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Articles

Advances in Ni(0)-Catalyzed Coupling for the Synthesis of Polythiophenes and Polyphenylenes

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ABSTRACT: The effects of solvent and monomer structure on the Ni(0)-catalyzed polymerization of 2,5-dichloro-3-(2′-thiophenecarbonyl)thiophene, 3-benzenesulfonyl-2,5-dichlorothiophene, 2,5-dichlorobenzophenone, and 2-benzenesulfonyl-1,4-dichlorobenzene were explored. Poly[3-(2′-thiophenecarbonyl)-2,5-thiophene] with an intrinsic viscosity of 0.38 dL/g and a 10% weight loss temperature in nitrogen of 480 °C (T_g = 149 °C) was synthesized. Oligomeric material was prepared from 3-benzenesulfonyl-2,5-dichlorothiophene. Poly(2,5-benzophenone) of 58×10^3 g/mol ($[\eta] = 1.15$ dL/g) with a T_g of 180 °C and a 10% weight loss temperature in nitrogen of 576 °C was synthesized. Oligomeric materials were also obtained from the polymerization of 2-benzenesulfonyl-1,4-dichlorobenzene. It was shown that the solvent choice has drastic effects upon the catalyst system and the final polymer. The differences in the catalyst resulting from solvent choice were explored by nuclear magnetic resonance. Effects arising from the structure of the monomer are discussed in relationship to the results obtained and the proposed mechanism.

Introduction

Since its development by Colon and Kelsey, nickel(0)-catalyzed coupling has proven to be a powerful synthetic method for the formation of carbon−carbon aryl bonds. The reaction conditions tolerate many functionalities with the only known exceptions being protic, nitro, and amine-containing substituents. A wide range of polymeric materials have been synthesized from inexpensive arylene chlorides[1] and mesylates[2,3] as well as the more costly bromide, iodide, and triflate derivatives.[4−6] The mechanism of the reaction has been of great interest, and many advances have been made in understanding the role of ligands, temperature, and reducing metal on the polymerization.[7]

Our interests are in the synthesis of polythiophenes and polyphenylenes substituted with electron-withdrawing substituents. The presence of electron-withdrawing groups ortho or para to the reactive site accelerates the reaction rate by activating that site to oxidative addition by the Ni(0) complex.[8] Substituents such as the benzoyl and benzenesulfonyl pendant group have been shown to exhibit many additional beneficial properties. The benzoyl pendant is known to increase the solubility of the wholly aromatic polyphenylene material, while maintaining the outstanding thermal and mechanical properties of the conjugated backbone.[9] The benzenesulfonyl pendant imparts very high thermal stability with 10% weight loss temperatures for oligomeric materials near 500 °C.[10]

Despite the numerous materials that have been synthesized and the current level of understanding of these Ni(0)-catalyzed polymerizations, many issues remain to be addressed, specifically with polythiophenes and polyphenylenes containing electron-withdrawing side groups. Previously, our group explored the polymerization of 3-benzoyl-2,5-dichlorothiophene (M1) as a route to high-performance materials for applications such as field-effect transistors (FET), optical sensors, and light-emitting diodes.[11] Polymers with intrinsic viscosities of 0.37 dL/g were synthesized, but several problems were encountered. Purification of the monomer, a viscous, yellow oil, was difficult. The removal of all protic impurities, which is essential for Ni(0) coupling, presented particular difficulty. During the polymerization partial degradation of this material, leading to a mixture of polymer and low molecular weight side product, was observed. Degradation of polythiophene derivatives at long reaction times in Ni(0) polymerization was also seen by Ueda.[12] In addition, the final product only exhibited partial solubility in most common solvents, including tetrahydrofuran and *N*,*N*-dimethylacetamide, which led to difficult processing and characterization.

In our work with polyphenylenes we noted the excellent reactivity of benzophenone derivatives. Materials with number-average molecular weights of up to 25×10^3 g/mol with outstanding mechanical and thermal properties were synthesized, but these polymers formed brittle films.[13] The formation of flexible films is a requirement for many of the potential applications of this material, such as separation membranes and organic electronics. Also, reduction of nearly 15% of the carbonyl group was observed.[14] When the carbonyl

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group was replaced with a sulfone functionality, only oligomeric materials were synthesized.[10]

In this paper, the synthesis of a new polymer from 2,5-dichloro-3-(2′-thiophenecarbonyl)thiophene (M2) and a study of the behavior of 3-benzenesulfonyl-2,5-dichlorothiophene (M3), 2,5-dichlorobenzophenone (M4), and 2-benzenesulfonyl-1,4-dichlorobenzene (M5) are presented. Reaction conditions were varied and analyzed to address the limitations presented above. The factors considered were the monomer structure, type of solvent, and type of ligand present. The catalytic systems were explored via the use of proton (^{1}H) and phosphorus (^{31}P) nuclear magnetic resonance (NMR). The polymers and oligomers were analyzed by gel permeation chromatography (GPC), viscometry, thermal gravimetric analysis (TGA), differential scanning calorimetry (DSC), UV−vis spectroscopy, and fluorescence spectroscopy.

