

Exploration of the Stille Coupling Reaction for the Syntheses of Functional Polymers

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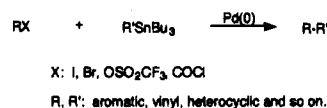
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Abstract: The palladium-catalyzed Stille coupling reaction was used for preparing functionalized, conjugated polymers. This reaction has several advantages, two of which are that it requires mild reaction conditions and produces high yields. Several factors which affect the polymerization processes were investigated, such as the catalyst composition and concentration, different solvents and ligands, and structures of monomers. It was found that solvents that could keep the macromolecules in solution and stabilize the palladium(0) catalyst would yield polymers with high molecular weights. If a Pd(II) compound was used as the catalyst, a stoichiometric adjustment of the distannyl monomer was necessary to enhance the molecular weight of the resulting polymer. In general, it was found that a combination of an electron-rich distannyl monomer and an electron-deficient dihalide (ditriflate) monomer forms polymers with relatively high molecular weights. To further demonstrate the versatility of the Stille reaction for polycondensations, different types of conjugated polymers with different properties and applications, such as liquid crystalline conjugated polymers and conjugated photorefractive polymers, were synthesized.

Introduction

Conjugated polymers possess interesting electronic and optical properties due to their unique delocalized π -electron systems. These properties are being explored for practical applications in electronic and optoelectronic devices, such as rechargeable batteries and electroluminescent devices.¹ To fully harvest these interesting physical properties, soluble and fusible polymers are desirable because they offer advantages in both fundamental characterizations and device fabrications. However, conjugated polymers without any substitutions are usually insoluble and infusible. Structural modifications of these polymers have thus been strongly pursued in different research groups.^{1,2} Recently, palladium-catalyzed reactions have been extensively investigated to synthesize conjugated or other functional polymers. For example, the Heck reaction was successfully utilized to synthesize poly(phenylenevinylene) (PPV) and its derivatives,^{3–8} the Suzuki reaction was explored to synthesize poly(*p*-phenylene) (PPP),^{9–12} and the Stille coupling reaction was applied to synthesize poly(phenylenethiophene) (PPT).¹³ The main reason for these research efforts is that these reactions only require mild conditions and can tolerate many functional groups. This is especially important for the syntheses of functional and

Scheme 1. General Scheme for the Stille Coupling Reaction



multifunctional polymers. For example, the Stille coupling reaction enabled us to synthesize photorefractive polymers with conjugated backbones and pendant nonlinear optical chromophores.^{14–16} Approaches other than the palladium-catalyzed reactions will encounter problems of intolerance for many of these functional groups. However, to effectively utilize these reactions for polycondensations, reaction conditions and scopes must be studied. In this paper we report the detailed studies of the Stille reaction for polycondensations.

The Stille reaction involves the coupling of an organic halide, triflate, or carbonyl chloride with organotin compound catalyzed by a palladium(0) catalyst.^{17,18} The organic groups can be aryl, heterocyclic, or vinyl types. The reaction has been shown to tolerate many functional groups, such as amines, aldehydes, esters, ethers, and nitro groups. The reaction yield is usually high, which is essential to obtain high molecular weight polymers. A general reaction is shown in Scheme 1.

A proposed mechanism is shown in Scheme 2 which has been well accepted by many groups after a great amount of research. A palladium(II) or palladium(0) complex is generally introduced as the catalyst. When a palladium(II) compound is used, it is believed that the palladium(II) complex is first reduced to the palladium(0) species by the organotin compound.¹⁹ The resulting Pd(0) reacts with the organic halide or triflate to form the organopalladium halide (triflate) intermediate by oxidative addition. This intermediate then undergoes transmetalation. In the case of triflates, LiCl has to be used to facilitate this

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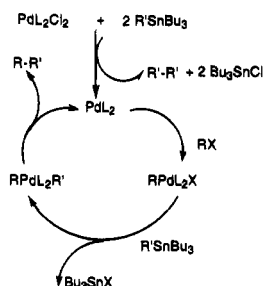
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Scheme 2. Mechanism for the Stille Coupling Reaction



process.²⁰ Finally, a reductive elimination affords the product and the palladium(0) species to complete the catalytic cycle. Several review papers are available on the Stille coupling reaction where various examples of the Stille reaction in organic synthesis are cited.^{17,18}

The general reaction conditions in the syntheses of small molecules via the Stille coupling reaction have been developed.^{17,18,20} However, studies on the reaction conditions for polymerizations are limited. Many of the factors that may not affect the reactions for small molecules could drastically affect the molecular weight for polymerizations; examples are the monomer stoichiometric imbalance caused by the conversion of the palladium(II) catalyst to the palladium(0), the solubility of the polymer in the reaction medium, the nature of the reactants and solvents, and the composition of the catalyst systems. To synthesize high molecular weight materials, it is of great importance to investigate these factors. Furthermore, the Stille reaction also allows us to synthesize many new conjugated polymer systems which exhibit interesting physical properties, such as liquid crystallinity and electroactivity. Some of these physical studies are reported in this paper. Finally, examples of utilizing the Stille reaction to prepare functional and multifunctional conjugated polymers are given to demonstrate the versatility of this reaction.

Experimental Section

Dioxane was purified by distillation with calcium hydride and stored over 3 Å molecular sieves. DMF was purified by distillation with phosphorus pentoxide. All of the other chemicals were purchased from the Aldrich Chemical Co. and were used as received unless otherwise stated. The synthetic schemes for monomer syntheses are shown in Schemes 2, 4, and 6. The following compounds were prepared according to literature procedures: 1,4-diiodo-2,5-bis(octyloxy)benzene (1),³ 1,4-dibromo-2,5-bis(octyloxy)benzene (2),³ 2,5-bis(octyloxy)phenyl 1,4-bistriflate (3),²¹ 4-diiodo-2,5-dioctylbenzene (4),²² 1,4-dibromo-2,5-dioctylbenzene (5),²² 2,5-bis(tributylstannyl)thiophene (9),¹³ 1,2-bis(tributylstannyl)ethene (10),²³ compound 17,²⁴ compound 22,¹⁴ 1-(6-bromohexyl)-2,5-dimethoxybenzene (23),¹⁴ dihydropyrrolopyrroledione 27.¹⁴

2,5-Dioctylphenyl 1,4-Bistriflate (6). To an ice-cooled pyridine solution (8 mL) of 2,5-dioctylhydroquinone (16) (2.88 g, 8.6 mmol) was added triflic anhydride (3.05 mL, 18.1 mmol) dropwise. The reaction mixture was warmed to room temperature 30 min after the addition and stirred at room temperature for an additional 48 h. This mixture was then poured into water (30 mL) and extracted with ether (20 mL, 2×). The organic layers were combined and washed consecutively with water (20 mL), 10% hydrochloric acid aqueous solution (10 mL, 2×), saturated sodium chloride aqueous solution (20 mL), and water (20 mL). The solution was dried over anhydrous

magnesium sulfate, and the solvent was evaporated under a vacuum. The crude product was purified by a short silica gel column using hexane/ethyl acetate (40:1, v/v) as the eluent. Recrystallization from hexane gave a white solid: yield 95%; mp 30–30.5 °C; ¹H NMR (CDCl₃) δ 0.87 (t, *J* = 6.68 Hz, –CH₃, 6H), 1.27 (m, –(CH₂)₅–, 20H), 1.58 (m, –CH₂–, 4H), 2.65 (t, *J* = 7.83 Hz, ArCH₂–, 4H), 7.14 (s, phenyl protons, 2H) ppm; ¹³C NMR (CDCl₃) δ 14.03, 22.60, 29.11, 29.18 (2 carbons), 29.52, 29.63, 31.76, 118.12 (d, *J* = 320.29 Hz), 123.53, 135.42, 146.47 ppm. Anal. Calcd for C₂₄H₃₆O₆S₂F₆: C, 48.15; H, 6.06. Found: C, 47.82; H, 6.00.

Phenyl *p*-Bistriflate (8). This compound was synthesized in the same way as described for compound 6 from hydroquinone: yield 75%; mp 50–52 °C; ¹H NMR (CDCl₃) δ 7.35 (s, phenyl protons, 4H) ppm; ¹³C NMR (CDCl₃) δ 118.12 (d, *J* = 320.18 Hz), 123.41, 148.41 ppm. Anal. Calcd for C₈H₄O₆S₂F₆: C, 25.68; H, 1.08. Found: C, 25.69; H, 1.08.

1,4-Bis(trimethylstannyl)benzene (11). The Grignard reagent of *p*-dibromobenzene was prepared by refluxing the mixture of *p*-dibromobenzene (6.60 g, 20 mmol) and magnesium powder (1.03 g, 42 mmol) in THF for 2 h. To this solution, cooled in an ice bath, was added a 2.5 M THF solution of trimethyltin chloride (16.4 mL, 41 mmol). The mixture was refluxed for 24 h and then cooled in an ice bath. After it was quenched with saturated ammonium chloride aqueous solution, THF was evaporated under a reduced pressure, and the resulting suspension was extracted with ether (20 mL, 3×). The combined organic layer was washed with water (20 mL, 2×). It was then dried with anhydrous magnesium sulfate, and the solvent was evaporated under a reduced pressure to give a white solid. This solid was run through a silica gel filtration column (hexane as the eluent) and recrystallized twice from methanol/ethyl acetate (20:1, v/v): yield 30%; mp 117–120 °C; ¹H NMR (CDCl₃) δ 0.27 (s, –Sn(CH₃)₃, 18H), 7.41 (s, phenyl protons, 4H) ppm; ¹³C NMR (CDCl₃) δ –9.39, 135.79, 142.41 ppm. Anal. Calcd for C₁₂H₂₂Sn₂: C, 35.70; H, 5.50. Found: C, 35.67; H, 5.19.

