Room-Temperature Carbonization of Poly(diiododiacetylene) by Reaction with Lewis Bases

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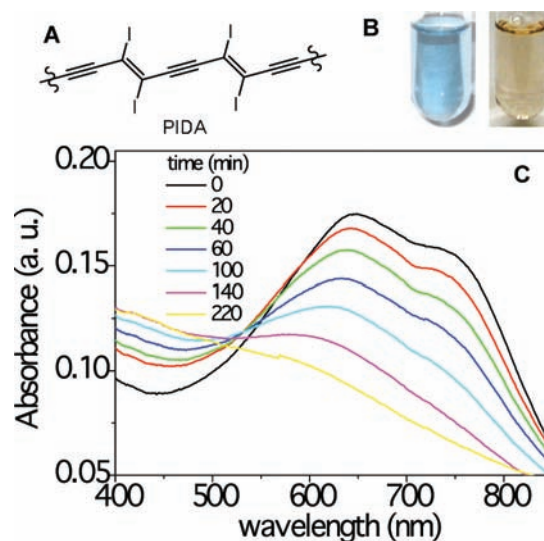
S *Supporting Information*

ABSTRACT: Poly(diiododiacetylene) (PIDA) is a conjugated polymer containing an all-carbon backbone and only iodine atom substituents. Adding a Lewis base to the blue PIDA suspension at room temperature leads first to rapid disappearance of the absorption peaks attributed to PIDA, followed more slowly by release of free iodine. The resulting solid material gives a Raman scattering spectrum consistent with graphitic carbon, and it has a much higher conductivity than PIDA itself. Further investigation has led to the discovery of a previously unreported transformation, the reaction of a Lewis base such as pyrrolidine with a *trans*-diiodo-alkene to form the corresponding alkyne. The generality of this iodine elimination further suggests that reaction of PIDA with Lewis bases dehalogenates the polymer, presenting a new method to prepare carbon nanomaterials at room temperature under very mild conditions.

Figure 1. (A) Structure of PIDA. (B) A blue suspension of 5 mg of PIDA dispersed in 5 mL of methanol (left) turns dark yellow (right) 4 h after 50 μL of triethylamine is added. (C) UV−vis absorption spectroscopic change of the blue suspension in (B) after addition of triethylamine.

Recently, our group reported the highly carbon-rich conjugated polymer poly(diiododiacetylene) (PIDA, Figure 1A), with an all-carbon backbone and single iodine atom substituents.[1−3] PIDA is prepared by topochemical polymerization of monomer diiodobutadiyne within host−guest cocrystals. It forms highly oriented nanofibers upon isolation from the cocrystals.[2,4] The PIDA fibers are stable at room temperature when undisturbed, *but become explosive under external energy such as shock or pressure*.[4] Under thermal conditions, carbonization of PIDA fibers starts at 120 °C, and complete carbonization can be achieved by pyrolysis at 900 °C for 1 h.[4] In addition, when irradiated with a 532-nm Raman laser, the PIDA fibers transform irreversibly at room temperature to sp[2]-hybridized carbon.[4]

The facile carbonization of the PIDA fibers indicates that dissociation of the carbon−iodine bonds in PIDA requires relatively little energy. Here we report that Lewis bases, such as pyrrolidine, pyridine, and other amines, can react with PIDA to release iodine and thus carbonize the polymer at room temperature. Graphitic nanomaterials are of great interest both in fundamental research and for potential applications.[5−9] In general, the preparation of these materials requires complicated steps[10−12] and harsh conditions, such as transition metal complex intermediates[13−15] and/or very high temperature.[12,14−17] The reaction between PIDA and Lewis bases provides a possible route to carbon nanomaterials under very mild conditions.

