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Acetylene Gas: A Reagent in the Synthesis of High Molecular Weight Poly(*p*-phenyleneethynylene)s Utilizing Very Low Catalyst Loadings

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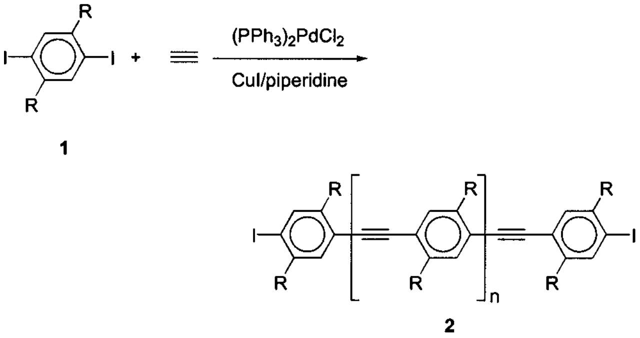
We describe the coupling of diiodobenzenes with acetylene gas as reagent in the efficient Pd-catalyzed synthesis of high-quality poly(*p*-phenyleneethynylene)s (PPEs). Catalyst loadings in the range 0.1−0.2 mol % $(PPh_3)_2PPdCl_2$ are sufficient to afford complete conversion of the starting materials.

PPEs are conjugated polymers of importance as active materials in light-emitting diodes, as sheet polarizers, and as sensory materials in the detection of explosives.[1−3] The PPEs are of high stability and display attractive photophysical behavior in absorption and emission.[4] PPEs are made either by alkyne metatathesis or by the Pd-catalyzed coupling of aromatic diiodides to aromatic diynes.[1,6−9] The Pd-catalyzed reactions have a broad scope, and their experimental setup is facile. However, catalyst loadings are mostly in the range 1−5 mol %, and two monomers, the diiodobenzene and the dialkynylbenzene, have to be synthesized.[1] Only in a few cases acetylene gas has been utilized as reagent in these couplings.[5] The such obtained PPEs were dark brown, suggesting defective polymers to have been formed; structurally intact PPEs are either colorless (*meta*-PPE), bright yellow (dialkyl-PPE), or orange (dialkoxy-PPE). We were able to optimize the process of the Pd-catalyzed coupling of diiodoarenes to acetylene gas that allows an industrial scale synthesis of defect-free PPEs of high molecular weight. In a preliminary experiment, a Schlenk flask of known volume was used to react **1a** with 2 equiv of acetylene gas in the presence of 1 mol % of catalyst $[(PPh_3)_2PPdCl_2]$ and cocatalyst [CuI] in a small volume of piperidine. The oligomer produced was of promising quality in appearance, but of low molecular weight. A set of experiments determined the best solvent to be a 1:1 mixture of toluene and piperidine. Piperidine alone as well as dichloromethane or chloroform as cosolvents gave polymers of low molecular weight. A second set of experiments determined that the optimum molar ratio of diiodobenzene to acetylene gas was between 1.0 and 1.1. Scale-ups based on these stoichiometries utilizing monomer **1a** yielded polymers of exceptionally high quality and high molecular weight.

We found that this approach was not only successful for the synthesis of **2a**,[6] but likewise efficient for the synthesis of dioctyl-PPE **2b**,[7] and to our surprise it also worked well for the synthesis of the dialkoxy-PPEs **2c**,**d**[8] that were obtained in high yields and with a substantial degree of polymerization.[10] We furthermore discovered that we could decrease the amount of Pd catalyst to 0.1 mol % without impeding the catalytic activity of the system. The coupling must be a highly efficient process.

Table 1. Reaction Conditions, Yields, and Properties of PPEs Made with Acetylene Gas



entry	substituent key for **1**, **2**	amt of Pd catalyst (%)	yield of **2** (%)	P_n GPC	M_w/M_n GPC	UV−vis max	emission max
1	**a** ethylhexyl	0.2	87	259	2.7	369	423
2	**a** ethylhexyl	0.1	72	181	3.6	370	423
3	**b** octyl	0.2	56	91	1.8	391	428
4	**b** octyl	0.1	85	127	4.1	389	428
5	**c** hexyloxy	0.2	74	55	1.4	440	471
6	**c** hexyloxy	0.1	63	33	3.2	438	468
7	**d** ethylhexyloxy	0.2	92	316	2.4	460	480
8	**d** ethylhexyloxy	0.1	88	104	3.1	460	480

Polycondensations that involve AA + BB monomers are sensitive toward imbalanced stoichiometry, and while the amount of acetylene gas we utilize is not excessive and according to the known flask volume and the general gas law represents approximately 1.1 equiv, that number can be off by 10−15% to either side. As a consequence, it would be expected that only low molecular weight materials could form. However, this experimental setup is advantageous insofar that the acetylene gas has to diffuse into the reaction mixture. And while slow stirring is maintained through the whole polymerization process, the concentration of free acetylene gas is perhaps low at any given moment *in* the reaction mixture. As a consequence, there is always a large excess of iodine-containing reactive groups present, even in later stages of the reaction. Phenyleneethynylene oligomers with alkyne termini will immediately couple to more monomer or iodine-substituted oligomers. Because of the additional concentration decrease of acetylene gas in the vapor phase, the influx of acetylene will decrease over time, which then leads to an efficient formation of relatively high molecular weight PPEs even if only very little Pd catalyst is present.

