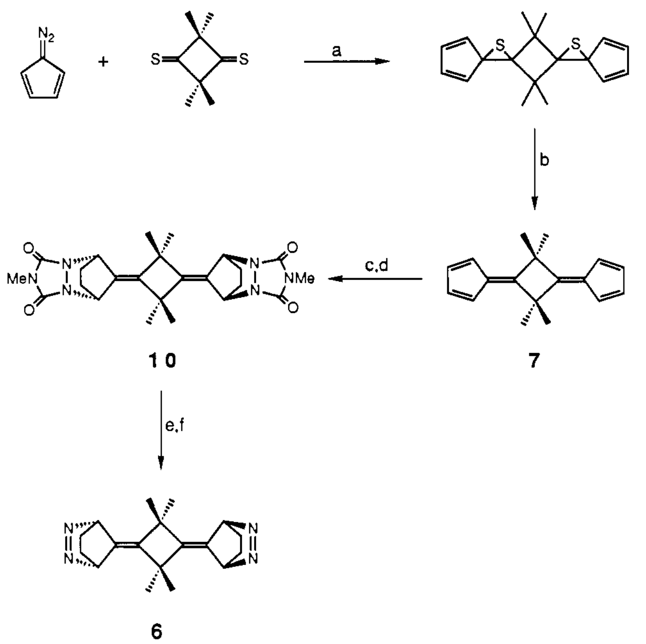
Scheme I[a]



[a] (a) Mixture of products (syn/anti dithiiranes, monothiirane and **7**), 4 weeks, room temperature, dark; (b) PPh_3; (c) *N*-methyltriazolinedione; (d) $NH_2NH_2{\cdot}H_2O$, O_2; syn isomer unstable to hydrogenation conditions; (e) KOH, 2-PrOH, reflux, 2 h; (f) NiO_x.

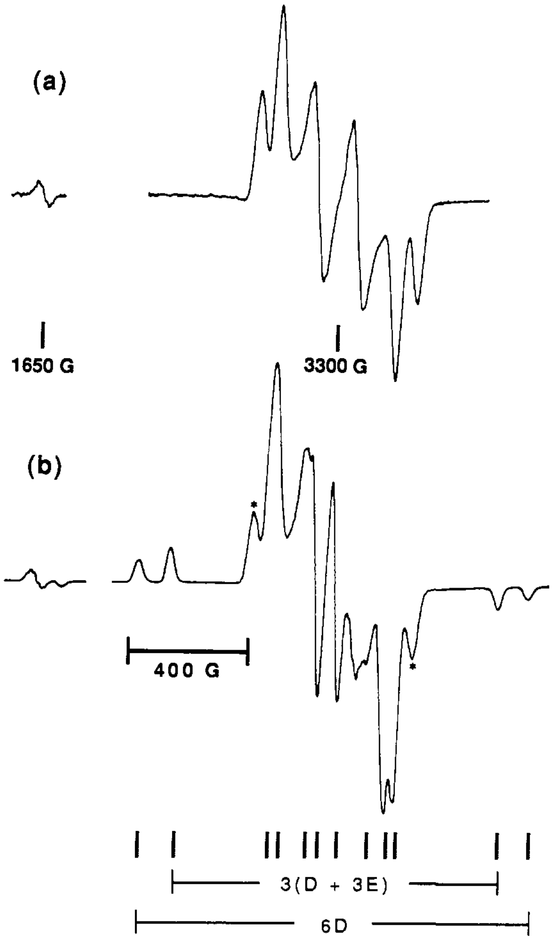


Figure 1. (a) Triplet EPR spectrum of **8** obtained upon brief photolysis of **6**. $|D/hc| = 0.0253$ cm^{-1} and $|E/hc| = 0.0042$ cm^{-1}. (b) Quintet EPR spectrum of **3** obtained upon extended photolysis of **6**. The vertical bars indicate the expected positions of the 12 transitions, from which the quintet zfs parameters can be obtained, as shown. Some **8** is also present, and the starred peaks are pure triplet **8** signals.

peratures as low as 3.8 K. Second, a Curie plot is linear in the range 17–80 K.[17] The usual interpretation of such observations is that the quintet is the ground state, although exact degeneracies among differing spin states cannot be ruled out.

