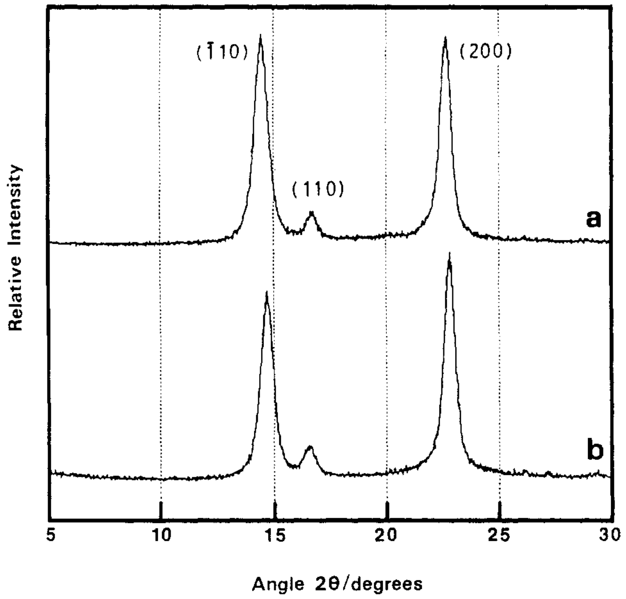

Figure 3. X-ray diffractograms of valonia cellulose (a) and the sample annealed at 260 °C in the 0.1 N NaOH solution (b).

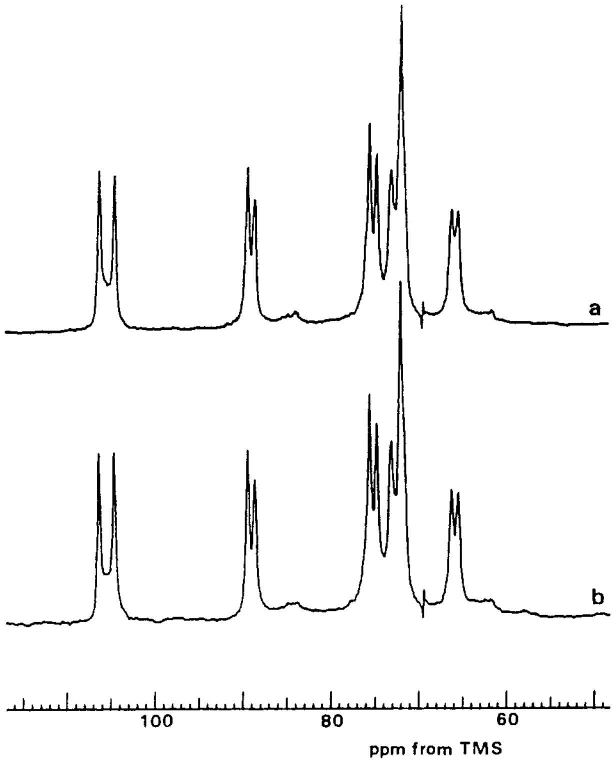

Figure 4. 50-MHz CP/MAS ^{13}C NMR spectra of tunicate cellulose (a) and the sample annealed at 260 °C in the 0.1 N NaOH solution (b).

cellulose sample seems to be very close to that of cellulose I_α' or cellulose I_β, which was defined by Atalla and VanderHart,[6,7] as first pointed out by Belton et al.[11] Figure 4 shows CP/MAS ^{13}C NMR spectra of tunicate cellulose and the sample annealed at 260 °C in the 0.1 N NaOH solution. In accord with the previous report,[11] the multiplets of the C1, C4, and C6 lines of the intact sample, which are virtually doublets, are very similar to those of cellulose I_α' or cellulose I_β. Moreover, no change in the multiplicities can be observed for the annealed sample. This may confirm that the crystal structure of tunicate cellulose is originally cellulose I_α' or cellulose I_β. Further discussion will be given elsewhere after detailed line-shape analyses are conducted for the C1 and C4 lines.

Registry No. NaOH, 1310-73-2; HCl, 7647-01-0; cellulose, 9004-34-6.

