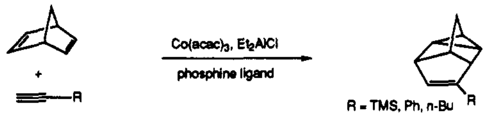
Communications to the Editor

Preparation and Ring-Opening Metathesis Polymerizations of 5-Siloxydeltacyclene and Deltacyclene Using the Schrock Molybdenum Alkylidene Catalyst

The development of "living catalysts" has created a resurgence of interest in ring-opening metathesis polymerization (ROMP) for the preparation of polyolefinic polymers.[2-5] Schrock, Osborn, and Grubbs have each developed metal alkylidene complexes that act as catalysts for the living ROMP of various cyclic olefins.[3,4] The advantages of these new catalysts include mild reaction conditions, control of the microstructure of the polymer, and the ability to prepare block copolymers.

We have recently reported the first study of the ring-opening metathesis polymerization of deltacyclene, 1.[6a] Our objectives in this program are to develop simple and efficient routes to novel monomers and polymeric materials, which are both rigid (due to the nortricyclane framework) and highly strained (due to the cyclopropane). Further modification of the thermal and mechanical properties of the polymers can be envisioned either by direct reaction of the polymer or via the synthesis of modified monomers and their subsequent polymerization. We have already reported our studies on the former approach by selective hydrogenation or epoxidation of the olefins.[6b] In this paper, we describe the use of a novel rearrangement reaction for the incorporation of a hydroxyl substituent into a deltacyclene monomer and the polymerization of this hydroxylated monomer using the Schrock molybdenum alkylidene catalyst 3, $Mo(=CHCMe_2Ph)(=N\text{-}2,6\text{-}(i\text{Pr})_2Ph)(OtBu)_2$. We also report that the oxygenated polymer has substantially increased solubility and a higher glass transition temperature than polydeltacyclene (PDC).

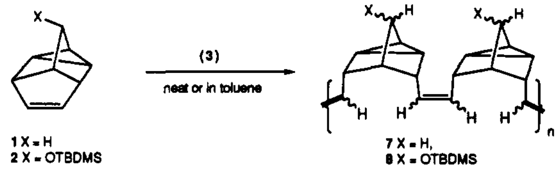
The most direct route to the preparation of a functionalized polydeltacyclene would involve the ROMP of deltacyclene bearing a substituent on the olefin, since a large variety of these compounds are now readily available via a cobalt-catalyzed [2 + 2 + 2] homo-Diels–Alder reaction between norbornadiene and a substituted acetylene, eq 1.[7] Unfortunately, substituted deltacyclenes where R = TMS, Ph, or *n*-Bu failed to undergo appreciable degrees of ROMP under our previously successful reaction conditions or with the Schrock catalyst.[8] Therefore, we sought an efficient preparation of an oxygenated deltacyclene where the substituent would act as a site for modification of the polymer but would be at a site other than directly on the olefin. The application of a rearrangement reaction of deltacyclene epoxides presented an attractive strategy to address this problem.[9]



(1)

Deltacyclene epoxide, 4, is known to undergo a homocyclopropyl rearrangement when treated with an aqueous acid. In this reaction, an alcohol appears at the carbon that is destined to become C-5 and solvent is trapped at C-8, giving 5, Scheme I. We decided to take advantage of this rearrangement by trapping the intermediate cation with a nucleophile capable of subsequent elimination to reform an olefin. Since sulfoxides are known to undergo thermal elimination, the reaction was run in thiophenol[10] and the sulfide 5 obtained was then oxidized to a mixture of diastereomeric sulfoxides 6 in 94% yield.[11] Protection of the alcohol as its silyl ether[12] provided the precursor to 2 in quantitative yield. The elimination of the siloxy sulfoxide was first examined in neat *N,O*-bis(trimethylsilyl)acetamide[13] at 160 °C, but only one diastereomer was reactive at this temperature. When the reflux temperature was increased to 180 °C by carrying out the reaction in *p*-bromotoluene in the presence of 2–3 equiv of *N,O*-bis(trimethylsilyl)acetamide, both diastereomers underwent elimination, providing the desired product 2 in 75% yield after purification.[14] The overall yield for this five-step procedure was 63%. Alternately, treatment of 6 with 1.5 equiv of 1,8-diazabicycloundecene (DBU) in decalins at 180 °C gave the unprotected 5-hydroxydeltacyclene in 91% yield, which was converted to 2 by silylation of the alcohol.[15] Either of these routes provides access to multiple-gram quantities of the monomer without resorting to chromatographic separation of the intermediates.

