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Polymerization of Norbornene by Olefin Metathesis Catalysts: Insertion and Ring Opening in the Same Chain

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ABSTRACT: Investigation of the homopolymer of norbornene prepared with Re or Mo catalysts showed that propagation occurs by an insertion process with an occasional ring-opening step in the same chain. Evidence comes from NMR spectrometry, where DEPT spectra of the polymer show the disappearance of some olefinic carbons that do not have hydrogen atoms attached to them. Ozonolysis of the polymer supports the NMR indications. Finally, polymerization of 2,3-dideuterionorborene and $^{13}C\{^2H\}$ polarization transfer NMR studies on the polymer show that deuterium is transferred, likely by α-D migration to the metal, from the 2-position on norbornene to a methylene group. To the best of our knowledge, this $^{13}C\{^2H\}$ polarization transfer NMR experiment represents the first application of the method to the selective detection of small amounts of unique structural components in a polymer. An inverse temperature relationship on the extent of ring opening was found for both catalysts.

Introduction

In previous reports we showed that $Re(CO)_5Cl/C_2H_5AlCl_2$ and $Mo(CO)_5py/C_2H_5AlCl_2/R_4NCl$ are effective catalysts for the metathesis of acyclic olefins.[1,2] A preliminary report on this work showed that, under certain reaction conditions using the $Re(CO)_5Cl$ catalyst system, norbornene was converted to high molecular weight polymers (M_n = 154 200; M_w = 443 000; polydispersity = 2.9), and the composition of the polymer was determined to have, by integration of olefinic to aliphatic proton signals in the ^1H NMR spectrum, 10 monomers with ring retention for every ring-opened monomer.[3]

Several cases of polymerization of cyclic olefins have been reported in which the structure of the final polymer indicated that ring-opening metathesis polymerization (ROMP) and ring-retention (insertion process) polymerization occur simultaneously on the same catalyst in the same chain. For example, a variety of cyclobutenes were reported to give polymers containing both ring-retained and ring-opened units.[4,5] *endo*-Dicyclopentadiene polymerization with a variety of catalysts gave polymers with varying degrees of unsaturation in the main chain.[6] This type of behavior has also been observed in the polymerizations of *exo,exo*- and *endo,endo*-hexacyclo-[9.2.1.0^{2,10}.0^{3,8}.0^{4,6}.0^{5,9}]tetradec-12-ene,[7] bicyclo[3.2.0]hepta-2,6-diene,[5] and bicyclo[4.2.0]octa-7-ene.[5] Polymers of norbornadiene[6] and norbornene[8] have been prepared that show saturated and unsaturated repeat units in the polymer backbone.

Ivin has proposed a mechanism that can account for saturated and unsaturated monomer units occurring in the same chain, by invoking insertion and α-H migration on the same catalyst,[9] as shown below.

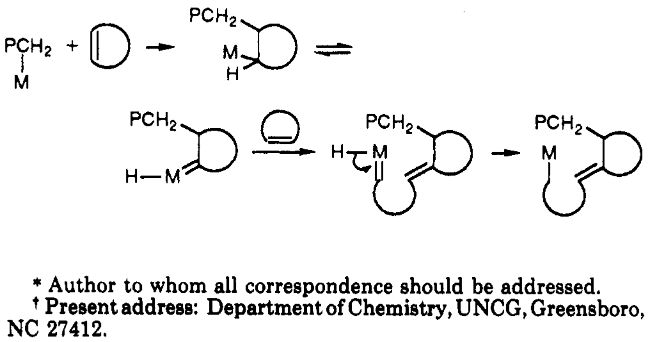

Table I
Polymerization of Norbornene at Various Temperatures[a]

catalyst	temp, °C	yield, %	O:A	ROMP, %
A	26	100	1:4.0	100
A	100	89.7	1:6.0	83
A	110	84.6	1:15	48
B	100	10	1:4.07	99.3
B	110	77.2	1:97.5	9.7
B	120	41.4	1:175	5.5
B	132	25.4	0:100	0.0

[a] A = $Mo(CO)_5py/C_2H_5AlCl_2/R_4NCl$; B = $Re(CO)_5Cl/C_2H_5AlCl_2$; O:A = olefinic to aliphatic proton ratio.

