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Construction of an *ortho*-phenol polymer

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Abstract—Synthesis and study of an *ortho*-phenol polymer, a highly functionalized polyphenylene, have been conducted. A dibromo *ortho*-biphenol monomer was synthesized and its homocoupling in the presence of Ni(1,5-cyclooctadiene)$_2$ followed by hydrolysis led to the formation of an *ortho*-phenol polymer. This polymer was soluble in common organic solvents. It was characterized by gel permeation chromatography, UV–vis, IR, ^{1}H and ^{13}C NMR spectroscopic methods. The use of this polymer in the Lewis acid-catalyzed reaction of phenylacetylene with benzaldehyde in the presence of diethylzinc was studied. It was found that the polymer when treated with 1/4 equiv. (relative to the phenol unit of the polymer) of Ti(O^{i}Pr)$_4$ generated a much more active Lewis acid catalyst than when treated with excess Ti(O^{i}Pr)$_4$. This indicates that different types of catalytic sites in the polymer have been produced under these conditions. © 2001 Elsevier Science Ltd. All rights reserved.

Since the discovery of the high doped conductivity of polyacetylene by Shirakawa, MacDiarmid, Heeger and co-workers in 1977,[1] tremendous amounts of study have been conducted on conjugated polymers.[2] These materials have exhibited many important and potentially very useful electrical and optical properties. Polyphenylenes are one class of conjugated polymers whose polymer chains are made of all phenyl rings linked at various positions, but in most cases at the *para* positions. Extensive work on these polymers has been reported.[2,3] In our laboratory, we are particularly interested in constructing functionalized polyphenylenes. The functional groups of conjugated polymers may allow them to interact with various organic molecules for optical and electrical sensor development.[4] Catalysts based on functionalized rigid conjugated polymers may have more easily accessible catalytic sites than flexible polymer catalysts when used for organic synthesis.[5] Properly designed functional groups may also allow the polymers to undergo either intrachain self-organization or interchain self-assembly for materials applications.

ortho-Phenol polymers are one type of functionalized polyphenylenes in which their phenol units are connected at the *ortho* positions by forming carbon–carbon bonds. An *ortho*-phenol polymer is expected to have two conformations, *cisoid* and *transoid*, as shown below. The adjacent biphenol dihedral angle is less than 90° for the *cisoid* conformation and larger than 90° for the *transoid* conformation. In a chiral environment, e.g. in the presence of optically active guest molecules or substituents, the polymer chain could also achieve a preferred one-handed helical sense because of the induced chiral conformation at the biaryl units.[6] How factors such as temperature, solvent polarity, guest molecules, metal ions, and substituents X on the phenol rings influence the polymer conformation is of significant fundamental interest. In addition, the conformation of the polymer might greatly influence its materials properties. The conformation change of *m*-phenylene ethynylene oligomers was investigated by Moore and co-workers.[7a,b] A poly(*m*-phenylenevinylene) was recently used to helically wrap around carbon nanotubes by Stoddart, Heath and co-workers.[7c] Macrocyclic oliogo-*ortho*-anisoles (spherands) were studied extensively by Cram and co-workers.[8] Stepwise couplings of substituted phenols to generate *ortho*-phenol oligomers were reported.[9] Although enzymatic methods have been developed for the polymerization of phenol and its derivatives, the resulting polymers were often found to contain a mixture of structural units due to the formation of both carbon–carbon bonds and carbon–oxygen bonds at different positions of the phenol rings.[10,11] In order to generate structurally well-defined *ortho*-phenol polymers, we have studied transition metal-mediated cross-coupling polymerizations of *ortho* bromophenols. Herein, our preliminary results are reported.

Keywords: *ortho*-phenol polymer; conjugated polymer; polyphenylene; polymer catalyst; alkynylzinc addition.

