature, stirred for 24 h, poured into water, and extracted with Et$_2$O (2×). The organic extracts were washed with water (1×), 10% HCl$_{(aq)}$, (2×), water (1×), and saturated NaCl solution (2×), dried (MgSO$_4$), and evaporated to afford a liquid (bis(triflate)s of substituted hydroquinones) or solid (bis(triflate)s of substituted 4,4′-dihydroxybiphenyls).

2-(Trifluoromethoxy)-1,4-bis[[(trifluoromethyl)sulfonyl]oxy]benzene (5) was purified by flash chromatography (petroleum ether), distillation, and crystallization at 5 °C to afford white crystals (90%): ^{1}H NMR (CDCl$_3$) δ 7.54 (d, 1H, J = 9 Hz), 7.42−7.32 (m, 2H); ^{13}C{^{1}H} NMR (CDCl$_3$) δ 148.01 (s), 141.50 (s), 140.16 (s), 125.09 (s), 121.07 (s), 120.11 (q, J = 262.9 Hz), 118.70 (q, J = 321 Hz), 118.63 (q, J = 321 Hz), 116.31 (s) ^{19}F NMR (CDCl$_3$) δ −73.74 (TfO), −72.95 (TfO), −58.88 (OCF$_3$).

2-Trifluoromethyl-1,4-bis[[(trifluoromethyl)sulfonyl]oxy]benzene (8) was purified by flash chromatography (petroleum ether) and distillation (90%): mp 16 °C; ^{1}H NMR (CDCl$_3$) δ 7.70−7.58 (m, 3H); ^{13}C{^{1}H} NMR (CDCl$_3$) δ 147.59 (s), 145.22 (s), 127.02 (s), 125.56 (q, J = 34.2 Hz), 124.70 (s), 121.77 (q, J = 4.7 Hz), 120.94 (q, J = 274 Hz), 118.73 (q, J = 321 Hz), 118.46 (q, J = 320 Hz); ^{19}F NMR (CDCl$_3$) δ −73.74 (TfO), −72.92 (TfO), −61.84 (CF$_3$). Anal. Calcd for $C_9H_3O_6F_9S_2$: C, 24.44; H, 3.02; O, 21.71; F, 38.67; S, 14.50. Found: C, 24.35; H, 2.96; F, 38.42; S, 14,46.

2-Methoxy-1,4-bis[[(trifluoromethyl)sulfonyl]oxy]benzene (10) was purified by sublimation (2×) (80.1%): white crystals; mp 69 °C; ^{1}H NMR (CDCl$_3$) δ 7.70 (d, 1H, J = 9.1 Hz), 7.62 (d, 1H, J = 2.9 Hz), 7.23 (dd, 1H, J = 9.1, 2.9 Hz), 3.97 (s, 3H); ^{13}C{^{1}H} NMR (CDCl$_3$) δ 152.18 (s), 148.82 (s), 137.46 (s), 124.15 (s), 118.26 (q, J = 321 Hz), 118.22 (q, J = 320 Hz), 113.92 (s), 108.64 (s), 57.50 (s); ^{19}F NMR (CDCl$_3$) δ −73.25, −73.23. Anal. Calcd for $C_9H_3O_7F_9S_2$: C, 23.59; H, 0.66; O, 24.44; F, 37.32; S, 13.99. Found: C, 23.49; H, 0.60; F, 37.22; S, 13.89.

4,4′-Diamino-2,2′-bis(trifluoromethoxy)biphenyl (11a) was synthesized as reported previously.[12e]

4,4′-Diamino-2,2′-bis(trifluoromethyl)biphenyl (11b) was prepared by a literature procedure.[12d]

4,4′-Dihydroxy-2,2′-bis(trifluoromethoxy)biphenyl (13a). (a) Procedure A. 4,4′-Diamino-2,2′-bis(trifluoromethoxy)biphenyl (**11a**; 3.71 g, 10.5 mmol) was dissolved in a solution of concentrated HCl (22 mL) and water (100 mL) and cooled to 5 °C. A solution of NaNO$_2$ (1.45 g, 21.0 mmol) in water (10 mL) was added while the reaction temperature was maintained at 0−5 °C. This solution was added to a cool solution of H$_3$PO$_4$ (20 mL) in water (1.8 L).[16] After stirring for 5 min, the orange mixture was heated to the boiling point. After 10 min, the mixture was cooled and extracted with Et$_2$O. The organic phase was extracted with 2 N NaOH solution; the aqueous phase was acidified with concentrated HCl, extracted with Et$_2$O, dried (MgSO$_4$), evaporated, and dried under high vacuum to afford an orange product. This product was combined with the product of a second reaction, which was performed in the same manner from 7.99 g (22.7 mmol) of starting material. These combined raw materials were purified by sublimation at 140 °C (0.02 mmHg), giving 7.71 g (21.8 mmol, 65.7% yield): mp 145 °C; ^{1}H NMR (DMSO-d_6) δ 10.15 (s, 2H), 7.18 (d, 2H, J = 8.4 Hz), 6.86 (dd, J = 8.4, 2H, 2.4 Hz), 6.83 (d, 2H, J = 2.4 Hz); ^{13}C{^{1}H} NMR (DMSO-d_6) δ 158.23 (s), 148.50 (s), 132.69 (s), 119.99 (q, J = 256.5 Hz), 119.81 (s), 114.29 (s), 107.10 (s); ^{19}F NMR (DMSO-d_6) δ −55.72.

Procedure B. 4,4′-Diamino-2,2′-bis(trifluoromethoxy)biphenyl (**11a**; 24.7 g, 70.1 mmol) was dissolved in a solution of concentrated HCl (70 mL) in water (140 mL) and cooled to 0 °C. A solution of NaNO$_2$ (10.6 g, 154 mmol) in water (20 mL) was added, and the reaction was stirred for 30 min at 0 °C. NaBF$_4$ (22.0 g, 200 mmol) in water (70 mL) was added, and the reaction was stirred for 30 min.[17] The resulting white solid was collected by filtration, washed with ice/water (1 × 50 mL) and Et$_2$O (1 × 100 mL), and dried under reduced pressure (1 × 10^{-3} mmHg) for 12 h to afford 35.4 g (64.4 mmol, 91.9%) of white crystals (**12a**) which were used in the next step without further purification. **12a** (13.0 g, 23.6 mmol) was added to a solution prepared by mixing K$_2$CO$_3$ (3.8 g) and CF$_3$CO$_2$H (120 mL) at 0 °C. The reaction was stirred at the reflux temperature for 28 h and then poured into water (300 mL). The solid was collected by filtration, recrystallized (EtOH), and purified by column chromatography (silica gel, hexane/EtOAc 3:1) to afford 6.10 g (17.2 mmol, 72.9% from **12a**, 67.0% from **11a**) of slightly yellow crystals: mp 143 °C; ^{1}H NMR (DMSO-d_6) δ 10.17 (s, 2H), 7.18 (d, 2H, J = 8.4 Hz), 6.86 (dd, 2H, J = 8.4, 2.4 Hz), 6.81 (d, 2H, J = 2.4 Hz).