1,4-Bis(trimethylstannyl)-2,5-dimethoxybenzene (12). To a mixture of hydroquinone dimethyl ether (1.38 g, 10 mmol) and *N,N,N',N'*-tetramethylethylenediamine (4.53 mL, 30 mmol) in 40 mL of dry hexane was added a 2.5 M hexane solution of butyllithium (15 mL, 37.5 mmol). The mixture was stirred for 20 h at room temperature. After the solution was cooled in an ice bath, a 1.0 M hexane solution of trimethyltin chloride (43 mL, 43 mmol) was added dropwise. The mixture was then stirred at room temperature for 2 h. After being quenched with water, the organic layer was separated and the aqueous layer was extracted with ether (20 mL, 2×). The organic layers were combined and washed with water. The solution was dried over anhydrous magnesium sulfate, and the solvent was evaporated under reduced pressure. The resulting solid was purified chromatographically using a silica gel column and hexane/ethyl acetate (40:1, v/v) as the eluent. The crude product was recrystallized from methanol to give 2.52 g of white solid: yield 54%; mp 114.5–115 °C; ¹H NMR (CDCl₃) δ 0.26 (s, –Sn(CH₃)₃, 18H), 3.75 (s, –OCH₃, 6H), 6.82 (s, phenyl protons, 2H) ppm; ¹³C NMR (CDCl₃) δ –8.92, 56.36, 117.78, 132.28, 158.61 ppm. Anal. Calcd for C₁₄H₂₆Sn₂O₂: C, 36.26; H, 5.65. Found: C, 36.27; H, 5.82.

1,4-Bis(tributylstannyl)-2,5-dimethoxybenzene (13). This compound was prepared using a method similar to that for 1,4-bis(trimethylstannyl)-2,5-dimethoxybenzene (12) except that tributyltin chloride was used instead of trimethyltin chloride. The resulting product was a colorless liquid. It was first vacuum distilled, and then the component was collected at 102–110 °C (1.3 Torr). Further purification was carried out by using a silica gel column with hexane as the eluent: yield 26%; ¹H NMR (CDCl₃) δ 0.88 (t, *J* = 7.12 Hz, –CH₃, 18H), 1.01 (m, –CH₂–, 12H), 1.32 (m, –CH₂–, 12H), 1.52 (m, –SnCH₂–, 12H), 3.71 (s, –OCH₃, 6H), 6.79 (s, phenyl protons, 2H) ppm; ¹³C NMR (CDCl₃) δ 10.02, 13.85, 27.57, 29.41, 55.75, 117.22, 131.54, 158.41 ppm. Anal. Calcd for C₃₂H₆₂Sn₂O₂: C, 53.66; H, 8.73. Found: C, 53.68; H, 9.01.

1,4-Bis(trimethylstannyl)-2,5-bis(heptyloxy)benzene (14). This compound was prepared using a method similar to that for 1,4-bis(trimethylstannyl)-2,5-dimethoxybenzene (12) from *p*-bis(heptyloxy)benzene. The resulting product was a white solid: yield 35%; mp 74–76 °C; ¹H NMR (CDCl₃) δ 0.26 (s, –Sn(CH₃)₃, 18H), 0.89 (t, *J* =

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6.95 Hz, $-\text{CH}_3$, 6H), 1.30 (m, $-(\text{CH}_2)_3-$, 12H), 1.45 (m, $-\text{CH}_2-$, 4H), 1.73 (m, $-\text{CH}_2-$, 4H), 3.87 (t, $J = 6.95$ Hz, $-\text{OCH}_2-$, 4H), 6.79 (s, phenyl protons, 2H) ppm; ^{13}C NMR (CDCl_3) δ -8.96, 14.11, 22.64, 26.13, 28.97, 29.13, 29.69, 31.84, 68.21, 117.11, 131.77, 157.54 ppm. Anal. Calcd for $\text{C}_{26}\text{H}_{50}\text{Sn}_2\text{O}_2$: C, 49.41; H, 7.97. Found: C, 49.66; H, 8.13.

1,4-Dimethoxy-2,5-diethylbenzene (15). To a mixture of hydroquinone dimethyl ether (2.76 g, 20 mmol) and *N,N,N',N'*-tetramethylethylenediamine (9.1 mL, 60 mmol) in 40 mL of dry hexane was added a 1.6 M hexane solution of butyllithium (37.5 mL, 60 mmol). The mixture was stirred at room temperature for 20 h. After the solution was cooled in an ice bath, 1-bromooctane (16 mL, 92 mmol) was added dropwise. The mixture was then stirred at room temperature for 12 h. After being quenched with water, the organic layer was separated, and the aqueous layer was extracted with ether (20 mL, 2 \times). The organic layers were combined and washed with water. The solution was dried over anhydrous magnesium sulfate and the solvent was evaporated under reduced pressure. The resulting liquid was vacuum distilled, and the component was collected at 90–100 $^\circ\text{C}$ (0.3 Torr). It was then purified using a silica gel column and hexane/chloroform (1:1 v/v) as the eluent. The crude product was recrystallized from methanol to give needle-like white crystals: yield 48%; mp 50–51 $^\circ\text{C}$; ^1H NMR (CDCl_3) δ 0.87 (t, $J = 6.26$ Hz, $-\text{CH}_3$, 6H), 1.29 (m, $-(\text{CH}_2)_5-$, 20H), 1.55 (m, $-\text{CH}_2-$, 4H), 2.54 (t, $J = 7.79$ Hz, ArCH_2- , 4H), 3.75 (s, $-\text{OCH}_3$, 6H), 6.60 (s, phenyl protons, 2H) ppm; ^{13}C NMR (CDCl_3) δ 14.14, 22.72, 29.36, 29.57, 29.71, 30.21, 30.28, 31.97, 56.18, 113.01, 129.25, 151.23 ppm.

2,5-Diethylhydroquinone (16). To a methylene chloride solution (60 mL) of 1,4-dimethoxy-2,5-diethylbenzene (15) (3.41 g, 9.4 mmol) cooled to -78 $^\circ\text{C}$ was added a solution of 3.6 M boron tribromide in methylene chloride (5.49 mL, 9.8 mmol). The solution was slowly warmed to room temperature and stirred for 12 h. It was then quenched with water. The methylene chloride was then evaporated under reduced pressure. The white solid was filtered and rinsed with water. Recrystallization from hexane gave white flakes: yield 92%; mp 102.5–103 $^\circ\text{C}$; ^1H NMR (CDCl_3) δ 0.87 (t, $J = 6.26$ Hz, $-\text{CH}_3$, 6H), 1.26 (m, $-(\text{CH}_2)_5-$, 20H), 1.56 (m, $-\text{CH}_2-$, 4H), 2.49 (t, $J = 7.72$ Hz, ArCH_2- , 4H), 4.20 (s, $-\text{OH}$, 2H), 6.50 (s, phenyl protons, 2H) ppm.

Compound 18. A mixture of compound 17 (1.867 g, 5.45 mmol),²⁴ *p*-anisaldehyde (0.68 mL, 5.45 mmol), and trichloroacetic acid (0.151 g) in acetonitrile (50 mL) was stirred for 12 h in the dark at room temperature. A solution of *p*-chloranil (2.18 g) in THF (40 mL) was added and allowed to react for 4 h under room temperature. The solvent was then evaporated under reduced pressure, which gave a purple black solid. This solid was dissolved in CH_2Cl_2 (50 mL) and washed with a saturated NaHCO_3 solution (2 \times 20 mL) followed by water (2 \times 20 mL). The organic layer was collected and dried over anhydrous magnesium sulfate, and the solvent was evaporated under reduced pressure. The crude product was purified by a short silica gel column using CH_2Cl_2 as the eluent: yield 57%; ^1H NMR (CDCl_3) δ -2.42 (s, NH, 2H), 0.89 (t, $J = 7.24$ Hz, $-\text{CH}_3$, 12H), 1.35 (m, $-\text{CH}_2-$, 8H), 1.46 (m, $-\text{CH}_2-$, 8H), 1.72 (m, $-\text{CH}_2-$, 8H), 2.17 (m, $-\text{CH}_2-$, 8H), 2.53 (s, porphyrin- CH_3 , 12H), 3.98 (t, $J = 7.82$ Hz, porphyrin- CH_2- , 8H), 4.10 (s, $-\text{OCH}_3$, 12H), 7.26 (d, $J = 8.2$ Hz, phenyl, 4H), 7.93 (d, $J = 8.2$ Hz, phenyl, 4H), 10.22 (s, meso-proton on porphyrin, 2H) ppm; ^{13}C NMR (CDCl_3) δ 14.17, 14.80, 22.77, 26.79, 29.99, 32.02, 33.33, 55.52, 96.84, 112.93, 117.54, 133.74, 134.64, 136.30, 141.38, 143.11, 145.51, 159.81 ppm. Anal. Calcd for $\text{C}_{62}\text{H}_{82}\text{N}_4\text{O}_2$: C, 81.35; H, 9.03; N, 6.12. Found: C, 81.53; H, 9.12; N, 6.13.