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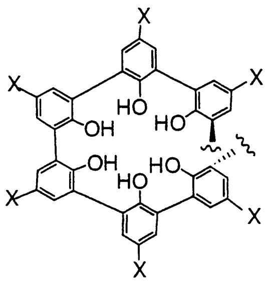
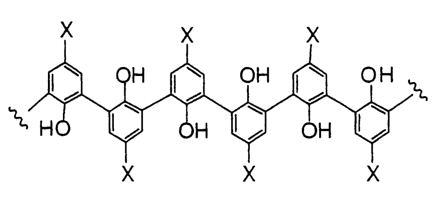
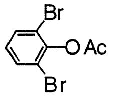


cisoid

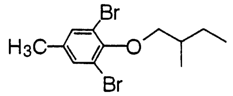


transoid

We first examined the direct polymerization of *ortho*-dibromo phenyl acetate **1** in the presence of Ni(cyclooctadiene)$_2$ or $NiCl_2/Zn$.[12] However, only low molecular weight materials were observed from these reactions and no polymer was obtained. Another alkylated *ortho*-dibromophenol **2** was prepared, which again could not be polymerized. It seems that directly making two phenyl–phenyl bonds on the phenyl ring of these monomers might not be suitable for polymer production.



1



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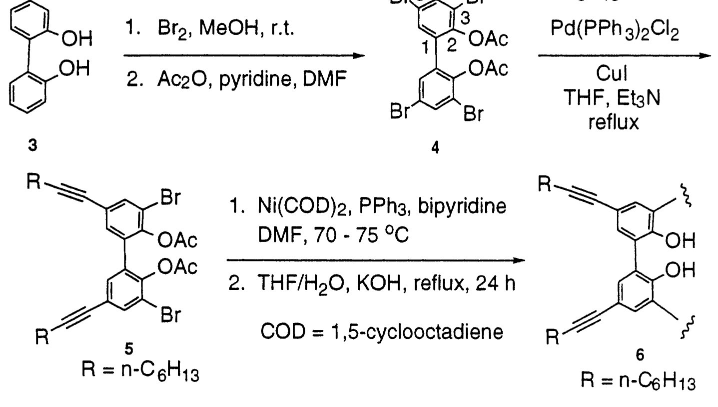
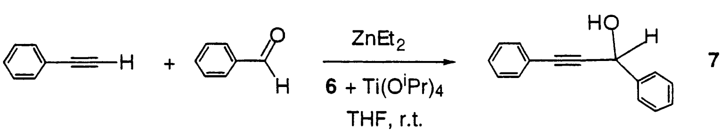
A different approach was then taken which involved the synthesis of a 3,3′-dibromo-1,1′-bi-2-phenol monomer and its polymerization. By using such a biphenol monomer, the cross-coupling reactions to make carbon–carbon bonds for the polymer formation would be conducted on two phenyl rings rather than on one phenyl ring. Following the literature procedures, the tetrabromo biphenyl acetate **4** was prepared in high yield from *ortho*-biphenol (**3**) (Scheme 1).[13] Gómez-Lor et al found that the 5,5′-bromine atoms of **4** were much more reactive than the 3,3′-bromines in the Sonogashira coupling.[13c,14] We thus reacted 1-octyne with **4** in the presence of $Pd(PPh_3)_2Cl_2$, which generated the 5,5′-dialkynyl substituted monomer **5**.[15] Introduction of the two alkynyl groups in monomer **5** serves the following purposes: (1) they block the 5,5′-positions and allow polymerization to take place specifically at the 3,3′-positions; (2) these substituents should increase the solubility of the resulting polymer in organic solvents and make it easy for characterization and spectroscopic study; (3) the triple bonds extend the conjugation of the substrates and should also allow further functionalization of the polymer. Unlike compounds **1** and **2**, the biphenyl monomer **5** underwent the aryl–aryl cross-coupling polymerization smoothly in the presence of Ni(cycloocatadiene)$_2$.[16] Therefore, making two carbon–carbon bonds on the two phenyl rings of **5** might have greatly reduced the interference when the coupling was conducted on the single phenyl ring of monomer **1** or **2**. After the Ni-mediated polymerization of **5** followed by hydrolysis under basic conditions, the desired *ortho*-phenol polymer **6** was obtained.[16] This polymer was a brown solid and soluble in common organic solvents such as methylene chloride, chloroform and THF. The molecular weight of the polymer was analyzed by gel permeation chromatography (GPC) relative to polystyrene standards, which showed $M_w = 10{,}400$ and $M_n = 4{,}500$ (PDI = 2.3). The UV spectrum of **6** in methylene chloride showed λ_{max} 302 (sh, $\varepsilon = 4{,}100$) and 246 ($\varepsilon = 15{,}100$) nm. The longest wavelength absorption of the polymer matches with that calculated for *p*-hydroxyphenylacetylene,[17] consistent with the expected absence of extended conjugation along the polymer chain of 1,3-linked polyphenylenes. In the IR spectrum of **6**, a strong and broad OH stretch at 3393 cm^{-1} appeared with the disappearance of the original ester stretch at 1762 cm^{-1}. A broad absorption was observed at ~1700 cm^{-1} probably due to partial oxidation of the polymer. Both the ^1H and ^{13}C NMR spectra of the polymer displayed well-defined alkyl signals. However, the aromatic (δ 110.0–155.0) and alkynyl (δ 79.7 and 88.8) carbon signals in the ^{13}C NMR spectrum were broad and weak.



