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IN *AQUA* SYNTHESIS OF A HIGH MOLECULAR WEIGHT ARYLETHYNYLENE POLYMER EXHIBITING REVERSIBLE HYDROGEL PROPERTIES

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Key Words: Poly(aryleneethynylene), Hydrogel, Palladium Copolymerization, Aqueous Media

ABSTRACT

A high molecular weight poly(aryleneethynylene) ($M_w \sim 60{,}000$) is prepared by the palladium catalyzed copolymerization of 3,5-diiodobenzoic acid and acetylene gas in a basic aqueous medium. The polymer has a "zig-zag", fully conjugated backbone. The

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polymer has been characterized by a variety of methods and exhibits high thermal stability. Furthermore, the polymer is readily soluble in aqueous base and is reversibly switchable from the solution state to a hydrogel state, in water, by changing the pH of the solvent.

INTRODUCTION

Poly(aryleneethynylene)s [1] (PAEs) compose one important class of highly conjugated polymers exhibiting photoluminescence [2], electrical conductivity [3], and non-linear optical [4] properties. These polymer systems have also been observed to demonstrate exceptionally high fluorescence quantum yields in comparison to other highly conjugated polymers [5]. Such properties render PAEs as useful tools for the construction of polymer light emitting diodes (polymer LEDs) [6], organic magnetic materials [7], molecular wires and antennas [8], and fluorescence sensors [9]. Recently, it has been shown by Nelson *et al.* that an aryleneethynylene based oligomer mimics protein folding, thus opening the potential that such polymer systems could be used for biological applications [10]. The useful application of PAE materials is often limited by their low solubility in solvents as well as relatively low degrees of polymerization. The increased interest in the properties of poly(aryleneethynylene) type materials has led various groups to attach a series of bulky substituents in an effort to increase solubility in organic solvents [1]. Alternatively, Kondo *et al.* have introduced irregularity into the polymer chain backbone in an effort to increase solubility [11]. However, introducing such structural irregularity may adversely affect the electronic and optical properties of the PAEs. During our studies of aqueous organic reactions [12], and as a part of our continuing interests in preparing aryleneethynylene-type polymers and oligomers [13], we recently reported an efficient synthesis of aryleneethynylene polymers and oligomers through polymerization of aryl halides with acetylene gas in an aqueous medium [14]. However, the prepared polymers suffered from limited solubility and low molecular weights of the soluble fractions. In an effort to address these difficulties, we decided to explore the preparation of water soluble poly(aryleneethynylene)s. Previously, there has been a very limited treatment in the literature regarding the synthesis of water-soluble rigid-chain polyelectrolytes. Two of the more notable advances in this area were presented by Wallow and Novak, who prepared a water soluble poly(p-phenylene) via the Suzuki reaction [15], and a water soluble poly(thiophene) sensor material reported by McCullough *et al.* [16]. Here, we report that the palladium catalyzed copolymerization of 3,5-diiodobenzoic acid (1) and acetylene gas in an aqueous basic medium affords a high molecular weight, "zig-zag" poly(aryleneethyny-lene) [17].

EXPERIMENTAL

General

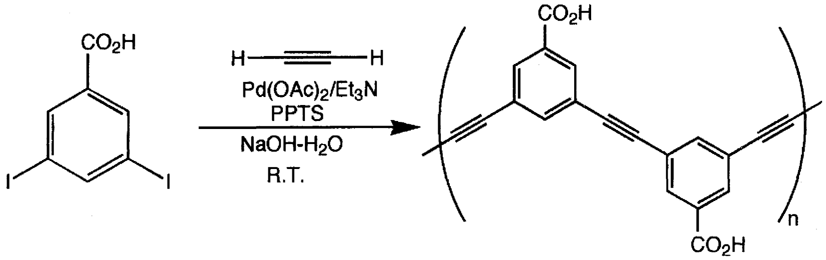
All reagents for this research were commercially available and were used without further purification. NMR analysis was performed on General Electric 400 MHz NMR. UV-VIS analysis was conducted with Hewlett Packard 8452A Diode Array Spectrophotometer utilizing a quartz cell. Thermogravimetric analysis was performed on a TA Instruments Hi-Res TGA 2950 Thermogravimetric Analyzer. DSC measurements were obtained with a TA Instruments DSC 2920 Modulated DSC. Molecular weight was determined on a Hybaid PS 3000P Gel Electrophoresis on agarose gel (1%) at 120 volts. Raman data was determined on a Coherent Ionpure Plasma Tube Innova 70 spectrophotometer with an argon ion laser at 514.5 nm. Infrared analysis was performed on a Mattson Instruments Galaxy Series FT-IR with a KBr pellet.

