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Poly(trimethylsilylcyclooctatetraene): A Soluble Conjugated Polyacetylene via Olefin Metathesis

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Highly conjugated polymers, such as polyacetylene, polythiophene, and poly(*p*-phenylene vinylene), have been the subject of intensive research due to their intriguing optical and electronic properties.² These parent systems are highly desirable for experimental and theoretical studies due to their simplicity. Their intractability, however, has made characterization an arduous task, and insolubility has severely limited their applications. Researchers have successfully circumvented these obstacles by synthesizing soluble alkyl- and alkoxy-substituted polythiophenes and poly(*p*-phenylene vinylenes).³ Analogous soluble highly conjugated polyacetylene derivatives have proven more elusive.^{4,5} We report here the synthesis of such a polymer using ring-opening metathesis polymerization (ROMP).⁶

Recently, Klavetter and Grubbs reported the synthesis of polyacetylene by the ring-opening metathesis polymerization of cyclooctatetraene with a well-defined non-Lewis acidic tungsten alkylidene catalyst.^{7,8} ROMP of substituted cyclooctatetraenes

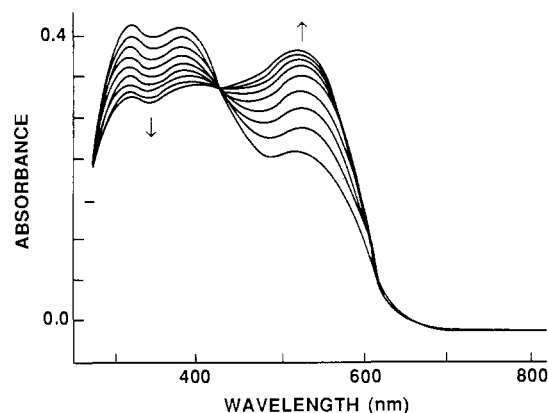


Figure 1. UV-vis spectra of poly(TMSCOT) in carbon tetrachloride (10^{-6} M) obtained between eight periods of photolysis (10 s each).

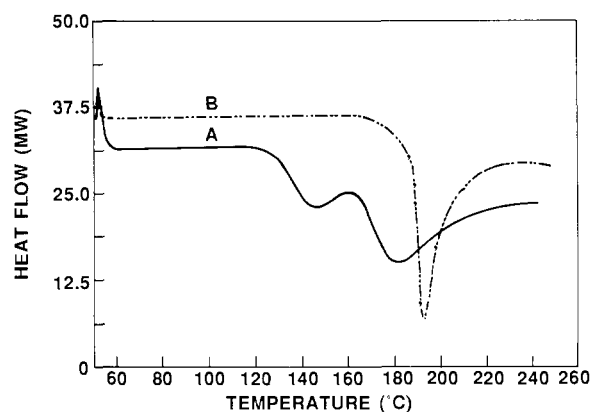
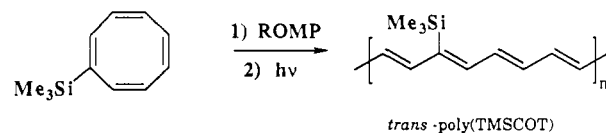


Figure 2. Differential scanning calorimetry thermogram of poly(TMSCOT) (9 mg) (A) prior to photolysis and (B) after photolysis.¹²

provides a convenient route to a variety of substituted poly-cyclooctatetraenes whose properties may be "tuned" by changing the substituent. We focus here on the properties of poly(trimethylsilylcyclooctatetraene) (poly(TMSCOT)). Other derivatives will be reported elsewhere.⁹



Poly(TMSCOT) is readily prepared on a multigram scale in a nitrogen drybox. In a typical small-scale polymerization, the tungsten catalyst¹⁰ (2 mg, 2.5 μ mol) is dissolved in a solution of 20 μ L of tetrahydrofuran and trimethylsilylcyclooctatetraene¹¹ (100 mg, 0.6 mmol). The yellow solution is then transferred by pipette onto a glass slide. During the course of the polymerization, the color of the material changes to red as it solidifies. The resulting free-standing polymer film is readily soluble (>1 mg/mL) in carbon tetrachloride, benzene, and tetrahydrofuran. Gel permeation chromatography indicates that the polymer is of high molecular weight.^{12,13}

(9) Gorman, C. B.; Ginsburg, E. J.; Marder, S. R.; Perry, J. W.; Grubbs, R. H., submitted.

