Macromolecules 1993, *26*, 4072-4073

Air- and Water-Stable 1,2-Vinyl-Insertion Polymerizations of Bicyclic Olefins: A Simple Precursor Route to Polyacetylene

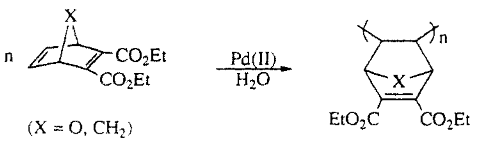
Adam L. Safir and Bruce M. Novak*

Department of Chemistry, University of California at Berkeley, and The Center for Advanced Materials, Materials Science Division, Lawrence Berkeley Laboratories, Berkeley, California 94720

Received December 14, 1992
Revised Manuscript Received May 20, 1993

Although a wide variety of conjugated polymers have been studied,[1] polyacetylene remains the defining example of a conducting organic material. Because of its insolubility and intractability, at least two recent synthetic efforts have been directed at the preparation of soluble precursor polymers that can be transformed into polyacetylene.[2] Although successful, these methods utilize monomers that are either difficult to synthesize or thermally unstable and catalyst systems that are highly sensitive to temperature, air, and moisture. We have therefore been interested in developing a simple, benchtop precursor route into polyacetylene using readily available monomers and catalysts. We would now like to report the synthesis of a stable, soluble polyacetylene precursor polymer prepared from a palladium(II)-catalyzed aqueous emulsion polymerization and its subsequent thermal conversion to polyacetylene.

It has been reported that palladium(II) salts will polymerize bicyclo[2.2.1]hept-2-ene derivatives and bicyclo[2.2.1]hepta-2,5-diene via a 1,2-vinyl-insertion mechanism.[3] We became interested in expanding the scope of this reaction by incorporating functional groups in the monomers to yield highly reactive precursor polymers. To this end, we synthesized the monomers diethyl 7-oxabicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate (1) and diethyl bicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate (2) via simple Diels–Alder reactions of diethyl acetylenedicarboxylate with furan or cyclopentadiene, respectively.[4] During preliminary test reactions we found that $Pd(CH_3CN)_4(BF_4)_2$, normally a highly reactive insertion catalyst, failed to polymerize either 1 or 2 under all conditions. We did find, however, that in rigorously anhydrous organic solvents $Pd(OAc)_2$ catalyzed the slow oligomerization of 1 over the course of several days. Surprisingly, addition of water to the reaction mixture led to a subsequent increase in the activity of the catalyst (4–5 fold increase in polymer yield at comparable times). The exact role of water remains unknown; the possibilities include nucleophilic attack by water on a Pd-bound monomer to yield a Pd–alkyl species similar to the Wacker process[5] or the water-induced breakup of inactive palladium aggregates.[6] Because excess water does not act as an inhibitor, the most convenient reaction conditions involve a simple aqueous emulsion polymerization of 1 or 2 initiated by $PdCl_2$ (eq 1).



(1)

Both poly(diethyl 7-oxabicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate) (**poly-1**) and poly(diethyl bicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate) (**poly-2**) are readily soluble in a variety of organic solvents. A typical polymerization with $Pd(OAc)_2$ using a monomer to initiator ratio of 200 gives a polymer in 75% yield with a molecular weight (GPC, relative to polystyrene) of 28 000 and a polydispersity of 1.8. The structures of **poly-1** and **poly-2** were confirmed by IR, ^1H NMR, and $\{^1H\}$ ^{13}C NMR spectroscopic methods as well as by elemental analysis.[7] Both the ^1H NMR and ^{13}C NMR spectra of **poly-1** and **poly-2** show evidence of microstructure, the nature of which has yet to be elucidated. Kinetic studies of the homogeneous polymerization of 1 in wet chloroform-*d* revealed a zero-order rate dependence on monomer, a first-order rate dependence on catalyst, and a k_{obs} of 4.2×10^{-4} s^{-1} (i.e., $-d[1]/dt = k_{obs}[Pd^{2+}]$).[8] This rate behavior suggests that propagation involves a monomer-independent, rate-determining insertion process.