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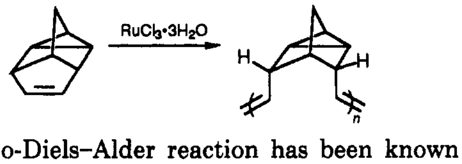
Ring-Opening Metathesis Polymerization of Deltacyclene via a Ruthenium Catalyst

The ring-opening metathesis polymerization (ROMP) of cycloalkenes was first reported in a patent in 1957 by Eleuterio and in the open literature by Truett in 1960.[2] Both synthetic and mechanistic aspects of the reaction have held the attention of chemists since that time.[3,4] We were intrigued by the possibility of preparing new materials having a combination of rigidity and strain through ROMP of suitable monomers. The homo-Diels–Alder reaction,[5] in which a highly strained deltacyclic olefin-containing compound is synthesized by cycloaddition of norbornadiene with an acetylene, provides such a monomer. The polymers derived from metathesis of this cycloalkene meet these criteria since they contain an inflexible carbon backbone, a cyclopropane ring, and a repeating sequence of olefins, which are held in close proximity due to the diendo orientation in the nortricyclane framework (eq 1).



(1)

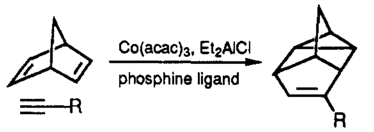
The homo-Diels–Alder reaction has been known for almost 30 years, and the synthesis of deltacyclene was first reported in 1965.[6] Of the two routes available to provide large quantities of deltacyclene, we preferred the method developed by Lyons since it requires a single step and proceeds at room temperature.[7] However, the yields ob-

Table I
Effect of Increasing Water on Molecular Weight

entry	ratio, mol SM/Cat/S	ratio, mol EtOH/H_2O	MW	yield, %
1	100/1/400	1/0	2000[a]	31
2	100/1/400	1/1	103000[b]	72
3	100/1/400	1/100	206000[c]	90
4	100/1/400	0/1	207000[c]	85

[a] Ratio of cis to trans isomers = 1/1.3. [b] Ratio cis to trans = 1/1. [c] Ratio of cis to trans isomers = 1/1.5.

tained are modest (ca. 45%). Our recent work has focused on expanding the scope and improving the yield of the reaction through activation of the catalyst.[8] We have shown that by azeotropically drying the cobalt complex, the catalyst generated upon reduction is substantially more effective in promoting this cycloaddition. The catalyst is prepared by in situ reduction of $Co(acac)_3$ with Et_2AlCl (DEAC) in the presence of the ligand 1,2-bis(diphenylphosphino)ethane (dppe). Thus far, acetylene, several sterically hindered acetylenes, and alkyl acetylenes bearing remote oxygen functionality participate in the reaction (eq 2).[8] Yields in excess of 80% are routinely observed. In this communication we report a study of the ROMP of deltacyclene in the presence of a ruthenium catalyst.[9] High molecular weight polymers are readily available through this methodology.



(2)

The crude products from the polymerization reactions described below were dark brown solids that were easily purified. The two methods found to be most convenient were precipitation or column chromatography on silica gel. The former method was the preferred one due to the simplicity of purification and ease of scale up. Specifically, the solid was dissolved in chloroform and then precipitated by slow addition of methanol while maintaining vigorous stirring. A white fibrous solid was obtained after a single purification. The highest molecular weight polymers, which were the least soluble, were soluble in halogenated solvents, THF, cyclohexane, and aromatic solvents such as benzene and xylenes.

The initial metathesis experiments were carried out under conditions previously described for the polymerization of norbornene (i.e., 1 mol % $RuCl_3 \cdot H_2O$ in anhydrous ethanol at 60 °C).[10,11] A solid precipitated during the course of the reaction, which GPC showed to be a low molecular weight polymer (Table I, entry 1).[12,13] In an attempt to increase the length of the polymer chains, the reaction was carried out in varying mixtures of ethanol/water. These experiments were guided by Grubbs' observation that addition of water to a ruthenium-catalyzed polymerization caused an increase in the rate of reaction and was effective for the preparation of high molecular weight macromolecules.[14] As shown in Table I, the addition of varying amounts of water to ethanol resulted in a similar dramatic increase (100-fold) in the molecular weight of the polymer derived from deltacyclene. Polymerization also occurred in water as the only solvent in spite of the insolubility of the monomer, entry 4. However, no further increase in M_w or yield was observed under these conditions. An increase in the polydispersity index (PDI) as a function of increasing water content (2.04 in ethanol and 3.46 in water) was noted. The M_w of the polymer was also affected by changes in the catalyst/monomer ratio. Decreasing the ratio of catalyst to monomer from 1 mol % to 0.17 mol % resulted in a substantial increase in M_w (Table II). Molecules with molecular weights approaching 10^6 were routinely isolated.