4,4′-Dihydroxy-2,2′-bis(trifluoromethyl)biphenyl (13b). (a) Procedure A. 4,4′-Diamino-2,2′-bis(trifluoromethyl)biphenyl (**11b**; 7.26 g, 22.7 mmol) suspended in a solution of concentrated HCl (47 mL) and water (215 mL) was heated until the diamine dissolved. A fine powder precipitated after cooling to 0 °C. A solution of NaNO$_2$ (3.13 g, 45.4 mmol) in water (20 mL) was slowly added to the suspension while the temperature was maintained between 0 and 5 °C. After the completion of the addition, stirring was continued for 20 min. The resulting mixture was divided into two parts. Each half was poured into a solution of H$_3$PO$_4$ (20 mL) in water (1.8 L). The orange solutions were stirred at the reflux temperature for 20 min, cooled to 22 °C, extracted with Et$_2$O, dried (MgSO$_4$), and concentrated to afford an orange oil. Purification by flash chromatography (petroleum ether/acetone, 4:1) followed by sublimation afforded 4.24 g of white solid (13.2 mmol, 58.1%): mp 149 °C (lit.[18] mp 152−152.5 °C); ^{1}H NMR (DMSO-d_6) δ 10.20 (s, 2H), 7.16−7.08 (m, 4H), 7.02 (dd, 2H, J = 8.4, 2.3 Hz); ^{13}C{^{1}H} NMR (DMSO-d_6) δ 157.04 (s), 133.48 (s), 128.63 (q, J = 28.6 Hz), 127.28 (s), 123.75 (q, J = 274.2 Hz), 117.94 (s), 112.32 (s); ^{19}F NMR (DMSO-d_6) δ −56.85.

(b) Procedure B. 13b was obtained by a literature procedure[18] (74.0% (57%[18]), mp 143 °C (152−152.5 °C[18]) and directly converted to **14b** without further purification.

2,2′-Bis(trifluoromethoxy)-4,4′-bis[[(trifluoromethyl)sulfonyl]oxy]biphenyl (14a): purified by flash chromatography (petroleum ether) followed by sublimation (90%); mp 73 °C; ^{1}H NMR (CDCl$_3$) δ 7.47 (d, 2H, J = 8.6 Hz), 7.37 (dd, 2H, J = 8.5, 2.4 Hz), 7.35 (d, 2H, J = 2.4 Hz); ^{13}C{^{1}H} NMR (CDCl$_3$) δ 149.61 (s), 147.60 (s), 133.00 (s), 128.59 (s), 120.13 (q, J = 267 Hz), 119.91 (s), 118.77 (q, J = 321 Hz), 114.38 (s); ^{19}F NMR (CDCl$_3$) δ −73.06 (OTf), −58.29 (OCF$_3$). Anal. Calcd for $C_{16}H_6O_8S_2$: C, 31.08; H, 0.98; O, 20.70; F, 36.87; S, 10.37. Found: C, 30.99; H, 0.91; F, 36.77; S, 10.25.

2,2′-Bis(trifluoromethyl)-4,4′-bis[[(trifluoromethyl)sulfonyl]oxy]biphenyl (14b): purified by chromatography (petroleum ether) (70.1%); mp 48 °C; ^{1}H NMR (CDCl$_3$) δ 7.69 (d, 2H, J = 2.5 Hz),7.55 (dd, 2H, J = 8.6, 2.5 Hz), 7.45 (d, 2H, J = 8.6 Hz); ^{13}C{^{1}H} NMR (CDCl$_3$) δ 149.27 (s), 135.82 (s), 133.77 (s), 131.46 (q, J = 32.4 Hz), 124.17 (s), 122.46 (q, J = 275 Hz), 119.93 (s), 118.82 (q, J = 321 Hz); ^{19}F NMR (CDCl$_3$) δ −73.07 (OTf), −59.19 (CF$_3$). Anal. Calcd for $C_{16}H_6O_6F_{12}S_2$: C, 32.77; H, 1.03; O, 16.37; F, 38.89; S, 10.94. Found: C, 32. 53; H, 1.09; F, 38.82; S, 10.88.

Aryl Bis(mesylate)s: Aryl bis(mesylate)s were synthesized by the reaction of methanesulfonyl chloride with the corresponding phenol in pyridine.[19] 2,2′-Bis(p-fluorobenzoyl)-4,4′-bis[(methylsulfonyl)oxy]biphenyl (**15c**),[11c] and 2,2′-dimethyl-4,4′-bis[(methylsulfonyl)oxy]biphenyl (**15d**),[10d] were synthesized by published procedures.

2,2′-Bis(trifluoromethoxy)-4,4′-bis[(methylsulfonyl)oxy]biphenyl (15a). Methanesulfonyl chloride (6.9 g, 60 mmol) was added dropwise to a solution of **13a** (7.10 g, 20.0 mmol), N,N-dimethylaminopyridine (0.10 g), and pyridine (50

Table 1. Ni(0)-Catalyzed Polymerization of 2-Substituted-1,4-bis[[(trifluoromethyl)sulfonyl]oxy]benzenes and 2,2′-Disubstituted-4,4′-bis[[(trifluoromethyl)sulfonyl]oxy]biphenyls[a]

entry	monomer[b]	mol % Ni	polymer, yield (%)	M_n[k]	M_w/M_n[k]	DP[k]
1[c]	**5** (2.6)	12.9	**16a**, 44.8	7560	2.22	47
2	**5** (3.1)	6.4	**16a**, 5.9	8420	1.57	53
3	**5** (19.0)	10.8	**16a**, 17.8	11200	2.14	70
4	**5** (13.3)	20.0	**16a**, 49.0	25600	1.95	160
5	**5** (21.1)	13.0	**16a**, 43.7	35200	2.76	220
6[d]	**5** (19.5)	10.2	**16a**, 17.6	5150	1.24	32
7	**5** (13.4)	33.4	**16a**, 31.6	8070	1.53	50
8	**8**(19.8)	7.7	**16b**, 18.1	12400	1.40	86
9	**8**(13.8)	13.1	**16b**, 22.7	10800	1.38	75
10	**8**(14.5)	13.1	**16b**, 4.0	8460	1.41	59
11	**8**(13.1)	21.0	**16b**, 35.1	9250	1.89	64
12[e]	**8**(13.0)	21.0	**16b**, 5.5	7830	1.77	54
13	**8**(11.0)	21.0	**16b**, 38.0	11500	1.69	80
14	**10** (4.75)	13.8	**16c**, 44.8[f]		insoluble	
15	**10** (10.5)	13.8	**16c**, 53.1[f]		insoluble	
16[g]	**14a** (11.2)	13.4	**17a**, 9.2	54500	1.82	340[h]
17[g,i]	**14a** (18.1)	17.5	**17a**, 17.5	2860	1.22	18[h]
18[j]	**14b** (7.7)	13.4	**17b**, 36.6	9450	2.00	66[h]

[a] $NiCl_2(PPh_3)_2$, Zn (25.7 mmol), Et_4NI (3.07 mmol), THF (1 mL), 22 °C, 20 min, 70 °C, 8 h (see Experimental Section). [b] For monomer numbers, see Scheme 3. Numbers in parentheses are millimoles used. [c] Reaction time 1 h. [d] Added 5.9 equiv of PPh_3 (vs Ni). [e] Reaction performed in an ultrasonic bath at 70 °C. [f] The yield was determined after thoroughly washing with 10% HCl in methanol. [g] Monomer added at beginning of reaction as a solid. [h] Number of phenyl groups in backbone (i.e., 2 × DP). [i] Added 6.1 equiv of PPh_3 (vs Ni). [j] Reaction time = 1.5 h. [k] By GPC.

mL) at 0 °C under nitrogen. The mixture was stirred at 0 °C for 1 h and at 23 °C for 12 h. The mixture was poured into water (200 mL), and the precipitate was isolated by filtration. Recrystallization (ether/hexanes 1:1) afforded 6.50 g of colorless crystals (12.7 mmol, 63.5%): mp 102−103 °C; ^1H NMR ($CDCl_3$) δ 7.39−7.33 (m, 6H), 3.24 (s, 6H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 149.30 (s) 146.88 (s), 132.74 (s), 127.66 (s), 120.27 (s), 120.07 (q, J = 260 Hz), 114.59 (s), 37.76 (s). Anal. Calcd for $C_{16}H_{12}O_8F_6S_2$: C, 37.65; H, 2.37; S, 12.56. Found: C, 37.59; H, 2.28; S, 12.50.