This work concerns the polymerization of norbornene with catalysts that give polymers that appear to be of the type where insertion and ROMP have both occurred. Experiments were designed to test the validity of Ivin's proposed mechanism. Among these experiments is the novel application of the $^{13}C\{^2H\}$ INEPT NMR technique combined with ^2H labeling. The label was incorporated in the starting material to produce CD_2 groups if Ivin's mechanism is operative. The $^{13}C\{^2H\}$ INEPT experiment permitted selective detection of these CD_2 fragments without interference from CH or CH_2 signals from the rest of the polymer backbone.

Results and Discussion

Before considering the studies on the mechanism of polymerization, it should be pointed out that the polymers were prepared for solution studies by column chromatography. According to gel permeation chromatography, which shows a single, relatively narrow peak for the polynorbornene polymers prepared from the two catalyst systems, the polymers are single species composed of saturated and unsaturated linkages in the same chain. It is unlikely that a mixture of polymers, one totally saturated and one ring-opened, is present in the final sample, in light of the purification procedures and GPC results.

A first aspect is that, if competing steps of insertion and metathesis occur on the same catalyst, then a temperature dependence would be expected; i.e., one process or the other would be favored at lower or higher temperature. From first principles, noting that both catalysts are effective metathesis catalysts for acyclic olefins, it might be expected that α-H abstraction is a lower energy process than insertion. Therefore, a greater degree of ROMP might be expected at lower temperatures whereas insertion would be more facile at higher temperatures. Table I shows

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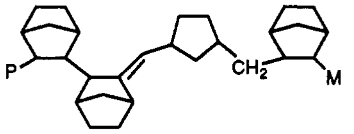
the results of a temperature-dependence study on the polymerization of norbornene with the two catalysts.

It is clear that there is a temperature effect on the relative amount of ROMP observed for each catalyst. The temperature window for the Re catalyst is much narrower, but activation of the catalyst requires a minimum temperature of 90 °C.[1]

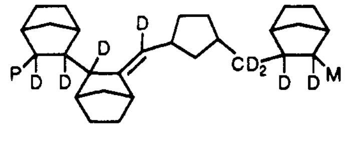
A second aspect in the investigation of the propagation steps of the catalyst is to examine the proposed structure of the polymer of norbornene where both insertion and ROMP are involved. This is shown below.



Since a hydrogen atom leaves the 2-position of a norbornene monomer and ends up on a methylene group, there must now be an olefinic carbon without a hydrogen attached to it. Furthermore, the stereochemistry about that carbon can be of four configurations: *E*, exo; *E*, endo; *Z*, exo; and *Z*, endo. Examination of the ^{13}C NMR spectrum of the polymer reveals four sets of resonances in the olefinic region at 131.8, 132.3, 132.5, and 132.8 ppm whose signals disappear in a $^{13}C\{^1H\}$[10] DEPT (distortionless enhancement by polarization transfer) spectrum, showing that these carbons are not protonated. The spectrum of polynorbornene obtained from the Re catalyst is similar.

In order to obtain confirmatory evidence as to the structure of the polymer, ozonolysis was carried out. If the proposed structure is correct, as indicated by the DEPT NMR spectra, then a ketone carbonyl derived from the olefinic 2-carbon of the norbornene ring should be produced. In fact, the ^{13}C spectrum of the products from ozonolysis of the polymer exhibits a resonance at 218.4 ppm, consistent with the presence of an aliphatic ketone similar to that in norcamphor (216 ppm).

As a final test of the mechanism of propagation of the polymer, 2,3-dideuterionorbornene was synthesized and polymerized with the Re catalyst. The object of this experiment was to track the migration of a deuterium atom from the 2-position of norbornene to the methylene group. This was accomplished by $^{13}C\{^2H\}$ INEPT (insensitive nuclei enhanced by polarization transfer) NMR spectroscopy.[11] As can be seen in the structure of the deuterated polymer below, aliphatic CD resonances arise from the labeled corners of the norbornene rings, and methylene CD_2 resonances arise from migration of D. By combining the use of $^{13}C\{^2H\}$ INEPT with incorporation of the ^2H label at the 2- and 3-positions of the norbornene monomer, the appearance of CD_2 groups from ROMP can be detected without interference from the CH and CH_2 resonances in the rest of the norbornene structures in the polymer. The $^{13}C\{^2H\}$ INEPT spectrum (Figure 1) shows clearly an enhanced CD_2 signal at ca. 27 ppm.