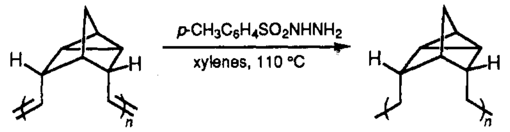
Table II
Effect of Catalyst/Monomer

entry	ratio[a] of SM/Cat, mol	MW[b]	yield, %
1	100/1	103000	72
2	200/1	447000	78
3	600/1	856000	85

[a] All reactions carried out in ethanol/water (1/1). [b] Ratio of cis to trans isomers = 1/1.

In the determination of the polymer microstructure from the ring opening of deltacyclene, both olefin stereochemistry and ring diad tacticity must be considered.[15] Similar issues of stereoselectivity have been addressed in the ring opening of norbornene and oxabicycloheptenes whose ^1H and ^{13}C NMR spectra have been analyzed in detail.[3,14,15] The spectral data described below are all in agreement with a mixture of olefin isomers being formed in the ROMP. The ^1H NMR at 200 MHz in $CDCl_3$ showed two broad resonances at 5.82 and 5.63 ppm, which were assigned to the olefinic protons in the cis and trans isomers, respectively.[16a] Integration of these signals provided the ratio of cis/trans isomers reported in the tables. When the solvent was changed to xylenes-d_{10} and the field was increased to 400 MHz, a total of four lines was now observed (6.10, 6.04, 5.97, 5.94 ppm). The total area of the two upfield lines vs the two downfield lines indicated these pairs were associated with the two resonances observed in $CDCl_3$. The ^{13}C NMR spectrum also showed two groups of closely spaced signals at 132.2 and 131.6 ppm, which were assigned to the trans and cis isomers, respectively. Integration of these signals give ratios in agreement with those from the proton spectra. Several of the other signals in the aliphatic region of the ^{13}C NMR spectrum showed a similar series of closely spaced signals.[16b] Ruthenium catalysts have been reported to yield polymers containing *trans*-olefins, and thus it is surprising to observe such low stereoselectivity.[17]

It was also important to demonstrate that a selective reaction could be performed on these difunctional polymers. Diimide was generated and reacted in situ by heating a solution of *p*-tosylhydrazine and the polymer in xylene at 110 °C for 3 h (eq 3).[18] The NMR spectrum of the gel in $CDCl_3$ of the white highly insoluble solid isolated from these experiments indicated that a clean reaction at the olefinic moiety was indeed possible. Six lines were observed in the ^{13}C NMR spectrum in $CDCl_3$ including those assigned to the cyclopropane (11.4, 15.2 ppm) and the aliphatic carbons (46.5, 46.4, 36.2, 31.0 ppm). No olefinic signals were observed in either the ^1H or ^{13}C NMR nor was there any fine structure in the aliphatic carbons. Ivin has observed a similar loss of tacticity information upon hydrogenation of polynorbornene.[19]



(3)

A series of experiments were carried out with the goal of changing the stereoselectivity of the ROMP. Formamide has been reported to have such an effect by increasing the amount of the trans isomer in the ring opening of norbornene.[20] In fact, increasing the proportion of formamide to ethanol did not result in any change in stereoselectivity as measured by ^1H NMR. However, the

Table III
Effect of Formamide/Ethanol

entry	EtOH/$HCONH_2$[a]	MW[b]	yield, %
1	5/1	86 000	42
2	1/1	259 000	54
3	1/7	929 000	42

[a] Ratio of SM/Cat/S = 100/1/400. [b] Ratio of cis to trans isomers = 1/1.8.