2,2′-Bis(trifluoromethyl)-4,4′-bis[(methylsulfonyl)oxy]biphenyl (15b): (72%); colorless crystals; mp 135−136 °C; ^1H NMR ($CDCl_3$) δ 7.67 (d, 2H, J = 2 Hz), 7.51 (d, 2H, J = 8 Hz), 7.36 (d, 2H, J = 8 Hz), 3.26 (s, 6H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 148.71 (s) 134.96 (s), 133.43 (s), 130.83 (q, J = 32 Hz), 124.53 (s), 120.70 (q, J = 275 Hz), 120.15 (s), 38.04 (s). Anal. Calcd for $C_{16}H_{12}O_6F_6S_2$: C, 40.17; H, 2.53; S, 13.40. Found: C, 40.07; H, 2.48; S, 13.35.

4,4′-Bis[(methylsulfonyl)oxy]biphenyl (15e): (81%); colorless crystals; mp 186 °C (DMF); ^1H NMR (DMSO-d_6) δ 7.80 (d, 4H, J = 8.2 Hz), 7.46 (d, 4H, J = 8.2 Hz), 3.38 (s, 6H). Anal. Calcd for $C_{14}H_{14}O_6S_2$: C, 49.11; H, 4.12; S, 18.73. Found: C, 49.08; H, 4.09; S, 18.70.

General Procedure for Polymerization of Aryl Triflates.[9a] The polymerization conditions and results are summarized in Table 1. In a typical polymerization (Table 1, entry 1), a 50-mL round-bottom flask equipped with a reflux condenser was charged under nitrogen with $NiCl_2(PPh_3)_2$ (0.216 g, 0.33 mmol), Zn (1.678 g, 25.67 mmol), and Et_4NI (0.790 g, 3.07 mmol). The flask was evacuated and purged with nitrogen three times. Then freshly distilled THF (1 mL) was added and the mixture was stirred for 15 min (the color gradually became dark red). **5** (1.17 g, 2.55 mmol) was added with a syringe. After stirring for 20 min, the temperature was raised to 70 °C for 2 h. The suspension was cooled to 22 °C and poured into 100 mL of methanol acidified with concentrated HCl (25% v/v). The precipitate was filtered and dried. The solid was dissolved in 10 mL of THF, filtered, evaporated to 3 mL, and poured into methanol acidified with concentrated HCl. The solid was isolated by filtration and dried in vacuo to afford 0.183 g (44.8%) of white polymer **16a**.

Polymer **16a** (Table 1, entry 1): ^1H NMR ($CDCl_3$) δ 7.8−7.4 (m, br); ^{19}F NMR ($CDCl_3$) δ −57.91 (m), −57.73 (m), −57.57 (m); IR (KBr) 2952 (w), 2922 (m), 2851 (m), 1617 (w), 1478 (m), 1390 (w), 1266 (s), 1215 (s), 1167 (s), 818 (m) cm^{-1}; UV-(THF) λ_{max} = 307 nm; ϵ = 85. Anal. Calcd for $C_7H_3F_3O$: C, 52.51; H, 1.89; F, 35.60. Found (entry 5, Table 1): C, 52.38; H, 1.90; F, 35.22. Mark−Houwink coefficient (entry 5): M_w = 21 800, $[\eta]$ = 0.455, log K = −7.353, a = 1.60.

Polymer **16b** (Table 1, entry 8). ^1H NMR (THF-d_8) δ 8.4−7.5 (m, br); ^{19}F NMR (THF-d_8) δ −57.52 (m, CF_3), −56.24 (m, CF_3, very weak), −73.93 (OTf), −73.88 (OTf); IR (KBr) 1617 (w), 1480 (m), 1430 (w), 1428 (w), 1411 (w), 1394 (sh), 1325 (s), 1292 (m), 1252 (m), 1175 (s), 1136 (s), 1087 (w), 1069 (w), 1060 (w), 1047 (w), 1026 (w), 1005 (w), 900 (w), 833 (w), 653 (w); UV (THF, 1 cm) λ_{max} = 271 nm; ϵ = 74. Anal. Calcd for $C_7H_3F_3$: C, 58.34; H, 2.10; F, 39.56. Found (entry 8, Table 1): C, 58.24; H, 2.14; F, 40.57. Mark−Houwink coefficient (entry 11): M_w = 11 600, $[\eta]$ = 0.235, log K = −7.132, a = 1.59.

Polymer **16c** (Table 1, entry 14): IR (KBr) 3436 (s), 2996 (w), 2952 (w), 2935 (w), 2910 (w), 2831 (w), 1604 (s), 1569 (m), 1480 (s), 1463 (s), 1419 (m), 1388 (s), 1306 (m), 1288 (w), 1260 (m), 1238 (s), 1216 (s), 1179 (m), 1139 (m), 1039 (m), 1027 (m), 1003 (m), 944 (w), 892 (w), 854 (w), 813 (m), 752 (w), 724 (w), 703 (w).

Polymer **17a** (Table 1, entry 16): ^1H NMR (THF-d_8) δ 8.0−7.4 (m, br); $^{13}C\{^1H\}$ NMR (THF-d_8) δ 148.21 (s) 142.30 (s), 133.82 (s), 130.72 (s), 126.89 (s), 121.72 (q, J = 258 Hz), 120.53 (s); ^{19}F NMR (THF-d_8) δ −56.49 (m); IR (KBr) 1614 (w), 1478 (m), 1391 (w), 1271 (s), 1264 (sh), 1250 (s), 1216 (s), 1167 (s), 820 (m); UV (THF, 1 cm) λ_{max} = 302 nm; ϵ = 76. Anal. Calcd for $C_7H_3F_3O$: C, 52.51; H, 1.89; F, 35.60. Found (entry 16, Table 1): C, 52.50; H, 1.94; F, 35.13.

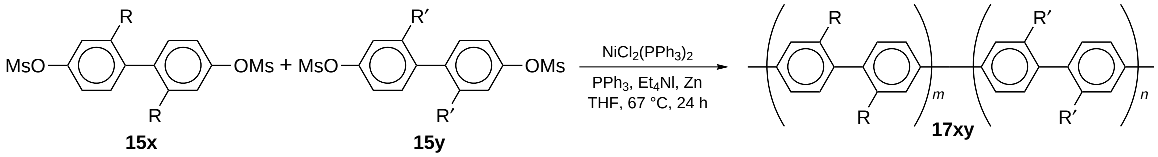
Polymer **17b** (Table 1, entry 18): ^1H NMR (THF-d_8) δ 8.27 (s (br), 1H), 8.14 (d, J = 7.3 Hz, 1H), 7.60 (d, J = 7.2 Hz, 1H); $^{13}C\{^1H\}$ NMR (THF-d_8) δ 140.24 (s) 137.50 (s), 133.16 (s), 130.38 (s), 129.90 (q, J = 30.5 Hz), 125.37 (s); 124.66 (q, J = 258 Hz); ^{19}F NMR (THF-d_8) δ −57.50 (CF_3, very weak); −73.11 (OTf); IR (KBr) 1480 (m), 1422 (w), 1408 (w), 1388 (m), 1313 (s), 1285 (sh), 1249 (m), 1174 (s), 1134 (s), 1084 (m), 1059 (w), 1047 (w), 1002 (w), 916 (w), 900 (w), 834 (w), 681 (w), 556 (w); UV (THF, 1 cm) λ_{max} = 273 nm; ϵ = 90. Anal. Calcd for $C_7H_3F_3$: C, 53.34; H, 2.10; F, 39.56. Found (entry 18, Table 1): C, 53.73; H, 2.15; F, 39.98.