An especially intriguing feature of **3** is its thermal stability. All cyclobutanediyls (**5**) prepared to date, including those with radical-stabilizing substituents, decay in the 20–55 K range and are not easily observed at temperatures above 60 K.[18] However, **3** is indefinitely stable at liquid nitrogen temperatures (77 K) and can be readily generated at this temperature. The cause of this enhanced stability is under further investigation.

Clearly, the localized biradical, 1,3-cyclobutanediyl, does ferromagnetically couple the two TMM triplets. This is the first rationally designed organic quintet that does not owe its high spin preference to the topology of a delocalized π system.[19] It has long been appreciated that magnetism, unlike conductivity, does not require delocalization, but **3** is the first organic realization of this concept. Our results suggest that cyclobutane is a general, ferromagnetic coupling unit, and further studies of this effect and extensions to still higher spin states are underway.

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(17) The limitations on the usefulness of Curie plots have been discussed in detail. See: (a) Platz, M. S. In *Diradicals*; Borden, W. T., Ed.; Wiley: New York, 1982; p 195. (b) Wertz, J. E.; Bolton, J. R. *Electron Spin Resonance: Elementary Theory and Practical Applications*; McGraw-Hill: New York, 1972. (c) In the present system, as in most related studies, signal saturation occurs at $T < 15$ K, making this temperature range unusable for the Curie plot. (d) For a thorough discussion of the complexities involved in Curie plots for $S = 2$ molecules, see ref 14a, p 205.

(18) Sponsler, M. B.; Jain, R.; Coms, F. D.; Dougherty, D. A. *J. Am. Chem. Soc.* **1989**, *111*, 2240–2252.

(19) A variety of structures containing four stable radicals, such as galvinoxyls, appended to a central atom have been prepared and quintet states observed. The nature of the spin coupling mechanism and the relative energies of the various spin states are not known. See, for example: Kirste, B.; Grimm, M.; Kurreck, H. *J. Am. Chem. Soc.* **1989**, *111*, 108–114, and references therein.

Ab Initio Molecular Orbital Studies of Chemical Shielding in Transition-Metal Compounds: ^{95}Mo Shielding in Molybdate and Thiomolybdate $[MoO_nS_{(4-n)}]^{2-}$ Anions

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Ab initio molecular orbital methods for chemical shielding have been extensively applied to first- and second-row elements[1-5] but

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(1) Kutzelnigg, W. *Israel J. Chem.* **1980**, *19*, 193. Schindler, M.; Kutzelnigg, W. *J. Chem. Phys.* **1982**, *76*, 1919. Schindler, M.; Kutzelnigg, W. *J. Am. Chem. Soc.* **1985**, *105*, 1360. Schindler, M. *J. Am. Chem. Soc.* **1988**, *110*, 6623 and references cited therein.

(2) Hansen, Aa. E.; Bouman, T. D. *J. Chem. Phys.* **1985**, *82*, 5035. Bouman, T. D.; Hansen, Aa. E.; Voight, B.; Rettrup, S. *Int. J. Quantum Chem.* **1983**, *23*, 595. Bouman, T. D.; Hansen, Aa. E. *Chem. Phys. Lett.* **1988**, *149*, 510.

(3) Facelli, J. C.; Grant, D. M.; Bouman, T. D.; Hansen, Aa. E. *J. Comput. Chem.*, in press.

Table I. Ab Initio LORG/GAUSSIAN 86 Results for Mo Shielding in the Series of Thiomolybdates Compared with the Experimental Values (Values in ppm) and Mo Atomic Charges[a]

species[b]	σ_d	σ_p	σ_T	δ[c] calc	δ[c] exp[d]	Mo atomic charge
$[MoO_4]^{2-}$	5388.2	−6395.5	−1007.3	0.0	0	1.590
$[MoSO_3]^{2-}$	5399.8	−7219.1	−1819.3	812.0	497	0.964
$[MoS_2O_2]^{2-}$	5361.8	−8168.6	−2806.8	1799.5	1067	0.312
$[MoS_3O]^{2-}$	5508.0	−9208.3	−3700.3	2693.0	1654	−0.387
$[MoS_4]^{2-}$	5589.4	−10334.8	−4744.4	3737.1	2259	−0.961