Poly(m-benzoic acid ethynylene)

In a large test tube, equipped with a magnetic stir bar, palladium acetate (9.4 mg, 0.042 mmol (3 mol%)), tris(*m*-sulfophenyl) phosphine trisodium salt (0.1524 g, 0.27 mmol (20 mol%)), and cuprous iodide (25.7 mg, 0.14 mmol (10 mol%)) are purged under nitrogen for five minutes. Eight mL of deionized water is added and the solution is gently warmed for one minute to generate the palladium catalyst. In a separate 100 mL round bottom flask equipped with a magnetic stir bar, 3,5-diiodobenzoic acid (0.5001 g, 1.34 mmol), previously prepared from 3,5-diaminobenzoic acid according to the method of Wheeler and Johns [18], and triethyl amine (0.4064 g, 4.02 mmol) are combined with 50 mL of 1 N NaOH and purged with nitrogen. Using a cannula, the palladium solution is transferred to the round bottom flask. The flask is then thoroughly purged with acetylene gas. Two balloons of acetylene gas are attached to the system, and the solution is allowed to stir for three days. During the stirring, the balloons are continually replenished with more acetylene gas. After stirring, the solution is filtered, and the flask and solid are washed with 50 mL of 1 N NaOH. The solution is acidified with 1 N HCl, resulting in precipitation of a gelatinous solid. The solid is allowed to settle for an hour, at which time the solid and solution are centrifuged. The solution is decanted, leaving a brown jelly like solid. The solid is lyophilized, resulting in a dark brown solid (0.1172 g, 60.8%).

RESULTS AND DISCUSSION

The starting point for the preparation of the polymer involved preparation of the monomer, 3,5-diiodo benzoic acid. This monomer was prepared according to literature methods [18], with particular attention being paid to the purification of the acid, as the presence of the monohalogenated species in the reaction would be chain terminating and thus counterproductive to our efforts of preparing a high molecular weight polymer. Once purified thoroughly, the monomer was polymerized according to Equation 1. The monomer was reacted with acetylene gas in the presence of a water soluble palladium catalyst, cuprous iodide as a co-catalyst, one equivalent of NaOH and three equivalents of Et_3N in water. The water soluble palladium catalyst was prepared in situ from palladium acetate and tris(*m*-sulfophenyl) phosphine trisodium salt, as used by Casalnuovo and others [19]. After stirring for three days, the polymer was isolated by addition of dilute HCl, giving a dark brown solid in its free acid form. It should be noted that throughout the entire polymerization process, the polymer remained soluble in the reaction medium, which is essential for formation of high molecular weight polymer chains.



(1)

The polymer thus generated has no substantial solubility in the solvents tested except in dilute aqueous NaOH, where it is readily soluble. Upon changing the pH of the NaOH solution to neutral and subsequently acidic, the polymer becomes a hydrogel, which holds water about eight times its weight after centrifuging. While the hydrogel can be obtained by direct treatment of the lyophilized polymer, it often requires considerable time and sonication, thus the