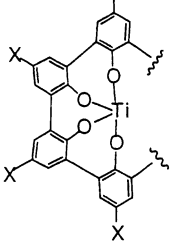
Scheme 1. Synthesis of an *ortho*-phenol polymer.



Scheme 2. Reaction of phenylacetylene with benzaldehyde catalyzed by polymer **6** and Ti(O^{i}Pr)$_4$.

As an example to explore the application of the *ortho*-phenol polymer in catalysis, we have studied the titanium(IV)-based Lewis acid-catalyzed alkynylzinc addition to aldehydes.[18] This reaction is very useful for the synthesis of propargyl alcohols that are versatile precursors to many organic compounds of biological significance. In this reaction, an alkynylzinc intermediate is generated from the reaction of a terminal alkyne with diethylzinc, which then undergoes nucleophilic addition to aldehydes in the presence of Lewis acids.[18a,b] In our experiment, a polymeric titanium complex based on **6** was prepared which was used to catalyze the reaction of phenylacetylene with benzaldehyde in the presence of diethylzinc to generate 1,3-diphenyl-2-propynol (**7**) (Scheme 2). Polymer **6** was first treated with Ti(O^{i}Pr)$_4$ in THF, and then combined with phenylacetylene, diethylzinc, and benzaldehyde at room temperature. It was found that the catalytic activity of the polymer–Ti complex generated from the reaction of **6** with 1/4 equivalent (relative to the polymer phenol unit) of Ti(O^{i}Pr)$_4$ is much higher than the polymer–Ti complex generated from the reaction with excess Ti(O^{i}Pr)$_4$.[19] In the presence of 20 mol% (the phenol unit of the polymer relative to benzaldehyde) of the polymer and 5 mol% of Ti(O^{i}Pr)$_4$, **7** was obtained in 71% isolated yield after 80 h at room temperature. However, under the same conditions, in the presence of 20 mol% of polymer **6** and 100 mol% of Ti(O^{i}Pr)$_4$, the yield of **7** was only 16%. Without Ti(O^{i}Pr)$_4$ and/or without the polymer, similar low yields of **7** were observed.

In order to explain the observed dramatic reactivity difference between the use of small and excess amounts of Ti(O^{i}Pr)$_4$, we propose that when polymer **6** was treated with 1/4 equiv. of Ti(O^{i}Pr)$_4$, the polymeric complex **8** that contains tetradentate aryloxy coordinated Ti sites might have been generated. Such tetradentate complex may have higher catalytic activity than the monodentate Ti complex **9** generated from the reaction of the polymer with excess Ti(O^{i}Pr)$_4$. A similar but chiral tetradentate aryloxy coordinated Ti complex was found by Yamamoto and co-workers to be a very efficient Lewis acid catalyst.[20] Besides as a very interesting polymeric ligand for catalysis, the highly functionalized *ortho*-phenol polymer is also potentially useful for electrical and optical applications.



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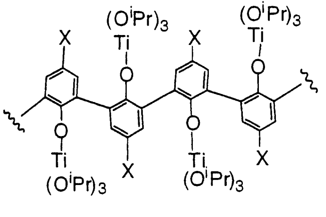

