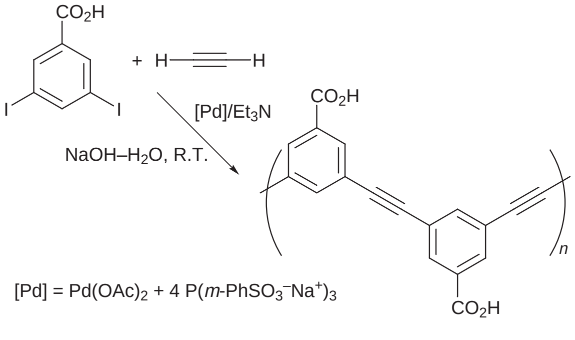
In aqua synthesis of a high molecular weight arylethynylene polymer with reversible hydrogel properties

Chao-Jun Li,*[a]† William T. Slaven IV,[a] Yi-Ping Chen,[b] Vijay T. John[c] and Suguna H. Rachakonda[c]

[a] *Department of Chemistry, Tulane University, New Orleans, LA 70118, USA*
[b] *Department of Cell and Molecular Biology, Tulane University, New Orleans, LA 70118, USA*
[c] *Department of Chemical Engineering, Tulane University, New Orleans, LA 70118, USA*

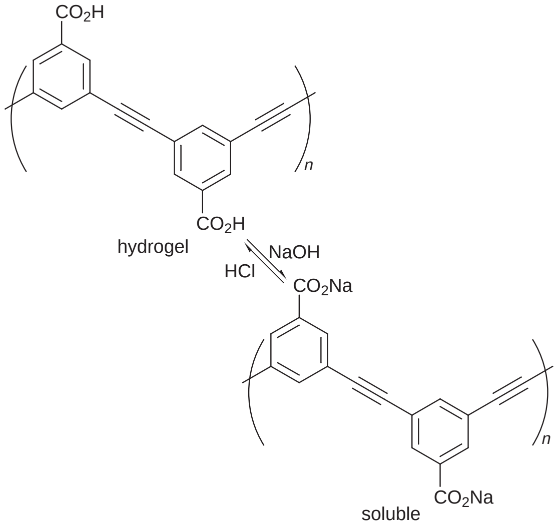
Palladium catalyzed copolymerization of 3,5-diiodobenzoic acid with acetylene gas in a basic aqueous medium provides a high molecular weight (~ 60 000), zig-zag phenylethynylene polymer; the polymer has been characterized by a variety of methods and has a high thermostability, is soluble in basic solutions and is reversibly switchable from soluble to hydrogel states in water by changing the pH of the solvent.

Poly(arylethynylene)[1] is an important class of conjugated polymer exhibiting properties such as photoluminescence,[2] electronic conductivity[3] and non-linear optical properties.[4] These polymers also exhibit exceptionally high quantum yields of fluorescence in comparison to other conjugated polymers.[5] Such properties render the polymer useful for applications in constructing polymer light emitting diodes (polymer LEDs),[6] organic magnetic materials,[7] molecular wires and antennas[8] and fluorescence sensors.[9] Recently, Nelson *et al.* have also shown that an arylethynylene-based oligomer mimics protein folding, which has exciting potential for biological applications.[10] However, the potential applications of these materials for electronic and optical purposes are often limited by their low solubility and low degree of the polymerization. The increased interest in the properties of polyarylethynylene-type materials has led to the attachment of various bulky substituents by various groups to increase their solubility in organic solvent.[1] Alternatively, Kondo *et al.* introduced irregularity in the polymer chain to increase their solubility and degree of polymerization.[11] However, the structural irregularity may also change its electronic and optical properties. During our studies of aqueous organic reactions,[12] and as part of our continuing interests in synthesizing arylethynylene-type polymers and oligomers,[13] we recently reported an efficient synthesis of arylethynylene polymer and oligomers through polymerization of aryl halides with acetylene gas in an aqueous medium.[14] However, the polymers that we generated had the same limitation of insolubility and low molecular weight. In an attempt to overcome these difficulties, we decided to explore the synthesis of water-soluble polyarylethynylenes. Here we report that the palladium catalyzed copolymerization of 3,5-diiodobenzoic acid with acetylene gas in a basic aqueous medium provides a high molecular weight, zig-zag arylethynylene polymer [eqn. (1)] which can be processed readily.



