pK = 5.4 for $T^{\pm}$. The solid line in Figure 1A shows the Brønsted correlation calculated[14] for the trapping mechanism of eq 1 and pK = 5.3 for $T^{\pm}$; it gives a satisfactory fit to the experimental data.

The Brønsted slope of $\beta = 0$ for bifunctional catalysts is consistent with diffusion-controlled encounter being largely or entirely rate-limiting, regardless of buffer pK. A rapid bifunctional proton transfer that converts $T^{\pm}$ to T^0 can explain why proton transfer and diffusional separation do not become rate-limiting for very weak bases.[15,16]

The results presented here provide what we believe to be the first direct evidence that the bimolecular aminolysis of an ester involves a trapping mechanism, in which general base catalysis involves rate-limiting diffusion-controlled proton transfer.

---

(13) A pK of $T^{\pm}$ = 5.4 ± 1.0 was calculated by using procedures described in the following: Fox, J. P.; Jencks, W. P. *J. Am. Chem. Soc.* **1974**, *96*, 1436.

(14) The theoretical curve that provides a satisfactory fit for the data in Figure 1A was calculated with eq 2 from ref 14, with $pK_{T\pm} = 5.3$, $K_1 = 3 \times 10^{-12}$ M^{-1}, $k_a = 10^9$ M^{-1} s^{-1}, $k_{-a} = k_b = 10^{10}$ s^{-1}, $\log k_p = 9.4 + 0.5\Delta pK$, and $\log k_{-p} = 9.4 - 0.5\Delta pK$ ($\Delta pK = pK_A - pK_{T\pm}$). The solid curve in Figure 1B was calculated assuming $k_H/k_D = 6.5$ for k_p and k_{-p}.

(15) Barnett, R. E.; Jencks, W. P. *J. Am. Chem. Soc.* **1969**, *91*, 2358.

(16) Cox, M. M.; Jencks, W. P. *J. Am. Chem. Soc.* **1981**, *103*, 572, 580.

(17) The aminolysis of alkyl esters shows a change in rate-limiting step on a pH-log rate profile (ref 2, Blackburn, G. M.; Jencks, W. P. *J. Am. Chem. Soc.* **1968**, *90*, 2638). This has been attributed to rate-limiting breakdown of the neutral intermediate T^0 to products at low pH, changing to rate-limiting formation of T^0 from $T^{\pm}$ at high pH.[2] Between pH 7 and 9, the uncatalyzed aminolysis of methyl formate by aniline is pH-independent (results not shown) and is consistent with the latter step being rate-limiting as previously described.[2]

(18) Plots of observed second-order rate constants against total buffer concentration show curvature with increasing buffer concentration, consistent with a change in rate-limiting step to T^0 breakdown at high buffer concentrations. Third-order rate constants for base catalysis at low buffer concentrations, k_B, were determined by fitting the data to eq 2. The rate constants

$$k_2\text{obsd} = K_T \frac{(k_a + k_1[B])(k^0 + k_2[B])}{(k_{-a} + k_{-1}[B]) + (k^0 + k_1[B])} \qquad (2)$$

k_a, k_{-a}, and k_1, k_{-1} are buffer independent and base-catalyzed rate constants, respectively, for interconversion of $T^{\pm}$ to T^0, whereas k^0 and k_2 are the buffer independent and base-catalyzed rate constants, respectively, for the breakdown of T^0 to products as outlined in eq 1, and $k_B = K_T k_1$. Rate constants for general base catalysis were obtained by either the determination of rate constants for buffer catalysis at several fractions of buffer base and extrapolating to 100% base or by a single experiment at a pH value >1.5 units above the buffer pK.

Strained Rings as a Source of Unsaturation: Polybenzvalene, a New Soluble Polyacetylene Precursor

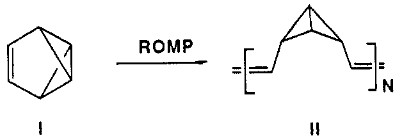
Timothy M. Swager, Dennis A. Dougherty, and
Robert H. Grubbs*

Contribution No. 7721, Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, California 91125

Received December 21, 1987

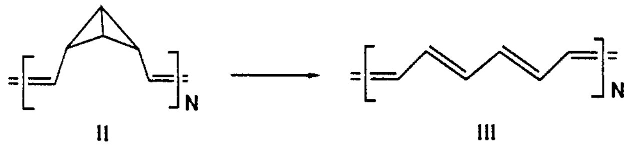
Conductive polymers currently represent an active area of research in polymer science.[1] Polyacetylene (PA) has been at center stage throughout the evolution of this field,[2] with a conductivity that can be increased with doping to values that rival copper.[3] PA and many other conductive polymers are insoluble, infusable materials with low tensile strength, and thus the manipulation of these materials into useful shapes and morphologies is limited. One solution to these material and processing problems has been the use of soluble precursor polymers that can be transformed into conductive polymers.[4] Precursor routes have afforded the synthesis of materials with higher molecular weights and highly ordered anisotropic morphologies.[4] One major drawback to the existing precursor routes is that they generally rely on the extrusion of molecular fragments. These extruded fragments may comprise a substantial fraction of the total mass and thus potentially limit the usefulness of these processes. The development of precursor routes that do not rely on the extrusion of small molecules is therefore desirable. We report herein the synthesis of polybenzvalene, an unusual polymer that can be transformed into PA without the extrusion of molecular fragments.