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X = n-C$_6$H$_{13}$—≡

Acknowledgements

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15. Preparation and characterization of monomer **5**: Under nitrogen, a solution of 1-octyne (1.525 mL, 10.32 mmol) in THF (10 mL) and freshly distilled triethylamine (20 mL) were syringed into a 50 mL dried Schlenk flask charged with $Pd(PPh_3)_2Cl_2$ (604 mg, 0.86 mmol), copper(I) iodide (164 mg, 0.86 mmol) and tetrabromide **4** (2.520 g, 4.30 mmol). After the reaction mixture was heated at reflux for 20 h, it was diluted with THF at room temperature, filtered through a pad of Celite, concentrated and dissolved in CH_2Cl_2. The CH_2Cl_2 solution was then washed with 1N HCl and brine, dried over Na_2SO_4 and concentrated under vacuum. Flash chromatography of the residue on silica gel using hexane/ethyl acetate as eluent gave **5** as a white solid in 66% yield (1.820 g). Mp 85–86°C; IR (KBr, cm^{-1}) 2951 (s), 2926 (s), 2857 (s), 2228 (w), 1762 (s), 1445 (s), 1367 (s), 1187 (s), 1017 (m), 905 (m), 876 (m). ^1H NMR (300 MHz, $CDCl_3$) δ 0.90 (t, $J=6.6$ Hz, 6H), 1.23–1.48 (m, 12H), 1.53–1.62 (m, 4H), 2.10 (s, 6H), 2.38 (t, $J=6.6$ Hz, 4H), 7.22 (d, $J=1.8$ Hz, 2H), 7.65 (d, $J=1.8$ Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.27, 19.53, 20.60, 22.73, 28.68, 28.77, 31.52, 78.30, 92.87, 117.14, 123.78, 131.75, 133.37, 136.23, 145.44, 167.84. APCI-MS m/z: $M+H^+$ peaks at 643, 645 and 647 with a 1:2:1 ratio indicate a dibromide.
16. Preparation and characterization of polymer **6**: Under nitrogen, a mixture of **5** (322 mg, 0.50 mmol), 2,2′-bipyridine (117 mg, 0.75 mmol), bis(1,5-cyclooctadiene)nickel(0) (172 mg, 0.63 mmol), 1,5-cyclooctadiene (212 μL, 1.73 mmol) was added DMF (8 mL). After the mixture was stirred at 70–75°C for 36 h, it was diluted with CH_2Cl_2 at room temperature, washed with 1N HCl and brine and dried over Na_2SO_4. The solution was concentrated and precipitated with MeOH. Centrifugation and filtration gave a solid, which was re-dissolved in CH_2Cl_2 and precipitated with MeOH again. The resulting solid was dried under vacuum to give a polymer as a brown powder (166 mg). GPC showed $M_w=18{,}000$ and $M_n=8{,}700$ (PDI = 2.1). This polymer was then dissolved in THF, combined with aqueous KOH (2 M), and heated at reflux for 24 h. The resulting mixture was acidified with 1N HCl, extracted with CH_2Cl_2, washed with water and dried over Na_2SO_4. The solution was concentrated under vacuum, and precipitated with MeOH. After centrifugation and filtration, polymer **6** was obtained as a brown solid in 62% yield. IR (KBr, cm^{-1}) 3393 (br s), 2954 (s), 2929 (s), 2857 (s), 2229 (w), 2190 (w), ~1700 (br, m), 1596 (m), 1465 (s), 1233 (br, s). ^1H NMR (300 MHz, $CDCl_3$) δ 0.88 (br, 6H), 0.96–1.70 (m, br, 16H), 2.37 (br, 4H), 3.45 (br, 2H), 6.82–7.82 (m, br, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.8, 19.2, 22.4, 28.6, 29.5, 31.3, 79.7 (br), 88.8 (br), 110.0–155.0 (br, weak peaks).
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19. Experimental procedure for the catalysis: Under nitrogen, $Ti(O^iPr)_4$ (4 μL, 5 mol%) was added via a syringe to a solution of polymer **6** (10 mg, 20 mol%) in freshly distilled THF (1.0 mL) at room temperature. The mixture was stirred for about 10 min and was then slowly added into a 10 mL Schlenk flask containing a solution of phenylacetylene (34 μL, 0.31 mmol), diethylzinc (32 μL, 0.31 mmol) in THF (2.0 mL). After the homogenous solution was stirred at room temperature for 30 min, benzaldehyde (26 μL, 0.25 mmol) was added via a syringe. The stirring continued and the reaction progress was monitored by TLC. After 80 h, the reaction was quenched with 1N HCl (1.5 mL). The resulting mixture was then diluted with CH_2Cl_2, washed with water and dried over Na_2SO_4. The solvent was removed under vacuum, and the residue was purified by column chromatography on silica gel using hexane/ethyl acetate as eluent to give pure **7** in 71% yield (37 mg). When 1.0 equiv. (relative to benzaldehyde) of $Ti(O^iPr)_4$ was used, the reaction gave only 16% yield of **7** under the above conditions.
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