[a] Basis sets on Mo were obtained with an extra diffuse *d*-function (orbital exponent 0.045) with a triple-ζ (433321/43311/4211) basis set on Mo and 4-31+G functions on the O and S ligands. (Huzinaga, S. *Gaussian Basis Sets for Molecular Calculations*; Elsevier: New York, 1984. Binkley, J. S.; Pople, J. A.; Hehre, W. J. *J. Am. Chem. Soc.* **1980**, *102*, 939). [b] All of the anions were assumed to be tetrahedral; bond lengths which were optimized for $[MoO_4]^{2-}$ and $[MoS_4]^{2-}$ using GAUSSIAN 86 with the basis set above [r(Mo–O) = 1.7841 Å and r(Mo–S) = 2.15 Å] were used for all of the anions. [c] Values relative to $[MoO_4]^{2-}$. [d] Reference 15.

have not generally been applied to transition-metal complexes. It is demonstrated that the localized orbital–local origin (LORG)[2] method satisfactorily reproduces the experimental NMR trends in the series of molybdate and thiomolybdate anions. Moreover, both the calculated and experimental shift data for Mo on successive replacement of oxygen by sulfur in this series give good correlations with the calculated increase (more negative) of the molybdenum atomic charge.

Although experimental chemical shift data for transition-metal compounds are extensive,[6-9] there are only two previous nonempirical studies.[10,11] These were for several compounds of transition elements (Cu, Zn, Ag, Cd, and Mn) and used finite perturbation theory (FPT) methods of SCF-MO theory. The calculated results reproduced many of the experimental trends, but all except the Mn compounds have filled *d*-subshells so that the shieldings are dominated by the diamagnetic terms.[12]

To perform the LORG/GAUSSIAN 86 computations the requisite modules were prepared to link the LORG algorithm in the RPAC program of Bouman and co-workers[2] to the output of the GAUSSIAN 86 program.[13] Entered in Table I are the calculated diamagnetic contributions, σ_d, paramagnetic contributions, σ_p, and the total shielding, σ_T, of Mo in a series of $[MoO_nS_{(4-n)}]^{2-}$ (n = 0–4) anions compared with the experimental data.[14,15] Clearly, both the total shielding and the changes in the shielding are dominated by the paramagnetic contributions; in fact, the change in the diamagnetic contributions is less than 5% throughout the series. In existing calculations of shielding in transition-metal compounds, this behavior has only been noted for Mn.[11] The data for the atomic charges on Mo in Table I strongly suggest that oxygen atoms attract electrons more strongly than the sulfur atoms in this series, and the resulting increase in the electron density on the molybdenum as oxygens are replaced by sulfur atoms is primarily due to the increases in the populations of the 5p and 4d orbitals on Mo. It is the increasing occupation of Mo orbitals having nonzero angular momentum which leads to the increasing (negative) paramagnetic contributions σ_p in column 3 of Table I. The excellent correlation of *both the experimental and calculated* Mo shifts with the calculated Mo atomic charges should be noted.

Calculated and experimental chemical shift data in columns 5 and 6 in Table I are referenced to the $[MoO_4]^{2-}$ values. Since these calculations are only at the triple-ζ level for the valence orbitals of the metal, overestimation (larger absolute value) of the paramagnetic contributions was expected.[16,17] Qualitatively, however, the monotonic deshielding resulting from successive replacement of oxygen by sulfur is well-reproduced by the calculated results in Table I. In fact, the correlation coefficient r^2 is 0.9997 in the linear regression between the calculated and experimental ^{95}Mo shift data ($\delta_{calc} = 1.65\delta_{exp} - 2$ ppm). In the last column of Table I are the calculated atomic charges on Mo, which were obtained with the same basis set. Because of the big change in the charges on Mo in calculations performed here at the triple-ζ and double-ζ levels for the metal and ligands, respectively, it was of interest to investigate the metal atomic charges upon introducing a diffuse *d*-function on Mo in accordance with the suggestion by Hay[18] that this procedure would improve the representation of 3d^{n+2} systems. Although the total range of charges is somewhat smaller, the sign reversal is reproduced in this series of anions. This big change in the electron distributions of thiomolybdates probably accounts for the very different chemistry for molybdate and thiomolybdates,[19] including the tendency of thiomolybdates to undergo intramolecular redox reactions.[20]