Scheme I



I II

Scheme II



II III

Polybenzvalene (II) was synthesized by the ring opening metathesis polymerization (ROMP) of the highly reactive but readily available monomer benzvalene (I),[5] as shown in Scheme I. We have previously demonstrated the utility of ROMP with titanocene metallacycle catalysts in the synthesis of living polymers,[6a] block copolymers,[6b] and a cross-conjugated conducting polymer precursor.[6c] However, these titanium catalysts proved ineffective in the polymerization of I.[7] The ROMP of I has only been made possible by the development of non-Lewis acidic[8] well-defined active tungsten alkylidene metathesis catalysts.[9,10] The catalytic systems of both Schrock[9] and Osborn[10] were effective for the ROMP of I. We have used the catalysts of Schrock[12] in our studies as a result of their selectivity for the formation of cis olefins.[9b]

II is an interesting material in its own right. The bicyclobutane moiety has approximately 64 kcal/mol of strain energy,[13] and thus the polymer has about 11 kcal of strain energy per carbon atom. High-energy polymers such as II may have applications in pro-

---

(1) *Handbook of Conducting Polymers*; Skotheim, T. J., ed.; Dekker: New York, 1986.

(2) Chien, J. C. W. *Polyacetylene: Chemistry, Physics, and Material Science*; Academic Press: 1984.

(3) Naarman, H.; Theophilou, N. *Synth. Metals* **1987**, *22*, 1.

(4) (a) Karasz, F. E.; Capistran, J. D.; Gagnon, D. R.; Lenz, R. W. *Mol. Cryst. Liq. Cryst.* **1982**, *118*, 567. (b) Edwards, J. H.; Feast, W. J. *Polymer* **1980**, *21*, 595. (c) Ballard, D. G.; Couris, A.; Shirley, I. M.; Taylor, S. C. *J. Chem. Soc., Chem. Commun.* **1983**, 954.

(5) (a) Katz, T. J.; Wang, E. J.; Acton, N. *J. Am. Chem. Soc.* **1971**, *93*, 3783. (b) Katz, T. J.; Roth, J.; Acton, N.; Carnahan, E. *Org. Synth.* **1973**, *53*, 157.

(6) (a) Gilliom, L. R.; Grubbs, R. H. *J. Am. Chem. Soc.* **1986**, *108*, 733. (b) Cannizzo, L. F.; Grubbs, R. H. *Macromolecules* **1988**, in press. (c) Swager, T. M.; Grubbs, R. H. *J. Am. Chem. Soc.* **1987**, *109*, 894.

(7) Reaction of I with titanocene alkylidenes resulted in metallacycles that were thermally unreactive at temperatures less than 80 °C. At these temperatures I is rapidly converted to benzene.

(8) I was found to react exothermically with Lewis acidic catalysts WCl_6:$Sn(Me)_4$, $WOCl_4$:$Sn(Me)_4$, and $((Me)_3CCH_2O)_2W(Br)_2CHC(Me)_3$:$GaBr_3$ to give a dark brown intractable material.

(9) (a) Schaverien, C. J.; Dewan, J. C.; Schrock, R. R. *J. Am. Chem. Soc.* **1986**, *108*, 2771. (b) Schrock, R. R.; Feldman, J.; Cannizzo, L. F.; Grubbs, R. H. *Macromolecules* **1987**, *20*, 1169.

(10) Kress, J.; Aguero, A.; Osborn, J. A. *J. Mol. Catal.* **1986**, *36*, 1.

(11) The non-Lewis acidic metathesis catalysts, $(CO)_5WC(OMe)Ph$ and $(CO)_5WC(Ph)_2$, in which the chain carrying species are not known or observed were investigated and found to be ineffective. However, these catalysts have been shown to be effective for other monomers: Katz, T. J.; Savage, E. B.; Lee, S. J.; Nair, M. *J. Am. Chem. Soc.* **1980**, *102*, 7940 and 7942.

(12) The catalysts employed were $(RO)_2W(N(2,6\text{-}(i\text{-}Pr)_2Ph))CHC(Me)_3$ where R = *tert*-butyl, or hexafluoro-*tert*-butyl (ref 8). The catalysts were used at room temperature and −20 °C, respectively, in benzene or toluene and were found to give the same material by NMR (ref 15).