Experimental Section

Materials. All reagents were purchased from Aldrich, unless otherwise noted, and used without further purification. *N*,*N*-Dimethylacetamide (DMAc) and anisole were dried over CaH_2 and vacuum-distilled before use. Tetrahydrofuran (THF) was distilled from sodium and benzophenone. 2,2′-Bipyridine (bipy) and triphenylphosphine were purified by recrystallization from ethanol and cyclohexane, respectively.

Monomer Synthesis. The monomers were synthesized by adding aluminum chloride (1 equiv) to a stirring mixture of the aromatic substrate (1 equiv) and acid chloride (1.1 equiv) in 5 equiv of nitromethane at 0 °C. The reaction was allowed to warm to room temperature and stir for 24 h. The reaction was stopped by pouring the solution into acidic ice water. The resulting oil was separated by extraction with ethyl acetate. For solid products, the crude monomer was isolated by filtration. The oil was concentrated by removal of the ethyl acetate under vacuum. The oil (or crude solid) was treated with activated carbon in boiling ethyl acetate/heptane (1:8) and filtered. Upon cooling to room temperature, the resulting crystals were isolated by filtration on a glass frit and dried under vacuum.

2,5-Dichloro-3-(2′-thiophenecarbonyl)thiophene). From 2,5-dichlorothiophene and thiophene-2-carbonyl chloride (76% yield). Yellow-orange crystalline solid, melting point 64 °C. ^{1}H NMR: δ (ppm) = 7.06 (s, 1H), 7.17 (dd, 1H, J = 3.9, 2.7 Hz), 7.64 (d, 1H, J = 2.7 Hz), 7.76 (d, 1H, J = 3.9 Hz). ^{13}C NMR: δ (ppm) = 126.76 (CH), 127.27 (q-C), 128.28 (CH), 130.05 (q-C), 135.18 (CH), 135.45 (CH), 136.23 (q-C), 143.30 (q-C), 180.23 (CO). Anal. Calcd for $C_9H_4OS_2Cl_2$: C, 41.08; H, 1.54; S, 24.37. Found: C, 41.09; H, 2.03; S, 24.49.

3-Benzenesulfonyl-2,5-dichlorothiophene. From 2,5-dichlorothiophene and benzenesulfonyl chloride (60% yield). White crystalline solid, melting point 134 °C. ^{1}H NMR: δ (ppm) = 7.25 (s, 1H), 7.56 (dd, 2H, J = 7.2, 7.2 Hz), 7.65 (t, 1H, J = 7.2 Hz), 8.00 (d, 2H, J = 7.2 Hz). ^{13}C NMR: δ (ppm) = 126.18 (CH), 127.68 (q-C), 127.82 (CH), 129.31 (CH), 131.89 (q-C), 133.97 (CH), 137.37 (q-C), 140.33 (CH). Anal. Calcd for $C_{10}H_6O_2S_2Cl_2$: C, 40.97; H, 2.06; S, 21.87. Found: C, 40.75; H, 2.36; S, 21.82.

2,5-Dichlorobenzophenone. From benzene and 2,5-dichlorobenzoyl chloride (72% yield). White crystalline solid, melting point 93 °C. ^{1}H NMR: δ (ppm) = 7.37 (s, 1H), 7.41 (m, 2H), 7.49 (dd, 2H, J = 7.2, 7.2 Hz), 7.63 (t, 1H, J = 7.2 Hz), 7.80 (d, 2H, J = 7.2 Hz). ^{13}C NMR: δ (ppm) = 128.75 (CH), 128.86 (CH), 129.54 (q-C), 130.03 (CH), 131.07 (CH), 131.24 (CH), 132.89 (q-C), 134.07 (CH), 135.79 (q-C), 139.83 (q-C), 193.67 (CO). Anal. Calcd for $C_{13}H_8OCl_2$: C, 62.18; H, 3.22. Found: C, 62.47; H, 3.28.

2-Benzenesulfonyl-1,4-dichorobenzene. From benzene and 2,5-dichlorobenzenesulfonyl chloride (54% yield). White crystalline solid, melting point 134 °C. ^{1}H NMR: δ (ppm) = 7.36 (d, 1H, J = 8.4 Hz), 7.50 (dd, 1H, J = 8.4, 2.4 Hz), 7.54 (dd, 2H, J = 7.8, 7.8 Hz), 7.64 (t, 1H, J = 7.8 Hz), 7.96 (d, 2H, J = 7.8 Hz), 8.50 (d, 1H, J = 2.4 Hz). ^{13}C NMR: δ (ppm) = 128.95 (CH), 129.23 (CH), 131.05 (CH), 131.42 (q-C), 132.45 (q-C), 132.51 (q-C), 133.38 (CH), 133.07 (CH), 134.76 (CH), 139.63 (q-C). Anal. Calcd for $C_{12}H_8O_2SCl_2$: C, 50.19; H, 2.81; S, 11.17. Found: C, 49.06; H, 3.38; S, 11.09.

Polymer Synthesis. In DMAc: Nickel(II) chloride (0.1 equiv), zinc, (3.1 equiv), triphenylphosphine (0.4 equiv), and bipy (0.1 equiv) under an inert atmosphere were added to a flask equipped with an overhead stirrer and a nitrogen inlet. Solvent (10 equiv) was added via a syringe, and the mixture was stirred at 80 °C until a deep red color was observed. The monomer (1 equiv) was added and allowed to react for a specified amount of time or until the reaction mixture became too viscous to stir. The polymer was then precipitated in hydrochloric acid and methanol (1:4), filtered, washed on a glass frit, and reprecipitated from DMAc.