In conclusion, we have developed a straightforward and valuable method to make high molecular weight PPEs utilizing acetylene gas in a Pd-catalyzed process. These PPEs are of better quality than many of the PPEs reported by Pd-catalyzed couplings of dialkynylarenes to diiodobenzenes;[1] the PPEs we have made here are of similar purity and quality as the metathesis-made materials.[6] Low catalyst loadings, the negligible price of acetylene gas, and the facile large-scale synthesis of diiodobenzene derivatives bodes well for the exploitation of this reaction scheme to the synthesis of large (kilogram) amounts of high-quality PPEs, which we are currently exploring in collaboration with a process engineer.

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References and Notes

(1) Bunz, U. H. F. *Chem. Rev.* **2000**, *100*, 1605. Bunz, U. H. F. *Acc. Chem. Res.* **2001**, *34*, 998.

(2) Schmitz, C.; Posch, P.; Thelakkat, M.; Schmidt, H. W.; Montali, A.; Feldman, K.; Smith, P.; Weder, C. *Adv. Funct. Mater.* **2001**, *11*, 41. Weder, C.; Sarwa, C.; Montali, A.; Bastiaansen, G.; Smith, P. *Science* **1998**, *279*, 835. Pschirer, N. G.; Miteva, T. Evans, U.; Roberts, R. S.; Marshall, A. R. Neher, D.; Myrick, M. L.; Bunz, U. H. F. *Chem. Mater.* **2001**, *13*, 2691.

(3) Yang, J. S.; Swager, T. M. *J. Am. Chem. Soc.* **1998**, *120*, 5321. Rose, A.; Lugmair, C. G.; Swager, T. M. *J. Am. Chem. Soc.* **2001**, *123*, 11298.

(4) Halkyard, C. E.; Rampey, M. E.; Kloppenburg, L.; Studer-Martinez, S. L.; Bunz, U. H. F. *Macromolecules* **1998**, *31*, 8655. Kim, J.; Swager, T. M. *Nature (London)* **2001**, *411*, 1030.

(5) (a) Li, C. J.; Slaven, W. T.; John, V. T.; Banerjee, S. *Chem. Commun.* **1997**, 1569. Li, C. J.; Slaven, W. T.; Chen, Y. P.; John, V. T.; Rachakonda, S. H.; *Chem. Commun.* **1998**, 1351. (b) Iyoda, M.; Kabir, S. M. H.; Vorasingha, A.; Kuwatani, Y.; Yoshida, M. *Tetrahedron Lett.* **1998**, *39*, 4701.

(6) Kloppenburg, L.; Song, D.; Bunz, U. H. F. *J. Am. Chem. Soc.* **1997**, *1200*, 7973. Kloppenburg, L.; Jones, D.; Bunz, U. H. F. *Macromolecules* **1999**, *32*, 4194.

(7) Huang, W. Y.; Gao, W.; Kwei, K. T.; Okamoto, Y. *Macromolecules* **2001**, *34*, 1570.

(8) Swanson, L. S.; Lu, F.; Shinar, J. *Proc. SPIEE* **1993**, *191*, 101.

(9) Giesa, R.; Schulz, R. C. *Macromol. Chem.* **1990**, *191*, 857. Mangel, T.; Eberhardt, A.; Scherf, U.; Bunz, U. H. F.; Müllen, K. *Macromol. Rapid Commun.* **1995**, *16*, 571. Weder, C.; Wrighton, M. S. *Macromolecules* **1996**, *29*, 5157.

(10) (a) Representative experimental procedure for the synthesis of **2a**: A nitrogen-flushed tubular 25 mL Schlenk flask (total volume 37 mL) was charged with 0.772 g (1.39 mmol) of the diiodo monomer **1a**, 2 mg of $(PPh_3)_2PdCl_2$ (0.2 mol %), and 1 mg of CuI (0.4 mol %). Toluene and piperidine, 1.5 mL each, were introduced with a syringe to wash down the sides of the flask. The flask was capped with a previously unused septum and degassed by three freeze−thaw cycles. After the final freezing and evacuation, the reaction was thawed with cold water (heating will introduce piperidine and toluene vapor into the evacuated Schlenk). The sidearm was purged with nitrogen and then fitted with a balloon slightly inflated with acetylene. The stopcock was briefly opened, allowing the acetylene gas to replace the vacuum but not to be absorbed into the thawing reaction mixture (approximate volume of acetylene gas is 34 mL or approximately 1.4 mmol). The reaction was allowed to stir at 50 °C for 36 h. Aqueous workup[6,9] furnishes **2a**. (b) A control experiment was performed without the presence of the diiodobenzene, and reaction for 36 h without admission of air led to a very slight dark clouding of the solution, suggesting the reduction of the Pd catalyst to Pd black. Without air, homocoupling of the acetylene does not seem to play a role. Only after the admission of air, a thick dark precipitate starts to form after several hours.

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