(1)

Previously, there has been a very limited study of the synthesis of water-soluble rigid-chain polyelectrolytes in the literature. The more noticeable advance in this area was the synthesis of a water-soluble poly(*p*-phenylene) reported by Wallow and Novak through the Suzuki reaction,[15] and a water-soluble poly(thiophene) sensor material reported by McCullough *et al.*[16] In the present investigation, the polymerization was carried out by reacting 3,5-diiodobenzoic acid with acetylene gas in the presence of a water-soluble palladium catalyst, cuprous iodide as a co-catalyst, 1 equiv. NaOH and 3 equiv. Et_3N in water. The water-soluble palladium catalyst was generated *in situ* from palladium acetate and tris(*m*-sulfophenyl)phosphine trisodium salt, as used by Casalnuovo and others.[17] The monomer used in the present study was prepared according to literature procedure.[18] After stirring the reaction mixture for three days at room temperature, the polymer was readily isolated by addition of dilute HCl, giving a dark brown solid in its free acid form. The polymer thus generated has no substantial solubility in all other solvents tested except in dilute aqueous NaOH solution. On the other hand, the polymer is readily soluble in dilute NaOH. Under neutral or slightly acidic conditions, the polymer becomes a hydrogel which holds water about eight times of its original weight after centrifuging. It can be reversibly transformed into the water-soluble and hydrogel states by changing the pH of the medium [eqn. (2)], which has potential biomedical and environmental applications.[19] It should be noted that throughout the polymerization process, the polymer remained soluble in the reaction medium, which is essential for the formation of high molecular weight polymers.



(2)

The polymer thus generated has been characterized by a number of methods. The two potential types of aromatic hydrogens exhibited a broad resonance around 8.2–8.4 ppm in the ^1H NMR spectrum (D_2O–NaOD). The IR (KBr pellet) spectrum displays typical absorption peaks corresponding to free carboxylic acid (3700–3100 and 1772 cm^{-1}) and aromatic functionality.[20] Absorption due to the acetylene stretch vibration (2100–2210 cm^{-1}) is insignificant. Raman spectroscopy of the aqueous solution of the corresponding sodium carboxylate salt showed several absorption peaks in the acetylene region, indicating the presence of polymers with different lengths.[21] The UV–VIS spectrum shows two major bands with absorption maxima at 210 and 288 nm respectively. The molecular weight (M_w = 66 000 g mol^{-1}) of the polymer was determined by agarose gel electrophoreses relative to double-stranded DNA markers.[22] Trace amounts of even higher molecular weight polymers were also observed. Thermogravimetric analysis (TGA) of the polymer showed the expected high thermal stability of common poly(arylethylene)s.[1] The polymer is stable up to 300 °C. It exhibited a one stage degradation with an onset decomposition at *ca.* 400 °C. Differential scanning calorimetry (DSC) measurements show an endotherm at 100 °C which may be due to removal of adsorbed water.

In conclusion, we have developed a simple process for obtaining high molecular mass poly(arylethylene)s. The polymer shows hydrogel properties in its carboxylic form and is reversibly switchable from water-soluble to hydrogel states. Presently, we are evaluating the potential applications of such water-soluble arylethynylene polymers.

Support of this research was provided in part by the Center of Bioenvironmental Research (DOD) and the Center for Photoinduced Processes (NSF-LEQSF). We thank the reviewers for their valuable comments. C. J. L. is an NSF CAREER Awardee (98-02).

Notes and References

† E-mail: cjli@mailhost.tcs.tulane.edu

1 For an excellent review on the synthesis and properties of poly(arylethynylene)s, see: R. Giesa, *J. Macromol. Sci., Rev. Macromol. Chem. Phys.,* 1996, C**36**, 631.

2 T. Yamamoto, M. Takagi, K. Kizu, T. Maruyama, K. Kubota, H. Kanbara, T. Kurihara and T. Kaino, *J. Chem. Soc., Chem. Commun.,* 1993, 797.

3 M. V. Lakshmikantham, J. Vartikar, K. Y. Jen, M. P. Cava, W. S. Huang and A. G. MacDiarmid, *Am. Chem. Soc., Polym. Prepr.,* 1983, **24**, 75; M. Tateishi, H. Nishihara and K. Aramaki, *Chem. Lett.,* 1987, 1727.