We have carried out preliminary polymerization experiments of 1 and 2 with catalyst 3 either neat or as solutions in toluene or chloroform. As the catalyst was sensitive to both moisture and oxygen, all reactions were performed in a glovebox and the monomers were rigorously dried over calcium hydride prior to use. The neat polymerizations were initiated by the addition of 0.02–3.0 mol % of 3 to the monomer with vigorous stirring, eq 2. For those polymerizations run in solution, the catalyst was dissolved in the appropriate solvent (see Table I) and added in one portion to a stirred solution of the monomer in the same solvent. After 5–10 min,[16] the polymerization was judged to be complete, resulting in a clear glassy solid or a viscous solution for both substrates. The reaction mixtures were then purified by dissolution of the solid in chloroform and precipitation with methanol. This procedure produced white fibrous polymers in >90% yield, which were identified by their ^1H and ^{13}C NMR spectra. The spectral data for polydeltacyclene (7, PDC), prepared as described above, were identical with those obtained previously.[6] The ratio of trans to cis alkene (as determined by ^1H NMR) varied from 2.7:1 to 1.9:1. The PDI's of these high molecular weight polymers were found to be 1.58 and 1.27, entries 1 and 2 in Table I.[17] Upon decreasing the chain length, the PDI improved to 1.09, entry 3.



(2)

Polymerization of 5-siloxydeltacyclene (SDC) gave poly(siloxydeltacyclene) (PSDC, 8), which showed increased solubility in common organic solvents such as benzene or chloroform compared to PDC. The polymer and monomer

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Scheme I

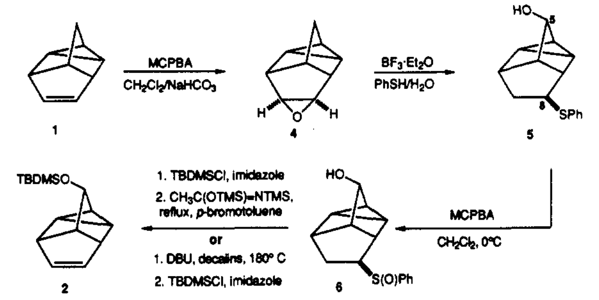


Table I
Polymerization Conditions and Molecular Weight Data

entry	M	GPC M_W(uncorr)	GPC M_N	DP	PDI	solvent
1	PDC	466 000	295 000	3950	1.58	neat
2	PDC	74 100	58 190	630	1.27	toluene
3	PDC	16 200	14 970	138	1.09	toluene
4	PSDC	78 200	44 300	315	1.77	neat
5	PSDC	13 300	9 300	55	1.44	toluene