(13) Wiberg, K. B. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 312.

pulsion technologies.[14] Differential scanning calorimetry reveals the liberation of 59 kcal/mol of energy from II upon heating from 50 to 420 °C. As a result of this high strain energy, II is a sensitive material that has been observed to undergo spontaneous exothermic decomposition upon the application of severe mechanical stress or rapid heating. Concentrated solutions of II gel upon standing, and after precipitation or evaporation II cannot be redissolved. The tendency for II to crosslink and spontaneously decompose has made it necessary to handle it in solution.[15] Gels of II that have been washed with a nonsolvent (e.g., acetone, MeOH), give solids which display elastomeric properties. On several occasions these samples could be stretched to more than 30 times their original length, although spontaneous decomposition often occurred before reaching these lengths. Preliminary experiments indicate that fibers may be drawn from concentrated solutions. Films of II are strong, transparent, amorphous,[17] and smooth when observed by scanning electron microscopy.

We envisioned II as a PA precursor via the isomerization of the bicyclobutane rings to 1,3-dienes (Scheme II). This type of isomerization has been promoted thermally,[18] photochemically,[19] and by transition metals[20] in a variety of substituted bicyclobutane compounds. Thermal and photochemical isomerizations of II were unsuccessful at producing high yields of PA;[21] however, we were successful with transition-metal catalysts. Solutions of HgCl$_2$, HgBr$_2$, and Ag$^+$ salts in THF transformed films of II into shiny silvery materials resembling polyacetylene in appearance. The conductivities of the resulting materials were 10^{-5}, 10^{-7}, and 10^{-8} S/cm, respectively, and were increased to 1, 10^{-1}, and 10^{-4}–10^{-6} S/cm upon I$_2$ doping.[22] We have focused our characterization on materials from the HgCl$_2$ isomerization as a result of the higher conductivity and superior mechanical properties exhibited by these samples.

Characterization of the films obtained from the HgCl$_2$ isomerization (III) by solid-state CP-MAS ^{13}C NMR and infrared spectroscopy indicated that we had formed PA.[23] Both spectroscopic methods reveal residual saturation. Integration of the CP-MAS ^{13}C NMR of III determined the degree of saturation to be approximately 19%. We attribute the saturation to crosslinking,[25] which may be promoted by residual HgCl$_2$ in the film.[26] The films of III have approximately a 40:60 cis:trans double bond content as determined by infrared spectroscopy. Since II was greater than 90% cis,[15] it appears that the isomerization of the bicyclobutanes produces mainly trans olefins. Films of III are strong, flexible, and of much lower crystallinity than polyacetylene prepared by other routes.[27] Our results are best compared with "Durham PA" prepared by the method of Feast[4b] which can also yield a material of low crystallinity.[28] This amorphous morphology results in lower conjugation length and conductivity than is observed in the extensively studied "Shirakawa PA".[2] The conductivities we report herein are comparable to unoriented Durham PA in spite of the above-mentioned crosslinking. Films of III have a conjugation length that is less than that of unoriented Durham polyacetylene, as evidenced by Raman spectroscopy.[28,29] This lower conjugation length may be the result of the crosslinking and/or a more amorphous morphology in III. The amorphous morphology of III is also apparent in the fact that samples of this material swell noticeably with solvents.

Our results demonstrate a new precursor route to polyacetylene that does not involve the extrusion of molecular fragments. The use of this method to form highly ordered polyacetylene is under investigation, as is the use of other transition metals in the isomerization reaction. We are also investigating the generality of this precursor method in the syntheses of other conductive polymers.

Acknowledgment. We are grateful to Professor R. R. Schrock for catalyst samples used in preliminary studies and for communicating results prior to publication. We gratefully acknowledge Scott C. Virgil for his assistance in the catalyst synthesis. We are thankful for financial support provided by the NSF and acknowledge the Southern California Regional NMR facility for the use of the solid-state NMR spectrometer. T.M.S. gratefully acknowledges IBM for a graduate fellowship. T.M.S. was supported in part by a fellowship from Caltech's Program in Advanced Technologies, sponsored by Aerojet General, General Motors, and TRW.

Supplementary Material Available: Experimental procedures for the preparation of II and III (3 pages). Ordering information is given on any current masthead page.

---

(14) Wardle, R. B., personal communication.