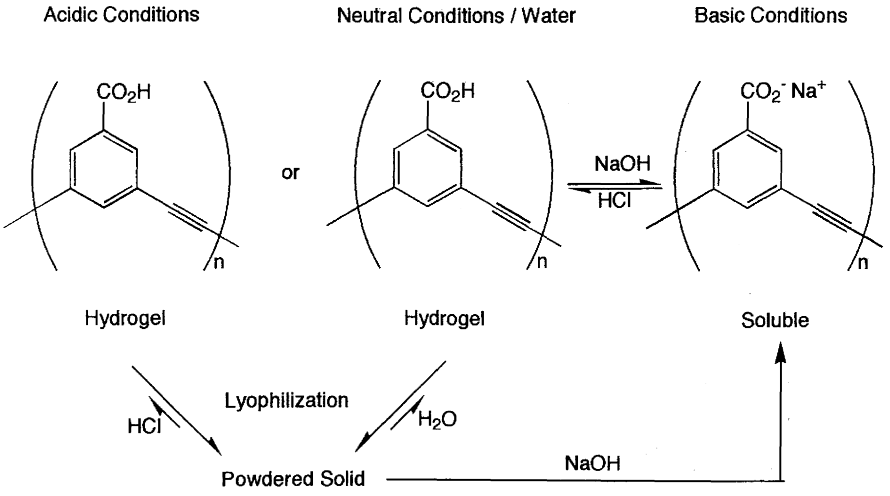


Figure 1. Treatment with NaOH.

gel is much more accessible by treatment with NaOH solution first and subsequent acidification to the desired pH (Figure 1). The ability to reversiblity switch between the water soluble and hydrogel states by changing the pH of the solution renders the polymer a potentially useful material for biomedical and environmental applications [20]. The prepared polymer has been characterized by a variety of methods and further characterizations are still being explored. The two potential types of aromatic protons exhibited extremely broad resonance around 8.2-8.4 ppm in the ^1H spectrum (D_2O-NaOD). The NMR sample is prepared by dissolving some of the polymer in minimal amounts of NaOH solution and repeatedly adding D_2O and lyophilizing the sample to exchange the hydroxide proton with deuterium. The infrared spectrum (KBr pellet) displays typical absorption peaks corresponding to free carboxylic acid (3700-3100 and 1772 cm^{-1}) and aromatic functionality [21]. Absorption due to acetylene stretching (2100-2210 cm^{-1}) was minimal. The Raman spectrum (Figure 2) of the aqueous solution of the corresponding sodium carboxylate salt displayed several peaks in the acetylene region, which has been attributed to the presence of polymers of varying lengths [22]. The molecular weight (M_w = 66,000 g mol^{-1}) was determined by agarose gel electrophoresis relative to double stranded DNA markers [23]. However, as described by Wallow and Novak [15], the determination of molecular weight by gel electrophoresis only provides an approximate molecular weight, not an absolute determination. The inaccuracy is attributed to rigidity of the PAE, compared to DNA, resulting in coagulation and aggregationof the