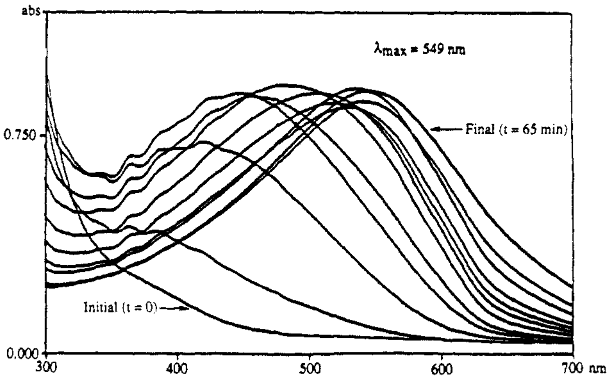


Figure 1. UV/vis study of the thermal transformation of **poly-1** at 120 °C to form polyacetylene. (Traces taken every 6 min.)

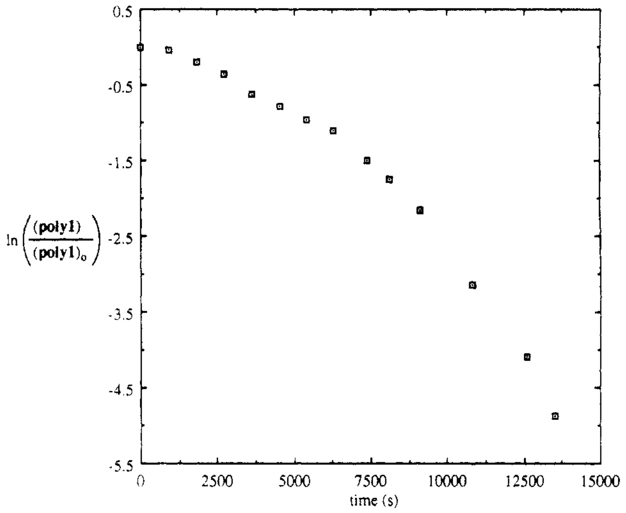
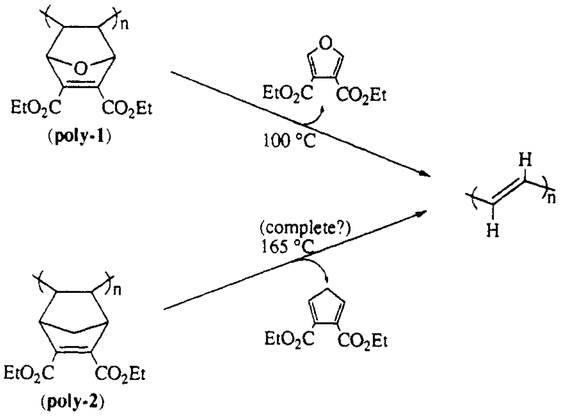


Figure 2. ^1H NMR solution kinetics in *o*-dichlorobenzene-d_4 of the conversion of **poly-1** to polyacetylene at 120 °C.