In THF or anisole: Dichlorobis(triphenylphosphine)nickel(II) (0.1 equiv), zinc (3.1 equiv), triphenylphosphine (0.2 equiv), and bipy (0.1 equiv) were added to a flask equipped with an overhead stirrer in a glovebox. The same procedure was followed as above, except in THF the reaction was carried out at 60 °C.

Poly[3-(2′-thiophenecarbonyl)-2,5-thiophene]. ^{1}H NMR: δ = (ppm) 7.15 (broad), 7.53 (broad), 7.64 (broad), 7.79 (broad). ^{13}C NMR: δ (ppm) = 131.94 (CH), 133.57 (CH), 135.31 (CH), 136.80 (CH), 139.06 (q-C), 140.30 (q-C), 141.93 (q-C), 148.39 (q-C), 187.37 (CO). Anal. Calcd for $C_9H_4OS_2$: C, 56.22; H, 2.10; S, 33.35. Found: C, 55.57; H, 2.39; S, 31.05.

Poly(3-benzenesulfonyl-2,5-thiophene). ^{1}H NMR: δ (ppm) = 7.19 (broad), 7.37 (broad), 7.46 (broad), 7.57 (broad). ^{13}C NMR: δ (ppm) = 126.79 (CH), 127.10 (q−C), 129.31 (CH), 131.75 (q-C), 133.82 (q-C), 133.98 (CH), 138.54 (q-C), 139.54 (CH). Anal. Calcd for $C_{10}H_6O_2S_2$: C, 54.03; H, 2.72; S, 28.85. Found: C, 53.69; H, 3.35; S, 26.88.

Poly(2,5-benzophenone). ^{1}H NMR: δ (ppm) = broad signal 6.5−8.2 (peaks at 6.5, 6.7, 7.2, 7.5, 7.75). ^{13}C NMR: δ (ppm) = broad signal 125−135 (peaks at 128.14, 129.22, 129.81, 131.03, 131.85), broad signal at 137.23, broad signal at 138.94, signal at 197.6 (CO). Anal. Calcd for $C_{13}H_8O$: C, 86.14; H, 4.48. Found: C, 87.23; H, 4.76.

Poly(3-benzenesulfonyl-1,4-benzene). ^{1}H NMR: δ (ppm) = broad signal 6.9−8.9 (peaks at 6.95, 7.4, 7.75, 8.0, 8.4, 8.8). ^{13}C NMR: δ (ppm) = 126.94, 127.34, 128.84, 129.56, 131.75, 133.615, 134.55, 138.15, 139.85. Anal. Calcd for $C_{12}H_8O_2S$: C, 66.65; H, 3.73; S, 14.83. Found: C, 62.46; H, 4.28; S, 14.10.

Catalyst Study. $NiCl_2$ (9.4×10^{-2} mmol, 12.2 mg), Zn (2.91 mmol, 190.2 mg), PPh_3 (0.38 mmol, 99.9 mg), and bipy (9.4×10^{-2} mmol, 14.7 mg) were added to an NMR tube along with 1 mL of deuterated *N*,*N*-dimethylformamide. Following three freeze−pump−thaw cycles, the tube was sealed and heated at 80 °C for 24 h. NMR spectra were obtained at 0, 4, 8, 16, and 24 h. With deuterated tetrahydrofuran as solvent (1 mL) the same procedure was followed except $NiCl_2(PPh_3)_2$ (9.4×10^{-2} mmol, 61.5 mg) and PPh_3 (0.19 mmol, 49.8 mg) were used, and the reaction was heated at 60 °C.

Characterization. ^{1}H and ^{13}C NMR spectra were acquired in deuterated DMSO, chloroform, or methylene chloride on a Varian VXR-300 or Bruker AC200. ^{31}P NMR were obtained on a Bruker AC200 in deuterated DMF or THF using triphenylphosphine as an internal reference (−5.2 ppm relative to 85% phosphoric acid external reference). Molecular weights, relative to narrow polystyrene standards, were measured using a Waters GPC system consisting of a Waters 510 pump, a Waters 717 autosampler, a Wyatt Optilab DSP interferometric refractometer, and a Wyatt Dawn EOS light scattering detector. The measurements were taken at 40 °C with THF as the mobile phase on four columns (Polymer Labs PLgel 100, 500, 1×10^4, 1×10^5 Å). Viscosity measurements were performed with an Ubbelohde capillary viscometer with DMAc as solvent at 30 °C. UV−vis spectra were measured on a HP 8542A diode array spectrophotometer, and fluorescence spectra were obtained on a Jobin Yvon Spex FluoroMax-2 with an excitation wavelength equal to that of the λ_{max} of absorbance. Thermogravimetric analysis was performed on a Perkin-Elmer TGA 7 with a heating rate of 10 °C/min. Glass transitions were