Compound 19. To a methylene chloride solution (40 mL) of compound 18 (1.39 g, 1.5 mmol) cooled to -78 $^\circ\text{C}$ was added a solution of 3.6 M boron tribromide in methylene chloride (2.56 mL, 9.2 mmol). The mixture was slowly warmed to room temperature and stirred for 12 h. It was then quenched with water. An aqueous solution of K_2CO_3 (2.2 g in 30 mL of water) was added and stirred for 10 min. The organic layer was separated and washed with water (2 \times 20 mL) and dried over anhydrous magnesium sulfate. The solvent was then evaporated under reduced pressure to give a purple solid: yield 93%; ^1H NMR (CDCl_3) δ -2.20 (s, NH, 2H), 0.88 (t, $J = 7.26$ Hz, $-\text{CH}_3$, 12H), 1.34 (m, $-\text{CH}_2-$, 8H), 1.46 (m, $-\text{CH}_2-$, 8H), 1.70 (m, $-\text{CH}_2-$, 8H), 2.15 (m, $-\text{CH}_2-$, 8H), 2.51 (s, porphyrin- CH_3 , 12H), 3.94 (t, $J = 7.62$ Hz, porphyrin- CH_2- , 8H), 7.05 (d, $J = 8.2$ Hz, phenyl, 4H),

7.80 (d, $J = 8.2$ Hz, phenyl, 4H), 10.15 (s, meso-proton on porphyrin, 2H) ppm; ^{13}C NMR (CDCl_3) δ 14.15, 14.83, 22.76, 26.78, 29.98, 32.00, 33.31, 96.85, 114.50, 117.40, 133.90, 134.84, 136.25, 141.38, 143.18, 145.48, 155.77 ppm. Anal. Calcd for $\text{C}_{60}\text{H}_{78}\text{N}_4\text{O}_2$: C, 81.22; H, 8.86; N, 6.31. Found: C, 80.96; H, 8.80; N, 6.28.

Compound 20. To an ice-cooled pyridine solution (10 mL) of compound 19 (1.22 g, 1.37 mmol) was added triflic anhydride (0.49 mL, 2.87 mmol) dropwise. The reaction mixture was warmed to room temperature 30 min after the completion of the addition and stirred under room temperature for 48 h. This mixture was poured into water (30 mL) and extracted with chloroform (20 mL, 2 \times). The organic layers were combined and washed consecutively with water (20 mL), 10% hydrochloric acid aqueous solution (10 mL, 2 \times), saturated sodium chloride aqueous solution (20 mL), and water (20 mL). The solution was dried over magnesium sulfate, and the solvent was evaporated under reduced pressure. The crude product was purified through a short silica gel column using chloroform as the eluent and then recrystallized from hexane/chloroform (20/1, v/v) to give a purple solid: yield 67%; ^1H NMR (CDCl_3) δ -2.40 (s, NH, 2H), 0.89 (t, $J = 7.29$ Hz, $-\text{CH}_3$, 12H), 1.36 (m, $-\text{CH}_2-$, 8H), 1.46 (m, $-\text{CH}_2-$, 8H), 1.71 (m, $-\text{CH}_2-$, 8H), 2.16 (m, $-\text{CH}_2-$, 8H), 2.44 (s, porphyrin- CH_3 , 12H), 3.94 (t, $J = 7.75$ Hz, porphyrin- CH_2- , 8H), 7.61 (d, $J = 8.19$ Hz, phenyl, 4H), 8.09 (d, $J = 8.19$ Hz, phenyl, 4H), 10.18 (s, meso-proton on porphyrin, 2H) ppm; ^{13}C NMR (CDCl_3) δ 14.20, 14.69, 22.83, 26.84, 30.09, 32.06, 33.40, 97.34, 115.39, 120.36, 134.38, 135.62, 141.64, 142.74, 143.89, 144.69, 149.85 ppm. Anal. Calcd for $\text{C}_{62}\text{H}_{76}\text{N}_4\text{O}_6\text{F}_6\text{S}_2$: C, 64.68; H, 6.65; N, 4.87. Found: C, 64.76; H, 6.71; N, 4.87.

Compound 21. A mixture of compound 20 (0.2455 g, 0.23 mmol) and zinc acetate dihydrate (0.5144 g, 2.3 mmol) in CHCl_3 /methanol (3:1, v/v) was refluxed for 3 h in the dark. The solution was then cooled in an ice bath, and a large amount of methanol was added to precipitate the product. The purple red solid was collected and recrystallized from hexane/ CHCl_3 (20:1 v/v): yield 99%; ^1H NMR (CDCl_3) δ 0.91 (t, $J = 6.86$ Hz, $-\text{CH}_3$, 12H), 1.38 (m, $-\text{CH}_2-$, 8H), 1.47 (m, $-\text{CH}_2-$, 8H), 1.71 (m, $-\text{CH}_2-$, 8H), 2.11 (m, $-\text{CH}_2-$, 8H), 2.34 (s, porphyrin- CH_3 , 12H), 3.81 (t, $J = 5.35$ Hz, porphyrin- CH_2- , 8H), 7.61 (d, $J = 7.75$ Hz, phenyl, 4H), 8.06 (d, $J = 7.63$ Hz, phenyl, 4H), 9.96 (s, meso-proton on porphyrin, 2H) ppm; ^{13}C NMR (CDCl_3) δ 14.15, 15.34, 22.77, 26.63, 30.07, 31.96, 33.34, 97.85, 116.78, 120.35, 134.72, 137.34, 144.02, 144.34, 146.39, 147.22, 149.87 ppm. Anal. Calcd for $\text{C}_{62}\text{H}_{74}\text{N}_4\text{O}_6\text{F}_6\text{S}_2\text{Zn}$: C, 61.30; H, 6.14; N, 4.61. Found: C, 61.02; H, 6.12; N, 4.55.

2-(6-Carbazol-9-ylhexyl)-1,4-dimethoxybenzene (24). Sodium hydride (0.36 g, 15 mmol) was added to a solution of carbazole (1.67 g, 10 mmol) in DMF (10 mL) under nitrogen. The solution was stirred at 50 $^\circ\text{C}$ for 1 h. 1-(6-Bromohexyl)-2,5-dimethoxybenzene (23) (3 g, 10 mmol)¹⁴ was then added, and the resulting mixture was stirred at 90 $^\circ\text{C}$ for 3 h. The reaction was stopped by adding water (30 mL) to the solution, and the mixture was extracted with ether (3 \times 15 mL). The combined organic solution was washed with water (20 mL) and brine (20 mL). After the solution was dried with anhydrous magnesium sulfate and the solvent was removed, the crude product was recrystallized from a mixture of methanol/chloroform. The product was collected as a white solid: yield 3.04 g, 78%; mp 83–85 $^\circ\text{C}$; ^1H NMR (CDCl_3) δ 1.40 (m, $-\text{CH}_2-$, 4H), 1.54 (m, $-\text{CH}_2-$, 2H), 1.86 (m, $-\text{CH}_2-$, 2H), 2.53 (t, $J = 7.2$ Hz, $-\text{phenyl-CH}_2-$, 2H), 3.71 (s, $-\text{OCH}_3$, 3H), 3.72 (s, $-\text{OCH}_3$, 3H), 4.26 (t, $J = 7.2$ Hz, $-\text{NCH}_2-$, 2H), 6.62 (m, phenyl, 2H), 6.69 (d, $J = 8.3$ Hz, phenyl, 1H), 7.17 (t, $J = 7.6$ Hz, carbazole, 2H), 7.34 (d, $J = 8.1$ Hz, carbazole, 2H), 7.40 (t, $J = 7.6$ Hz, carbazole, 2H), 8.04 (d, $J = 7.6$ Hz, carbazole, 2H) ppm; ^{13}C NMR (CDCl_3) δ 27.29, 29.01, 29.33, 29.85, 30.36, 43.10, 55.72, 55.97, 108.80, 110.71, 111.23, 116.39, 118.83, 120.45, 122.93, 125.71, 132.39, 140.53, 151.84, 153.52 ppm.

2-(6-Carbazol-9-ylhexyl)-1,4-hydroquinone (25). 1-(6-Carbazol-9-ylhexyl)-2,5-dimethoxybenzene (24) (2.90 g, 7.49 mmol) was dissolved in methylene chloride (20 mL). The mixture was cooled to -78 $^\circ\text{C}$, and then boron tribromide (3.6 M in methylene chloride, 8.3 mL, 4 equiv) was added dropwise. After the addition, the solution was warmed to room temperature and stirred for 18 h. The reaction mixture was quenched by adding water in small portions at 0 $^\circ\text{C}$ with stirring. The organic solution was dried with anhydrous sodium sulfate and concentrated under a vacuum. The crude solid was recrystallized

with a mixture of hexane/ethyl acetate. The product was then collected as a white solid: yield 2.60 g, 96%; mp 116–118 °C; ^1H NMR (CDCl_3) δ 1.27 (m, $-\text{CH}_2-$, 2H), 1.40 (m, $-\text{CH}_2-$, 2H), 1.55 (m, $-\text{CH}_2-$, 2H), 1.88 (m, $-\text{CH}_2-$, 2H), 2.48 (t, $J = 7.2$ Hz, $-\text{phenyl}-\text{CH}_2-$, 2H), 4.20 (s, $-\text{OH}$, 1H), 4.25 (s, $-\text{OH}$, 1H), 4.30 (t, $J = 7.2$ Hz, $-\text{NCH}_2-$, 2H), 6.51 (m, phenyl, 2H), 6.60 (d, $J = 8.4$ Hz, phenyl, 1H), 7.22 (d, $J = 7.6$ Hz, carbazole, 2H), 7.39 (d, $J = 8.1$ Hz, carbazole, 2H), 7.46 (t, $J = 7.6$ Hz, carbazole, 2H), 8.10 ppm (d, $J = 7.6$ Hz, carbazole, 2H).