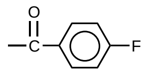
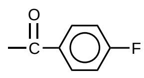
General Procedure for Polymerization of Aryl Mesylates.[10c] In a typical polymerization (Table 2, entry 3), a 25-mL Schlenk tube was charged with $NiCl_2(PPh_3)_2$ (1.75 g, 1.75 mmol), PPh_3 (2.75 g, 10.5 mmol), Zn (8.00 g, 123 mmol), Et_4NI (6.75 g, 26.3 mmol), **15a** (4.47 g, 8.75 mmol), **15b** (4.19 g, 8.75 mmol), and a magnetic stir bar. The tube was sealed with a rubber septum and placed under an Ar atmosphere (by three evacuation/fill cycles). Freshly distilled THF (16 mL) was added via 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) and at 70 °C for 24 h. After cooling to 22 °C, $CHCl_3$ (20 mL) was added and the reaction mixture was poured into methanol (300 mL) acidified with concentrated HCl (100 mL). The resulting precipitate was collected by filtration and dissolved in $CHCl_3$ (150 mL). The solution was filtered and poured into methanol (500 mL). The precipitate was collected by filtration and dried in vacuo (4.40 g, 83%). The polymer was purified by reprecipitation into MeOH from $CHCl_3$ solution before being analyzed by GPC. (M_n = 55 200, M_w/M_n = 2.04, phenylene repeat units = 2(m + n) = 363, DP = 182.) Elemental analyses of all polymers gave satisfactory results.

Results and Discussion

A. Synthesis of Monomers. Scheme 1 outlines the synthesis of hydroquinone substituted with OCF_3 (**4**) and CF_3 (**7**) groups and of the corresponding triflates **5** and **8**. Methoxyhydroquinone (**9**) and its corresponding bis(triflate) **10** were used as model for the nonfluorinated compound **4**. The polymerization of the bis(mesylate) of methylhydroquinone, which is a model for **8**, was described previously.[10c,d] The introduction of the OCF_3 group in **1** to produce **2** was performed by a general synthetic procedure elaborated by one of us.[14]

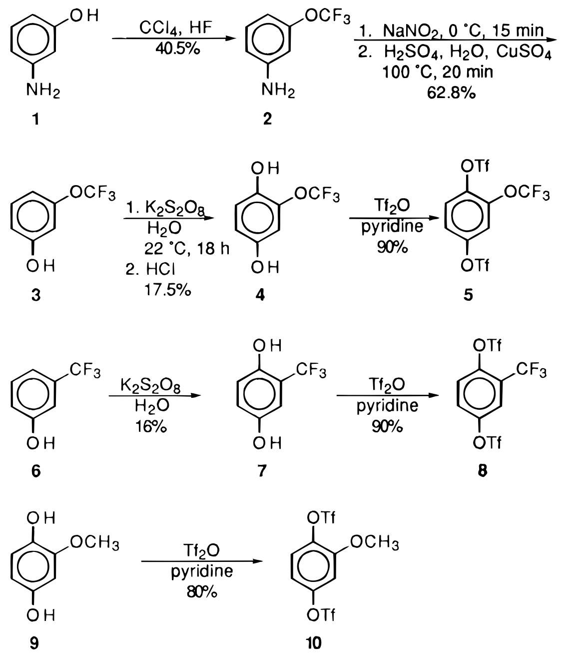
Table 2. Ni(0)-Catalyzed Polymerization and Copolymerization of 2,2′-Disubstituted-4,4′-bis[(methylsulfonyl)oxy]biphenyls



monomers								
entry	**15x**	R	15y	R′	polymer, yield (%)	M_n[b]	M_w/M_n[b]	$2(m + n)$[b]
1	**15a** (100)	OCF_3			**17a**, 86	13490	3.48	84
2	**15b** (100)	CF_3			**17b**, 81	8370	3.97	58
3	**15a** (50)	OCF_3	15b	CF_3	**17ab**, 83	55200	2.04	363
4	**15a** (50)	OCF_3	15c		**17ac**, 83	16630	2.86	93
5	**15a** (50)	OCF_3	15d	CH_3	**17ad**, 90		insoluble	
6	**15a** (50)	OCF_3	15e	H	**17ae**, 100		insoluble	
7	**15b** (50)	CF_3	15c		**17bc**, 92	10680	2.99	62
8	**15b** (50)	CF_3	15d	CH_3	**17bd**, 78	9430	2.81	81
9	**15b** (50)	CF_3	15e	H	**17be**, 88	6270	2.54	57

[a] Numbers in parentheses are mole percent. [b] By GPC.