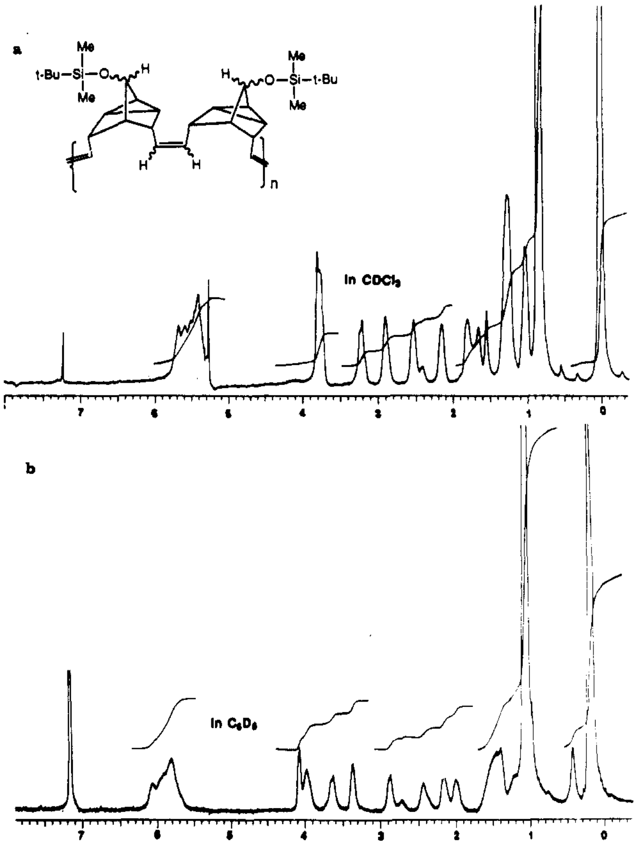
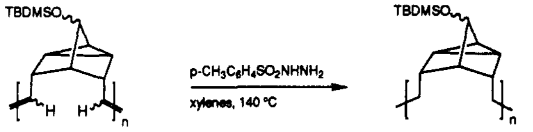


Figure 1.

were characterized by ${}^1H$ and ${}^{13}C$ NMR spectroscopy and GPC. The PDI's of the substituted polydeltacyclenes are shown in the Table I. In the ${}^1H$ NMR ($CDCl_3$) of monomer **2**, every proton has a distinct, observable resonance.[18] The olefinic protons appear at 6.14 and 5.98 ppm, the proton on the siloxy-bearing carbon is at 4.05 ppm, and the two allylic protons appear at 3.09 and 2.61 ppm. The spectra for poly(siloxydeltacyclene) (PSDC) were more complex than those obtained for PDC due to the lack of symmetry in the monomer and hence the polymer.[19,20] In the ${}^1H$ NMR spectrum ($CDCl_3$) of **8**, a broad olefinic resonance is observed, Figure 1a.[19] The proton at C-5 appears as a broad singlet at 3.78 ppm with the two allylic protons at 2.90 and 2.18 ppm. These peaks are accompanied by additional resonances at 3.25 and 2.55 ppm attributed to the minor isomer, the ratio of major to minor peaks being dependent on the polymerization conditions. The ${}^1H$ NMR spectrum in C_6D_6 shows similar patterns to that in $CDCl_3$ with the exception that the signal corresponding to the proton at H-5 now appears as two partially resolved signals at 4.09 and 3.99 ppm, Figure 1b. When the reaction was run without solvent, the ratio of peaks at 2.90 and 3.25 ppm was 1:1; as a solution in toluene with 0.5% catalyst, the ratio was ca. 4:1. We have assigned the resonance at 2.90 ppm to the trans isomer and the resonance at 3.25 ppm to the cis isomer in keeping with our previous observations on the selectivity of molybdenum catalysts toward the production of the trans isomer in reactions with deltacyclene. The polymerization was found to be a highly exothermic process, and the increase in selectivity observed may be due to a more controlled polymerization under higher dilution conditions. In principle, several types of isomeric units are possible from the ROMP of an unsymmetrical olefin including olefin isomers and orientational isomers (head-to-head vs head-to-tail and tacticity). The ${}^{13}C$ NMR spectra of PSDC were similar for all the polymers irrespective of the ratio of isomers. In an effort to identify the type of selectivity, **8** was hydrogenated so as to decrease the number of possible isomers, eq 3.[21] After 5 h of exposure to the diimide precursor *p*-toluenesulfonyl hydrazone in refluxing xylene, the reaction was complete as evidenced by the disappearance of the olefinic protons in the ${}^1H$ NMR. The ${}^1H$ NMR spectrum of **8** displayed a single resonance at 3.68 ppm in $CDCl_3$ and at 3.88 ppm in C_6D_6, which was assigned to the proton at C-5, but the ${}^{13}C$ NMR spectrum showed >13 signals.[22] We conclude that the polymerization has given a mixture of HH, TT, and HT isomers.



