Synthesis of Soluble, Organometallic Poly(phenylene sulfide) and Poly(phenylene oxide) Derivatives *via* Transition-Metal-Activated Nucleophilic Substitution[†]

Alexa A. Dembek,* Paul J. Fagan, and Marianne Marsi

DuPont Central Research and Development, Experimental Station, Wilmington, Delaware 19880-0328

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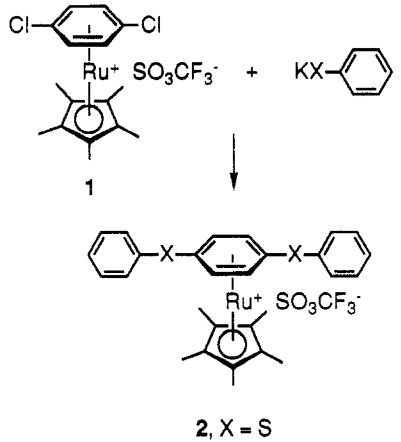
Poly(phenylene sulfides) and poly(phenylene oxides) are engineering thermoplastics with many desirable characteristics, including excellent thermal, oxidative, and chemical stabilities. Conventional syntheses must overcome the polymers' insolubility and therefore require drastic polymerization conditions, often limiting the range of polymer compositions that are accessible. Traditionally, poly(phenylene sulfide) is synthesized by polycondensation of 1,4-dichlorobenzene and sodium sulfide in polar solvents at high temperature and pressure.[1] The conventional route to poly(phenylene oxide) involves the metal-catalyzed oxidative coupling polymerization of 2,6-disubstituted phenols.[2] The development of new synthetic routes to this important class of engineering plastics based on nucleophilic aromatic substitution polymerization is an area of considerable interest.[3]

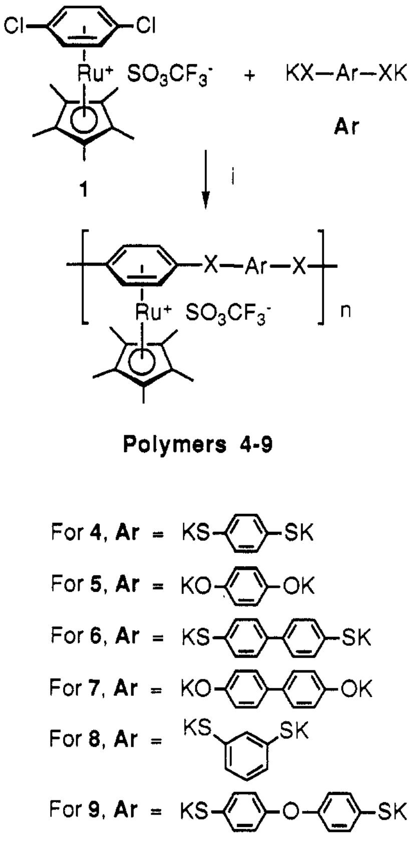
It is well-known that aromatic halides can be activated toward nucleophilic displacement by π-complexation with $Cr(CO)_3$, $CpFe^+$ (Cp = cyclopentadienyl), $CpRu^+$, or $Mn(CO)_3{}^+$.[4] An activating group of particular interest to us is the cationic Cp^*Ru^+ (Cp* = pentamethylcyclopentadienyl) fragment, which is a versatile organometallic building block that effectively binds arenes.[5] In our experience, the activating ability of this π-bonded complex tremendously exceeds that of the highly electron-withdrawing nitro substituent in aromatic systems. In the same manner as in S_NAr reactions, leaving groups on the η^6-arene complexes are readily displaced by nucleophiles. π-Coordinated transition-metal-activating groups for nucleophilic substitution offer new opportunities for aromatic polymer synthesis.[6] For example, activation by π-complexation allows use of monoaryl monomers, such as 1,4-dihalobenzene, instead of conventional bisaryl substrates containing carbonyl or sulfonyl electron-withdrawing groups. Polymer structure and composition are determined by the dinucleophile structure. Segal has reported previously on the synthesis of $CpRu^+$–poly(ether ether ketone) polymers.[7] Here we demonstrate the broad generality of this transition-metal-activated route by synthesis of a family of organometallic poly(phenylene sulfide) and poly(phenylene oxide) derivatives using the *Cp*Ru*$^+$ fragment as an activating group. Tailored design of polymer structures is illustrated by syntheses using a variety of sulfur- or oxygen-based dinucleophiles, including monomers containing biphenyl moieties and *meta* linkages. This methodology allows polymer synthesis under extremely mild conditions, even with *dichloro* aromatic substrates, overcomes polymer insolubility by using the Cp^*Ru^+ complex as a solubilizing agent, and ultimately provides opportunities for synthesis of compositions otherwise unaccessible.