Scheme 1. Synthesis of 2-Substituted-1,4-Bis(triflate) Monomers 5, 8, and 10

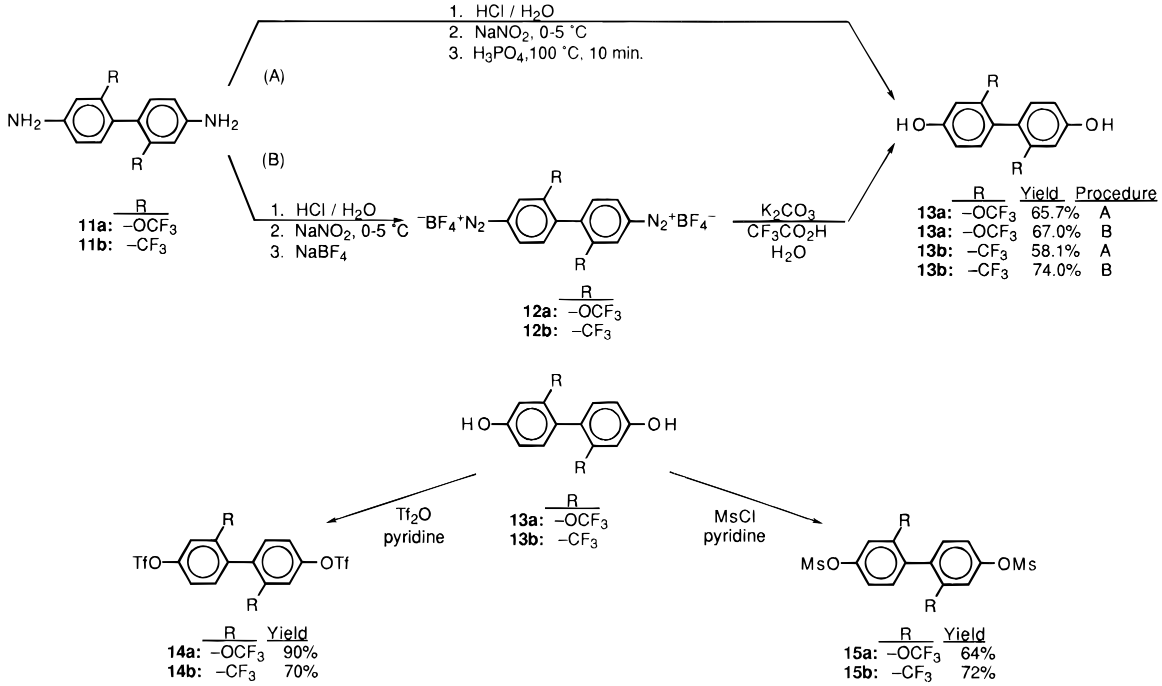


The new compound **2** was obtained in 62.8% yield and was transformed into the corresponding 3-(trifluoromethoxy)phenol (**3**) by a conventional Sandmeyer method for the synthesis of phenols by the decomposition of aromatic diazonium salt. The oxidation of **3** with $K_2S_2O_8$ in aqueous alkali followed by hydrolysis of the intermediate *p*-hydroxyphenyl potassium sulfate with dilute HCl under reaction conditions similar to those used for the oxidation of 2-fluorophenol[15] produced (trifluoromethoxy)hydroquinone (**4**) in 17.5% yield. (Trifluoromethyl)hydroquinone (**7**) was synthesized in 16% yield by the oxidation of 3-(trifluoromethyl)phenol (**6**) by the same procedure as that used for the oxidation of **3**. The synthesis of **7** was reported previously in only 6% yield.[15] The bis(triflate)s **5**, **8**, and **10** were prepared by esterification with Tf_2O in anhydrous pyridine and were purified by a combination of flash chromatography and crystallization (**5**), distillation (**8**), or sublimation (**10**), respectively.

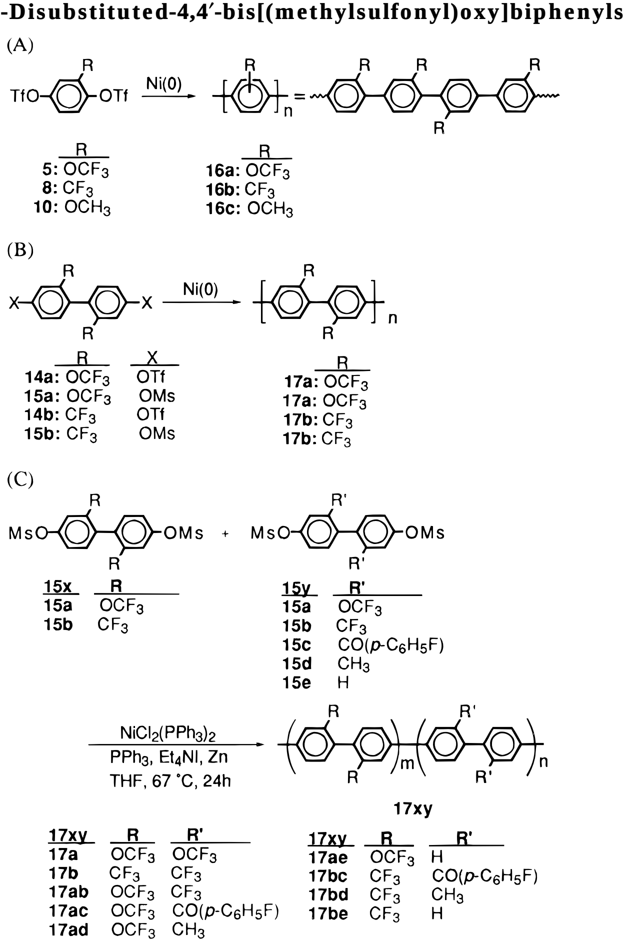
Scheme 2 describes the synthesis of 4,4′-dihydroxy-2,2′-bis(trifluoromethoxy)biphenyl (**13a**) and 4,4′-dihydroxy-2,2′-bis(trifluoromethyl)biphenyl (**13b**) of the corresponding bis(triflate)s **14a** and **14b** and bis(mesylate)s **15a** and **15b**. The starting materials 4,4′-diamino-2,2′-bis(trifluoromethoxy)biphenyl **(11a)**[12e] and 4,4′-diamino-2,2′-bis(trifluoromethyl)biphenyl **(11b)**[12d] were synthesized by methods available in the literature. Both **13a** and **13b** were obtained by the adaptation of two different Sandmeyer methods available in the literature for the preparation of phenols by the decomposition of aromatic diazonium salts. These two methods were named in the experimental section procedure A and procedure B. In procedure A, the diazonium chloride obtained from **11a** and **11b** was decomposed without separation in H_3PO_4.[16] In procedure B, the chloride anion of the diazonium salt was first exchanged with $NaBF_4$ to the tetrafluoroborate anion, and the resulting crystalline diazonium tetrafluoroborate was separated and then decomposed in refluxing trifluoroacetic acid containing CF_3CO_2K.[17] Even though procedure B produces higher yields (67.0% for **13a**, 74.8% for **13b**) than procedure A (65.7% for **13a**, 58.1% for **13b**), procedure A is preferred since it represents a three-step, one-pot reaction vs a four step, two-pot reaction. In addition, the overall reaction time is much shorter for procedure A. One synthesis of **13b**[18] according to procedure B was available in the literature. The literature reported yield (57%) is lower than that obtained by us with the same procedure B (74%) and only slightly lower than our yield obtained with procedure A (58.1%). The triflates (**14a**, **14b**) and mesylates (**15a**, **15b**, 4,4′-bis[(methylsulfonyl)oxy]biphenyl (**15e**)) of **13a**, **13b**, and **13e** were prepared by conventional methods and purified by column chromatography followed by sublimation or recrystallization when necessary. 2,2′-Bis(*p*-fluorobenzoyl)-4,4′-bis[(methylsulfonyl)oxy]biphenyl (**15c**) and 2,2′-dimethyl-4,4′-bis[(methylsulfonyl)oxy]biphenyl (**15d**), which were used in a few copolymerization experiments, were prepared as reported previously.[11c]

B. Polymerization Experiments. Scheme 3A,B outlines the polymerization of all monomers containing triflate leaving groups. The polymerization results are summarized in Table 1. All polymerization experiments with bis(triflate)s were carried out with our original

Scheme 2. Synthesis of 2,2′-Disubstituted Biphenyl Monomers 14a, 14b, 15a, and 15b



Scheme 3. Synthesis of (A) Regioirregular PPPs (16a–c) from 2-Substituted-1,4-Bis[[(trifluoromethyl)-sulfonyl]oxy]benzenes, (B) Regioregular Homopolymer PPPs (17a, 17b) from 2,2′-Disubstituted-4,4′-bis[[(trifluoromethyl)sulfonyl]-oxy]biphenyl and 2,2′-Disubstituted-4,4′-bis[(methylsulfonyl)oxy]biphenyls, and (C) Regioregular Copolymer PPPs (17x,y) from 2,2′-Disubstituted-4,4′-bis[(methylsulfonyl)oxy]biphenyls



reaction conditions,[9a,10a] which were not optimized. The polymerization experiments with bis(mesylate)s, which will be discussed later, were performed after optimum reaction conditions were elaborated.[10c,d,11] Nevertheless, even if the polymerization experiments carried out with bis(triflate)s can be improved, both series of experiments (i.e., bis(triflate)s and bis(mesylate)s) provide the same clear message.