This study provides strong evidence that Ivin's proposal is correct. A carbon atom in a norbornene unit without a hydrogen atom attached to it most likely arises from α-hydrogen abstraction to create a metal–carbene complex, which would then undergo metathesis to give a ring-opened monomer unit. Any subsequent ring-opening steps that occur before migration of the hydrogen to a methylene group, which terminates metathesis and initiates insertion, would give ring-opened units with a hydrogen on every carbon. This paper also illustrates the feasibility of using $^{13}C\{^2H\}$ INEPT techniques for the selective detection of structural defects in rigid, high molecular weight polymers, despite the relatively short ^2H relaxation times.

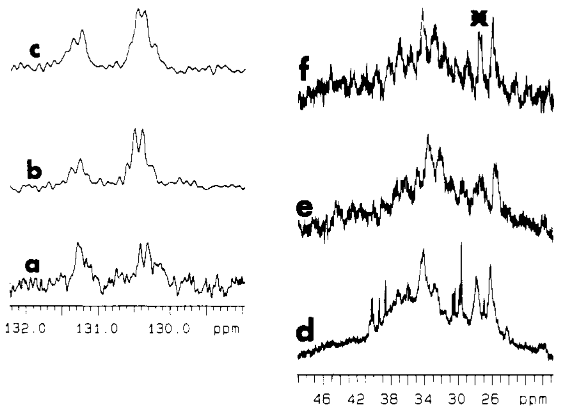


Figure 1. ^1H- and ^2H-decoupled ^{13}C NMR spectra of poly(2,3-dideuterionorbornene) showing expansions of the olefinic (a–c) and aliphatic (d–f) regions. Expansions from the normal ^{13}C spectrum without polarization transfer are shown in a and d; expansions from the $^{13}C\{^2H\}$ INEPT spectrum show CD resonances only (b and e) and CD/CD_2 resonances (c and f). Note the appearance of the CD_2 resonance in f at ca. 27 ppm.

Experimental Section

Physical Methods. Routine ^1H and ^{13}C NMR spectra were recorded on a Varian Gemini 300-MHz spectrometer. ^1H, ^{13}C, DEPT, and ^2H NMR spectra were taken on a Varian VXR 300-MHz spectrometer. The standard DEPT software package provided with the instrument was used. Proton and carbon spectra were recorded with $CDCl_3$ as solvent and internal reference. Tetramethylsilane was used as a reference when necessary. Deuterium spectra were recorded in $CHCl_3$ or toluene. $^{13}C\{^2H\}$ INEPT NMR spectra of 2,3-dideuterionorbornene and poly(2,3-dideuterionorbornene) were recorded on a modified Varian VXR-300 NMR spectrometer. A fourth broad-band radio-frequency channel was constructed for the spectrometer to permit simultaneous decoupling and pulsing at the ^1H, ^2H, and ^{13}C resonance frequencies. This channel was connected to four software-controlled auxiliary lines on the spectrometer where one line controls pulse gating of the decoupler, two lines are used for generation of 0/90/180/270° phase shifting, and one line simultaneously controls a hardwired WALTZ modulator and an attenuator. $^{13}C\{^2H\}$ INEPT spectra were obtained with a standard ^1H, ^{19}F/broad-band switchable probe, using ca. 50 mg of sample in 0.5 mL of $CHCl_3$ with a trace of $CDCl_3$, a 17-kHz spectral window, a 0.12-s relaxation delay (set based on the measured ^2H T_1's of 45–60-ms polarization transfer delay, refocusing delays of 9.6 (CD optimized subspectrum) and 4.8 ms (CD and CD_2 subspectrum), and a 0.15-s acquisition time. ^{13}C pulsing was performed with a 75-W, 13-μs 90° pulse (19.2-kHz B_1 field) using the instrument's standard broad-band radio-frequency channel and broad-band probe coil. Continuous ^1H Waltz-16 modulated decoupling was performed with 1 W (2.5-kHz B_2 field) using the instrument's standard ^1H decoupler radio-frequency channel and the probe's decoupler coil. ^2H irradiation was performed with a 125-W, 72-μs 90° pulse (3.5-kHz B_3 field) and Waltz-16 modulating decoupling during the acquisition time using the broad-band radio-frequency channel constructed at the University of Akron and the standard lock channel on the probe. Spectra were collected in the unlocked mode with a magnetic field drift, producing ca. 0.2 Hz/h of shift of the ^{13}C resonances, without significant degradation of magnetic field homogeneity. Two separate INEPT spectra were obtained (110 000 transients, ca. 9 h/spectrum), with delays optimized for detection of CD and CD/CD_2 resonances, respectively. Four sets of these spectra were obtained over a 72-h period. The eight spectra were processed with 5-Hz exponential line broadening and zero filling to 16K. In order to compensate for magnet drift while still achieving the signal-to-noise enhancement from long-term signal averaging, the four CD (and CD/CD_2) spectra were added with the necessary digital shifting to keep the $CDCl_3$ reference signal aligned.