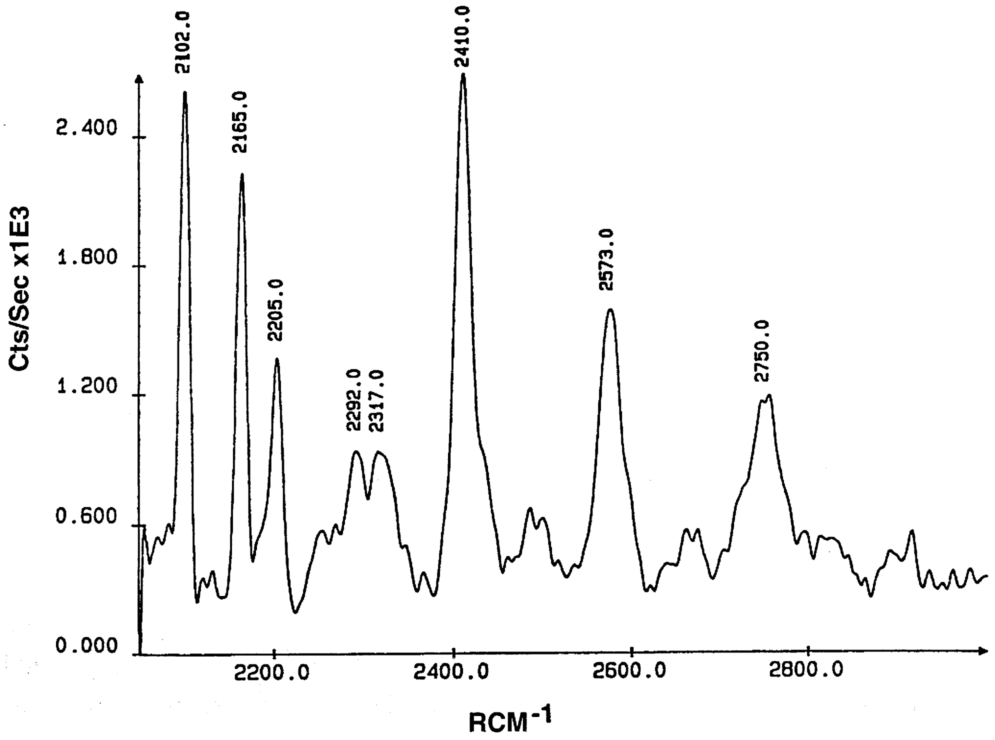


Figure 2. Raman spectrum.

polymer in solution over time. Consequently efforts are currently underway to determine the exact weight by light scattering methods in which the polymer solution is filtered through a fine filter (0.20 μm) and immediately tested. Preliminary results indicate that the M_w is slightly lower, but of the same magnitude as previously calculated, but we are still exploring this avenue and the results will be reported at a later time. The UV-VIS spectrum (0.0048 mg mL^{-1} 1 N NaOH) shows two major bands with absorption maxima at 226 nm and 284 nm respectively (Figure 3). The band at 226 nm is attributed to hydroxide. Thermal gravimetric analysis (TGA) of the polymer showed the the expected high thermal stability, which is common to poly(aryleneethynylene)s [1]. The polymer shows good stability up to about 300°C, while showing a one stage degradation with an onset of decomposition around 400°C (Figure 4). Differential scanning calorimetry (DSC) measurements show an endotherm at 100°C, which may be due to removal of adsorbed water (Figure 5).

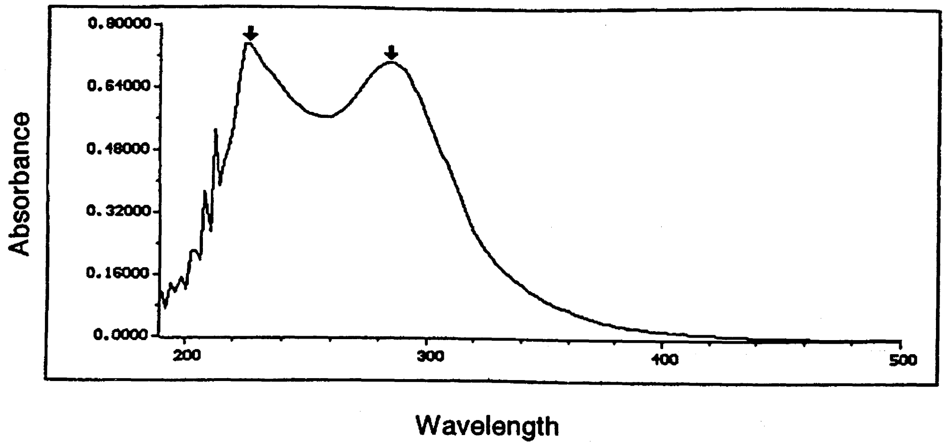


Figure 3. UV-Vis spectrum.