2-(6-Carbazol-9-ylhexyl)phenyl 1,4-Bis(trifluoromethanesulfonate) (26). The 2-(6-carbazol-9-ylhexyl)-1,4-hydroquinone (2.60 g, 7.24 mmol) was added to pyridine (10 mL) under nitrogen, and the solution was cooled to 0 °C. After the solid dissolved, trifluoromethanesulfonic anhydride (2.6 mL, 2.1 equiv) was added slowly. The solution was stirred at room temperature for an additional 18 h. Water (20 mL) and methylene chloride (30 mL) were added to the mixture. The organic layer was then washed with water (3×20 mL) and dried over anhydrous sodium sulfate, and the solvent was removed under vacuum. The crude product was subjected to silica gel chromatography, using hexane/ethyl acetate (4:1, v/v) as the eluent. The product was collected as a pale yellow viscous liquid: yield 4.1 g, 91%; ^1H NMR (CDCl_3) δ 1.40 (m, $-\text{CH}_2-$, 2H), 1.59 (m, $-\text{CH}_2-$, 2H), 1.79 (m, $-\text{CH}_2-$, 2H), 2.67 (t, $J = 7.2$ Hz, $-\text{phenyl}-\text{CH}_2-$, 2H), 4.31 (t, $J = 7.2$ Hz, $-\text{NCH}_2-$, 2H), 7.17 (m, phenyl, 2H), 7.22 (d, $J = 7.6$ Hz, carbazole, 2H), 7.32 (m, phenyl, 1H), 7.39 (d, $J = 8.1$ Hz, carbazole, 2H), 7.46 (t, $J = 7.6$ Hz, carbazole, 2H), 8.09 (d, $J = 7.6$ Hz, carbazole, 2H) ppm; ^{13}C NMR (CDCl_3) δ 26.59, 28.57, 28.64, 29.01, 29.59, 42.45, 108.53, 118.12 (d, $J = 320.10$ Hz), 118.67, 120.11, 120.21, 122.67, 122.87, 123.56, 125.49, 138.20, 140.25, 146.50, 147.99 ppm. Anal. Calcd for $\text{C}_{26}\text{H}_{23}\text{NO}_6\text{F}_6\text{S}_2$: C, 50.08; H, 3.72; N, 2.25. Found: C, 50.10; H, 3.74; N, 2.24.

Polymerization. The typical polymerization procedures were as follows: For the polymerization of a diiodo monomer with a distannyl monomer, the two monomers (1 mmol each) were dissolved in 10 mL of dry THF, and $\text{PdCl}_2(\text{PPh}_3)_2$ (2 mol % equiv) was added as the catalyst. The solution was refluxed under nitrogen until the black metallic palladium precipitated out. The mixture was filtered to remove the metallic palladium, and the filtrate was then concentrated to about 10 mL and precipitated into acetone. The precipitate was collected by filtration, redissolved, and precipitated into acetone again. The polymer was collected and extracted with acetone for over 20 h and then dried under a vacuum.

For the polymerization of ditriflate and distannyl monomers, $\text{Pd}(\text{PPh}_3)_4$ (2 mol % equiv) was used as the catalyst and 10 mL of dry 1,4-dioxane was added as the solvent. Lithium chloride (3 equiv) was added and the solution was refluxed until the catalyst decomposed. The polymer was purified using the same procedure described as above.

Data for Poly(2,5-dialkylphenylene-1,4-thiophene) (Polymer 1): ^1H NMR (CDCl_3) δ 0.86–1.94 (br peaks, $-(\text{CH}_2)_n\text{CH}_3$), 2.88 (br, $-\text{phenyl}-\text{CH}_2-$, 4H), 7.02 (br, thiophenyl protons, 2H), 7.34 (br, phenyl protons, 2H) ppm; ^{13}C NMR (CDCl_3 , polymer 1, $n = 6$) δ 14.11, 22.62, 29.37, 31.60, 31.66, 33.31, 126.41, 132.21, 133.40, 138.59, 142.66 ppm. Anal. Calcd for $(\text{C}_{22}\text{H}_{30}\text{S})_n$ ($n = 6$): C, 80.92; H, 9.26. Found: C, 80.13; H, 9.23; I, not detectable (from the end group).

Data for Poly(2,5-dialkoxyphenylene-1,4-thiophene) (Polymer 2): ^1H NMR (CDCl_3) δ 0.86–1.94 (br peaks, $-(\text{CH}_2)_n\text{CH}_3$), 4.10 (br, $-\text{OCH}_2-$, 4H), 7.25 (br, thiophenyl protons, 2H), 7.53 (br, phenyl protons, 2H) ppm; ^{13}C NMR (CDCl_3 , polymer 2, $n = 16$) δ 14.22, 22.85, 26.31, 26.44, 29.56, 29.67, 29.90, 32.11, 69.86, 112.80, 124.08, 126.06, 139.46, 149.65 ppm. Anal. Calcd for $(\text{C}_{42}\text{H}_{70}\text{O}_2\text{S})_n$ ($n = 16$): C, 78.94; H, 11.04. Found: C, 76.97; H, 11.46; I, 2.59 (from the end group).

Data for Polymer 9: yield 45%; ^1H NMR (CDCl_3) δ 1.25–1.80 (br, H_2-H_5 , $\text{H}_{11}-\text{H}_{14}$), 2.85 (br, H_{10}), 2.90 (s, H_{16}), 3.00 (s, H_{23}), 3.30 (br, H_{15}), 6.55 (br, H_{17}), 6.80 (d, H_{19}), 7.05 (br, H_{20}), 7.40 (br, H_9), 7.45–7.55 (br, H_{18} , H_{21} , H_{27}), 7.75 (br, H_{22}) ppm. Anal. Calcd for $(\text{C}_{32.32}\text{H}_{33.43}\text{N}_{1.03}\text{S}_{1.99}\text{Zn}_{0.01}\text{O}_{1.98})_m$: C, 72.91; H, 6.33; N, 2.71. Found: C, 70.20; H, 6.19; N, 2.56.

Data for Polymer 10: yield 41%; ^1H NMR (CDCl_3) δ 0.90 (br, H_1), 1.25–1.80 (br, H_2-H_5 , $\text{H}_{11}-\text{H}_{14}$), 2.65 (s, H_{24}), 2.85 (br, H_{10}), 2.90 (s, H_{16}), 3.00 (s, H_{23}), 3.30 (br, H_{15}), 3.95 (br, H_6), 6.55 (br, H_{17}), 6.80 (d, H_{19}), 7.05 (br, H_{20}), 7.40 (br, H_9), 7.45–7.55 (br, H_{18} , H_{21} ,

H_{27}), 7.75 (br, H_{22}) ppm. Anal. Calcd for $(\text{C}_{32.64}\text{H}_{33.86}\text{N}_{1.06}\text{S}_{1.98}\text{Zn}_{0.02}\text{O}_{1.96})_m$: C, 72.98; H, 6.35; N, 2.76. Found: C, 71.42; H, 6.22; N, 2.70.

Data for Polymer 11: yield 43%; ^1H NMR (CDCl_3) δ 0.90 (br, H_1), 1.25–1.80 (br, H_2-H_5 , $\text{H}_{11}-\text{H}_{14}$), 2.65 (s, H_{24}), 2.85 (br, H_{10}), 2.90 (s, H_{16}), 3.00 (s, H_{23}), 3.30 (br, H_{15}), 3.95 (br, H_6), 6.55 (br, H_{17}), 6.80 (d, H_{19}), 7.05 (br, H_{20}), 7.40 (br, H_9), 7.45–7.55 (br, H_{18} , H_{21} , H_{27}), 7.75 (br, H_{22}), 7.98–8.02 (br, H_7-H_8), 10.15 (s, H_{25}) ppm.

Data for Polymer 12: yield 41%; ^1H NMR (CDCl_3) δ 1.25–1.80 (br, H_2-H_5 , $\text{H}_{11}-\text{H}_{14}$), 2.85 (br, H_{10}), 2.90 (s, H_{16}), 3.00 (s, H_{23}), 3.30 (br, H_{15}), 6.55 (br, H_{17}), 6.80 (d, H_{19}), 7.05 (br, H_{20}), 7.40 (br, H_9), 7.45–7.55 (br, H_{18} , H_{21} , H_{27}), 7.75 (br, H_{22}) ppm. Anal. Calcd for $\text{C}_{32.32}\text{H}_{33.43}\text{N}_{1.03}\text{S}_{1.99}\text{Cu}_{0.01}\text{O}_{1.98}$: C, 72.91; H, 6.33; N, 2.71. Found: C, 71.49; H, 6.16; N, 2.63.

Data for Polymer 13: yield 85%; ^1H NMR (CDCl_3) δ 1.00 (br, H_{23}), 1.30 (br, H_{22}), 1.40 (br, H_9-H_{10}), 1.55 (br, H_8), 1.80 (br, H_7), 2.67 (br, H_6), 3.60 (br, H_{18}), 4.31 (br, H_{11}), 6.80–6.90 (br, H_5 , H_3-H_4), 7.22 (br, H_{14}), 7.39 (br, H_{12}), 7.46 (br, H_{13}), 7.49 (br, H_1-H_2), 7.70–7.80 (br, $\text{H}_{16}-\text{H}_{17}$), 8.02 (br, H_{15}) ppm.

Data for Polymer 14: yield 91%; ^1H NMR (CDCl_3) δ 1.40 (br, H_9-H_{10}), 1.55 (br, H_8), 1.80 (br, H_7), 2.67 (br, H_6), 4.31 (br, H_{11}), 6.80–6.90 (br, H_5 , H_3-H_4), 7.22 (br, H_{14}), 7.39 (br, H_{12}), 7.46 (br, H_{13}), 7.49 (br, H_1-H_2), 8.02 (br, H_{15}) ppm. Anal. Calcd for $\text{C}_{28}\text{H}_{25}\text{NS}$: C, 82.52; H, 6.14; N, 3.20. Found: C, 79.80; H, 6.09; N, 3.28.