There exists a vast literature of chemical shift data for transition-metal compounds in which the many trends are largely unexplained.[6-9] The results presented here clearly show that ab initio MO computational techniques for nuclear shielding can be used very effectively for qualitative interpretation of the experimental trends in chemical shifts of transition-metal compounds. Although these results require large-scale computational efforts, it is important to note that the methods are feasible without an excessively large basis set, inclusion of configuration interaction, and relativistic effects (at least up to the second-row transition elements).

Acknowledgment. We extend thanks to Professor T. Bouman for providing a preliminary version of the RPAC program and to Professor W. Kutzelnigg and Dr. M. Schindler for permission to use the IGLO program, and J.C.F. thanks Prof. D. M. Grant for his hospitality. We also want to express our appreciation for support from the U.S. Department of Agriculture under Grant

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[4] For reviews of the theory of shielding see, for example: Jameson, C. J. In *Nuclear Magnetic Resonance*; (Specialist Periodical Reports); The Chemical Society London, Burlington House: London; 1987; No. 16, and previous chapters in this series.

[5] Ditchfield, R. *Mol. Phys.* **1974**, *27*, 789. Rohlfing, C. M.; Allen, L. C.; Ditchfield, R. *Chem. Phys.* **1984**, *87*, 9.

[6] Webb, G. A. In *NMR of Newly Accessible Nuclei*; Laszlo, P. Ed.; Academic Press: New York, 1983; Vol. 1, p 79.

[7] Harris, R. K.; Mann, B. E. *NMR and the Periodic Table*; Academic Press: New York, 1978.

[8] Mason, J. *Multinuclear NMR*; Plenum: New York, 1987.

[9] Minelli, M.; Enemark, J. H.; Brownlee, R. T. C.; O'Connor, M. J.; Wedd, A. G. *Coordination Chem. Rev.* **1985**, *68*, 169.

[10] Nakatsuji, H.; Kanda, K.; Endo, E.; Yonezawa, T. *J. Am. Chem. Soc.* **1984**, *106*, 4653.

[11] Kanda, K.; Nakatsuji, H.; Yonezawa, T. *J. Am. Chem. Soc.* **1984**, *106*, 5888.

[12] The improvement of the distributed origins method adopted here over the FPT method is attributable to the damping of basis set errors associated with long-range contributions to chemical shielding.[1,2] However, for the symmetrical, or nearly symmetrical, molecules studied here, differences from the coupled Hartree–Fock methods with the metal origins are expected to be small.[3] In fact, preliminary chemical shielding results from these laboratories are similar to those of Nakatsuji et al.[10] for transition-metal compounds in which the metals have a d^{10} configuration. An exception is the absolute Cu shielding value of −2246 ppm which was reported for CuCl.[10] This is almost certainly incorrect in view of the good correspondence of our calculated values of +2440 ppm (IGLO) and +2298 ppm (LORG).

[13] GAUSSIAN 86, Frisch, M. J.; Binkley, J. S.; Schlegel, H. B.; Raghavachari, K.; Melius, C. F.; Martin, R. L.; Stewart, J. J. P.; Bobrowicz, F. W.; Rohlfing, C. M.; Kahn, L. R.; Defrees, D. J.; Seeger, R.; Whiteside, R. A.; Fox, D. J.; Fleuder, E. M.; Pople, J. A. Carnegie-Mellon Quantum Chemistry Publishing Unit: Pittsburgh, PA, 1984.

[14] A preliminary shielding result for Mo(CO)$_6$ with a single-ζ basis set on Mo is σ_T = +364.1 ppm, which is qualitatively in accord with the experimental data[15] even with this small basis set.

