

Communications to the Editor

In Aqua Synthesis of Water-Soluble Poly(*p*-phenylene) Derivatives

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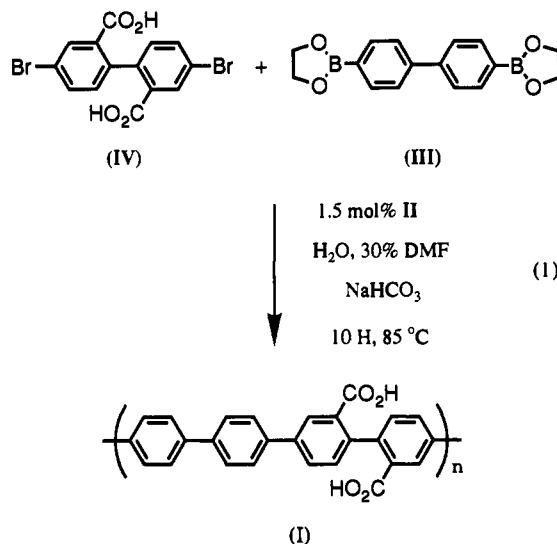
Aromatic, rigid-rod polymers play an important role in a number of diverse technologies including high-performance engineering materials,² conducting polymers,³ and nonlinear optical materials.⁴ The synthesis of these interesting macromolecules has been historically difficult and will face additional challenges in the coming decades as the design of superior materials, which may be synthesized and processed entirely under environmentally acceptable conditions, gains importance.⁵ It has been our goal to develop routes to soluble, rigid-rod polymers that can be synthesized and processed in water without the use of highly toxic and corrosive solvents. In this communication, we report the homogeneous, in aqua preparation of a structurally well defined, rigid-rod, poly(*p*-phenylene) derivative using a water-soluble palladium(0) catalyst.

Several well-known biological examples of water-soluble rodlike polymers exist, notably double-stranded DNA⁶ and xanthan.⁷ By comparison, synthetic water-soluble, rigid-chain polyelectrolytes are essentially unknown in the literature.⁸ To the best of our knowledge, no previous example of an aqueous, one-step synthesis of a soluble rigid-chain polyelectrolyte has been reported.

Rigid-chain polymers are typically difficult to synthesize, process, and characterize due to their intractability. This problem has been addressed in a number of ways, none of them without troubling aspects.⁹ High molecular weight rigid-chain polymers

possessing weakly basic functionalities (poly(*p*-phenyleneterephthalamide¹⁰ (PPTA; Kevlar), poly(*p*-phenylenebenzobisoxazole¹¹ (PBO), etc.) are only soluble in neat strong acids. Rigid-chain polymers bearing bulky substituents tend to be soluble in common organic solvents;¹² in these cases, however, solubility comes at the price of increased synthetic difficulty and inferior physical properties.¹³

We have prepared poly(*p*-quaterphenylene-2,2'-dicarboxylic acid) (I) by an adaptation of a Pd(0) cross coupling of boronic acids and aryl halides¹⁴ (eq 1). Following its synthesis, polymer I is readily isolated by addition of dilute hydrochloric acid to yield the free acid form as a golden solid. While the free acid is completely insoluble in all common organic solvents, I may be dissolved in dilute aqueous base as its sodium, potassium, or triethylammonium salt. We note that, in contrast to these monovalent cations, addition of divalent magnesium or zinc salts causes immediate precipitation of I to yield solvent and water-resistant, insoluble films. Concentrated solutions of I (>5% w/v) can be prepared in basic aqueous dimethylformamide (75:25, water/DMF). Liquid crystallinity has not yet been observed in solutions of I; however, thin films cast from concentrated solutions of I are highly birefringent, confirming the polymer's anisotropic structure.



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The successful preparation of high molecular weight rigid-rod polymers via step-growth processes requires that the growing polymer chains remain soluble during all stages of the polymerization. (Poly(*p*-phenylene), being the quintessential rigid rod, is a completely intractable material that precipitates as an oligomer

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when synthesized by classical methods.)¹⁵ Therefore, the synthesis of a water-soluble, high molecular weight polymer requires converting all reaction components, catalyst as well as monomers, into water-soluble species. To this end, a water-soluble zerovalent palladium catalyst (PdL₃, L = P(C₆H₅)₂(*m*-C₆H₄SO₃Na) (II)) was prepared from PdCl₂ and monosulfonated triphenylphosphine¹⁶ by an adaptation (see supplementary material) of Coulson's method for the synthesis of tetrakis(triphenylphosphine)palladium.¹⁷ Complex II proved to be identical with the catalyst reported by Calabrese.¹⁸ The ethylene glycol diester of 4,4'-biphenylenebis(boronic acid) (III) served as one water-soluble monomer precursor (rapid hydrolysis of the water-insoluble III affords the sparingly soluble bis(boronic acid) hydroxyl adduct), while 4,4'-dibromodiphenic acid (IV) served as the second. Both monomers were prepared by modifications of known literature syntheses and were fully characterized.^{19,20} The dibromide IV was chosen as a synthetic target after model studies revealed that Pd(0) cross couplings under homogeneous aqueous conditions exhibit a strong regiochemical limitation: Coupling of bromobenzoic acids and tolylboric acid proceeds readily and in essentially quantitative yield (as determined by ¹H NMR) for *m*-bromobenzoic acid, but gave no identifiable product for *o*-bromobenzoic acid.