Polymer Characterization. The GPC measurements were performed on a Waters RI system equipped with a UV detector, a differential refractometer detector, and an Ultrastaygel linear column at 35 °C using THF (HPLC grade; Aldrich) as the eluent. The molecular weight and the molecular weight distribution were calculated on the basis of monodispersed polystyrene standards. The ^1H NMR spectra were collected on a GE 500 MHz FT NMR spectrometer. A Perkin-Elmer Lambda 6 UV/vis spectrophotometer and a Perkin-Elmer MPR-4 spectrofluorimeter were also used. The thermal analyses were performed using the DSC-10 system of TA Instruments with a heating rate of 10 °C/min under a nitrogen atmosphere. The polarizing microscopy was performed with a Nikon (OPTIPHOT-2) microscope equipped with a Creative Device 50–600 hot stage. The cyclic voltammetry measurements were performed using an EG&G Princeton Applied Research Potentiostat interfaced to a personal computer. A thin polymer film was casted onto a Pt disk working electrode (diameter 2 mm). The counter and reference electrodes were both Pt wires, and the system was calibrated against the formal potential of the $[\text{Cp}_2\text{Fe}]/[\text{Cp}_2\text{Fe}^+]$ couple (+0.40 V vs SCE). The experiment was carried out in anhydrous acetonitrile (10 mL) with tetrabutylammonium tetraborofluorate (0.33 g) as the supporting electrolyte under a nitrogen atmosphere.

Results and Discussion

Reaction Scope. In our previous work, we demonstrated the feasibility of the Stille coupling reaction for the synthesis of conjugated and photorefractive polymers.^{13,14} This paper involves more detailed studies to define the reaction scope and to optimize the reaction conditions. Figures 1 and 2 list all of the monomers involved in this study, and the syntheses of some of the monomers are shown in Scheme 3.

Catalyst Amount. According to the proposed mechanism, if a $\text{Pd}(\text{II})$ compound is used as the catalyst, it has to be reduced to a $\text{Pd}(\text{0})$ species by the organotin compounds. It was found earlier in the Stille coupling reaction of aromatic acid chloride with (trimethylstannyl)benzene using $\text{Pd}(\text{II})$ as the catalyst that the catalytically active zero-valent palladium species were generated by the reduction of the divalent catalyst by (trimethylstannyl)benzene through the formation of biphenyl as shown in eq 1.¹⁹ As a result, a part of the tin monomer was consumed, leading to an imbalance in the monomer stoichiometry. However, in order to obtain high molecular weight polymers, the monomer stoichiometry should be carefully balanced. Therefore, the effect of the catalyst concentration on the polymerization was studied. A simple reaction system was chosen for

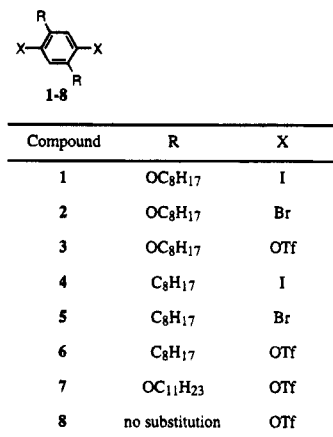


Figure 1. Structures of the organohalides and triflates for the Stille coupling reactions.

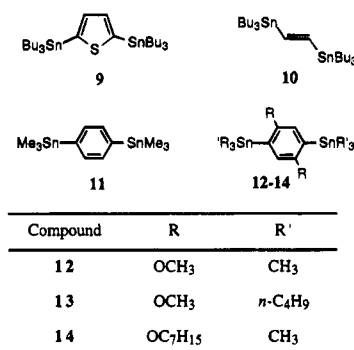
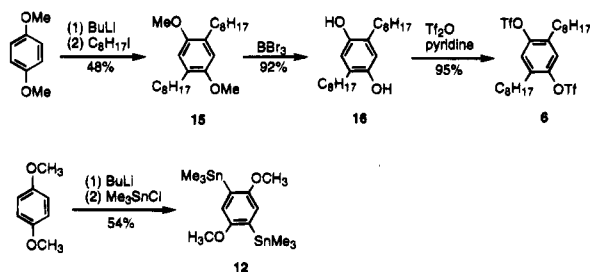
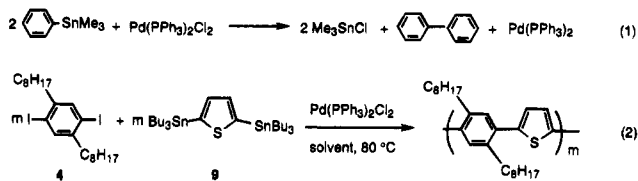


Figure 2. Structures of the organotin monomers for the Stille coupling reactions.

Scheme 3. Syntheses of Monomers



this purpose (shown on eq 2). The amount of catalyst, Pd(PPh₃)₂-



Cl₂, was varied under conditions where either equivalent amounts of both monomers were used or the amount of monomer 9 was adjusted by compensating the amount that may be consumed by the Pd(II) in the catalytic cycle. The results are shown in Table 1.

It can be seen that the molecular weights obtained with corrections in monomer 9 are higher than those without corrections regardless of the amount of catalyst used. It should be pointed out that the molecular weight is determined by using polystyrenes as the standard samples which clearly cannot give rise to the absolute molecular weight. However, the results should still be meaningful since the same polymer structure is compared. Thus, in these two cases, the effect of the catalyst

Table 1. Molecular Weights of Polymers from Eq 2^a

entry	[Pd(II)] ^b (%)	<i>M_n</i> (C) ^c	DP(C) ^f	<i>M_n</i> ^d	DP ^g
1	1	16 000 ^e	42	12 000	31
2	2	22 000	57	9 800	26
3	3	17 000	44	9 100	24
4	4	16 000	42	11 000	29
5	5	13 000	34	12 000	31

^a Determined by GPC using polystyrenes as standards and THF as the eluent. ^b Mol % equiv of palladium catalyst (Pd(PPh₃)₂Cl₂) (THF at 80 °C). ^c *M_n*(C) is the number-averaged molecular weight obtained when the amount of monomer 2 was adjusted according to the amount of palladium catalyst used. For example, if 2 mol % equiv of Pd(II) was adapted, 1.02 equiv of monomer 2 would be used. ^d *M_n* is the number-averaged molecular weight using equivalent amounts of monomers. ^e Polymer partially soluble in THF. ^f DP(C) is the degree of polymerization obtained when the amount of monomer 2 was adjusted according to the amount of palladium catalyst used. ^g DP is the degree of polymerization using equivalent amounts of monomers.

Table 2. Molecular Weights for Polymerization of 2,5-Dioctyl-1,4-diiodobenzene with 1,4-Bis(tributylstannyl)thiophene Catalyzed by Pd(PPh₃)₂Cl₂ (2 mol % equiv) in Different Solvents at 80 °C

solvent	<i>M_n</i> ^a	<i>M_w</i> ^b	polydispersity	DP ^c
dioxane	14 300	31 400	2.19	37
DMF	18 700	47 500	2.54	49
NMP	5 300	10 900	2.06	14
THF	21 700	60 200	2.77	57

^a Number-averaged molecular weight. ^b Weight-averaged molecular weight. ^c Degree of polymerization.

concentration is different. For the reactions that the monomer amount was adjusted, the higher the catalyst concentration, the lower the molecular weight of the resulting polymer. When both monomers were used in equivalent amounts, the molecular weight first decreased when the catalyst concentration increased from 1 to 3 mol % equiv and then increased when the catalyst concentration increased from 4 and 5 mol % equiv. If all the initially active catalyst palladium(0) was formed as described in eq 1, the higher the catalyst concentration the lower the molecular weight should be. When the monomer stoichiometry is adjusted, the molecular weight should not be greatly affected by the catalyst concentration. Our results indicate that the tin monomer is indeed responsible for the initial reduction of the palladium(II) catalyst since the adjustment of the monomer amount does improve the molecular weights. However, the exact amount of tin monomer that is consumed is not clear, and this amount may also depend on the concentration of the catalyst initially used. However, from the above results, the best reaction condition was identified and used in our further studies involving diiodo monomers: catalyst, Pd(PPh₃)₂Cl₂ (2 mol % equiv); amount of tin monomer, 1.02 equiv of the diiodo monomer.

Solvent Effect. The solvent is known to play an important role in the Stille reaction.^{20,25} In the polymerization process, the solvent affects both the catalyst stability and the molecular weights of the resulting polymers. The ideal solvent for the palladium-catalyzed polymerization should be able to maintain the polymeric molecules in solution and at the same time be able to stabilize the catalyst. Studies on several solvents commonly used in the Stille coupling reaction (eq 2) showed that the highest molecular weight of the polymer was obtained when THF was used as the solvent (Table 2). This is due to the good solubility of the resulting polymers and the good stability of the Pd catalyst in THF solution. No precipitation of the catalyst was observed until after reacting for 7 days. The reactions proceeded to completion quickly in DMF and NMP

Table 3. Molecular Weights for Polymerization of 2,5-Dioctyl-1,4-diiodobenzene with 1,4-Bis(tributylstannyl)thiophene Catalyzed by Pd₂dba₃ (1 mol %) in the Presence of Ligands at 80 °C in THF

entry	ligand (L)	Pd:L	M _n ^a	M _w ^b	DP ^d	polydispersity	reaction time ^c
1	PPh ₃	1:1	8 500	18 000	22	2.10	4.5 days
2		1:2	13 000	28 000	34	2.17	7 days
3		1:4	13 000	24 000	34	1.83	7 days
4	AsPh ₃	1:1	13 000	33 000	34	2.49	12 h
5		1:2	18 000	46 000	47	2.55	24 h
6		1:4	22 000	56 000	57	2.50	24 h
7	(2-MeC ₆ H ₄) ₃ P	1:4	9 000	21 000	23	2.27	24 h
8	P(OPh) ₃	1:4	7 200	13 000	19	1.79	24 h
9	(2-furyl) ₃ P	1:4	18 000	40 000	47	2.23	7 days

^a Number-averaged molecular weight. ^b Weight-averaged molecular weight. ^c The time for the palladium catalyst to decompose and precipitate out from the solution, after which the reaction was stopped. ^d Degree of polymerization.

which are known to accelerate the palladium-catalyzed reactions by acting as ligands to the palladium center.²⁵ However, the solubility of the resulting polymers was very limited in NMP and moderate in DMF. They precipitated out from the reaction medium, therefore limiting the molecular weights. The polymerization in dioxane was slow. The Pd catalyst was not as stable in this solvent as in THF and precipitated as the palladium black from the solution after 2 days. The molecular weight in this case was much lower than that obtained from the THF medium. Overall, we found that THF is a good solvent for the Stille coupling reaction. DMF would also be a good solvent if the desired polymer has a high solubility in it.