(10) W(CHR)(NAr)[OC(CH₃)(CF₃)₂]₂ was used. (a) For R = *t*-Bu, Ar = 2,6-diisopropylphenyl, see: Schrock, R. R.; DePue, R. T.; Feldman, J.; Schaverien, C. J.; Dewan, J. C.; Liu, A. H. *J. Am. Chem. Soc.* **1988**, *110*, 1423. (b) Johnson, L. K.; Virgil, S. C.; Grubbs, R. H., manuscript in preparation.

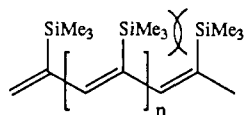
(11) Cooke, M.; Russ, C. R.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1975**, 256.

(12) Prior to obtaining thermograms, elemental analyses, and gel permeation chromatograms, the films were rinsed repeatedly with dry pentane and methanol under argon in order to remove soluble components such as residual monomer, catalyst decomposition products, and trimethylsilylbenzene produced by "back-biting" during the polymerization.⁸

- (1) (a) California Institute of Technology. (b) Jet Propulsion Laboratory.
(2) See discussions in: (a) *Handbook of Conducting Polymers*; Skotheim, T. A., Ed.; Marcel Dekker: New York, 1986; two volumes. (b) *Electroresponsive Molecular and Polymeric Systems*; Skotheim, T. A., Ed.; Marcel Dekker: New York, 1988; Vol. 1.
(3) See, for example: (a) Jen, K. Y.; Oboodi, R. L.; Elsenbaumer, R. L. *Polym. Mat. Sci. Eng.* **1985**, *53*, 79. (b) Hotta, S.; Rughooputh, S. D. D. V.; Heeger, A. J.; Wudl, F. *Macromolecules* **1987**, *20*, 212. (c) Rughooputh, S. D. D. V.; Nowak, M.; Hotta, S.; Heeger, A. J.; Wudl, F. *Synthetic Metals* **1987**, *21*, 41. (d) Askari, S. H.; Rughooputh, S. D.; Wudl, F.; Heeger, A. J. *Polym. Prepr.* **1989**, *30*, 157.
(4) A number of polyacetylene graft copolymers have been made. See: (a) Armes, S. P.; Vincent, B.; White, J. W. *J. Chem. Soc., Chem. Commun.* **1986**, 1525. (b) Dorsinville, R.; Tubino, R.; Krimchansky, S.; Alfano, R. R.; Birman, J. L.; Bolognesi, A.; Destri, S.; Catellani, M.; Porzio, W. *Phys. Rev. B* **1985**, *32*, 3377. (c) Tubino, R.; Dorsinville, R.; Lam, W.; Alfano, R. R.; Birman, J. L.; Bolognesi, A.; Destri, S.; Catellani, M.; Porzio, W. *Phys. Rev. B* **1984**, *30*, 6601. (d) Baker, G. L.; Bates, F. S. *Macromolecules* **1984**, *17*, 2619. (e) Stowell, J. A.; Amass, A. J.; Beevers, M. S.; Farren, T. R. *Makromol. Chem.* **1987**, *188*, 1635.
(5) Nonconjugated polyacetylenes have been prepared: (a) Zeigler, J. M. U.S. Patent Appl. US 760 433 AO, November 21, 1986; *Chem. Abstr.* **1986**, *20*, 157042. (b) Zeigler, J. M. *Polym. Prepr.* **1984**, *25*, 223. (c) Okano, Y.; Masuda, T.; Higashimura, T. *J. Polym. Sci.: Polym. Chem. Ed.* **1984**, *22*, 1603. (d) Masuda, T.; Higashimura, T. *Adv. Polymer Science* **1987**, *81*, 121.
(6) (a) Grubbs, R. H. In *Comprehensive Organometallic Chemistry*; Wilkinson, G.; Stone, F. G. A.; Abel, E. W., Eds.; Pergamon: Oxford, 1982; Chapter 54. (b) Ivin, K. J. *Olefin Metathesis*; Academic: London, 1983. (c) Novak, B. M.; Grubbs, R. H. In *Encyclopedia of Polymer Science and Engineering*; Kroschwitz, J. I., Ed.; John Wiley & Sons: New York, 1989, in press.
(7) Lewis acidic metathesis catalysts have been used to polymerize cyclooctatetraene, resulting in a polymer containing many sp³ defects: (a) Tlenkopachev, M. A.; Korshak, Yu. V.; Orlov, A. V.; Korshak, V. V. *Dokl. Akad. Nauk SSSR (Engl. Transl.)* **1986**, *291*, 1036; *Dokl. Akad. Nauk SSSR* **1986**, *291*, 409. (b) Korshak, Yu. V.; Korshak, V.; Kansichka, G.; Höcker, H. *Makromol. Chem. Rapid Commun.* **1985**, *6*, 685.
(8) Klavetter, F. L.; Grubbs, R. H. *J. Am. Chem. Soc.* **1988**, *110*, 7807.

