

Palladium catalysed polymerization of aryl diiodides with acetylene gas in aqueous medium: a novel synthesis of areneethynylene polymers and oligomers

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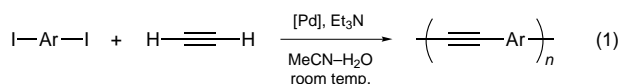
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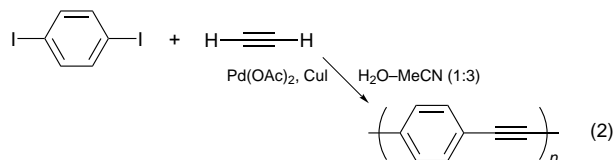
Palladium catalysed copolymerization of aryl iodides with acetylene gas in an aqueous medium provides areneethynylene polymers and oligomers.

Poly(areneethynylene) is an important class of conjugated polymer exhibiting properties such as photoluminescence,¹ electronic conductivity and nonlinear optics.² These polymers also exhibit exceptionally high quantum yields of fluorescence in comparison to other conjugated polymers.³ Such properties render the polymers potentially useful for applications in constructing light emitting diodes (polymer LEDs)⁴ and fluorescence sensors.⁵ Previously, areneethynylene polymers and oligomers have been synthesized by the polymerization of aryl dihalides with aryl diacetylenes (requiring multistep syntheses) through Sonogashira coupling.⁶ The reaction also requires the use of triethylamine as solvent and refluxing conditions.

As part of our continuing interest in synthesizing areneethynylene-type polymers and oligomers,⁷ we required a simple and practical method for ready access to these materials. Conceptually, a convenient and economical way of generating these polymers is *via* the copolymerization of aryl dihalides with acetylene gas. During our studies of aqueous organic reactions,⁸ we became interested in synthesizing poly(areneethynylene)s *via* polymerization of aryl halides with acetylene gas in aqueous medium [eqn. (1)].

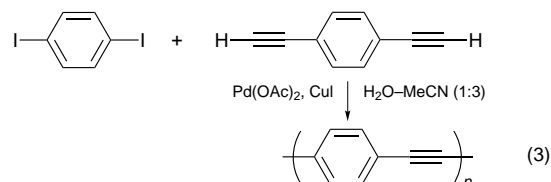


To ensure that the reactants were soluble, a mixture of water–MeCN was used as the reaction solvent. The average molecular weights (M_w and M_n) of the polymer were characterized by gel permeation chromatography (GPC) using polystyrene as standard and THF as the eluent. Thus, 1,4-diiodobenzene was stirred with acetylene gas in a mixture of MeCN and water (3 : 1) in the presence of a catalytic amount of palladium acetate and cuprous iodide, together with 3 equiv. of triethylamine at room temperature. After three days, a dark brown polymeric solid was generated quantitatively [eqn. (2)]. The polymer thus



generated had very low solubility in common solvents, *e.g.* THF, benzene, CH_2Cl_2 . We were unable to determine the molecular weight of this insoluble polymer. However, the molecular weights of the soluble fraction indicate oligomers with $M_n = 828$ and $M_w = 4326$. The polymer generated through this method appears very similar to those prepared by

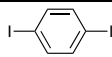
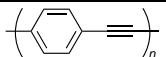
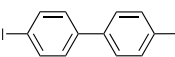
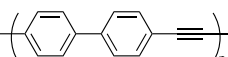
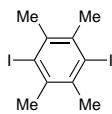
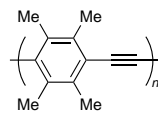
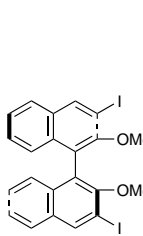
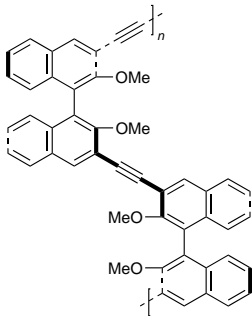
the polymerization of aryl dihalides with aryl diacetylenes [eqn. (3)]. The effectiveness of this preliminary investigation led us



investigate the preparation of other areneethynylene polymers and oligomers by this convenient method. The results are listed in Table 1.⁹

The polymerization of 1,4-diiodo-2,3,5,6-tetramethylbenzene and acetylene gas generated a polymer (yield 51%) which is slightly more soluble in THF than the phenylethynylene polymer. GPC measurement of the soluble portion showed $M_n = 1185$ and $M_w = 3495$. Polymerization of 4,4'-diiodobiphenyl and acetylene gas again generated an insoluble polymer. The soluble, low molecular weight portion