Ligand Effect. The polymerization of 2,5-dioctyl-1,4-diiodobenzene with 1,4-bis(tributylstannyl)thiophene (eq 2) was studied in the presence of different ligands. Here the tris-(dibenzylideneacetone)dipalladium (Pd₂dba₃) was used as the catalyst. When the reaction was carried out with a stoichiometric amount of the two monomers and 1 mol % equiv of Pd₂dba₃ (2 mol % equiv of Pd), palladium black precipitated out from the solution when the mixture was heated to 80 °C. No reaction was observed, and only the monomers were recovered. When different ligands were added, the effective catalyst PdL₄ was formed *in situ* by ligand exchange between the weakly coordinated Pd₂dba₃ and the ligand (4 equiv for each Pd) under study. The purple-red color of the Pd₂dba₃ usually turned into a pale yellow color within 5–10 min at room temperature.

When AsPh₃ was used as the ligand, the reaction was found to go to completion quickly, resulting in the polymer with the highest molecular weight (Table 3, entry 6). When tri-2-furylphosphine was used as the ligand, the reaction mixture became very viscous after 24 h, but the palladium catalyst did not decompose until after 7 days (Table 3, entry 9). The molecular weight obtained under this condition was relatively high. If triphenylphosphine was used, the solution became viscous only after 3–4 days under the same conditions (Table 3, entry 3). Thus, the polymerization was faster with tri-2-furylphosphine as the ligand than with triphenylphosphine. If (2-MeC₆H₄)₃P or P(OPh)₃ was used, the catalyst appeared to be unstable (Table 3, entries 7 and 8) and decomposed before high molecular weights of the polymers were formed.

Catalysts with unsaturated coordination were examined by treating Pd₂dba₃ with 1 or 2 equiv of ligand (for each Pd) *in situ*. If only 1 equiv of ligand was used, the resulting catalyst was unstable and decomposed before the reaction went to completion (Table 3, entries 1 and 4). Low molecular weight oligomers were formed. If 2 equiv of ligand was used, the catalysts formed were much more stable (Table 3, entries 2 and

Table 4. Preparations of Different Conjugated Polymers from the Reaction of Monomer A and Monomer B under the Stille Coupling Conditions

entry	monomer A	monomer B	M _n ^a	M _w ^b	DP ^c	polydispersity
1	9	1	4 300	8 300	10	1.96
2	9	2	2 100	4 300	5	2.04
3	9	3	5 600	9 100	14	1.61
4	9	4	12 400	29 600	32	2.39
5	9	5	9 500	26 700	25	2.81
6	9	6	8 300	11 200	22	1.36
7	10	1	2 600	5 100	7	1.92
8	10	2	1 800	2 100	5	1.15
9	10	3	3 200	4 800	9	1.48
10	10	4	4 200	11 500	13	2.75
11	10	5	1 900	6 900	6	3.72
12	10	6	3 900	8 000	12	2.05
13	11	1	no reaction			
14	11	3	4 900	9 100	12	1.88
15	11	4	no reaction			
16	11	6	4 300	5 200	11	1.22

^a Number-averaged molecular weight. ^b Weight-averaged molecular weight. ^c Degree of polymerization.

5) and the molecular weights were significantly higher than in the former situation. When the ligand amount was increased to 4 equiv, a higher molecular weight was obtained if AsPh₃ was used and no difference was observed in molecular weight between 2 and 4 equivalents of PPh₃. Therefore, to ensure the highest molecular weight, 4 equiv of ligand should be used in polymerization. From these results, the reactivity of the ligand can be ranked as AsPh₃ > (2-furyl)₃P > PPh₃ which has a similar trend for other examples of the Stille coupling reactions.²⁰

Recently, some modified conditions for the Stille coupling reaction have been reported, such as using phosphine-free palladium sources to minimize the aryl–phenyl scrambling or by using Pd(0)/Cu(I) cocatalyst to accelerate the transmetalation.^{26–29} When Cu(I) salt is applied, it reacts with organostannanes to produce transient organocopper intermediates which are presumably more reactive than organostannanes in transmetalation with the palladium species.²⁷ We studied the effect of the addition of copper iodide (same condition as Table 3, entry 3, except 20% equiv of CuI is added). Compared with the same reaction condition without copper iodide (Table 3, entry 3), the addition of CuI did not have a positive effect on the molecular weight. A weight-averaged molecular weight of 11 000 with a polydispersity of 1.65 was obtained. This might be due to the limited solubility of copper iodide in the reaction medium THF. In the DMF or NMP medium, the effect of copper iodide cannot be observed because our polymer precipitates out from these solvents before a higher molecular weight is reached.

Reactivity of Different Monomers. In order to expand the scope of the Stille coupling reaction to different conjugated polymer systems, we studied the reactivities of various monomers (Table 4). In general, it was found that diiodo-substituted monomers are more reactive than dibromo-substituted monomers. In the case of PPT and PPV, diiodo monomers lead to higher molecular weights than dibromo monomers (Table 4, entries 1, 4, 7, and 10). On the other hand, the dialkyl-substituted monomers gave higher molecular weights than the similar dialkoxy-substituted monomers. However, very low reactivity was found for these monomers in preparing PPP type

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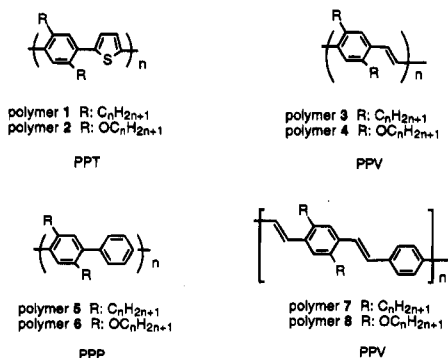
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polymers (Table 4, entries 13 and 15). The reaction could not proceed further after forming dimers or trimers. There are two factors that might be responsible for this difference. First, the oxidative addition step in a palladium-catalyzed reaction is usually facilitated by electron-withdrawing or less electron-donating groups. Second, the dialkyl-substituted polymers have better solubility than the similar dialkoxy-substituted polymers. The triflate monomers reacted under conditions different from those of the dihalides. Low molecular weight polymers were obtained from DMF due to the low solubility of the polymer. Low molecular weights were also obtained when THF was used as the solvent because the reaction temperature could not be increased above 80 °C under ambient pressure.

The reactivities of the three tin monomers **9**, **10**, and **11** were very different. The thiophenyl monomer **9** was the most reactive. High molecular weight polymers could be obtained (Table 4, entries 1–6). The electron-donating property of the sulfur atom may accelerate the transmetalation step which is generally accepted as the rate-determining step for palladium-catalyzed cross-coupling reactions.^{30,31} The distannyl-substituted ethylene appeared to be much less reactive. Under the same conditions, only low molecular weight oligomers were obtained (Table 4, entries 7–12). Stannylbenzenes were usually found to be not very active under the Stille coupling conditions. We tested several types of stannylbenzenes; none of the substituted ones produced polymers. Only dimers or trimers were obtained (reactions of compounds **12** and **6**, compounds **13** and **6**, and compounds **14** and **8**). When a more hindered triflate monomer such as 2,5-di-*tert*-butyl-*p*-bis[(trifluoromethyl)sulfonyl]benzene was used, no reaction occurred and the starting monomers were recovered. These results indicate that both the oxidative addition and the transmetalation steps in the Stille reaction are sensitive to the steric bulkiness of the substituent on the reactants. Furthermore, the molecular weight was also increased by polymerizing monomer **7** with *p*-bis(tributylstannyl)benzene instead of *p*-bis(trimethylstannyl)benzene (**11**).³² This might be due to a slower alkyl transfer than aryl transfer when the alkyl group is butyl.²⁰

Polymer Characterizations. Structural Characterizations.

The polymers synthesized above have been characterized by different techniques, the results of which are partially discussed in this section to provide support for the claimed polycondensations. Since the final polymers are soluble in common organic solvents, such as THF, chloroform, toluene, and dichloroethane, many physical characterizations can be performed.



The ¹H NMR spectra of all the polymers exhibit the chemical shifts of alkyl side chains at 0.90–1.95 ppm. The methylene protons next to the oxygen atom (–OCH₂–) appear at 4.20 ppm,

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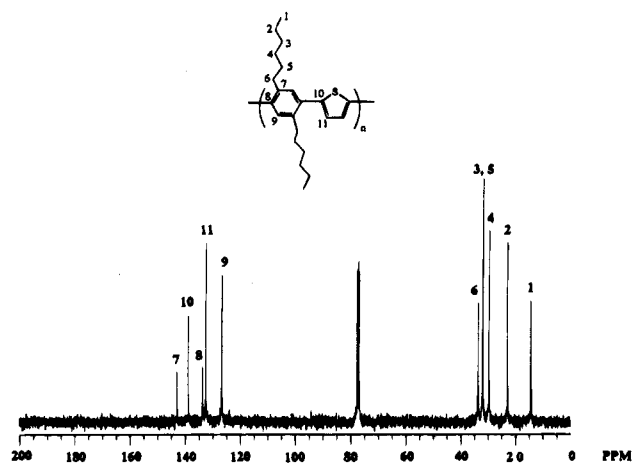


Figure 3. ¹³C NMR of polymer **1** (*n* = 6).

and the methylene protons adjacent to the phenyl rings are found at 2.88 ppm. In polymer **1**, the chemical shifts of the thiophenyl proton and the phenyl proton appear at 7.02 and 7.34 ppm, respectively, while they are found at 7.25 and 7.53 ppm in polymer **2**. The vinyl protons of polymers **3** and **4** are at 7.20 and 7.11 ppm, respectively. The protons on the phenyl ring are found at 7.37 ppm for polymer **3**, and at 7.44 ppm for polymer **4**. The chemical shifts of the substituted phenyl ring protons appear at 7.17 ppm for polymer **5** and at 7.06 ppm for polymer **6**. The unsubstituted phenyl ring protons are found at 7.40 and 7.66 ppm for polymers **5** and **6**.