Polymer I has been characterized by a number of techniques in order to confirm its composition, structure, and molecular weight.²¹ NMR analysis of I is complicated by extreme peak broadening: The ¹H NMR spectrum (D₂O/NaOD) shows a broad resonance with secondary peaks from 6.0 to 8.2 ppm. The ¹³C NMR spectrum consists of six broad resonances (width at half-height 2-3 ppm). The 11 individual resonances expected for I are apparently concealed by significant overlap. The IR (KBr pellet) spectrum displays expected bands at 3500-3100 cm⁻¹ and 1709 cm⁻¹ and a number of bands from 900 to 700 cm⁻¹ associated with aromatic C-H out-of-plane bending modes of di- and tri-substituted benzenes.²²

Polymer I exhibits the outstanding thermal stability typically found in rigid-chain polymers:²³ Thermogravimetric analysis (under N₂) shows the onset of thermal decomposition above 520 °C, while differential scanning calorimetry shows no apparent softening temperature. Both methods indicate that I undergoes dehydration at 300-330 °C to form a poly(anhydride) structure; this process has been confirmed by IR spectroscopy.²⁴

Poly(acrylamide) gel electrophoresis²⁵ of I gives an approximate molecular weight (*M_w*) of 50 000 g/mol relative to single-stranded DNA. In the absence of an absolute reference, it is unreasonable to expect this method to give an accurate molecular weight, since I is much more rigid than single-stranded DNA. Thus, this result is best taken as an order-of-magnitude estimate. Viscometry experiments (standard Ubbelohde viscometers; identical results with different capillary diameters indicate that flow-induced shearing is not a significant complication²⁶) yield an intrinsic viscosity of 0.49 dL/g for I in 0.100 M Na₂CO₃. A solution viscosity of 1.9 cP for a 1% solution of I in 0.1 M Na₂CO₃ compares favorably with a reported viscosity for a 10% aqueous solution of 45% sulfonated PPTA of 3 cP.^{8a}

Current work is directed at determining the absolute molecular weight of I and at extending this aqueous coupling strategy to a number of monomer substrates to provide a host of architecturally diverse polymers ranging from rigid rods to flexible chains.

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Supplementary Material Available: Experimental procedures for the syntheses of water-soluble Pd complex II and polymer I, ¹H and ¹³C NMR and IR spectra of I, IR spectrum of dehydrated polymer, and TGA trace of I (5 pages). Ordering information is given on any current masthead page.

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The Intramolecular Salt Effect. An Acrylate Ester Bearing an Ion Pair Shows Enhanced Rates and Stereoselectivity in a Nitron Cycloaddition¹

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Understanding the effects that a nearby (4-25 Å) ion pair can exert on reaction processes will have practical applications in the area of chemical synthesis and will help to illuminate the necessary and sufficient components of biocatalysis. Here we show that in chloroform an acrylate ester tethered to an ion pair reacts faster than comparable neutral acrylates. Importantly, the three major diastereomeric pathways in this nitron cycloaddition differ in sensitivity to this intramolecular salt effect.³ The charged acrylate is both more reactive and more selective than its neutral congeners.

The effects of salts on ionization rates of organic substrates in nonpolar solvents have been studied for many years.⁴ Simple salt effects are due to the Coulombic effects of ion pairs on the reactants and transition states of ionic processes, and a quantitative model of these effects has been proposed.^{5,6} Effects of unreactive

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(21) ¹H NMR (500 MHz): δ = 6.38, 6.75, 7.01, 7.30, 7.68, 8.07 (all br). ¹³C NMR (125 MHz): δ = 128, 129, 130, 139.5, 141, 179 (all br). Elemental anal. Expected for (C₁₃H₉O₂)_n: C, 79.58; H, 4.07. Found: C, 77.55; H, 4.31. (Poly(*p*-phenylenes) reported in the literature do not yield clean combustion analyses. (See refs 3 and 12b.) This has been attributed to difficulties in burning these materials quantitatively. Impurities and residual end-groups on oligomeric species have also been implicated. I leaves detectable residues in both combustion analysis and thermogravimetric analysis. Additionally, it has proven to be extremely difficult to remove trace amounts of water from I.

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(24) Disappearance of the OH stretch; replacement of the broad carbonyl stretch by a ragged, intense anhydride carbonyl stretching band at 1708 cm⁻¹; and considerable disturbance of both aromatic in-plane skeletal deformation modes (1400-1500 cm⁻¹) and aromatic C-H out-of-plane bending modes (900-700 cm⁻¹) are observed.

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