Table 1 Data for areneethynylene polymers and oligomers^a

Entry	Diiodoarene	Polymer (oligomer)	Reaction conditions ^b	M_n/M_w
A			A	828 4326
B			B	504 1291
B			B	1185 3495
C			C	1250 3180

^a All reactions were carried out at room temperature under an atmosphere of acetylene gas. M_n and M_w distributions are based only on the soluble portion of the polymerized material. ^b Reaction conditions: A = Pd(OAc)₂ (5%), PPh₃ (10%), CuI (5%), Et₃N (5 equiv.), 3 days, in MeCN–H₂O (3 : 1); B = Pd(OAc)₂ (5%), PPh₃ (10%), CuI (5%), Et₃N (5 equiv.), 3 days in THF–H₂O (3 : 1); C = Pd(OAc)₂ (5%), P(*m*-PhSO₃Na)₃ (10%), CuI (5%), Et₃N (5 equiv.), 5 days, in THF–MeCN–H₂O (1 : 1 : 2).

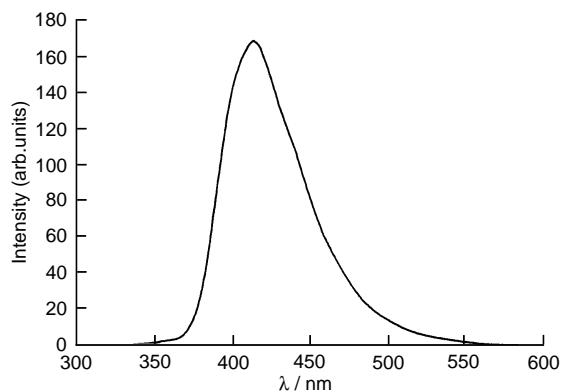


Fig. 1 Fluorescence of the binaphthyl polymer in THF (excitation wavelength = 324 nm)

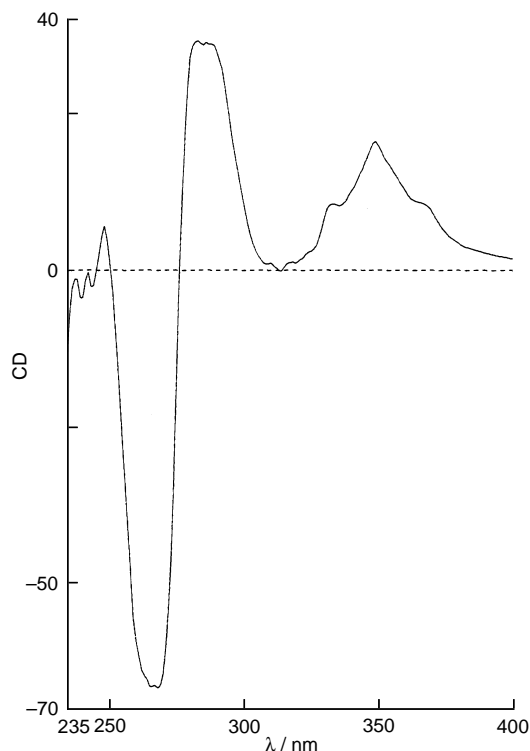


Fig. 2 Circular dichroism spectrum of the binaphthyl polymer

showed $M_n = 504$ and $M_w = 1291$. On the other hand, polymerization of 3,3'-diiodo-2,2'-dimethoxy-1,1'-binaphthyl

and acetylene gas generated a polymer (yield 48%) which is soluble in a variety of common organic solvents (*e.g.* THF, CH_2Cl_2 , CHCl_3). Characterization showed $M_n = 1250$ and $M_w = 3180$, which are similar to those of the corresponding polymer that was prepared *via* the palladium-catalysed Stille reaction¹⁰ by a modified procedure of Cummins¹¹ using bis(tributylstannyl)acetylene in refluxing 1,4-dioxane ($M_n = 1860$ and $M_w = 3200$). The polymer shows a strong fluorescence, which suggests the potential for LED applications. The fluorescence spectrum of the polymer (Fig. 1) shows an emission maxima of 435 nm when excited at 324 nm. Both ^1H and ^{13}C NMR showed significant broadening of all the corresponding peaks. The circular dichroism (CD) spectrum of the polymer in chloroform (Fig. 2) shows a negative Cotton effect at $\lambda = 245$ nm and a positive effect at $\lambda = 277$ nm. Attempts to obtain information about the endgroups of the oligomers *via* MALDI MS were not successful. Further evaluation of the method for synthesis of areneethynylene polymers and oligomers as well as the characterization of the polymers and oligomers is in progress.

Footnotes and References

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