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Polymerization of Acetylene with a Ruthenium Olefin Metathesis Catalyst

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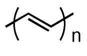
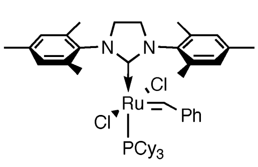
The ring opening metathesis polymerization of 1,3,5,7-cyclooctatetraene (COT) to afford polyacetylene (**PA**) was recently reported by Grubbs and co-workers.[1,2] This procedure makes use of a readily available ruthenium metathesis catalyst (**1**) developed by Grubbs and can be performed easily at ambient temperature to produce films of **PA**[1] or soluble **PA** block copolymers.[2] However, the expense of the monomer and the low **PA** yields (15−30%) make this process inefficient.[1,2] The Durham method uses metathesis to prepare a precursor polymer that is then converted to **PA** by thermolysis.[3] Other methods, such as Shirakawa's method,[4] Naarmann's modification,[5] or alkyne metathesis[6] use the more cost-effective monomer acetylene. Herein we report that a more active analogue of **1**, the 3-bromopyridine complex **2**,[7] readily polymerizes acetylene to produce **PA** as a black powder. We have characterized the product, explored variations in procedure, and produced shiny **PA** films by pressing the powder.



PA



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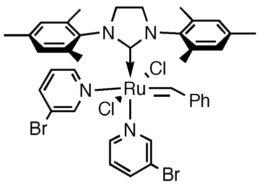

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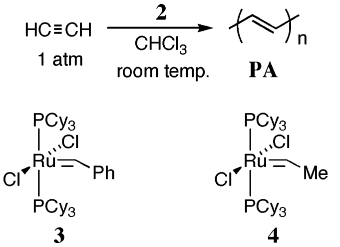
Scheme 1. Polymerization of Acetylene



When a pale green solution of **2** (7 mg in 3 mL $CHCl_3$) was exposed to acetylene gas at ambient temperature, the solution darkened through red to black, followed by the precipitation of a black solid. The visible changes occurred over a minute or two if the acetylene was introduced over the solution but within seconds if the acetylene was bubbled through the solution. After 1 h of bubbling, the yield of black solid, after evaporation of solvent, was 61 mg. Washing the solid with $CHCl_3$ gave most of the catalyst back[8] and 56 mg of **PA**.

Both **1** and the first-generation Grubbs catalyst, **3**,[9] undergo color changes in the presence of acetylene, but neither causes the formation of any solids. The failure of both **3**[10] and **1**[11] to polymerize acetylenes has been previously noted, though stoichiometric reactions with ethylidene **4**[12] and with **1**[11] have been reported.

The **PA** formed as in Scheme 1 was characterized by a variety of methods (Table 1). The results verify the chemical identity and show that the polymer is mostly trans. The IR, UV−vis, and CP-MAS NMR data are all consistent with *trans*-**PA**, though smaller peaks corresponding to *cis*-**PA** were observed in the IR and CP-MAS NMR spectra of fresh samples. As reported for the **PA** produced from COT,[1] isomerization to trans occurs at room temperature, presumably catalyzed by incorporated catalyst, since **PA** from other methods isomerizes less readily.[4,13] The isomerization was observed to occur in ca. 2 h. A cyclic voltammogram (CV), obtained on a film deposited onto an indium−tin oxide coated glass plate, was a perfect match for a literature

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Table 1. PA Characterization Data

property	Shirakawa **PA**[a]	**PA** from **1** (polyCOT)[a]	**PA** from **2**[b]
appearance	shiny, silver films	shiny, gold films	black powder or shiny, silver films
σ(undoped) (S/cm)	10^{-5} (trans), 10^{-9} (cis)	$<10^{-8}$ (mostly trans)	$<10^{-8}$
σ(doped with I_2) (S/cm)	160 (trans), 550 (cis)	>25 (mostly trans)	10^2
SS CP-MAS ^{13}C NMR δ (ppm)	136−139 (trans),126−139 (cis)	133 (trans), 127 (cis)	135, 127 (fresh sample, ca. 3:1)
IR major peaks (cm^{-1})	1015 (trans), 740 (cis)	1010, 992, 930, 773, 745 (mostly trans)	999, 769 (fresh sample, ∼33% *cis*[d]) 1010[e]
UV−vis maximum (10^3 cm^{-1})	15.5 (trans), 18.7 (cis)[c]		15.5

[a] Reference 1. [b] This work. [c] Tanaka, J.; Tanaka, M. In *Handbook of Conducting Polymers*; Skotheim, T. A., Ed.; Dekker: New York, 1986; Vol. 2, Chapter 35. [d] Using the method from ref 4. [e] Several hours at room temperature.

PA thick-film CV.[14] Conductivities, measured by using a four-point probe on pressed films, were also consistent with literature values.

The **PA** obtained as in Scheme 1 could be handled in several forms. An insoluble powder was obtained after vaporization of solvent. Coatings of **PA** on glass plates or other substrates were obtained by simply inserting the substrate in a solution of the catalyst under acetylene; by varying exposure times, loose and porous films of various thicknesses were deposited. A wet "gel" with a sponge or pastelike consistency was obtained directly without filtration or evaporation of solvent. This material, similar in properties to that described by Shirakawa,[15] was spread onto substrates and allowed to dry, or was sandwiched between glass plates, clamped, and dried to create black, pressed films. The films were removable from the glass to form free-standing films.