(15) As a result of the instability of II, films were cast directly from the polymerization solution. Gel permeation chromatography revealed a very broad molecular weight distribution ranging from 600 000 to 1000 with the average molecular weight approximately 20 000 (relative to polystyrene standards). Viscous solutions were obtained from solutions with 2–5% II. Solutions tend to gel in a matter of hours and could only be stored in frozen benzene. Solution NMR spectra of II were obtained by subjecting reaction mixtures to repetitive partial evaporation and addition of C$_6$D$_6$. NMR data for II obtained with the Schrock catalysts (ref 12) is as follows: three approximately equal intensity ^{13}C signals at 133.0, 47.8, and 12.8 ppm and three approximately equal intensity ^{1}H signals at 5.83, 3.28, 1.73 ppm (C$_6$D$_6$). These shifts are compared to those of I (^{13}C 133.7, 48.3, 36.6 ppm and ^{1}H 5.95, 3.53, 1.84 ppm in C$_6$H$_6$). Multiple smaller ^{13}C peaks in the region of 40–20 ppm were observed, and the intensity of these peaks increased relative to the major peaks with increasing time; thus we attributed these peaks to crosslinking. UV–vis spectra of films of II displayed a maximum at 190 nm and a shoulder at 270 nm. Infrared spectra were complex (ref 16); however, the presence of cis olefins is confirmed by the strong absorption at 750 cm^{-1}. The infrared data and the observation of only one olefinic carbon in the ^{13}C NMR suggests that II has nearly exclusively cis olefins.

(16) There is extensive mixing in the infrared spectrum of II, as is also observed for I: Griffith, D. W. T.; Kent, J. E.; Dwyer, F. O. *Aust. J. Chem.* **1975**, *28*, 1397.

(17) X-ray diffraction of II showed only a diffuse amorphous halo.

(18) (a) Weinstein, S.; Leftin, J. H.; Kerbs, J.; Gil-Av, E. *J. Chem. Soc. D* **1971**, 1616. (b) Cristl, M.; Heinemann, U.; Kristof, W. *J. Am. Chem. Soc.* **1975**, *97*, 2299.

(19) Renner, C. A.; Katz, T. J.; Pouliquen, J.; Turro, N. J. *J. Am. Chem. Soc.* **1975**, *97*, 2568.

(20) (a) Mango, F. D. *Coord. Chem. Rev.* **1975**, *15*, 109 and references therein. (b) Gassman, P. G.; Atkins, T. J. *J. Am. Chem. Soc.* **1971**, *93*, 4597.

(21) Irradiation with 193-nm laser light produced no observable change in the material. Complete thermal analysis results will be reported in a forthcoming full paper.

(22) Conductivities were measured by the standard DC four-point probe method: Seeger, K. *Semiconductor Physics*; Springer-Verlag: New York, 1973.

(23) Details of the CP-MAS ^{13}C NMR experiment have been published elsewhere (ref 24). The HgCl$_2$ isomerized material was ductile and could not be ground fine enough to obtain the required spinning rates. *trans*-PA is known to be more brittle than *cis*-PA and hence III was thermally isomerized (ref 2) to *trans*-III which was readily ground. CP-MAS ^{13}C NMR spectra of the *trans*-III exhibited a sharp resonance at 135.5 ppm and a small broad signal at 40.0 ppm. Infrared spectroscopy revealed broad major absorptions at 3100, 1000 (trans), and 740 (cis) cm^{-1}. With thermal isomerization the spectrum sharpened, and the 740-cm^{-1} resonance dissappeared. The sharp 1329-cm^{-1} absorption usually observed in *cis*-PA is not present in III. This is most likely a result of the broadness of the spectra and/or isolated cis olefins. However, a slight decrease in the signal intensity of this region is observed with thermal isomerization to *trans*-III. Infrared spectra also displayed minor absorptions at 2800 and 1400 cm^{-1} characteristic of saturated material before and after thermal treatment.

(24) Eckert, H.; Yesinowski, J. P.; Sandman, D. J.; Velazquez, C. S. *J. Am. Chem. Soc.* **1987**, *109*, 761.

(25) DSC scans of III showed no exothermic transitions indicating residual bicyclobutanes. Variation of parameters in CP-MAS ^{13}C NMR experiments indicated that the resonance at 40 ppm had a shorter $T_{1\rho}$ than the 135-ppm peak, consistent with the 40-ppm peak having a more rigid environment.

(26) Elemental analysis (Spang Microanalytical Laboratories) showed samples that were extracted with THF to be 89.2% carbon and hydrogen (C/H = 1.09), suggesting the presence of residual metal. Efforts are underway to remove impurities and to minimize the crosslinking.

(27) X-ray diffraction experiments of III showed a somewhat broad peak at 23° (2θ Cu Kα) with no other observable peaks. The width at half height was 10° which is considerably broader than PA prepared by other methods (ref 26).

(28) (a) Bott, D. C., et al. *Synth. Metals* **1986**, *14*, 245 and references therein. (b) Bott, D. C.; Brown, C. S.; Winter, J. N.; Barker, J. *Polymer* **1987**, *28*, 601.

(29) Resonant Raman spectra showed two characteristic peaks at 1070 and 1520 cm^{-1} when the sample was excited with 488-nm laser light.