Dispersing the PIDA nanofibers in an organic solvent, such as tetrahydrofuran or methanol, results in a fine blue suspension (Figure 1B), which has a broad absorption peak centered at 680 nm and a longer-wavelength absorption shoulder that is associated with the aggregation of the polymer chains (black curve in Figure 1C).[2] Adding a Lewis base, such as pyrrolidine, pyridine, or triethylamine, to the blue PIDA suspension leads to the disappearance of the blue color, as shown in Figure 1B. The rate of the color change depends on the strength of the base, with pyrrolidine causing a faster color transition than pyridine or triethylamine at the same concentration. The absorption shoulder at 750 nm decreases immediately after the base is added, indicating that the polymer starts to deaggregate. The major absorption peak diminishes more gradually, with the center of the peak shifting to lower wavelength. Eventually, the absorption spectrum stops changing, with no apparent peak above 450 nm, as shown by the yellow curve in Figure 1C. The base-treated PIDA suspension can be separated by high-speed centrifuge into a supernatant solution and a bulk mass of solid material. The absorption intensity in the visible range (above 400 nm in wavelength) of the resulting
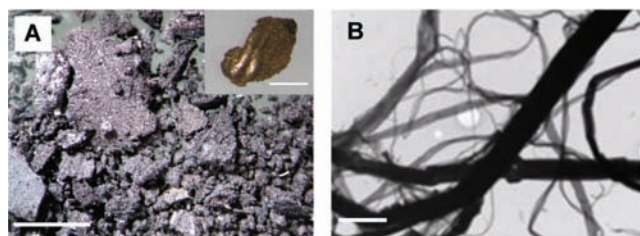
Figure 2. (A) Optical microscope image of bulk pyrrolidine-treated PIDA. Inset: bulk collection of PIDA from a blue suspension as shown in Figure 1B. Scale bars: 1 mm. (B) TEM image of pyrrolidine-treated PIDA dispersed in methanol. Scale bar: 500 nm.

Scheme 1[a]

1 R = CH$_2$CH$_2$CH$_3$
2 R = CH$_2$OH
3 R = C$_6$H$_5$

4 R = CH$_2$CH$_2$CH$_3$
5 R = CH$_2$OH
6 R = C$_6$H$_5$

[a] Reagents and conditions: (a) 0.2 M alkene solution in pyrrolidine, room temperature, dark, 15 h; (b) 1 equiv pyrrolidine, solvent THF, room temperature, dark, 15 h.

Figure 3. Raman spectra of isolated PIDA, pyrrolidine-reacted PIDA, and commercial graphite. The spectra were taken by a Raman spectrometer with a 785-nm Raman laser at a power of 3 mW.

supernatant is lower than in the mixed suspension. Taking the difference between these spectra (Figure S1, Supporting Information (SI)) indicates that the suspended solids have a broad absorption peak centered roughly at 550 nm. The bulk solid material also appears more amorphous and less reflective compared to pristine PIDA fiber aggregates. In addition, the color changes from a metallic luster to dark gray-black after reaction with Lewis base (Figure 2A). This bulk material does not give a well-defined powder X-ray diffraction spectrum, indicating a lack of long-range order in the sample. Redispersing this solid material in methanol leads to a dark suspension. Transmission electron microscopy (TEM) images reveal that the material maintains a fibrous morphology after reaction with the Lewis base, as shown in Figure 2B. However, mixing bulk PIDA with neat pyrrolidine results in a dark, opaque suspension which is difficult to separate.[18]

In the reaction between PIDA and neat pyridine, the resulting supernatant solution shows a maximum absorption at 370 nm, upon dilution with additional pyridine, consistent with molecular iodine. Adding Na$_2$S$_2$O$_3$ to the solution quenches the absorption, further evidence that molecular iodine (I$_2$) is formed during the reaction. On the other hand, in methanol, the reaction between PIDA and excess pyrrolidine forms iodide (I$^-$) instead, as indicated by the formation of a yellow precipitate upon addition of AgNO$_3$. In stoichiometric titration experiments in methanol-d_4, addition of pyrrolidine to a PIDA suspension leads to a gradual increase in the ^{1}H NMR shifts of the pyrrolidine protons (α and β, Figures S8 and S9, SI), indicating the formation of pyrrolidinium ions.[19] These experiments also indicate the presence, after several days, of formyl pyrrolidine (Figures S8 and S10, SI), suggesting a redox reaction between iodine and methanol to give the observed I$^-$.