The first instructive comparison considered involves the polymerization results of 2-substituted-1,4-bis[[(trifluoromethyl)sulfonyl]oxy]benzenes containing OCF_3 (**5**), CF_3 (**8**), and OCH_3 (**10**) substituents (Scheme 3A, Table 1). The polymerization of **5**, **8**, and **10** provides regioirregular PPPs which are more soluble than regioregular PPPs.[10d] The molecular weight of these polymers is determined by the solubility of the polymer[10c,d,11a] in the reaction mixture and by side reactions which terminate the polymerization process.[11a] Side reactions are favored by the presence of bulky and electron-donating substituents available in the ortho position of the leaving group.[11a] Electron-withdrawing substituents present in the same position increase the reactivity of the leaving group, while electron-donating substituents decrease it.[11a] The polymerization results from Table 1 provide a very clear conclusion. PPPs obtained from **5** have approximately 2.8 times larger molecular weights (M_n) than those obtained from **8** (e.g., compare entries 4 and 11). The solubility of the regioirregular PPPs with OCF_3 substituents is higher than that of the polymers with CF_3 substituents. At the same time, the polymers obtained from **10** are insoluble due to their crystallinity. Therefore, their molecular weights could not be measured by GPC. These results demonstrate that OCF_3 is more efficient than CF_3 in the production of soluble polymers. Although CF_3 has a stronger electron-withdrawing character than OCF_3, the latter displays a larger number of conformers due to rotation about C–O and O–CF_3 bonds, and therefore, generates a higher conformational entropy than the CF_3 group. At the same time, rotation about the C–O and O–CF_3 bonds of the OCF_3 group produces less steric hindrance to the triflate group than the CF_3 group. The replacement of OCF_3 with OCH_3 generates insoluble polymers. Similarly, the replacement of CF_3 with CH_3 also produces only very low molecular weight polymers.[10c,d]

Previously we demonstrated that regioregular PPPs are less soluble than regioirregular ones.[10d] Regioregular PPPs with OCF_3 and CF_3 substituents can be obtained by the polymerization of 2,2′-disubstituted-4,4′-bis[[(trifluoromethyl)sulfonyl]oxy]biphenyls containing OCF_3 (**14a**) and CF_3 (**14b**) substituents (Scheme 3B, Table 1). A regioregular PPP containing OCF_3 groups with $M_n = 54\,500$, which is higher than of the corresponding regioirregular polymers, was obtained. At the same time, the molecular weight of the regioregular PPP with CF_3 side groups is slightly lower than that of the regioirregular polymer. These two opposite trends are determined by a combination of polymer solubility and lack of steric hindrance of the leaving group. The solubility of both regioregular polymers **17a** and **17b** (Scheme 3) is lower than that of the corresponding regioirregular polymers **16a** and **16b**. However, the solubility of regioregular **17a** is much higher than that of **17b**. Since the monomer **17a** does not have any bulky ortho substituents to the triflate group to enhance side reactions, its polymerization yields a higher molecular weight polymer than that resulting from monomer **5**.

Table 2 and Scheme 3B,C summarize the polymerization experiments carried out with 2,2′-disubstituted-4,4′-bis[(methylsulfonyl)oxy]biphenyls. The molecular weight obtained by the polymerization of **15b** is in agreement with that obtained by the polymerization of **14b** (Scheme 2, Tables 1 and 2). The molecular weight of the polymer obtained from **15a** is higher than that obtained from **15b** but is lower than that obtained from **14a**. The solubility of the regioregular PPP with OCF_3 groups is higher than that with CF_3 groups. Copolymerization of a 1:1 molar ratio of **15a** and **15b** yields a soluble statistical copolymer with a $M_n = 55\,200$ (363 phenylenic repeat units). These results provide a strategy for the synthesis of even higher molecular weight PPPs. Copolymerization of **15a** and **15b** with 2,2′-bis(*p*-fluorobenzoyl)-4,4′-bis[(methylsulfonyl)oxy]biphenyl (**15c**); entries 4 and 7, Table 2), 2,2′-dimethyl-4,4′-bis[(methylsulfonyl)oxy]biphenyl (**15d**; entries 5 and 8, Table 2), and 4,4′-bis(methylsulfonyl]oxybiphenyl (**15e**; entries 6 and 9, Table 2) all produced lower molecular weight copolymers.

C. End-Group Analysis. Although complete end-group analysis is beyond the scope of this paper, some important preliminary results were obtained. Low molecular weight samples of polymers **16a** and **16b** (prepared from bis(triflate) monomers **5** and **8**, respectively) were analyzed by MALDI. In addition to multiples of the repeat unit mass, these experiments detected PPP molecular ion peaks (*M*) which correspond to multiples of the repeat unit mass plus 77 ± 2 and/or 149 ± 2. This indicates the incorporation of Ph and OTf end groups. The MALDI spectra were inconclusive for H end groups (mass of 1), since the resolution of the experiment was ±2. The MALDI spectral data indicate that PPh_2 (185 amu), PPh_3^+ (262 amu, from $PPh_3^+I^-$ or $PPh_3^+OTf^-$) and OH (17 amu) end groups were not present in detectable quantities. No masses corresponding to the incorporation of phosphorus in the endgroups or backbone were detected.[20] $^{31}P\{^1H\}$ NMR analysis of **17a** and **17b** did not detect any phosphorus resonances. At this time these results must be regarded as preliminary and definitive analyses of the end groups (i.e., complete analyses of **16**, **17**, and several model compounds by NMR (^1H, ^{13}C, ^{19}F, ^{31}P), MALDI, and elemental analysis) await a future study. However, since PPh_3 has been demonstrated to function as a potential trifunctional monomer capable of generating branch points and/or cross-links in Suzuki-type Pd-catalyzed polymerizations,[20] these preliminary analyses have important implications in regard to the rigidity and linearity of PPPs synthesized by this method.

The factors that influence the type(s) of end group(s) formed include (a) side reactions, (b) polymer solubility, and (c) end-group stability after reaction completion. Scheme 4 shows potential routes to several types of end groups. Chart 1 summarizes the structure and mass (in addition to the repeat unit mass) of these end groups. The initial end groups of growing polymers are OTf. The decomposition of Ni catalyst prior to the complete consumption of all OTf groups results in OTf end caps. Unless a growing polymer chain is able to react efficiently at the solid/liquid interface, the premature precipitation of a OTf-terminated polymer chain facilitates the formation of OTf-end-capped PPP. These groups can potentially be cleaved by a subsequent process (e.g., O−S bond cleavage to give **36**). All other end groups are formed by side reactions.