The ¹³C NMR spectrum of polymer **1** (*n* = 6) is shown in Figure 3, where the assignments of the chemical shifts are indicated.³³ The ¹³C NMR spectra of polymers **3**–**6** indicate that these materials are in fact oligomers for their end groups can be identified.

The UV/vis–fluorescence spectra of several polymers are shown in Figures 4 and 5. The absorptions of the alkoxy-substituted polymers are red-shifted compared to the corresponding alkyl-substituted polymers due to the electronic effect and less steric hindrance. With the same substitution (either dialkyl or dialkoxy), PPP type polymers absorbed at the highest energy region while PPTs absorbed at the lowest energy region. Similar trends were observed in the emission spectra of these polymers. It is interesting to observe that the emission spectra of these polymers prepared from the Stille coupling reaction cover almost the entire visible spectral region. It is known that conjugated polymers with similar backbones are electroluminescent materials.^{34,35} Polymers emitting different wavelengths of light can be used for full-color display.

Thermal Properties. Table 5 summarizes the thermal transitions of different polymers. The melting temperatures, determined by differential scanning calorimetry (DSC), were consistent with the polarizing microscopic observations. All of the polymers were found to be liquid crystalline materials under a polarizing microscope. We have previously demonstrated that liquid crystallinities of dialkoxy-substituted PPTs

(32) When *p*-bis(tributylstannyl)benzene was used to react with monomer **7**, a polymer with a weight-averaged molecular weight of 9000 and a polydispersity of 1.70 was obtained. With the same reaction conditions, while *p*-bis(trimethylstannyl)benzene was used, a polymer with a weight-averaged molecular weight of 8000 and a polydispersity of 1.72 was obtained.

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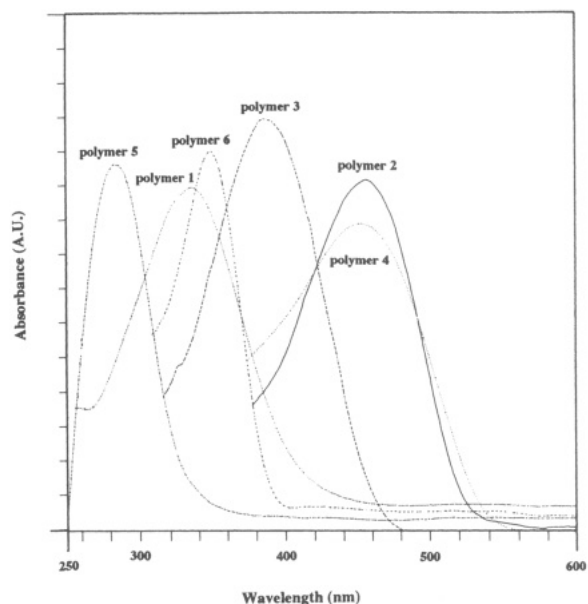


Figure 4. UV/vis spectra of different polymers measured in THF solutions.

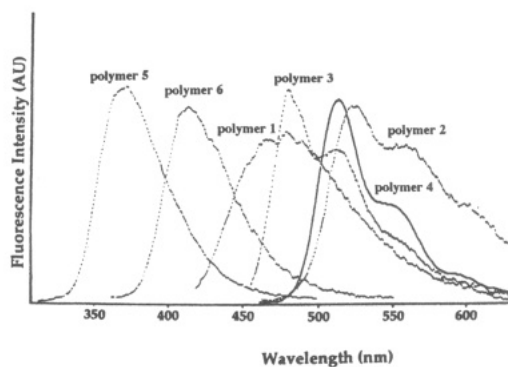


Figure 5. Photoluminescence spectra of different polymers measured in THF solutions.

Table 5. Thermal Transitions of Different Polymers

polymer	T_g^a (°C)	T_m^b (°C)	T_c^c (°C)
1 ^d	55	98	100
2 ^d	47	120	148
3 ^d	30	75	135
4 ^e	50	67	160
5 ^d	34	58	120
6 ^f	80	155	242

^a Glass transition temperature, determined by DSC. ^b Melting temperature, determined by DSC. ^c Clearing temperature, corresponding to the transition from the liquid crystalline state to the isotropic state, determined by a polarizing microscope. ^d The polymers were used as precipitated without any thermal treatment. ^e This polymer was annealed at 60 °C for 2 h. ^f This polymer was annealed at 50 °C for 2 h.

(polymer 2), PPPs (polymer 6), and PPVs (polymers 7 and 8).^{36,37} The dialkyl-substituted polymers are also liquid crystalline polymers (Figure 6). The PPVs prepared from the Heck reactions (polymer 7 and polymer 8) are structurally different from those prepared by the Stille coupling reactions (polymers 3 and polymer 4). However, both polymers 3 and 4 were found to be liquid crystalline (LC) polymers which may be due to their small molecular weights while similar polymers prepared from other approaches did not show LC properties.²

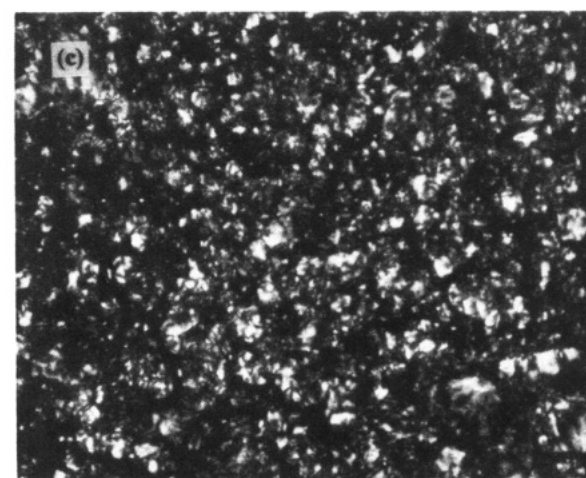
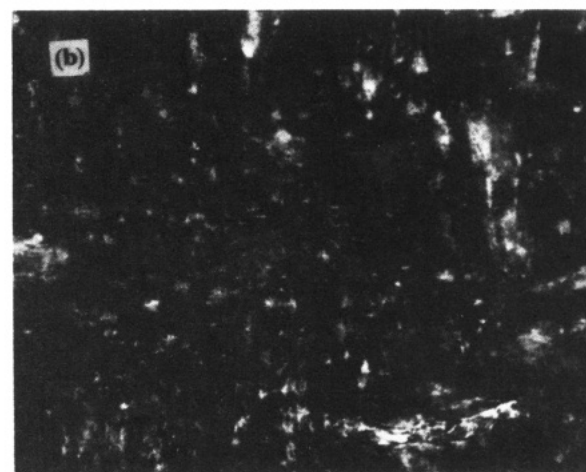
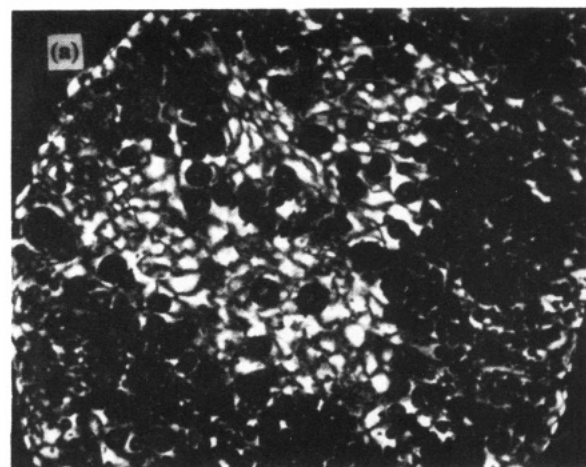


Figure 6. Typical Schlegel textures under a polarizing microscope, indicating a nematic liquid crystalline phase: (a) polymer 1 ($n = 7$), 90 °C, 100 \times ; (b) polymer 3 ($n = 8$), 173 °C, 100 \times ; (c) polymer 5 ($n = 8$), 95 °C, 100 \times . All parts were reproduced at 80% of the original size.

Cyclic Voltammetry. To examine the electroactivities of these conjugated polymers, we performed cyclic voltammetry measurements. All of the dialkoxy-substituted polymer films were oxidized irreversibly (Figure 7). A large electric current was noticed, and the color of the film changed to black after one cycle. The current was observed to drop dramatically after each scan. Changing the scan rate shifted the peak value for oxidation. This oxidation is most likely due to the oxidation of the conjugated backbone. Similar phenomena have also been reported for the alkoxy-substituted PPVs prepared by the Heck

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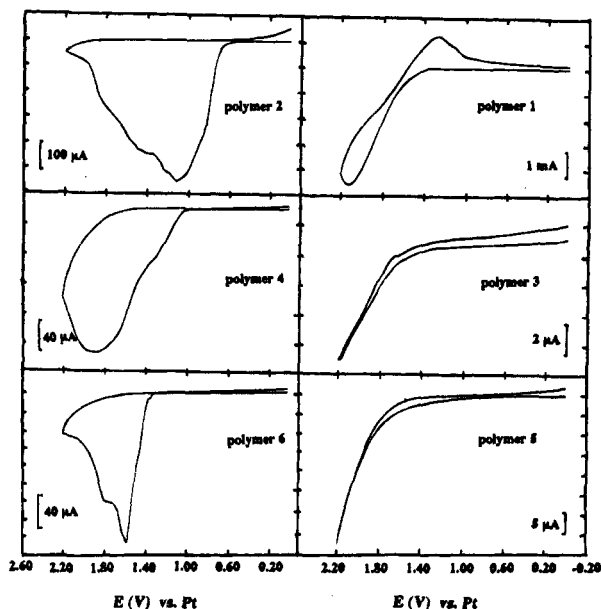


Figure 7. Cyclic voltammograms of different conjugated polymers (scan rate 200 mV/s).