Table IV
Homogeneous Polymerization of Deltacyclene

entry	ratio mol of SM/Cat/S	solvent (ratio)	MW[a]	yield, %
1	100/1/350	EtOH/PhH (1/3)	5 000	60
2	200/1/400	EtOH/THF (1/10)	35 000	68
3	100/1/400	H_2O/THF (1/10)	992 000	74

[a] Ratio of cis to trans isomers = 1/1-1.5.

M_w did increase with increasing amounts of formamide (Table III).

We also examined polymerization under conditions where the starting material and product would be completely soluble. Reaction in THF or benzene in the presence of hydroxylic solvents caused the solution to become highly viscous during the course of the reaction but remain as one phase. In general, these reaction conditions were inferior to those described above. However, when the polymerization was carried out in a mixture of water/THF, a high molecular weight polymer was isolated (Table IV, entry 3). No other changes were observed (i.e., olefin double-bond isomer ratio).

Measurement of the glass transition temperature, T_g, using differential scanning calorimetry (DSC) was attempted so as to more fully characterize the macromolecules. These experiments proved unsuccessful since no T_g was observed from −150 to +150 °C. Instead, a highly exothermic process was noted at ca. 135 °C. When the measurement was repeated on the same sample, a totally different curve was observed. When a sample of the polymer was heated in an inert atmosphere to 150 °C, the ratio of olefinic to aliphatic protons decreased. We have been unable to fully characterize this material to determine the nature of the reaction.

The chemistry described demonstrates the viability of preparing polymers from a ring-opening metathesis of deltacyclene. High molecular weight macromolecules have been isolated in excellent yield. The polymers synthesized have olefins that are rigidly held at defined distances due to the nortricyclane framework. Studies are in progress to exploit the unique features of these new molecules. The ROMP of substituted deltacyclenes is also under way, the results of which will be reported in due course.

Acknowledgment. This research was supported by the Natural Science and Engineering Research Council (NSERC) of Canada, the Bickell Foundation, the Ontario Centre for Materials Research (OCMR), and the University of Toronto. We thank Professors M. A. Winnik, J. E. Guillet, and W. F. Reynolds of the University of Toronto for helpful discussions and the DAAD (FRG) for the support of J.R. during his stay in Toronto. We also thank T. Huber of the University of Toronto for performing the ebuliometry measurements.

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(12) Gel permeation chromatography (GPC) was carried out on a Varian 5000 liquid chromatograph using an Ultrastyragel 10^4-Å or 500-Å column with THF as eluant.
(13) The M_w and M_n of the polymer were calculated from GPC analysis [vs poly(methyl methacrylate) standard]. To check the accuracy of this method, this value was compared to the M_n calculated from ebuliometry of a dilute solution of the polymer in refluxing benzene. The two values were within 15-20% of one another: Huber, T., unpublished results.
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(16) (a) The ^1H NMR also has diagnostic resonances at 2.40 and 2.10 ppm, which are assigned to the protons allylic to the olefin in the cis and trans isomers. Comparison of the integrals of these signals confirms the ratios determined from integration of the olefinic resonances. (b) The polymer from ROMP of deltacyclene has signals in the ^{13}C spectrum at 51.4, 46.8, 45.1, 44.6, 44.5, 44.4, 44.3, 44.2, 38.6, 19.6, 19.5, 19.3, 18.4, 18.3, and 14.6 ppm in xylenes-d_{10} at 100 MHz. It is not possible at this time to determine which local stereochemical effects (i.e., ct, tc, etc. or m/r diads) are responsible for these signals. Up to six signals (three assigned to the cis and three to the trans) have been observed in the ^{13}C NMR spectrum for the olefinic region of the polymer derived from ROMP of norbornene. All the carbons show cc, ct, and tt splitting, but no splittings that can be assigned to m/r effects are observed. See: ref 3.
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Supported Vanadium Catalyst for Isospecific Propylene Polymerization

Ziegler-Natta (ZN) catalysts for isospecific polymerization of α-olefins are mainly based on group IV transition elements. Vanadium compounds on the other hand have a propensity for syndioselectivity.[1] $V(acac)_3/AlEt_2Cl$[2a] and $V(mbd)_3/AlEt_2Cl$[2b] (mbd = 2-methyl-1,3-butanedianato) catalyze "living" syndiospecific polymerization of propylene