Scheme I



2, X = S
3, X = O

Scheme II



i: DMSO, 60°C for 1-2 h

Model reactions demonstrate the quantitative yield of Cp^*Ru^+-activated chloro displacement necessary for the synthesis of high polymers. The reaction of $[Cp^*Ru(\eta^6\text{-}1,4\text{-dichlorobenzene})]^+OTf^-$ (OTf = SO_3CF_3)[8] (**1**) with 2 equiv of potassium thiophenoxide or phenoxide in polar solvents affords the bis(thiophenoxy) or bis(phenoxy) derivatives **2** and **3** (Scheme I).[9] The reactions proceed rapidly to quantitative conversion at 25 °C, as determined by ^1H NMR spectroscopy, demonstrating that this metallo-activated reaction meets the requirements necessary for high polymer formation *via* a step-growth polymerization.

Reaction of metallo monomer **1** with a stoichiometric ratio of the preformed dipotassium salt[10] of 1,4-benzenedithiol[11] or hydroquinone in DMSO under an inert atmosphere gives *soluble*, organometallic derivatives of poly(phenylene sulfide) (**4**) or poly(phenylene oxide) (**5**) (Scheme II). The remarkable activating ability of the

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Table I. Polymer Characterization Data

	^{1}H NMR,[a] ppm					elem anal.	
polymer	uncomplexed aromatic	complexed aromatic[c]	Cp*[d]	^{13}C NMR,[a] ppm	η_{inh},[b] dL/g	calcd	found
4	7.59 (s, 4 H)	6.10	1.92	133.3, 132.1, 100.4, 97.1, 88.7, 9.5	1.21	C: 45.91 H: 3.85	C: 45.62 H: 3.86
5	7.29 (s, 4 H)	6.13	1.97	151.7, 127.0, 120.9, 96.3, 78.7, 9.8	0.81	C: 53.95 H: 4.21	C: 53.74 H: 4.29
6	7.83 (d, 4 H, J = 8.1 Hz), 7.63 (d, 4 H, J = 8.0 Hz)	6.06	1.92	139.4, 133.4, 130.1, 128.1, 101.9, 96.8, 87.9, 9.5	1.38	C: 51.39 H: 4.02	C: 50.53 H: 4.11
7	7.79 (d, 4 H, J = 8.5 Hz), 7.30 (d, 4 H, J = 8.6 Hz)	6.18	2.00	154.6, 135.8, 128.4, 126.7, 119.2, 96.3, 79.1, 9.8	1.49	C: 53.95 H: 4.21	C: 53.74 H: 4.29
8	7.70 (s, 1 H), 7.55 (s, 3 H)	6.09	1.89	135.9, 133.2, 132.5, 131.5, 100.6, 97.0, 88.6, 9.4	0.52	C: 45.91 H: 3.85	C: 45.52 H: 3.85
9	7.60 (d, 4 H, J = 8.7 Hz), 7.17 (d, 4 H, J = 8.7 Hz)	5.95	1.89	156.9, 135.8, 124.1, 120.2, 103.2, 96.5, 86.8, 9.4	1.07	C: 50.21 H: 3.92	C: 50.08 H: 3.93

[a] In DMSO-d_6. [b] 0.5% solution in DMF at 30 °C. [c] Singlet resonances, 4 H. [d] Singlet resonances, 15 H.

Cp*Ru$^+$ moiety allows the polymerizations to be carried out under extremely mild conditions (60 °C for 1–2 h) at high monomer concentration (ca. 30 wt %).

Tailored design of the polymer structure is straightforward and is accomplished by variation of the dinucleophile. For example, biphenyl units are incorporated into the polymer structure by reaction of 1 with the dipotassium salt of 4,4′-biphenyldithiol[12] or 4,4′-biphenol to afford novel derivatives 6 or 7. The introduction of *meta*-arylene linkages further exemplifies the generality of this synthetic approach. Specifically, reaction of 1 with the dipotassium salt of 1,3-benzenedithiol affords the alternating *meta*/*para* isomer of poly(phenylene sulfide) (8). Preparation of a mixed poly(phenylene sulfide)–poly(phenylene oxide) derivative is facile; reaction of 1 with the dipotassium salt of 4,4′-oxybis(thiophenol)[12] gives copolymer 9, which has both thioether and ether linkages in the polyarylene structure.

The π-complexed polymers are isolated as tan solids by precipitation of the viscous DMSO reaction mixtures into water. Polymers 4–9, which have a Cp*Ru$^+$ fragment coordinated to every repeat unit, are completely soluble at room temperature in polar organic media such as acetonitrile, DMSO, *N*,*N*-dimethylformamide (DMF), and *N*-methylpyrrolidinone (NMP), demonstrating the exceptional solubilizing power of the transition-metal π-complex. The solubility characteristics of these metallo polymers complement our previous results showing dramatically enhanced solubility of the rigid-rod poly(*p*-phenylene terephthalamide) resulting from chromium tricarbonyl π-complexation.[6a]

NMR spectra of metallo polymers 4–9 confirm the transformation of the Cp*Ru$^+$-complexed dichloro aromatic species into the corresponding diaryl–thioether or diaryl–ether polymers. Specifically, ^{1}H NMR analyses show resonances for the uncoordinated arenes in the range 7.8–7.3 ppm and singlet resonances for the coordinated arene at ca. 6.2 ppm and the methyl group of the Cp* ligand at 1.9 ppm (Table I). ^{13}C NMR spectra also show characteristic upfield shifts of ca. 30 ppm in the resonances of the coordinated arene carbon nuclei relative to the uncoordinated aromatics.[5] The inherent viscosities in DMF were in the range 0.52–1.49 dL/g (0.5%, 30 °C) (see below). Thermal gravimetric analysis under nitrogen for 4–9 shows the onset of weight loss at 350–380 °C, with a final weight retention of ca. 20% at 800 °C. At this time, no evidence for glass transition or melting temperatures has been determined by differential scanning calorimetry.