Scheme I



0024-9297/93/2226-4072$04.00/0

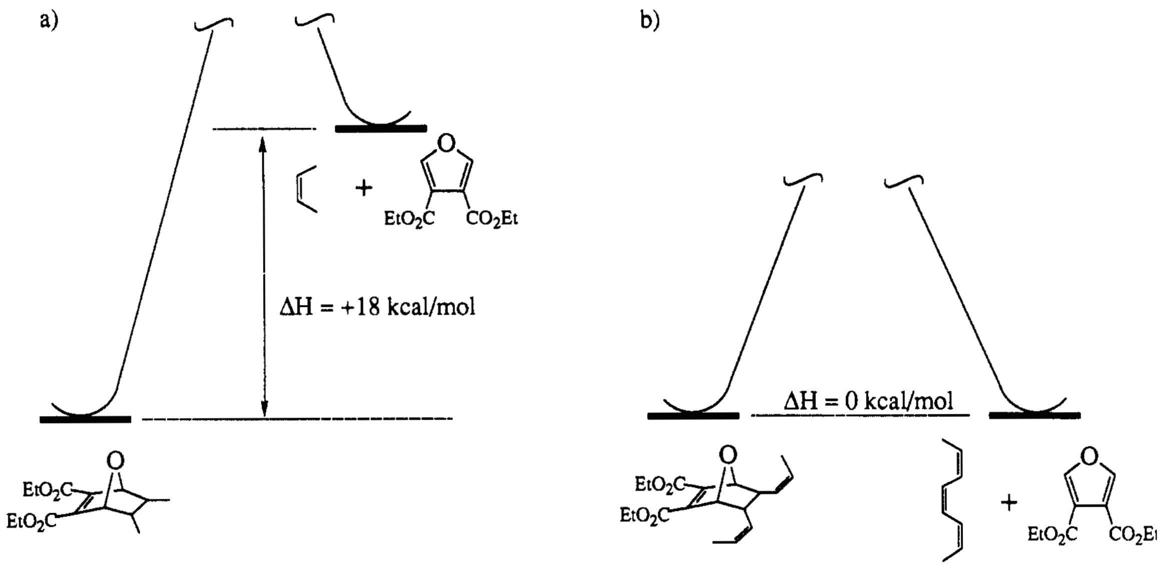


Figure 3. Group increment calculations for the retro Diels–Alder reactions of repeat units (a) adjacent to two saturated units and (b) adjacent to two unsaturated units.

Poly-1 is stable at room temperature; however, when heated at 100 °C either in solution or after being processed into thin films, this polymer is transformed into polyacetylene via a retro [4+2] Diels–Alder reaction which liberates 3,4-disubstituted furans (Scheme I).[9] During the thermal transformation process we observed a gradual color change from clear to deep purple which we attribute to an increase in the average degree of conjugation along the polymer backbone.[10] This color change can be monitored by UV/vis spectroscopy: a precursor polymer with a molecular eight of 29 100 (relative to polystyrene) displayed an absorbance that red-shifted over time and culminated in an ultimate wavelength of 549 nm (Figure 1).

Three additional independent techniques were used to characterize the polyacetylene produced as well as to probe the level of conversion of the precursor polymers. The IR absorbance at 1008 cm^{-1} and the fundamental *trans*-polyacetylene Raman resonances at 1086 and 1484 cm^{-1} (as well as the absence of any other signals in either spectrum) confirm the complete transformation of **poly-1** to *all-trans*-polyacetylene.[11] Presumably, the originally formed *cis*-polyacetylene is rapidly converted to *trans* at these temperatures.[12] Complete transformation of these precursor polymers was also confirmed by collecting the cyclic diene byproduct. When **poly-1** was heated under vacuum (25 mTorr), analytically pure diethyl furan-3,4-dicarboxylate was collected in 96% yield.[13]

An investigation of the kinetics associated with the conversion of **poly-1** to polyacetylene was conducted in the solid state using thermal gravimetric analysis (TGA) and in solution using ^1H NMR. As evidenced by curvature in the first-order plots (monitoring the loss of repeat units versus time) (Figure 2), both sets of kinetic data indicate that the retro Diels–Alder reaction is autoaccelerated. Using arguments based on the Hammond postulate, we attribute this rate acceleration to a decrease in the endothermicity of the retro Diels–Alder reaction. This favorable thermodynamic shift results from the continually changing electronic structure of the polymer backbone as it becomes more unsaturated during the reaction. Group increment calculations show that the retro Diels–Alder reaction for a repeat unit adjacent to two unsaturated units is 18 kcal/mol less endothermic than the retro Diels–Alder reaction for a repeat unit adjacent to two saturated units (Figure 3). Hence, the retro reaction should be faster for repeat units adjacent to unsaturated units in the polymer backbone that were formed by prior retro Diels–Alder reactions.