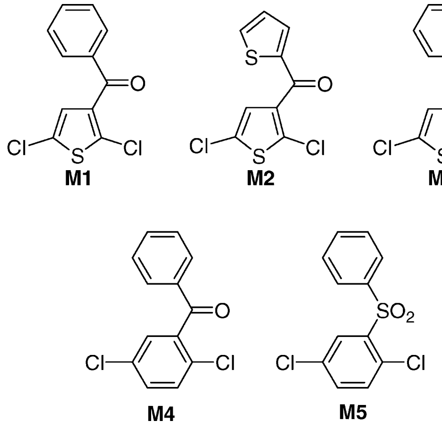


Figure 1. Structures of 3-benzoyl-2,5-dichlorothiophene (M1), 2,5-dichloro-3-(2′-thiophenecarbonyl)thiophene (M2), 3-benzenesulfonyl-2,5-dichlorothiophene (M3), 2,5-dichlorobenzophenone (M4), and 2-benzenesulfonyl-1,4-dichlorobenzene (M5).

determined at the inflection point of the endotherm with a Perkin-Elmer Pyris 1 differential scanning calorimeter with a heating rate of 10 °C/min.

Table 1. Conditions and Results for the Polymerization of 2,5-Dichloro-3-(2′-thiophenecarbonyl)thiophene (M2)

sample	solvent[a]	time (h)	% yield[b]	[η][c] dL/g
PTC1	DMAc	24	42	0.20
PTC2	anisole	4	78	*d*
PTC3	anisole	24	88	*d*
PTC4	THF	4	98	0.28
PTC5	THF	24	97	0.35

[a] DMAc = *N*,*N*-dimethylacetamide, THF = tetrahydrofuran. [b] Determined by mass recovered. [c] Determined using an Ubbelohde capillary viscometer with DMAc as solvent at 30 °C. [d] Intrinsic viscosities were too low to be measured.

Table 2. Physical Properties of Poly[3-(2′-thiophenecarbonyl)-2,5-thiophene]

sample	λ_{max}(abs) (nm)[a]	λ_{max}(em) (nm)[b]	10% weight loss temp[c]	T_g[d]
PTC1	412	560	391	134
PTC2	418	605	351	99
PTC3	414	610	387	92
PTC4	452	610	496	135
PTC5	450	610	480	149

[a] Determined by UV−vis spectroscopy; abs = absorbance. [b] Determined by fluorescence spectroscopy with an excitation wavelength equal the λ_{max}(abs); em = emission. [c] Determined by TGA. [d] Determined by DSC.

Results and Discussion

In previous work with the 2,5-dichloro-3-benzoylthiophene monomer (Figure 1, M1), limitations arising from monomer purity, polymer degradation during the reaction, and partial polymer solubility were encountered.[11] To overcome these difficulties, structurally similar derivatives of monomer M1 were synthesized. The monomers considered here are shown in Figure 1 and include the two thiophene derivatives, 2,5-dichloro-3-(2′-thiophenecarbonyl)thiophene (M2) and 3-benzenesulfonyl-2,5-dichlorothiophene (M3). Monomer M1 was a viscous oil and subsequently very difficult to purify. It was shown that monomer purity is highly important in Ni(0) polymerization due to reduction of the aryl chloride bond caused by protic impurities.[5] Side reactions, such as this reduction, result in low molecular weights. The purification issues associated with M1 were easily overcome when the benzoyl pendant was replaced with a thiophenecarbonyl or a benzenesulfonyl electron-withdrawing group. The resulting monomers, M2 and M3, were synthesized in high yield and greater than 99% purity by GC. As previously mentioned, the effects of the benzenesulfonyl group are known, but the structure−property relationships of the thiophenecarbonyl pendant are unknown. It is expected to have properties similar to the benzoyl pendant, but the effects on the glass transition temperature (T_g), solubility, and optoelectronic properties are undetermined.

The next step was to examine the polymerization behavior of these two monomers in addition to the final polymer properties. The question was whether the same problems of degradation and limited solubility observed with M1 would occur with M2 and M3. Polymerization of M2 was carried out in three solvents *N*,*N*-dimethylacetamide (DMAc), anisole, and tetrahydrofuran (THF) (Table 1). Polymerization in DMAc gave yields of only 40−50%. Increasing the reaction time led to similar degradation as observed with M1 and lowered the yield. Conducting the polymerization in anisole or THF increased the yields and, more importantly, did not lead to degradation. Using THF as a solvent led to near quantitative yields with short reaction times.

In addition to overcoming the degradation, the solubility of the final polymer from M2 was improved. This improvement allowed for the molecular weight characterization by GPC and intrinsic viscosity. All polymers from M2 were completely soluble in DMAc. The materials synthesized in anisole were completely soluble in THF. All other polymers of M2 exhibited partial solubility in THF. Molecular weights were measured by GPC for the fractions of material soluble in THF, and intrinsic viscosities were measured in DMAc. The polymers synthesized in near quantitative yields had the highest molecular weight THF soluble fractions of approximately 2.0 × 10^3 g/mol. The oligomers from the reactions in anisole were completely soluble in THF and had number-average molecular weights of 700−900 g/mol. The material from reaction in DMAc had a viscosity of 0.20 dL/g but a low yield due to side reactions that led to a large fraction of methanol-soluble material. The intrinsic viscosities of the material produced in anisole were too low to measure due to low molecular weights. However, 4 h in THF gave a polymer with an intrinsic viscosity of 0.28 dL/g. Increasing the reaction time to 24 h led to a polymer with an intrinsic viscosity of 0.35 dL/g.