To further understand the effect of pyrrolidine on PIDA, we have studied the reactions between pyrrolidine and a variety of *trans*-diiodoalkenes, as shown in Scheme 1. Reacting at room temperature overnight, each of the alkenes loses iodine, yielding the corresponding alkyne quantitatively. UV light has been shown previously to dehalogenate dihaloalkenes, while butyllithium has been reported to eliminate trimethylsilyl bromide.[20−22] However, to our knowledge, Lewis base-induced dehalogenation of a *trans*-diiodoalkene to form the corresponding alkyne has not been reported previously. Initial experiments suggest an ionic rather than a radical mechanism for this reaction: The dehalogenation of compound **1** occurs slowly or not at all in nonpolar solvents such as toluene and cyclohexane, but proceeds well in polar solvents such as THF and neat pyrrolidine. In addition, when carried out in the presence of the radical inhibitor hydroquinone, the reaction proceeds unaffected. Detailed investigations of the mechanism and kinetics of this reaction are still under way, but the generality of the elimination suggests that reaction
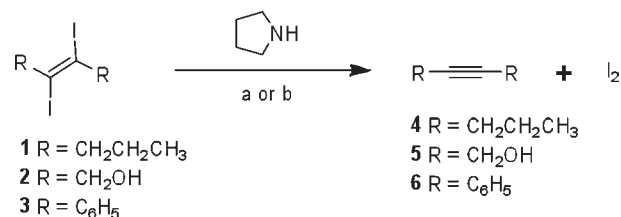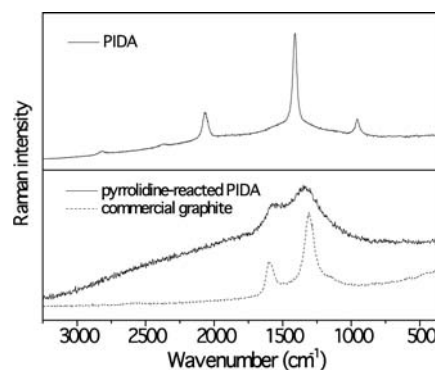
with Lewis bases can remove iodine to carbonize PIDA fibers at room temperature.

In fact, X-ray photoelectron spectroscopy data (XPS, Figure S4, SI) on the pyrrolidine-treated material suggest a significant decrease in the iodine present on the sample surface after reaction. In addition, elemental analysis of pyrrolidine-treated PIDA samples indicates that the carbon/iodine atom ratio in the solid product has increased to over 7:1 after the reaction,[23] significantly higher than that of the initial polymer. Full dehalogenation may be hindered by the inhomogeneity of the system: each individual PIDA strand is part of a large, insoluble aggregate, and the interiors of these polymer fibers may be inaccessible to base. The elemental analysis also indicates the presence of nitrogen, presumed to result from pyrrolidine or related byproduct.

Bulk PIDA loses iodine steadily when heated. Thermogravimetric analysis (TGA, Figure S5, SI) under inert atmosphere shows a steady mass loss from PIDA starting at ∼150 °C, with a residual mass of 18% at 550 °C. TGA of the pyrrolidine-treated PIDA, however, indicates much less mass loss, with most loss occurring above 550 °C, and residual mass of 44%. Differential scanning calorimetry (DSC, Figure S6, SI) on the same material also appears very different from DSC on the initial PIDA sample and includes an endothermic peak at ∼100 °C that may correspond to evaporation of some pyrrolidine-related byproduct. The endothermic peak disappeared in the DSC spectrum of pyrrolidine-treated PIDA that had been stored in air at room temperature for 2 weeks.