The visible absorption of undoped poly(TMSCOT) solutions shifts to lower energies irreversibly upon exposure to light. This is attributed to a cis-trans isomerization of the polymer.¹⁴ The course of a photolysis experiment¹⁵ was monitored by UV-vis (Figure 1) and ¹H NMR spectroscopy.¹⁶ Differential scanning calorimetry thermograms¹² of the polymer before and after photolysis are shown in Figure 2.¹⁷ An exotherm present at 145 °C in the nascent polymer is not observed after photolysis. Since polyacetylene thermally isomerizes from cis to trans at 150 °C,¹⁸ these data are consistent with the hypothesis that poly(TMSCOT) is undergoing a cis-trans isomerization upon photolysis in solution. The initially formed polymer is expected to have a high cis content since three of the four cis double bonds of the monomer are unlikely to be affected by the metathesis polymerization. Highly reflective soluble polymer films can be cast from a photolyzed purple solution.¹⁹

Upon doping with iodine, the conductivities of the cis films are less than 10⁻⁵ Ω⁻¹ cm⁻¹, while the conductivities of the trans films are typically 0.2 Ω⁻¹ cm⁻¹.^{18,20,21} By comparing the absorbance maximum of undoped trans-poly(TMSCOT) (512 nm) to the maxima of polyenes prepared by Schrock and co-workers,²² the effective conjugation length of trans-poly(TMSCOT) is thought to be greater than that of a polyene containing 15 unsubstituted double bonds. The lowest energy absorption maximum observed for the cis polymer is at 380 nm, implying an average effective conjugation length of less than nine double bonds. trans-Poly(TMSCOT) can also be compared to a polymer made from a substituted acetylene, for example, poly(trimethylsilylacetylene),⁵ depicted below, which shows a conductivity of 10⁻⁴ Ω⁻¹ cm⁻¹ when saturated with iodine. Presumably, the placement of substituents at every other carbon induces sufficient twisting of the poly(trimethylsilylacetylene) backbone to significantly decrease the effective conjugation length of the polymer π-system.²³ The poly(RCOT) methodology allows placement of the substituents at every eighth carbon atom, on the average, and consequently results in polymers of higher conjugation length. In the present case, where R = Me₃Si, this substitution pattern is sufficient to render the polyene soluble.



poly(trimethylsilylacetylene)

Because of its solubility and conductivity, poly(TMSCOT) is a candidate for study in a variety of investigations. For example,

(13) $M_n = 137\,000$ versus polystyrene by gel permeation chromatography.

(14) For a discussion of cis-trans photoisomerization, see: Turro, N. J. *Modern Molecular Photochemistry*; Benjamin/Cummings: Menlo Park, CA, 1978; Chapter 12.

(15) Light from a Pyrex-filtered, 450-W high pressure mercury Hanovia lamp was used for photolyses.

(16) NMR data for the cis-poly(TMSCOT) were obtained from a sample containing both isomers of the polymer. cis-Poly(TMSCOT): ¹H NMR (THF-*d*₆, 400 MHz) δ 0.15 (s), 5.8-7.1 (br m). trans-Poly(TMSCOT): ¹H NMR (THF-*d*₆) δ 0.23 (s, 9 H), 6.5 (br s, 5 H), 7.0 (br m, 2 H); ¹³C{¹H} NMR (methylene chloride-*d*₂) δ -0.25 (s), 128-145 (m). Elemental analysis, calculated for (C₁₁H₁₆Si)_n: C, 74.93; H, 9.14. Found: C, 74.2; H, 8.9.

(17) The exotherm observed at higher temperatures may be due to a cross-linking reaction, since samples which have been heated above 200 °C are totally insoluble.

(18) Chien, J. C. W. *Polyacetylene: Chemistry, Physics, and Material Science*; Academic: Orlando, FL, 1984.

(19) The polymer is treated as an air-sensitive material. After exposure of a 20-30-μm thick film to air for 2 h, approximately 20% of the material is no longer soluble in tetrahydrofuran.

(20) Conductivities were measured with a four-point probe in a nitrogen drybox or a four-wire probe attached to a Schlenk line. The films were exposed to iodine for several hours and then exposed to vacuum for at least 1 h to remove excess iodine.