The UV−vis and fluorescence spectra of the polymers and oligomers prepared from M2 were measured (Table 2). All spectra were measured with DMAc as the solvent. The polymers synthesized in THF had the longest measured λ_{max} of absorbance values, 450−452 nm (PTC4 and 5). The oligomers produced in anisole had shorter λ_{max} of absorbance values, corresponding with very low molecular weights. Comparison of the spectra shows a marked difference in the resulting material from the polymerizations conducted in DMAc and those conducted in anisole or THF. In Figure 2, the spectrum of the product of the reaction in DMAc (PTC1) does not show a large valley at 360 nm like the products from reaction in anisole or THF. The absorbance of the same material also extends further toward the red than the higher molecular weight polymers from reaction in THF. It is important to note that the spectra of the materials from the ether solvents are qualitatively the same and only differ in the values of the maxima and minima. This difference arises from the varying molecular

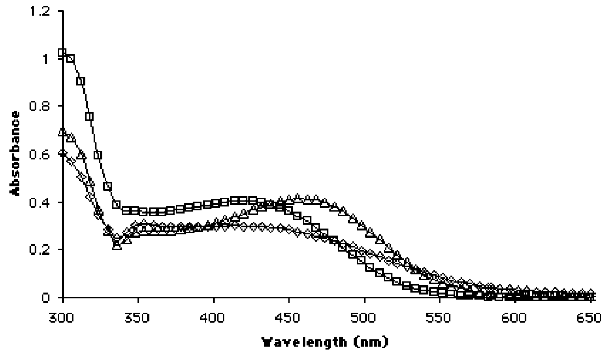


Figure 2. UV−vis spectra of poly[3-(2′-thiophenecarbonyl)-2,5-thiophene] synthesized in DMAc (◇), anisole (□), and THF (△).

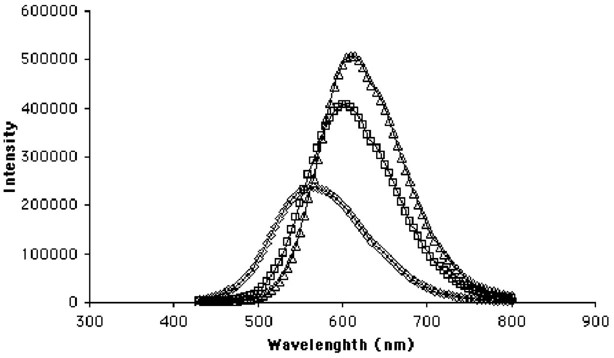


Figure 3. Fluorescence spectra of poly[3-(2′-thiophenecarbonyl)-2,5-thiophene] synthesized in DMAc (◇), anisole (□), and THF (△).

weights. A similar trend in the fluorescence spectra of the polymers was observed (Figure 3). The higher molecular weight material produced in THF had a longer λ_{max} of emission than did the lower molecular weight materials synthesized in anisole. Once again, these two spectra were very similar with their differences arising from the molecular weights of the materials. The material from reaction in DMAc exhibited a much lower λ_{max} of emission (560 nm) and broader emission spectra, different from the spectra of the materials produced in the ether solvents. Thermal analysis of these polymers again showed a difference between the materials produced in DMAc and those synthesized in ether solvents. PTC1 exhibited a 10% weight loss temperature of 391 °C and a glass transition temperature of 134 °C. The oligomers from anisole (PTC2 and -3) showed a similar weight loss to PTC1 but lower glass transition temperatures. The polymers synthesized in THF had respectable 10% weight loss temperatures near 500 °C and glass transitions of 135 and 149 °C. It was evident from the optical and thermal data that the polymers produced in anisole and THF were structurally the same and only differed in molecular weight, while the product from reaction in DMAc was a wholly different material. Possible reasons for these differences were determined and will be addressed later in the text.

Given the results for monomer M2, it was chosen to study the polymerization of monomer M3 in DMAc and THF (Table 3). A reaction time of 24 h in DMAc gave a yield of 77%. Upon increasing the reaction time, degradative side reactions again were evident, and the yield decreased to 62% in 72 h. When THF was employed as solvent, a yield of 99% was obtained. However, no large increase in molecular weight was observed when THF was used as solvent. The material resulting from the reaction in DMAc had poor general solubility. It was soluble only in DMAc and partly soluble in THF. The oligomer from reaction in THF was completely soluble in polar solvents such as THF, chloroform, and DMAc. Viscosity measurements were attempted, but only PTS1 exhibited a measurable intrinsic viscosity of 0.1 dL/g. The physical properties of the materials resulting from these two solvents again were quite different. PTS3 exhibited longer λ_{max} of absorbance and emission than the material produced in DMAc (PTS1) (λ_{max}(abs) = 378 nm, λ_{max}(em) = 555 nm from THF, λ_{max}(abs) = 340 nm and λ_{max}(em) = 470 nm from DMAc). In addition, the oligomer from THF had higher 10% weight loss temperature of 434 °C compared to 335 °C for the polymer from DMAc. A glass transition temperature of 146 °C was also observed for the material synthesized in THF. The material from DMAc (PTS1) had a lower T_g of 101 °C.