The best films obtained, however, were films pressed from the dry powder. Shiny, silver-colored films were obtained with application of high pressure (by using an IR KBr pellet press), moderate pressure (by using glass plates and a spring clamp), or low pressure (by drawing a spatula blade over the powder). In all cases, films were obtained that were readily removed from the substrate and were resistant to scratching or indentation. The free-standing films were much tougher than even thicker films from COT, due to microcracks that form in the latter.[1] Conductivity measurements on such films appear in Table 1. The ability to produce shiny films from a black powder of **PA** is reminiscent of Shirakawa's report,[15] except that those observations were made on *cis*-rich **PA**.

Scanning electron microscope (SEM) images of the **PA** (Figure 1) reveal that the morphology is a network of spherical particles near 0.5 μm in diameter. This differs from the usual fibrillar morphology for **PA**,[4,5] though globular forms have been observed.[6,16]

X-ray diffraction (XRD) patterns recorded for **PA** powder and pressed films were similar to each other and to patterns recorded and reported[17] for Shirakawa **PA**. All samples showed a single reflection with $d \approx 3.7$ Å and similar widths, suggesting similar crystallite sizes. Pressing the film caused both a slight increase in width (decrease in crystallite size) and the appearance of a significant shoulder at smaller angles, attributable to amorphous scattering.[17a]

Differential scanning calorimetry (DSC) experiments from 20 to 600 °C show a very small exotherm at 350 °C and a large endotherm near 475 °C. The endotherm is attributed to degradation of the polymer,[18] consistent with an 80% loss in mass.

Strong effects of solvent, concentration, and temperature were observed for the polymerization reaction. Of all solvents tried, $CHCl_3$ gave the highest yield of polymer, though **PA** was formed in most solvents tried. The **PA** formed at −30 °C was very fine and glittery black in appearance; SEM images showed roughly spherical particles near 0.1 μm in diameter.

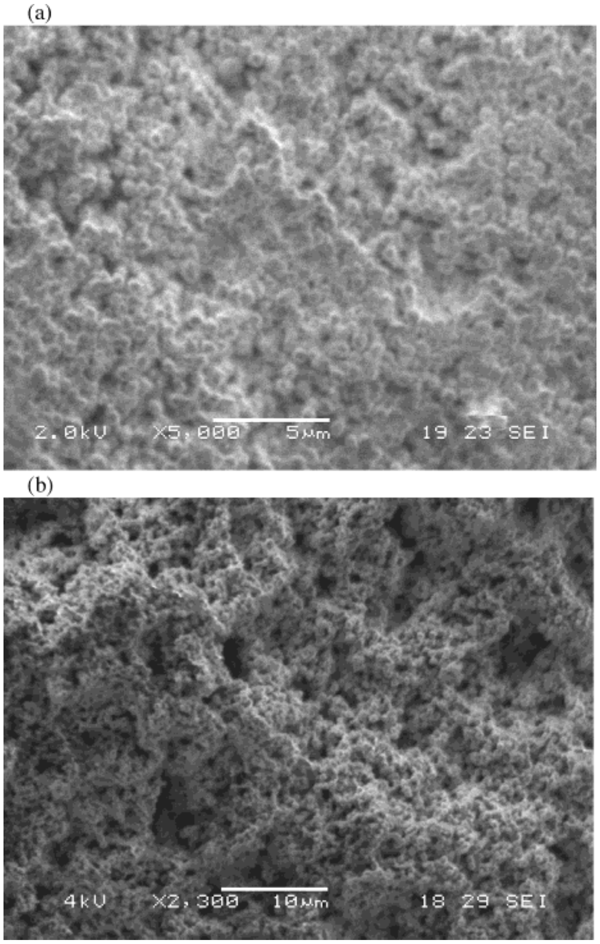

Figure 1. SEM images of **PA** prepared at 22 °C: (a) pressed film (by spatula); (b) dry powder.

Previous reports on **PA** formed from acetylene as a black powder[15,19] have appeared using several catalysts as has the formation of pressed films,[15,20] but the present method appears to be the most convenient from the standpoint of catalyst stability and availability.

The catalyst **2** was also tested in the polymerization of other acetylenes. 1-Hexyne, propargyl alcohol, and phenylacetylene each gave red to red-brown materials that were consistent with literature reports of the substituted polyacetylenes.[21] Catalyzed formation of substituted polyacetylenes has recently been reviewed.[22]

In summary, **PA** powder, paste, and films have been efficiently and cost-effectively prepared by passing acetylene through solutions of the readily available and easily handled catalyst **2**.

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Supporting Information Available: Text giving the procedure for **PA** formation and testing, tables of solvent, concentration, and temperature effects on **PA** formation, and figures showing **PA** characterization data (CPMAS NMR, IR, UV−vis, CV, XRD, DSC) and IR spectrum of poly(phenylacetylene). This material is available free of charge via the Internet at http://pubs.acs.org.

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