(21) Sze, S. M. *Physics of Semiconductor Devices*; John Wiley & Sons: New York, 1981; p 30.

(22) Schrock, R. R.; Krouse, S. A.; Knoll, K.; Feldman, J.; Murdzek, J. S.; Yang, D. C. *J. Mol. Catal.* **1988**, *46*, 243.

(23) Petit, M. A.; Soum, A. H.; Leclerc, M.; Prud'homme, R. E. *J. Polym. Sci.: Part B: Polym. Phys.* **1987**, *25*, 423.

we are examining spin-coated films for third-order nonlinear optical properties.²⁴ The polymer is amorphous, so losses due to light scattering are less than one observed for crystalline materials. Additionally, we have found that thin transparent films of I₂-doped poly(TMSCOT) can be used in Schottky barrier type solar cells.²⁵

In summary, ROMP of trimethylsilylcyclooctatetraene, followed by photolysis in solution, provides a soluble, trans-polyacetylene derivative in which the substituents are placed a sufficient distance apart to allow conjugation along the backbone. Work is underway using the RCOT/ROMP methodology to develop other polyacetylene derivatives which are soluble, more conductive, and air-stable.

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(24) For discussions of third-order nonlinear optical properties in organic materials, see: *Nonlinear Optical Properties of Organic Molecules and Crystals*, Vol. 2; Chemla, D. S., Zyss, J., Eds.; Academic: Orlando, FL, 1987.

(25) Sailor, M. J.; Lewis, N. S.; Ginsburg, E. J.; Gorman, C. B.; Marder, S. R.; Grubbs, R. H., manuscript in preparation.

[(Benzosemiquinone-18-crown-6)⁻Li⁺Na⁺]⁺: A Paramagnetic Triple Ion with Two Different Counter Cations¹

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The ability of host molecules M to discriminate among various guest cations Me⁺ is widely known.² Like this shape-selective encapsulation [MMe⁺], site-specific complexation at electron-rich centers may also successfully compete with cation solvation, especially, if additional Coulombic attraction by the negative charge, e.g., of a molecular radical anion M^{•-}, helps to stabilize the resulting contact ion pair radical [M^{•-}Me⁺].³⁻⁵ Moreover, if M^{•-} contains several appropriate docking sites and can be generated by single electron transfer in aprotic solution with surplus Me⁺X⁻ content, contact triple ion radical cations, [Me⁺M^{•-}Me⁺]^{•+}, with two identical counter cations readily form.⁶⁻⁸ They are best

(1) Electron Transfer and Ion Pairing. 12. Part 11, see: Bock, H.; Herrmann, H. F. *Helv. Chim. Acta* **1989**, *72*, in print.

(2) Cram, D. J. *Science (Washington, D.C.)* **1988**, *240*, 760. Lehn, J. M. *Angew. Chem.* **1988**, *100*, 91; *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 89. Pedersen, C. J. *Pure Appl. Chem.* **1988**, *60*, 450.

(3) Cf. e.g.: Lubitz, W.; Plato, M.; Möbius, K.; Biehl, R. *J. Phys. Chem.* **1979**, *83*, 3402 and the literature survey given.

(4) Bock, H.; Hierholzer, B.; Vögtle, F.; Hollmann, G. *Angew. Chem.* **1984**, *96*, 74; *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 57 and literature cited.

(5) Bock, H.; Hierholzer, B.; Schmalz, P. *Angew. Chem.* **1987**, *99*, 811; *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 791 and literature cited.

(6) Since their first ESR detection by Gough and Hindle (Gough, T. E.; Hindle, P. R. *Can. J. Chem.* **1968**, *47*, 1698) many triple ion radical cations have been characterized by ESR/ENDOR techniques, cf., e.g.:^{7,8} or Hierholzer, B. Ph.D. Thesis University of Frankfurt, 1988.

(7) Bock, H.; Solouki, B.; Rosmus, P.; Dammel, R.; Hänel, P.; Hierholzer, B.; Lechner-Knoblach, U.; Wolf, H. P. In *Organosilicon and Bioorganosilicon Chemistry*; Sakurai, H., Ed.; Horwood Lim.: Chichester, 1985; pp 59-65. See, also: Bock, H. *Polyhedron* **1988**, *7*, 2429 or Hänel, P. Ph.D. Thesis, University of Frankfurt, 1987.

(8) Cf., e.g.: Kurreck, H.; Kirste, B.; Lubitz, W. *Electron Nuclear Double Resonance Spectroscopy of Radicals in Solution*; VCH Publishers: New York, 1988; and literature cited.