(3)

We have also measured the glass transition temperatures of these materials using capillary rheometry.[23] The T_g increased from 64 to 88 to 108 °C for PNB, PDC, and PSDC, respectively. In conclusion, we have shown that rearrangement of deltacyclene epoxide and trapping with thiophenol represents an attractive route to deltacyclene monomers bearing a masked hydroxyl group. Polymerization of **1** or **2** is very facile using the Schrock catalyst, and control over the molecular weights and PDI's is possible. The successful polymerizations of **1** and **2** also demonstrates the compatibility of the Schrock catalyst toward the sensitive cyclopropane ring. Opportunities now exist for the preparation of modified rigid polymers through attachment of groups at the hydroxylic oxygen. Studies in this direction are in progress and will be reported in due course.

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References and Notes

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(6) For the use of Ru, Re, and W as catalysts for the polymerization of deltacyclene, see: (a) Lautens, M.; Abd-El-Aziz, A. S.; Reibel, J. *Macromolecules* **1989**, *22*, 4132. A typographical error appears in this paper. The assignment of the cis and trans olefin peaks were inadvertently reversed. The downfield resonance at ca. 5.65 ppm is assigned to the trans isomer and the upfield resonance at ca. 5.50 ppm is assigned to the cis isomer. The ratios in the table are correctly assigned. For complete spectral information for the cis isomer, see: (b) Lautens, M.; Abd-El-Aziz, A. S.; Schmidt, G. *Macromolecules* **1990**, *23*, 2819.

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(10) Compound **4** is dissolved in PhSH and added dropwise to 8 equiv of $BF_3 \cdot Et_2O$ in PhSH (5% H_2O, final concentration of **4** is 0.07 M). After 2 h, the reaction is quenched with $NaHCO_3$ and extracted. The ether and thiophenol are removed by distillation, and the mixture is purified by recrystallization from hexane–chloroform.

(11) The ratio of diastereomers varied from 1:1 to 5:1, depending on the oxidation temperature; see: Paquette, L. A.; Carr, R. V. C. *Org. Synth.* **1986**, *64*, 157. Pitchen, P.; Dunach, E.; Deshmukh, M. N.; Kagan, H. B. *J. Am. Chem. Soc.* **1984**, *106*, 8188.

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(14) The silyl-protected sulfoxide **6** is dissolved in *p*-bromotoluene, and 2 equiv of *N*,*O*-bis(trimethylsilyl)acetamide is added. After refluxing for 11 h, the solvent and acetamide byproducts are removed by vacuum distillation (using a steam condenser) and the product is then purified by bulb to bulb distillation [bp 60 °C (0.05 mm)].

(15) We thank Rudi Rulkens for performing these experiments.

(16) The solution polymerizations of 5-siloxydeltacyclene were run for a longer period of time because the polymer's high solubility in toluene made it difficult to assess when the polymerization was complete.

(17) Gel permeation chromatography (GPC) was carried out on a Varian 5000 liquid chromatograph using an Ultrastyragel 10^4-, 10^3-, or 500-Å column with THF as eluant.

(18) ^1H NMR (200 MHz, $CDCl_3$): δ 6.14 (m, 1 H), 5.98 (m, 1 H), 4.05 (br s, 1 H), 3.09 (br s, 1 H), 2.61 (br s, 1 H), 1.79 (br s, 1 H), 1.64 (m, 1 H), 1.46 (m, 1 H), 1.33 (m, 1 H), 0.88 (s, 9 H), 0.03 (s, 3 H), 0.02 (s, 3 H).

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(22) Compound **8**. ^{13}C NMR (50.1 MHz, C_6D_6): δ 79.4, 44.9, 44.5, 43.5, 42.2, 41.8, 32.3, 32.1, 31.5, 30.6, 26.1, 19.9, 19.0, 18.5, 17.1, −4.2. A complete analysis of the spectra will appear in the full paper on this work.

(23) T_g's were measured on a Shimadzu Flowtester by Dr. G. Sacripante of Xerox Research Centre of Canada. The M_N and PDI for each sample are as follows: PNB, 341 000 and 1.3; PDC, 58 190 and 1.27; PSDC, 89 000 and 1.3.

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