Table 3. Conditions and Results for the Polymerization of 3-Benzenesulfonyl-2,5-dichlorothiophene (M3)

sample	solvent[a]	time (h)	% yield[b]	$\langle M_n \rangle$ (g/mol)[c]	PDI[c]	$[\eta]^d$ (dL/g)
PTS1	DMAc	24	77	1700[e]	1.89	0.10
PTS2	DMAc	72	62	1300[e]	1.59	*f*
PTS3	THF	24	99	2200	2.05	*f*

[a] DMAc = *N*,*N*-dimethylacetamide, THF = tetrahydrofuran. [b] Determined by mass recovered. [c] Determined by GPC. [d] Determined using an Ubbelohde capillary viscometer with DMAc as solvent at 30 °C. [e] Not completely soluble in THF. [f] Intrinsic viscosities were too low to be measured.

With the knowledge of the differing results in these solvents, the polymerization chemistry of two materials that we earlier reported, 2,5-dichlorobenzophenone (M4) and 2-benzenesulfonyl-1,4-dichlorobenzene (M5), was revisited in order to address the limitations encountered. In previous experiments, polymers of M4 with number-average molecular weights of up to approximately 25 × 10^3 g/mol were synthesized in quantitative yields. Unfortunately, polymerization in amide solvents led to reduction of nearly 15% of the carbonyl functionalities.[14] This limitation was overcome by simply oxidizing the material postpolymerization or by the addition of small quantities of triphenylphosphine oxide (TPO) to the reaction mixture.[15] In addition to this difficulty, these polymers formed brittle films. Many of the target applications for polymers such as this require the formation of flexible, creasable films. In the case of the polymerization of M5 only oligomeric materials were produced. However, this material showed great promise with 10% weight loss temperatures near 450 °C.[10]

Utilizing THF as solvent and the conditions described for M2 and M3, polymerization of M4 resulted in a number-average molecular weight of 55.6 × 10^3 g/mol and an intrinsic viscosity of 1.15 dL/g. In addition to higher molecular weights than previously reported, no reduction of the carbonyl was observed, even without the addition of TPO. This result eliminated the need for oxidation reactions postpolymerization. The polymer was soluble in solvents such as chloroform, THF, and DMAc. Thin films of the polymer were cast from chloroform. Although not highly creasable, the films were flexible and showed much better overall film-forming properties than the polymers synthesized previously in amide solvents. In addition to overcoming the two previous limitations, the physical properties of this polymer were greatly enhanced as well. The polymer

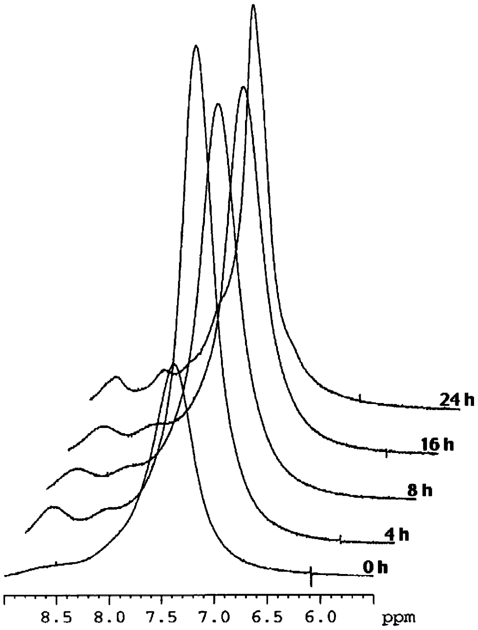


Figure 4. ^{1}H NMR spectra of the reaction of $NiCl_2$ (0.1 equiv), Zn (3.1 equiv), TPP (0.4 equiv), and bipy (0.1 equiv) over 24 h at 80 °C in DMF-d_7.

had a 10% weight loss temperature of 576 °C and a glass transition of 180 °C. Polymerization of M5 in THF only yielded soluble oligomeric material with an $\langle M_n \rangle$ of 1.6 × 10^3 g/mol and a PDI of 1.3. As in the previous study of this material, excellent potential thermal properties were observed with a 10% weight loss of 578 °C in nitrogen and a T_g of 136 °C. From these results, it was apparent that THF was the best solvent for coupling these arylene chlorides. Also, it was clear that the substitution of the carbonyl with a sulfone drastically changed the polymerization chemistry. No high molecular weight sulfone-containing materials were synthesized. It should be noted here that, on the basis of these data, high molecular weight polymer from M1 would be expected, if the monomer purity was sufficient. These results led to two questions. The first was regarding the role of solvent choice in the polymerization. The second was concerning the role of the monomer structure.