CONCLUSION

A high molecular weight poly(aryleneethynylene) polymer has been prepared through the palladium catalyzed copolymerization of 3,5-diiodobenzoic acid and acetylene gas in a basic aqeous medium. The polymer has a "zig-zag"

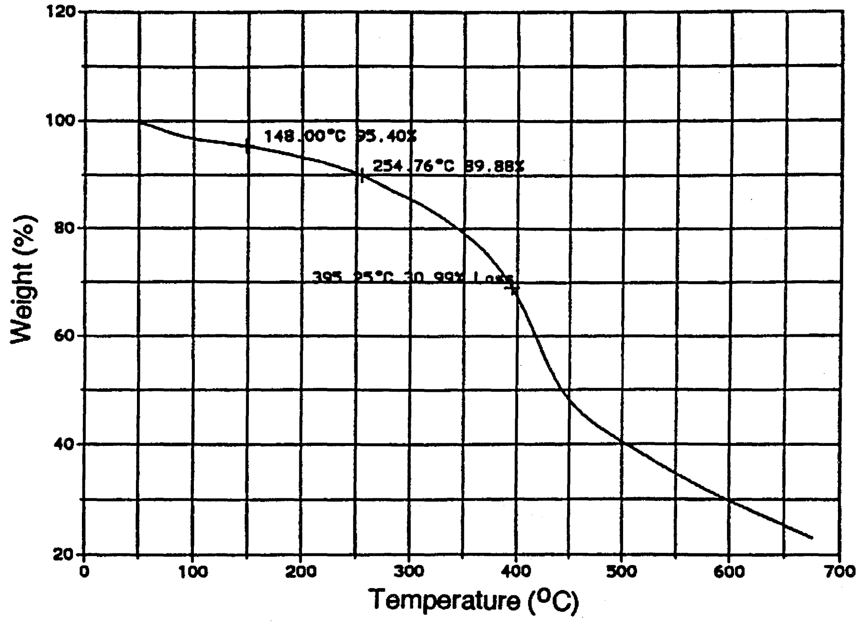


Figure 4. Thermogravimetric analysis.

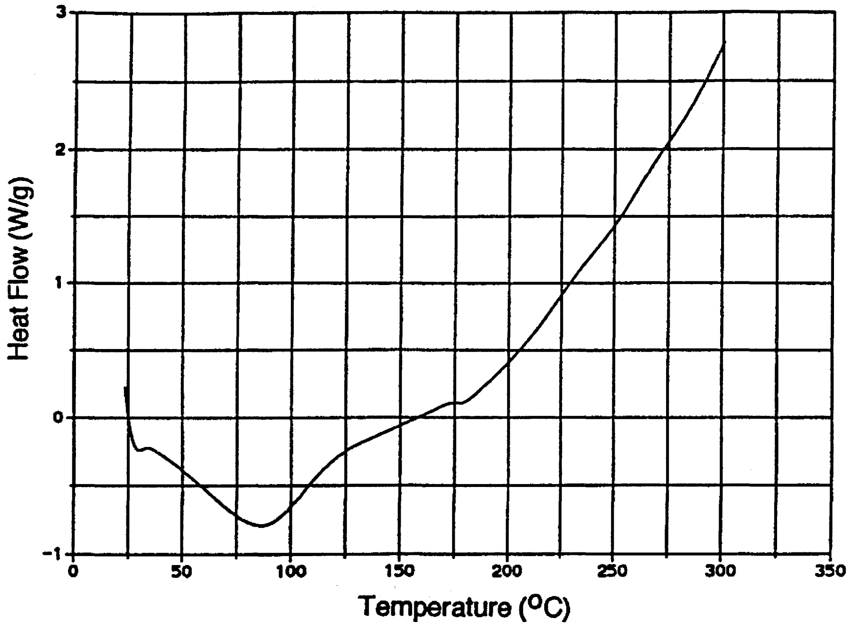


Figure 5. Differential scanning calorimetry.

main chain. The typical lack of solubility, characteristic of poly(aryleneethynylene)s, is overcome by the introduction of a hydrophillic side chain that renders the polymer readily soluble in aqeous base. The polymer exhibits reversible hydrogel properties by changing the pH of the solution; in aqeous base the polymer is soluble and upon changing the pH to neutral and subsequently acidic, a hydrogel forms. The hydrogel state holds water approximately eight times the sample weight. In the dry solid state, the polymer has high thermal stability, characteristic of other PAE systems. Current efforts are being directed at determining the absolute molecular weight as well as preparing related polymer systems based on the benzoic acid moiety.

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