Solutions of the Cp*Ru$^+$-complexed polymers 4–9 exhibit polyelectrolyte effects[13] in polar organic solvents, which are suppressed at high ionic strength (Figure 1). For example, the reduced viscosity of 7 at 0.5% is 1.95 dL/g and increases nonlinearly as concentration decreases due to expansion of the polymer chain from intramolecular repulsion between the cationic Cp*Ru$^+$ groups.[5a] By contrast, plots of the reduced viscosity of 7 in DMF containing 0.05 M LiCl are linear, giving an intrinsic viscosity of 0.40 dL/g. Polymer 7 adsorbs on conventional gel permeation chromatography columns, causing molecular weight measurements to be unreliable.

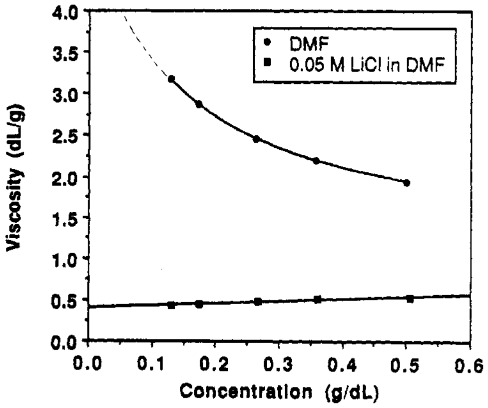

Figure 1. Reduced viscosity data for polymer 7 in DMF and 0.05 M LiCl in DMF (30 °C). Addition of LiCl suppresses the polyelectrolyte effect, giving an intrinsic viscosity of 0.40 dL/g.

Decomplexation of the Cp*Ru$^+$ moiety from polymers 4–9 to generate the parent poly(phenylene sulfide) and poly(phenylene oxide) derivatives would allow the π-complex to function as a reversible activating group and solubilizing agent. Although efficient decomplexation from models 2 and 3 is accomplished by an arene-displacement reaction (thermally in DMSO, 160 °C, 2 h or photochemically in CH_3CN, 450 W, 1 h),[4] decomplexation from polymers 4–9 is complicated by precipitation of the insoluble poly(phenylene sulfide) or poly(phenylene oxide) derivatives after partial Cp*Ru$^+$ removal. Investigation of alternative decomplexation procedures is in progress.

Additional studies are underway to extend further the generality of this transition-metal-activated nucleophilic substitution route to the synthesis of soluble, organometallic polyaniline derivatives, mixed aromatic–aliphatic polymers, and the corresponding 1,3-isomers of poly(phenylene sulfide) and poly(phenylene oxide). The extraordinary activating ability and solubilizing power of the Cp*Ru$^+$ complex may facilitate the design of new materials with controlled architectures, such as dendrimers or star polymers, by judicious nucleophile/electrophile selection.

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(8) Prepared by reaction of 1,4-dichlorobenzene with Cp*Ru-$(CH_3CN)_3{}^+OTf^-$. See ref 5b.

(9) For **2**: ^{1}H NMR (DMSO-d_6) 7.55–7.46 (m, 10 H, Ar H), 5.97 (s, 4 H, Ru-arene), 1.90 (s, 15 H, CH_3) ppm; ^{13}C NMR (DMSO-d_6) 132.9, 129.9, 129.2, 102.2, 96.5, 87.5, 9.3 ppm. MS (positive FAB). Calcd: *m/z* cation 531. Found: *m/z* cation 531. Anal. Calcd for $C_{29}H_{29}O_3S_3F_3Ru$: C, 51.24; H, 4.30. Found: C, 51.35; H, 4.23. For **3**: ^{1}H NMR (DMSO-d_6) 7.50–7.20 (m, 10 H, Ar H), 6.08 (s, 4 H, Ru-arene), 1.96 (s, 15 H, CH_3) ppm; ^{13}C NMR (DMSO-d_6) 155.0, 130.3, 126.8, 125.0, 118.8, 96.2, 78.9, 9.8 ppm. MS (positive FAB). Calcd: *m/z* cation 499. Found: *m/z* cation 499. Anal. Calcd for $C_{29}H_{29}O_5SF_3Ru$: C, 53.78, H, 4.51. Found: C, 53.70; H, 4.44.

(10) Prepared by reaction of the bisthiophenol or bisphenol with KO*t*Bu (2.05 equiv, THF, 60 °C), followed by filtration of the THF-insoluble salt, extraction of excess KO*t*Bu, and drying *in vacuo* (90 °C for 16 h).

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