Solvent choice was shown previously to play an important role in Ni(0) coupling, but the mechanism that gives rise to degradation and reduction was unclear.[3,16] Therefore, a study of the catalyst in the different solvents was undertaken. The catalyst components ($NiCl_2$ in DMF, $NiCl_2(PPh_3)_2$ in THF, Zn, PPh_3, and bipy) were sealed in NMR tubes and heated, and spectra were taken over a 24 h period (Figure 4). *N*,*N*-Dimethylformamide-d_7 (DMF-d_7) was substituted for DMAc due to availability. Several important differences in these series of spectra were apparent. Free bipy (8.4 and 8.7 ppm) was observed throughout the reaction in DMF-d_7 by ^{1}H NMR. No signal from free bipy was observed in THF-d_8 (Figure 5). The ^{31}P NMR in DMF-d_7 showed an increase in intensity and narrowing of the triphenylphosphine (TPP) signal (−5.2 ppm) from 8 to 24 h (Figure 6). In THF-d_8, the TPP signal remained broad and constant in intensity over the same time period (Figure 7).

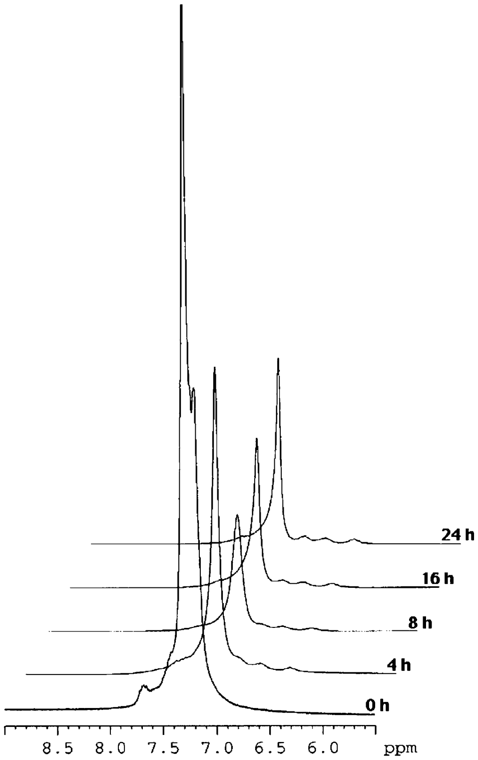


Figure 5. ^{1}H NMR spectra of the reaction of $NiCl_2(PPh_3)_2$ (0.1 equiv), Zn (3.1 equiv), TPP (0.2 equiv), and bipy (0.1 equiv) over 24 h at 60 °C in THF-d_8.

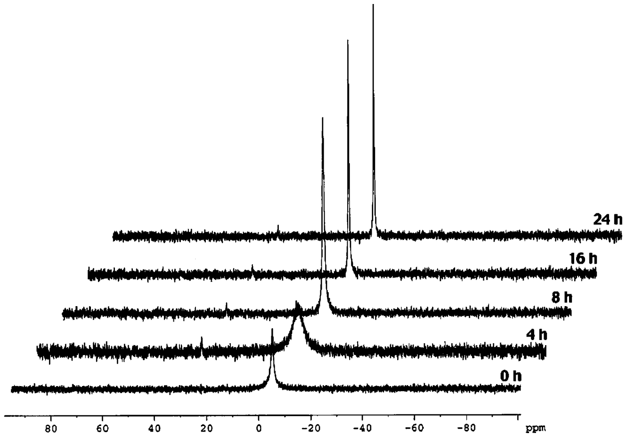


Figure 6. ^{31}P NMR spectra of the reaction of $NiCl_2$ (0.1 equiv), Zn (3.1 equiv), TPP (0.4 equiv), and bipy (0.1 equiv) over 24 h at 80 °C in DMF-d_7.

The observation of free TPP in solution was expected due to the large stoichiometric excess compared to the nickel salt. However, because of a greater binding affinity and a one-to-one ratio between the nickel and the bipy, free bipy was not expected to be observed in either solvent. The observation of free bipy in DMF suggested that less bipy is complexed to Ni in amide solvents than in THF. The ligands in Ni(0) coupling were shown to play an important role in preventing side reactions. In one example, the addition of bipy prevented phenyl migration from TPP to the Ni atom.[5] Bipy, not complexed with the Ni center, would be expected to have little utility in this role. Also, Ni(0)−phosphine complexes have been observed to insert into the carbon−sulfur bonds of certain thiophene derivatives.[17] A hydrodesulfurization mechanism, such as this insertion, could play a role in the degradation of polythiophene chains observed at long reaction times. Bipy, complexed to the Ni(0), may play a role in preventing such a side reaction.

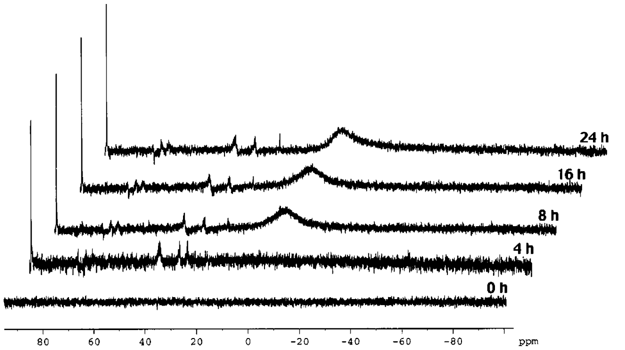
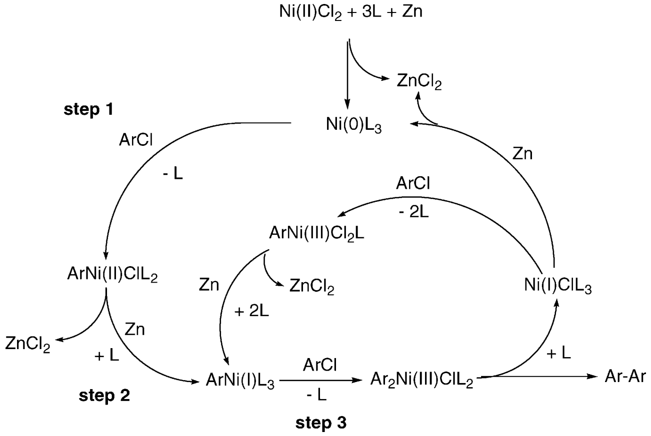