PIDA is a strong Raman scatterer, with peaks at 971, 1407, and 2074 cm^{-1}. The solid produced from reaction of PIDA with pyrrolidine, however, shows none of these peaks.[24] Instead, when irradiated at 785 nm, it exhibits a Raman spectrum with broad
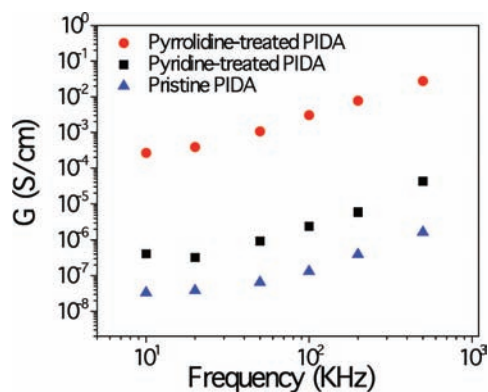
Figure 4. AC frequency-dependent conductivity of bulk samples of PIDA and base-treated PIDA at a fixed amplitude of 1.0 V.

peaks centered at 1360 and 1580 cm^{-1} (Figure 3), similar to graphitic carbon and carbon nanofibers.[25] The breadth of the peaks suggests significant disorder in the structure of base-treated samples, but may also be attributed to the amorphous surface of the materials after the reaction or incomplete carbonization of the PIDA.

The ^{13}C MAS NMR spectra of the solid products from reaction of PIDA with pyrrolidine or pyridine suggest that these products have distinct structure and properties, compared to the starting polymer. The original sp^2 and sp carbon peaks of PIDA are no longer distinguished after the reactions; they are replaced by very broad peaks from ~50 to 150 ppm (Figure S7, SI). Interestingly, the pyrrolidine-treated PIDA samples do not spin when placed in a rotor in high magnetic field unless diluted by a magnetically inactive salt.[26] This phenomenon indicates the generation of eddy currents,[27−29] suggesting that the conductivity of PIDA has been significantly enhanced by the reaction with Lewis base. The breadth of the observed peaks is therefore most likely due to the conducting or semiconducting nature of the material, but may also indicate some paramagnetic species in the sample.

To quantify the change in conductivity upon reaction with Lewis bases, the electrical properties of bulk samples have been measured by impedance spectroscopy. Figure 4 shows the frequency dependence of the alternating-current (AC) electrical conductivity of each sample. The conductivity of pyridine-treated PIDA is ~10 times higher than that of the pristine PIDA at a given AC frequency, while the conductivity increases by as much as 10^4 after reaction with pyrrolidine. This increase in conductivity is consistent with the observations from ^{13}C MAS NMR.

In summary, we have observed that Lewis bases can react with PIDA to dehalogenate the polymer at room temperature. This base-induced dehalogenation is a general reaction of *trans*-diiodoalkenes and pyrrolidine. With at least ~60% of the original iodine dissociating from the polymer upon reaction, the base-treated PIDA materials exhibit Raman spectra consistent with graphitic carbon, and have a significantly increased conductivity. The reaction between PIDA and Lewis bases presents a novel chemical method to generate one-dimensional carbon nanomaterials under mild conditions. Ongoing experiments are focused on optimizing the method to achieve complete dehalogenation of PIDA and to form ordered carbon nanomaterials at room temperature.

ASSOCIATED CONTENT

S **Supporting Information.** Experimental details for reactions of PIDA and model systems, and additional UV−vis

absorption and ^{13}C MAS NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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REFERENCES

(1) Sun, A. W.; Lauher, J. W.; Goroff, N. S. *Science* **2006**, *312*, 1030–1034.

(2) Luo, L.; Wilhelm, C.; Sun, A.; Grey, C. P.; Lauher, J. W.; Goroff, N. S. *J. Am. Chem. Soc.* **2008**, *130*, 7702–7709.

(3) Wilhelm, C.; Boyd, S. A.; Chawda, S.; Fowler, F. W.; Goroff, N. S.; Halada, G. P.; Grey, C. P.; Lauher, J. W.; Luo, L.; Martin, C. D.; Parise, J. B.; Tarabre, C.; Webb, J. A. *J. Am. Chem. Soc.* **2008**, *130*, 4415–4420.

(4) Luo, L.; Wilhelm, C.; Young, N. C.; Grey, C. P.; Halada, G. P.; Xiao, K.; Ivanov, I. N.; Howe, J. Y.; Geohagen, D. B.; Goroff, N. S. *Macromolecules* **2011**, *44*, 2626–2631.