Although, the exact polymerization mechanism has not been established, a working model based upon established mechanistic details of homocoupling reactions of aryl halides[21] was discussed in earlier publications.[9a,c,d,10c,11a] These studies include a comprehensive discussion of side reactions in the coupling reactions of aryl sulfonates[11a] and polymerization of arylene bis(sulfonate)s.[10c] According to this model, polymer chain growth occurs by a process of (a) oxidative addition of TfO−terminated polymer $\mathbf{18}_{\boldsymbol{n}}$ (Scheme 4) to the Ni(0) catalyst to form the Ni(II) species **19**, (b) reduction of Ni(II) to Ni(I) with Zn, (c) oxidative addition of monomer (or TfO-terminated oligomer or polymer) resulting in a Ni(III) species (e.g., **27**), and (d) reductive elimination of $\mathbf{18}_{\boldsymbol{n+m}}$ (where $n + m$ = repeat units). The occurrence of side reactions during this cycle either ends (H and Ph end groups) or greatly inhibits (PPh_2 and $PPh_3^+X^-$ end groups) chain growth at the polymer terminus. The reduction of the aryl ligand of intermediate **19** by adventitious proton or hydrogen sources results in the formation PPP **20** with an H end-group. The reductive elimination of phosphonium salt end-capped **21** can also occur. An exchange reaction of the aryl ligand of **19** with PPh_3 gives PPh_2 end-capped PPP **24** upon dissociation from **22**. The resulting Ni species (**23**) gives Ph end-capped PPP **26** upon reaction with another growing polymer chain. These side reactions (reduction,[21a] phosphonium salt formation,[22] aryl group exchange[23]) are also considered for intermediate **27**. Both aryl ligands of **27** may participate in aryl exchange reactions with the Ph group of the PPh_3 ligand to form **28** or **31**. These Ni complexes (**28** and **31**) have diphenylphosphine end-capped PPP ligands (**30** and **24**, respectively). Reductive coupling of the aryl and Ph ligands of **28** (or **31**) gives phenyl end-capped PPP **29** (or **26**, respectively). The pentacoordinate character of **27** may inhibit side reactions that require vacant coordination sites. Aryl group exchange reactions similar to the transformation of **19** to **22**, **27** to **28**, and **27** to **31** apparently proceed by prior ligand dissociation to give coordinatively unsaturated species.[23a] Therefore, these reactions are expected to be less important for **27** than **19**.

Another mechanistic pathway for aryl exchange is possible.[21a,23b−e] This route is the cross-coupling reaction of $\mathbf{18}_{\boldsymbol{n}}$ with $Ph{-}Ni(PPh_2)(PPh_3)$ (**33**) to give phenyl end-capped PPP **29**. Cross-coupling reactions of **33** with aryl halides were reported in $Ni(0)(PPh_3)_n$-catalyzed reactions.[21a] Ni species **33** can be formed from $Ni(PPh_3)_3$ (**34**) by dissociation of PPh_3 to give $Ni(PPh_3)_2$ (**35**), followed by insertion of Ni into a P−Ph bond. This

Scheme 4. Potential Pathways for End-Group Formation during the Synthesis of PPPs

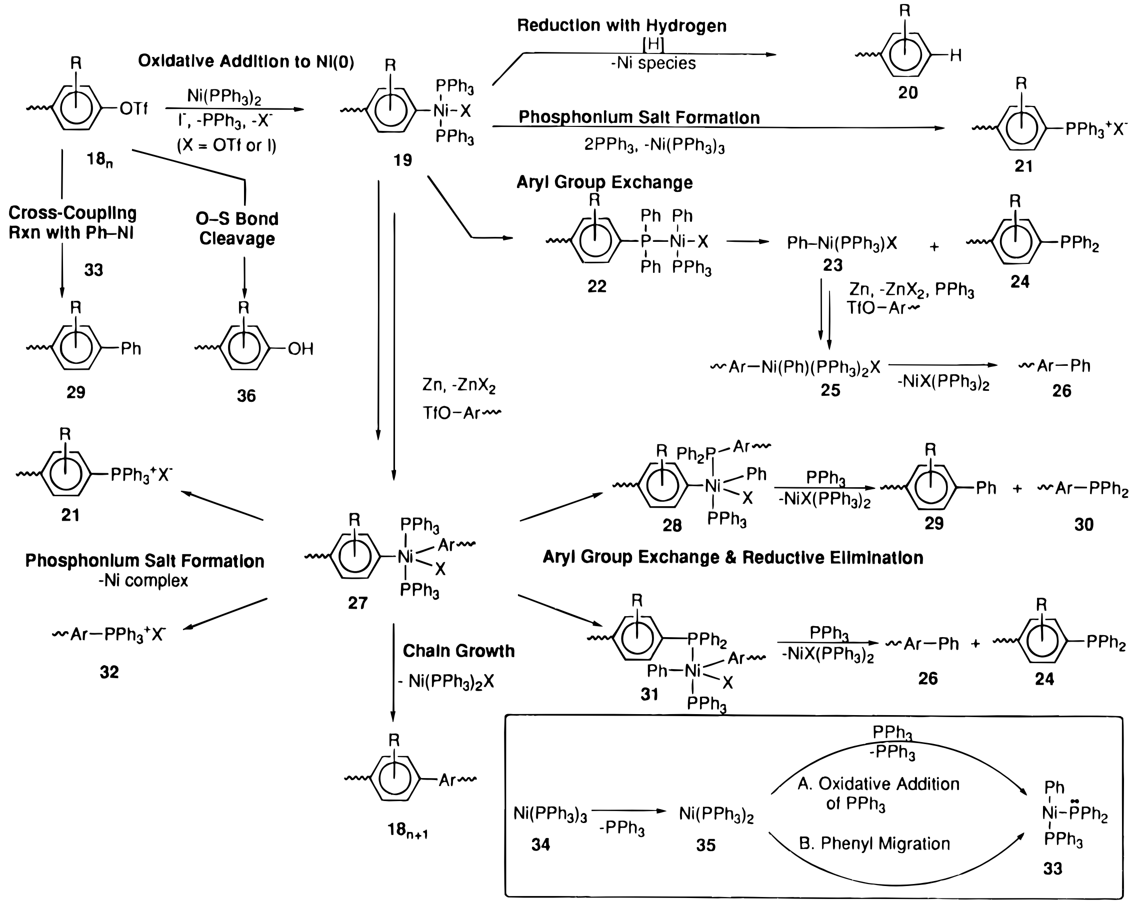


Chart 1. End-Group Masses of PPPs

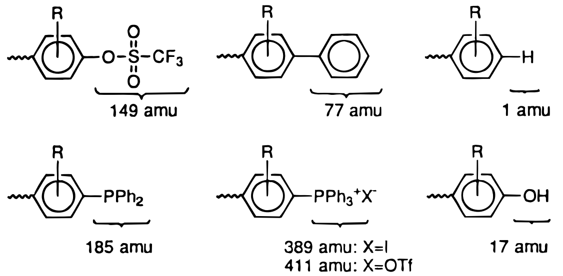


Table 3. Thermal Stability, UV Absorption, and Mark-Houwink Coefficient a of PPPs

polymer	R	λ_{max}[a] (nm) (ϵ)	10% weight loss[b] (° C)	Mark–Houwink coefficient *a*
16a	OCF_3	307 (85)	575	1.60
16b	CF_3	271 (74)	615	1.59
16b	CF_3			1.58
16c	OCH_3	insoluble	455	
17a	OCF_3	302 (76)	550	
17b	CF_3	273 (90)	580	
PPP[c]		420		

[a] Numbers in parentheses are the extinction coefficients ϵ. [b] TGA analysis under nitrogen. [c] Poly(*p*-phenylene).[24]

insertion has been proposed to occur through phenyl migration[23b,c] or oxidative addition of PPh_3.[23d,e] Unlike the previous aryl group exchange pathways, PPh_2 end-capped PPP is not formed. Therefore, the two types of aryl exchange reactions (i.e., that of **18_n** or those of **19** and **27**) can be distinguished by the amount of PPh_2 end cap formed in relationship to Ph end-capped PPP. The initial 1:1 ratio of **26**:**24** (or **29**:**30**) formed from aryl exchange reactions of **19** or **27** could be affected by the participation of **24** (or **30**) in a second aryl exchange reaction.