4 R. H. Baughman, J. L. Bredas, R. R. Chance, R. L. Elsenbaumer and L. W. Shacklett, *Chem. Rev.,* 1982, **82**, 209.

5 A. P. Davey, S. Elliott, O. O'Conner and W. Blau, *J. Chem. Soc., Chem. Commun.,* 1995, 1433.

6 D. D. C. Bradley, *Adv. Mater.,* 1992, **4**, 756; Q. X. Ni, L. S. Swanson, P. A. Lane, J. Shinar, Y. W. Ding, S. Ljadimaghsoodi and T. J. Barton, *Synth. Met.,* 1992, **49**–**50**, 447; L. S. Swanson, J. Shinar, Y. W. Ding and T. J. Barton, *ibid,* 1993, **55**–**57**, 1.

7 Y. Miura and Y. Ushitani, *Macromolcules,* 1993, **26**, 7079.

8 For a recent review, see: J. M. Tour, *Chem. Rev.,* 1996, **96**, 537. For representative examples, see: J. Zhang, J. S. Moore, Z. Xu and R. A. Arguirre, *J. Am. Chem. Soc.,* 1992, **114**, 2273; R. W. Wagener and J. S. Lindsey, *J. Am. Chem. Soc.,* 1994, **116**, 9759; J. S. Schumm, D. L. Pearson and J. M. Tour, *Angew. Chem., Int. Ed. Engl.,* 1994, **33**, 1360.

9 Q. Zhou and T. M. Swager, *J. Am. Chem. Soc.,* 1995, **117**, 7017; T. M. Swager, C. J. Gil and M. S. Wrighton, *J. Phys. Chem.,* 1995, **99**, 4886.

10 J. C. Nelson, J. G. Saven, J. S. Moore and P. G. Wolynes, *Science,* 1997, **277**, 1793.

11 K. Kondo, M. Okuda and T. Fujitani, *Macromolecules,* 1993, **26**, 7382.

12 C. J. Li, *Chem. Rev.,* 1993, **93**, 2023; C. J. Li, *Tetrahedron,* 1996, **52**, 5643; C. J. Li and T. H. Chan, *Organic Reactions in Aqueous Media,* Wiley, New York, 1997.

13 C. J. Li, D. Wang and W. T. Iv, Slaven, *Tetrahedron Lett.,* 1996, **37**, 4459; D. Wang, T. J. Liu, C. J. Li and W. T. Iv. Slaven, *Polym. Bull.,* 1997, **39**, 265; T. J. Liu, D. Wang, F. L. Bai, C. J. Li and W. T. Iv. Slaven, *Chin. J. Polym. Sci.,* in the press.

14 C. J. Li, W. T. Iv. Slaven, V. T. John and S. Banerjee, *Chem. Commun.,* 1997, 1569.

15 T. I. Wallow and B. M. Novak, *J. Am. Chem. Soc.,* 1991, **113**, 7411; see also references cited therein for other examples.

16 R. D. McCullough, P. C. Ewbank and R. S. Loewe, *J. Am. Chem. Soc.,* 1997, **119**, 633.

17 A. L. Casalnuovo and J. C. Calabrese, *J. Am. Chem. Soc.,* 1990, **112**, 4324. For other examples, see: M. Safi and D. Sinou, *Tetrahedron Lett.,* 1991, **32**, 2025; J. P. Genet, E. Blart and M. Savignac, *Synlett,* 1992, 715; N. A. Bumagin, V. V. Bykov and I. P. Beletskaya, *Russ. J. Org. Chem.,* 1995, **31**, 348; Z. Jiang and A. Sen, *Macromolecules,* 1994, **27**, 7215.

18 H. L. Wheeler and C. O. Johns, *Am. Chem. J.,* 1910, **43**, 398.

19 P. G. de Gennes, in *Physical Properties of Polymeric Gels,* ed. J. P. C. Addad, Wiley, Chichester, 1996; A. S. Hoffman, in *Polymer Gels, Fundamentals and Biomedical Applications,* ed. D. DeRossi, K. Kajiwara, Y. Osada and A. Yamauchi, Plenum Press, New York, 1991, p. 289–297.

20 R. M. Silverstein, G. C. Bassler and T. C. Morrill, *Spectrometric Identification of Organic Compounds,* Wiley, New York, 5th edn., 1991.

21 M. Moroni, J. L. Moigne and S. Luzzati, *Macromolecules,* 1994, **27**, 562.

22 J. Sambrook, E. F. Fritsch and T. Maniatis, *Molecular Cloning: A Laboratory Manual,* Cold Spring Harbor Laboratory Press, New York, 2nd edn., 1989.

Received in Columbia, MO, USA, 29th January 1998; 8/00843D