Acknowledgment. We gratefully acknowledge support of this work from the Office of Naval Research, the NSF Presidential Young Investigator Award, associated PYI industrial sponsors, the Alfred E. Sloan Foundation, and Lawrence Berkeley Laboratories. A.L.S. acknowledges the Department of Education for a predoctoral fellowship.

References and Notes

(1) Skotheim, T., Ed. *Handbook of Conducting Polymers*; Dekker: New York, 1968.
(2) (a) Edwards, J.; Feast, W.; Bott, D. *Polymer* **1984**, *22*, 395. (b) Swager, T.; Dougherty, D.; Grubbs, R. *J. Am. Chem. Soc.* **1988**, *110*, 2973.
(3) (a) Schultz, R. *Polym. Lett.* **1966**, *4*, 541. (b) Sen, A.; Lai, T.; Thomas, R. *J. Organomet. Chem.* **1988**, *358*, 567. (c) Mehler, C.; Risse, W. *Makromol. Chem., Rapid Commun.* **1991**, *12*, 255.
(4) (a) Alder, K.; Rickert, H. *Chem. Ber.* **1937**, *70*, 1354. (b) McCulloch, A.; Stanovik, B.; Smith, D.; McInnes, A. *Can. J. Chem.* **1969**, *47*, 4319. (c) Diels, L.; Alder, K.; Nienburg, H. *Liebigs Ann. Chem.* **1931**, *490*, 236.
(5) Gragor, N.; Henry, P. *J. Am. Chem. Soc.* **1981**, *103*, 681.
(6) Ketley, A. D.; Fischer, L. P.; Berlin, A. J.; Morgan, C. R.; Gorman, E. H.; Steadman, T. R. *Inorg. Chem.* **1967**, *6*, 657.
(7) (a) **poly-1**. IR (KBr): 1724, 1645 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ 1.27 (br, 6), 2.62 (br, 1.5), 3.93 (br, 0.5), 4.20 (br, 4), 5.21 (br, 1), 5.60 (br, 1). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 13.7 (br), 37.7 (br), 44.6 (br), 61.5 (br), 80.8 (br), 82.0 (br), 139.2 (br), 153.2 (br), 160.0 (br), 164.8 (br). Anal. Calcd for $C_{12}H_4O_5$: C, 60.50; H, 5.92. Found: C, 60.21; H, 5.98. **poly-2**. IR (KBr): 1718, 1628 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ 1.20 (br, 6), 1.82 (br, 2), 2.58 (br, 1), 2.82 (br, 1), 3.30 (br, 2), 4.19 (br, 4). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 14.2 (br), 39.6 (br), 44.7 (br), 48.0 (br), 60.5 (br), 139.6 (br), 154.9 (br), 161.6 (br), 166.0 (br). Anal. Calcd for $C_{13}H_{16}O_4$: C, 66.09; H, 6.83. Found: C, 65.88; H, 7.12.
(8) Kinetics were conducted in $CDCl_3$ at 25.5 ± 0.5 °C with [monomer] = 0.533 M and varying [palladium acetate].
(9) Heating **poly-2** at 165 °C promotes a similar retro [4 + 2] Diels–Alder reaction. However, the IR spectrum of the polyacetylene produced suggests that the retro reaction is not going to completion or that side reactions are occurring at this elevated temperature.
(10) (a) Edwards, J.; Feast, W. *Polymer* **1980**, *21*, 595. (b) Klavetter, F.; Grubbs, R. *J. Am. Chem. Soc.* **1988**, *110*, 7807.
(11) (a) Shirakawa, H.; Ikeda, S. *Polym. J.* **1971**, *2*, 231. (b) Porter, J.; Carter, P. *Phys. Rev.* **1991**, *B43*, 14478.
(12) Ito, T.; Shirakawa, H.; Ikeda, S. *J. Polym. Sci.* **1975**, *13*, 1943.
(13) Anal. Calcd for $C_{16}H_{12}O_5$: C, 56.60; H, 5.70. Found: C, 56.23; H, 5.81.