The detection of Ph end groups (by MALDI) combined with no evidence of phosphorus incorporation in the backbone or end groups (both MALDI and $^{31}P\{^1H\}$ NMR) is consistent with the primary pathway for formation of Ph end-capped PPP being the cross-coupling of **33** with the OTf end-group of monomers, oligomers, and polymers. This pathway does not involve the concurrent formation of PPh_2 end caps. It also suggests that the aryl group exchange reactions of **19** (to **22**) and **27** (to **28** and **31**) do not occur to a detectable extent. Aryl exchange reactions occurring by mechanisms similar to that depicted for the conversion of **19** to **22** have been reported for a number of Pd, Ni, and other transition metal-catalyzed processes including Suzuki-type Pd-catalyzed polymerizations.[20] Therefore, PPh_3 sometimes functions as a potential trifunctional monomer capable of generating branch points and/or cross-links.[20] These transarylation reactions are favored by the presence of electron-donating substituents upon the aryl moiety ligated to the metal.[20,21,23] The strongly electron-withdrawing OCF_3 and CF_3 substituents apparently suppress this reaction. This is supported by both the MALDI and $^{31}P\{^1H\}$ NMR data.

D. Characterization of PPPs. Some characterization experiments were carried out to assess the properties of these polymers and copolymers. The maxima of the absorption spectra of PPPs with OCF_3 and CF_3 substituents are reported in Table 3. The regioirregular **16a** absorbs at 307 nm, the regioregular **17a** at 302 nm, the regioirregular **16b** at 271 nm, and the regioregular **17b** at 273 nm. The first conclusion derived from these data is that both types of regioregular and regioirregular polymers have approximately the same conjugation length. However, the polymers containing OCF_3 sub-

Table 4. Phase transitions (°C) and corresponding enthalpy changes (J/g) of selected examples of PPPs[a]

polymer	M_n (GPC)	phase transitions (°C) and corresponding enthalpy changes[b] (J/g in parenthesis)	
		heating	cooling
17a	13 490	k_1 232, k_2 254 (13.8),[c] n	n 193 (0.7), S? 159 (11.5), k_2
17b	8 370	k_1 307 (6.3), k_2 343 (7.2), n	n 309 (1.02), S? 264 (11.96), k_2
17b	6 927	k_1 304 (6.25), k_2 338 (11.8), n	n 310 (1.71), S? 262 (22.6), k_2
17ab	17 640	g 206, k_1 241 (4.12), S? 254 (0.65), n	n 226, S? 219 (4.5),[c] k 202 g
17ab	55 200	g 206, k_1 S? 252 (2.6), n	n 236 (2.5) S?

[a] Numbers in parentheses are joules per gram. [b] Data are from first heating and cooling scans. Heating and cooling rates are 20 °C/min. [c] Overlapped transitions.

stituents are more conjugated than those with CF_3 substituents. The λ_{max} is about 30 nm higher for the polymers with OCF_3 groups than of those with CF_3 groups. This result is consistent with our discussion on the steric hindrance generated by OCF_3 and CF_3 groups placed in the ortho position of the leaving group. The angle between the two phenyl units of the 2,2′−disubstituted biphenyl is higher in the case of CF_3 than OCF_3. λ_{max} for unsubstituted PPP is 420 nm.[24] The thermal stability of these polymers was investigated under nitrogen. The 10% weight loss for the polymers with OCF_3 groups is in the range of 550−575 °C, while the same percent weight loss for polymers with CF_3 groups is in the range of 580−615 °C.

All homopolymers and copolymers display several first-order phase transitions both on heating and on cooling (Table 4). Homopolymers **17a** and **17b** exhibit two melting transitions on heating and most probably a monotropic smectic phase followed by a crystallization on cooling (Table 4). Above the highest first-order transition temperature, **17a**, **17b**, and **17ab** exhibit an enantiotropic nematic mesophase, observed on the optical polarized microscope, which does not undergo isotropization, up to the decomposition temperature. The nematic phases of **17a**, **17b**, and **17ab** exhibit a classic Schlieren texture. The first-order transition observed on cooling for **17a** and **17b** is strongly supercooled and has a much lower enthalpy change than the one observed during the heating process. Optical microscopy could not provide a definitive assessment of this phase due to the high viscosity of the sample in this phase. Samples of copolymer **17ab** exhibit a glass transition at about 206 °C. The lower molecular weight **17ab** also exhibits a melting and an enantiotropic smectic phase. The higher molecular weight polymer **17ab** exhibits only one first-order transition which most probably is associated with the smectic phase. Due to the high molecular weight, its crystallization is very slow. Therefore, the phase that becomes enantiotropic in **17ab** is most probably a higher ordered LC phase. The monotropic phase of homopolymers **17a** and **17b** seems to have been transformed into an enantiotropic phase by copolymerization (see **17ab**, Table 4).

It is known that *p*-sexiphenyl displays both nematic and S_A phases,[8b,25,26] while the hexamethylated *p*-sexiphenyl exhibits only crystalline, and isotropic phases.[8b,27] The octamethylated *p*-octaphenyl displays crystalline, nematic, and isotropic phases while the decamethylated *p*-decaphenyl exhibits crystalline, smectic, and nematic phases.[8b,27] Therefore, on the basis of the phase behavior of these model compounds which resemble the structure of the present polymers, we can speculate that the phase which becomes enantiotropic in **17ab** is most probably a LC phase. X-ray diffraction experiments are however required to fully assign the crystalline and liquid crystalline phases of these polymers.

Polymers **17a**, **17b**, and **17ab** with the molecular weights reported in Tables 1−3 are soluble in THF, $CHCl_3$, and dipolar aprotic solvents. The solubility of **17ab** is higher than that of **17b** and much higher than that of **17a**. Solutions of all these polymers become opalescent upon concentration, demonstrating the formation of a lyotropic mesophase. Free-standing anisotropic polymer films can be obtained from **17ab** by solution casting.

Several polymer samples were characterized by GPC coupled to refractomer, viscometer, and laser light scattering detectors in order to calculate the Mark−Houwink coefficient **a** (Table 3). The coefficient **a** is in the range of values available for the most rigid polymers reported so far.[28] MALDI experiments together with the present solution results suggest that the molecular weights of these polymers determined by GPC with polystyrene standards are overestimated by a factor between 1.5 and 2.

Conclusions

High molecular weight regioregular and regioirregular PPPs containing CF_3 and OCF_3 substituents were prepared via the Ni(0)-catalyzed homocoupling of the bis(triflate)s and bis(mesylate)s of the substituted hydroquinone and 4,4′-dihydroxy-2,2′-disubstituted biphenyls. The electron-withdrawing characteristic of these substituents facilitates high efficiency in the polymerization reaction, and the increased solubility imparted by these groups prevents premature precipitation of the growing polymer chain. The most dramatic increase in molecular weight (vs nonfluorinated substituent groups) was obtained with OCF_3. In comparison with the CF_3 group, OCF_3 imparts higher conformational entropy to PPP and produces less steric hindrance in the coupling reaction that gives regioirregular PPPs. These results demonstrate that fluorine-containing substituents are the most effective groups developed to date for the synthesis of soluble, high molecular weight PPPs. Preliminary characterization experiments showed that these polymers form both thermotropic and lyotropic liquid crystalline phases. The Mark-Houwink coefficient of **17a**, **17b**, and **17ab** is about 1.60. Experiments to investigate the rigidity of these PPPs in solution and compare it with that of other rigid polymers[29] as well as to elucidate their thermotropic liquid crystalline and crystalline phases by X−ray diffraction experiments are in progress.

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