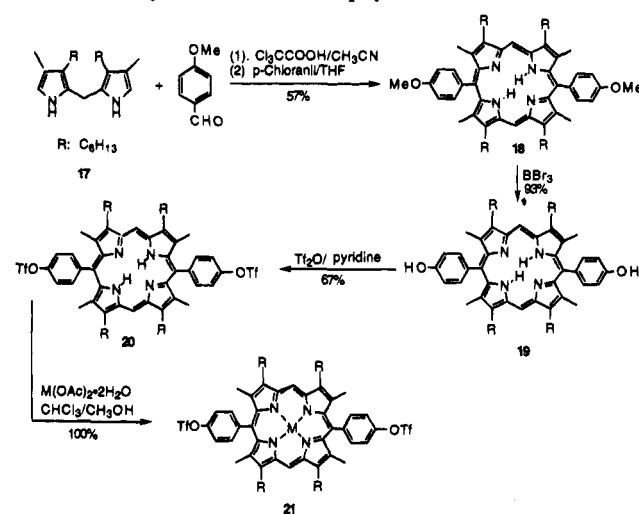
reaction.³⁸ Except the PPTs, the dialkyl-substituted polymers could not be oxidized when they were scanned from 0.0 to 2.2 V under different scan rates ranging from 20 to 1000 mV/s. This could be due to their lower HOMO orbital levels compared with the dialkoxy-substituted polymers. The oxidation of the dialkyl-PPT was also irreversible, resulting in a black substance. No reduction of the above polymer films from 0 to -3 V was observed at different scan rates.

Preparation of Multifunctional Polymers. Our main purpose in exploring the Stille reaction is to apply it to the syntheses of multifunctional conjugated polymers. We have previously reported the preparation of conjugated photorefractive polymers using this approach.¹⁴ In this paper, more examples are provided to demonstrate the versatility of the Stille coupling reactions.

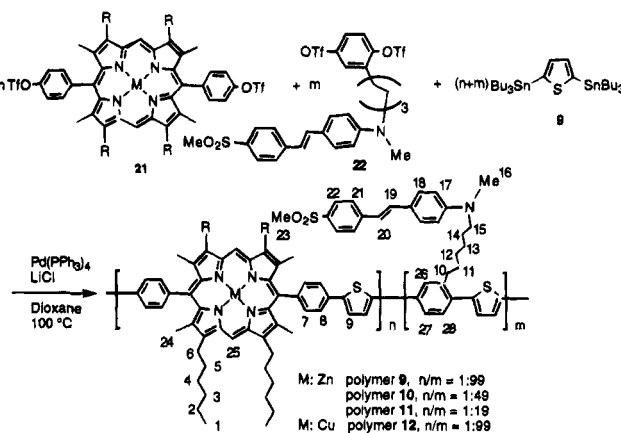
Metalloporphyrin-Containing Polymers. Photorefractive polymers are multifunctional polymers which require the material to be both photoconductive and electrooptically active.³⁹ In these polymers, the large quantum yield for the photocharge generation is essential in order to obtain a large two-beam coupling optical gain coefficient (an important measure of the photorefractive performance). It is known that metalloporphyrins are responsible for energy/electron transfer in the photosynthetic process,³⁶ and a relatively high quantum yield for the photocharge generation has been obtained with metalloporphyrin-containing conjugated polymers.²⁴ If nonlinear optical chromophores are also incorporated into the polymer, we expect to obtain a photorefractive polymer with possibly higher quantum yields for the photocharge generation. The Stille coupling reaction enabled us to synthesize polymers 9–12 which possessed ratios of 1:99, 1:49, and 1:19 between the zinc porphyrin monomer (21) and the chromophore (22) (Scheme 5). Other metalloporphyrins such as copper porphyrin could also be incorporated.

The polymerizations were carried out under the typical Stille reaction conditions as shown in Scheme 5. The red-colored polymers precipitated out after 4 h, and the reactions were stopped after 24 h. The crude polymer had almost a quantitative

Scheme 4. Syntheses of the Porphyrin Monomers



Scheme 5. Syntheses of Metalloporphyrin-Containing Polymers

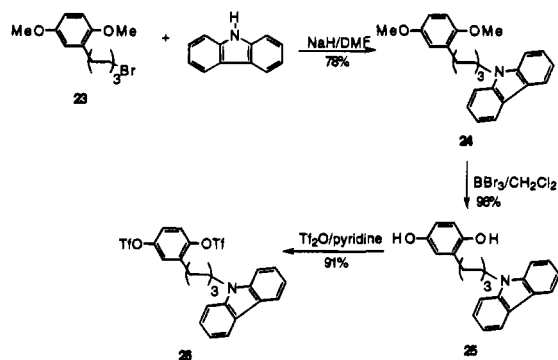
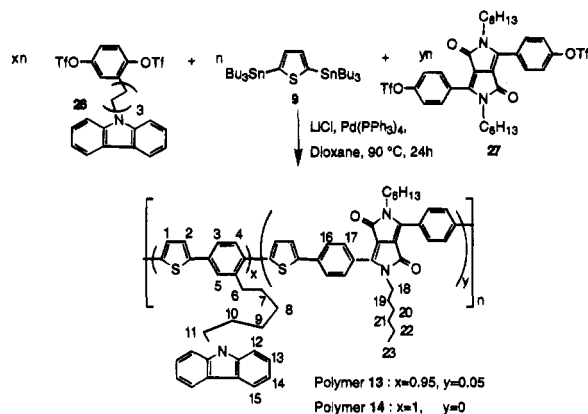


yield. The UV/vis spectra of these polymers showed a strong absorption at 380 nm due to the NLO chromophore, and the existence of the porphyrin moiety was evidenced by the absorptions of the porphyrin Soret band at 400 nm and the Q bands between 500 and 600 nm. The relative intensities of these peaks were proportional to the percentage of the metalloporphyrin existing in the polymer. The molecular weights of these polymers could not be determined by GPC since they were only partially soluble in THF. All of these polymers, however, were soluble in different chlorinated solvents such as chloroform and 1,1,2,2-tetrachloroethane. The viscosity measurements indicated that they had relatively high intrinsic viscosities; for example, for polymer 12 the intrinsic viscosity was found to be 0.347 dL/g using 1,1,2,2-tetrachloroethane as the solvent at 30 °C. Preliminary results indicated that the poled sample was photorefractive as evidenced by the asymmetric energy exchange in two-beam coupling experiments. Detailed physical measurements will be reported separately. This work indicates that the Stille coupling reaction can be utilized for the synthesis of metalloporphyrin-containing polymers.

Pendant Carbazole-Conjugated Polymers. A polymer with a poly(phenylenethiophene) backbone and carbazolyhexyl groups as the side chains was also prepared by the Stille reaction. It was synthesized for the purpose of investigating the photoconductivity and charge mobility which are two of the most important properties of photorefractive polymers. We also incorporated 5% dihydropyrrolopyrroledione (DPPD) compound 27 to serve as a photosensitizer in order to increase the absorption at the working laser wavelength (632.8 nm).

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Scheme 6. Syntheses of Monomers with Pendant Carbazole**Scheme 7.** Syntheses of Conjugated PPTs with Pendant Carbazole Moieties

The syntheses of the monomer and polymers are shown in Schemes 6 and 7. The polymers were soluble in chloroform, 1,2-dichloroethane, and 1,1,2,2-tetrachloroethane. They could be cast from solution to form optical quality films. The ^1H NMR spectra of polymers 13 and 14 were quite similar, except that additional small peaks at δ 7.8–7.9, 3.8, and 0.9 ppm, due to the resonance peaks of the DPPD unit, were observed for

polymer 14. TGA studies showed that both polymers were thermally stable up to 400 $^\circ\text{C}$ under a nitrogen atmosphere.

The UV/vis spectra of the polymers had strong absorptions at 340 and 380 nm corresponding to the absorptions from the carbazole and the conjugated backbone, respectively. The small peak at 530 nm in polymer 13 was due to the absorption of the DPPD unit. This peak has a red shift compared to the corresponding monomer 27 (480 nm), which indicated that the DPPD unit was indeed incorporated into the polymer backbone. The weight-averaged molecular weight M_w of polymer 14 was found to be 18 000 with a polydispersity of 2.68 determined by GPC using polystyrenes as standards and THF as the eluent while for polymer 13 the M_w was found to be 56 000 with a polydispersity of 3.35. This example again demonstrates that the Stille coupling reaction can be utilized to prepare functionalized conjugated polymers.

Conclusions

The Stille coupling reaction can be utilized for the syntheses of conjugated polymers. Due to its mild conditions, different functional groups can be incorporated. This reaction allowed us to prepare different types of functional conjugated polymers. Reaction conditions that affected the polymerization were investigated. It was found that judicious selections for the reaction conditions and the monomers were crucial for the preparation of high molecular weight material. The general trend is that the organotin monomer prefers to be electron-rich and the organohalide (or triflate) to be electron-deficient.

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