[15] Lutz, O.; Nolle, A.; Kronek, P. *Z. Naturforsch.* **1976**, *31A*, 454; **1977**, *32A*, 505.

[16] In the IGLO and LORG approaches reasonable chemical shift results are often obtained for the simpler cases of first- and second-row elements if the basis sets are at least double-ζ in quality.

[17] Orendt, A. M.; Facelli, J. C.; Beeler, A. J.; Reuter, K. J.; Horton, W. J.; Cutts, P.; Grant, D. M.; Michl, J. *J. Am. Chem. Soc.* **1988**, *110*, 3386.

[18] Hay, J. P. *J. Chem. Phys.* **1977**, *66*, 4377.

[19] Müller, A.; Diemann, E.; Jostes, R.; Bögge, H. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 934.

[20] Rittner, W.; Müller, A.; Neumann, A.; Bäther, W.; Sharma, R. C. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 530. Miller, K. F.; Bruce, A. E.; Corbin, J. L.; Wherland, S.; Stiefel, E. I. *J. Am. Chem. Soc.* **1980**, *102*, 5102.

No. 84-CrCr-1-1416 and the Cornell National Supercomputer Facility, a resource of the Center for Theory and Simulations in Science and Engineering, which receives major funding from the National Science Foundation and IBM Corporation, with additional support from New York State and members of the Corporate Research Institute.

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 provides a convenient route to a variety of substituted polycyclooctatetraenes 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]

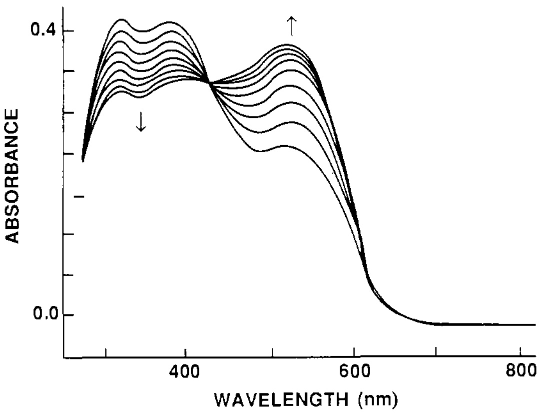


Figure 1. UV–vis spectra of poly(TMSCOT) in carbon tetrachloride (10^{-6} M) obtained between eight periods of photolysis (10 s each).

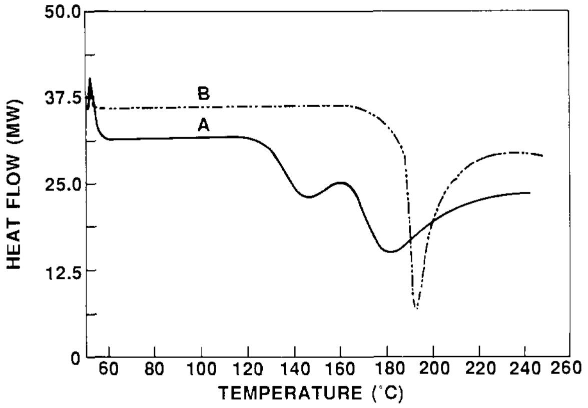
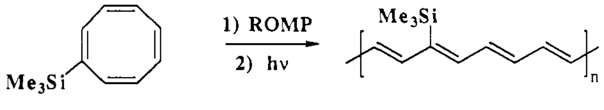


Figure 2. Differential scanning calorimetry thermogram of poly(TMSCOT) (9 mg) (A) prior to photolysis and (B) after photolysis.[12]



trans -poly(TMSCOT)

Poly(TMSCOT) is readily prepared on a multigram scale in a nitrogen drybox. In a typical small-scale polymerization, the tungsten catalyst[10] (2 mg, 2.5 μmol) is dissolved in a solution of 20 μL of tetrahydrofuran and trimethylsilylcyclooctatetraene[11] (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]

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(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. Prep.* **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 sp^3 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, Y. 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.

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

(10) $W(CHR)(NAr)[OC(CH_3)(CF_3)_2]_2$ 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 permation 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]

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