(5) Chung, D. D. L. *Carbon* **2001**, *39*, 279–285.

(6) Avouris, P. *Acc. Chem. Res.* **2002**, *35*, 1026–1034.

(7) De Jong, K. P.; Geus, J. W. *Catal. Rev.-Sci. Eng.* **2000**, *42*, 481–510.

(8) Wu, J. S.; Pisula, W.; Mullen, K. *Chem. Rev.* **2007**, *107*, 718–747.

(9) Hu, L. B.; Hecht, D. S.; Gruner, G. *Chem. Rev.* **2010**, *110*, 5790–5844.

(10) Zhi, L. J.; Wu, J. S.; Li, J. X.; Kolb, U.; Mullen, K. *Angew. Chem., Int. Ed.* **2005**, *44*, 2120–2123.

(11) Laskoski, M.; Steffen, W.; Morton, J. G. M.; Smith, M. D.; Bunz, U. H. F. *J. Am. Chem. Soc.* **2002**, *124*, 13814–13818.

(12) Gherghel, L.; Kubel, C.; Lieser, G.; Rader, H. J.; Mullen, K. *J. Am. Chem. Soc.* **2002**, *124*, 13130–13138.

(13) Guo, T.; Nikolaev, P.; Thess, A.; Colbert, D. T.; Smalley, R. E. *Chem. Phys. Lett.* **1995**, *243*, 49–54.

(14) Iyer, V. S.; Vollhardt, K. P. C.; Wilhelm, R. *Angew. Chem., Int. Ed.* **2003**, *42*, 4379–4383.

(15) Hu, J. Q.; Bando, Y.; Zhan, J. H.; Zhi, C. Y.; Xu, F. F.; Golberg, D. *Adv. Mater.* **2006**, *18*, 197–200.

(16) Partouche, E.; Margel, S. *Carbon* **2008**, *46*, 796–805.

(17) Kyotani, M.; Matsushita, S.; Nagai, T.; Matsui, Y.; Shimomura, M.; Kaito, A.; Akagi, K. *J. Am. Chem. Soc.* **2008**, *130*, 10880–10881.

(18) ***Caution!*** Mixing PIDA fibers directly with pyrrolidine may cause explosion in some cases. For more information, see Safety Statement in Supporting Information.

(19) Tassaing, T.; Besnard, M. *J. Phys. Chem. A* **1997**, *101*, 2803–2808.

(20) Friedrich, H. B.; Tardy, D. C.; Burton, D. J. *J. Fluorine Chem.* **1993**, *65*, 53–57.

(21) Bonin, J.; Costentin, C.; Mahet, M.; Mulon, J. B.; Robert, M. *Phys. Chem. Chem. Phys.* **2009**, *11*, 10275–10280.

(22) For an example of dehalogenation of a dibromoalkene by alkyllithium, see: Alhassan, M. I. *J. Organomet. Chem.* **1989**, *372*, 183–186.

(23) See SI for detailed calculation based on elemental analysis.

(24) We have observed that PIDA can be carbonized under 532-nm Raman laser irradiation but remains unaffected when irradiated with a 785-nm Raman laser.

(25) Wang, Y.; Serrano, S.; Santiago-Aviles, J. J. *Synth. Met.* **2003**, *138*, 423–427.

(26) Although we did not encounter any problems in our experiments when using this diluent (sodium nitrate), we do not recommend mixing the diluent with a shock explosive.

(27) Chapman, A. C.; Rhodes, P.; Seymour, E. F. W. *Proc. Phys. Soc. B* **1957**, *70*, 345–360.

(28) Xiong, J. C.; Lock, H.; Tao, T.; Keeler, C.; Maciel, G. E. *Solid State Nucl. Magn. Reson.* **1999**, *14*, 95–103.

(29) Krinichnyi, V. I.; Tokarev, S. V.; Roth, H. K.; Schrodner, M.; Wessling, B. *Synth. Met.* **2005**, *152*, 165–168.