Figure 7. ^{31}P NMR spectra of the reaction of $NiCl_2(PPh_3)_2$ (0.1 equiv), Zn (3.1 equiv), TPP (0.2 equiv), and bipy (0.1 equiv) over 24 h at 60 °C in THF-d_8.

Scheme 1. Reaction Mechanism Proposed by Colon for the Ni(0)-Catalyzed Polymerization of Aryl Chlorides



The difference in the catalyst stability observed in the two solvents was also of interest. In DMF, the increase in intensity and narrowing of the TPP signal showed that over time less ligand was complexed with nickel. It then follows that there was less active catalyst present over time in DMF. Observation of the color of the two systems supports this conclusion. In DMF, the solution turned the deep red color of the active Ni(0) species within minutes, but concurrently with the rise in the TPP signal a black precipitate formed. The reaction in THF remained the deep red color throughout the 24 h period. Although the active catalyst species could not be identified, the greater number and concentration of phosphorus species in THF pointed to higher active catalyst concentration.

To understand the role of the monomer structure in the reaction, the mechanism was considered. The catalytic cycle proposed by Colon and Kelsey contains three steps in which the structure of the monomer could possibly play a role (Scheme 1).[5] These steps were oxidative addition of Ni(0) across the aryl chloride bond (step 1), reduction resulting in an arylnickel(I) species (step 2), and oxidative addition of the arylnickel(I) species to a second aryl chloride (step 3). The first two steps were shown to be accelerated by the presence of an electron-withdrawing substituent on the aryl chloride.[8] In the third step, the presence of an electron-withdrawing group ortho to the Ni−C bond would be expected to increase the stability of the electron-rich $ArNi(I)L_3$ (where L = PPh_3 or L_2 = bipy) complex and thus slow the oxidative addition reaction of this complex with a second aryl chloride. Colon and Kelsey proposed that early in the reaction (conversions less than 80%) the reduction of the $ArNi(II)ClL_2$ (step 2) was the rate-limiting step. As the concentration of ArCl approached that of the nickel species, the oxidative addition of ArNi(I)L_3 (step 3) became rate limiting. The degree of polymerization is related to the conversion through eq 1 ($[X_n]$ = average degree of polymerization, ρ = conversion).[18] Oligomers of 10 repeat units (such as the sulfone materials presented here) equated to a 90% conversion of the aryl chloride. At this concentration, the oxidative addition of ArCl to the $ArNi(I)L_3$ would be rate limiting. Sulfonyl substituents are stronger withdrawing groups than ketones and thus deactivate the $ArNi(I)L_3$ complex for oxidative addition to a greater extent.

$$[X_n] = 1/(1 - \rho) \tag{1}$$

From this mechanism and our experimental results, we propose that in Ni(0)-catalyzed coupling there exists a window of reactivity in which the activating character of the electron-withdrawing ability of the subsistent in the first two steps is balanced with the deactivating character of the same group in the third step. Ketone pendants such as the benzoyl group or the thiophene-carbonyl group meet this requirement. Pendants, such as sulfones, deactivate the third step to a large enough degree to inhibit the reaction.

Conclusions

The choice of solvent and the monomer structure were shown to be key considerations in the Ni(0) polymerization of arylene dichloride monomers containing electron-withdrawing substituents. Polymerization in DMAc resulted in side reactions, such as degradation of the thiophene polymers in the reaction mixture and reduction of the carbonyl groups, which limited the materials utility. Through the use of THF as solvent, high molecular weight poly[3-(2′-thiophenecarbonyl)-2,5-thiophene] and poly(2,5-benzophenone) were synthesized with no side reactions being observed. Although the exact cause of the differing results was not found, drastic differences in the catalytic environments in the two solvents were observed by NMR. Also, high molecular weight materials from monomers containing carbonyl functionalities were obtained, while substitution with a sulfone resulted in oligomeric material. Analysis of the results and consideration of the mechanism showed that in Ni(0)-catalyzed polymerization there is a window of electron-withdrawing ability for which functionalities such as carbonyl-containing pendants meet the criteria and greatly accelerate the reaction. Increasing the electron-withdrawing ability by substitution with a sulfone slows the reaction due to the stabilization of a reactive intermediate. Further work is planned to quantify the electron-withdrawing effect through the study of benzophenone monomers with varying electron-donating and -withdrawing functionalities in the 4′-position.

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