Gas chromatographic analyses were run on a Hewlett-Packard 5890 GC, using helium as the carrier gas and a carbosieve S-II column for gases. Gas chromatography–mass spectrometry were carried out on a Hewlett-Packard 5890 GC equipped with a 7673 autoinjector. The detector was either a HP 5790 or a Finnigan Model 700 ion trap MS. Gel permeation chromatography was conducted on a Waters Associates Model 150 C GPC; the sample size was 0.25% in THF, and a μ-Styragel column was used. Molecular weight calibrations were run against a polystyrene standard. Differential scanning calorimetry was recorded on a Du Pont 9900 DSC. Ozone produced for ozonolysis of polymers was made with an Orec Ozone generator.

Starting Materials and Solvents. The following materials were used as received: *n*-butyllithium in pentane and hexanes (Aldrich); sodium *tert*-butoxide (Aesar); D_2O (Isochem). Chlorobenzene (Aldrich) was distilled over CaH_2 while norbornene was distilled over sodium through a Vigreux column and stored at −10 °C under an inert atmosphere. Ethylaluminum dichloride in hexanes was purchased from Aldrich in Sureseal bottles and used as received. Hexacarbonylmolybdenum was obtained from Climax, and decacarbonyldirhenium was purchased from Strem; both were used as received. (Pyridine)pentacarbonylmolybdenum[12] and chloropentacarbonylrhenium[13,14] were prepared according to literature methods. Tetrabutylammonium chloride was obtained from Aldrich and dried under vacuum for 24 h at 100 °C before use.

Preparation of 2,3-Dideuterionorbornene. *n*-Butylsodium was prepared by metal–metal exchange from *n*-butyllithium and sodium *tert*-butoxide.[15] To 16 g (0.2 mol) of *n*-butylsodium was added, slowly by means of a syringe pump,[16,17] norbornene (15.0 g, 0.16 mol) dissolved in 150 mL of pentane. The reaction mixture was allowed to stand overnight under nitrogen, and 9.0 mL of deuterium oxide (*Caution*! extremely exothermic reaction) was added very slowly with cooling to ice bath temperature. When the addition was complete, the mixture was refluxed for 15 min. The mixture was dried over anhydrous $MgSO_4$ and filtered through course filter paper. The pentane and then the crude product were distilled through a 20-cm fractionating column packed with glass helices. The fraction boiling from 85 to 106 °C was collected. The product was redistilled over Na metal; 10.25 g of 2,3-dideuterionorbornene (32.9% D as determined by ^1H NMR) was recovered. The sample of dideuterionorbornene was subjected to the same treatment two more times. The final sample distilled from 93 to 96 °C and contained 60.3% deuterium. ^{13}C NMR: δ 135.4, 135.1 (t), 48.4, 41.6, 41.5, 24.4. ^2H NMR: δ 5.95.

Polymerization of Norbornene with the Mo Catalyst. Norbornene (8.17 g, 86.7 mmol), 0.16 g (0.50 mmol) of $Mo(CO)_5py$, and 50 mL of chlorobenzene were placed in a 250-mL, four-neck, round-bottomed flask. The flask was equipped with a condenser, thermometer, thermometer adaptor, gas adaptor, magnetic stir bar, and two septums. Ethylaluminum dichloride in hexanes (4 mL, 4 mmol, 1 M) was added to the flask by means of a syringe. Separate reaction mixtures were heated to the temperatures indicated in Table I. The reaction was stopped after 20 h by the addition of 10 mL of methanol. The gelled, rubbery polymer was placed in 400 mL of methanol and stirred overnight. The methanol was poured off, and the polymer was dried under vacuum for 3 days at 60 °C. The polymer was purified for solution studies by column chromatography on Florisil, using chloroform as the eluting solvent. Yields and percent ROMP are indicated in Table I. The DSC plot of the sample prepared at 100 °C showed a T_g at 75 °C and a T_m at 130 °C.

Polymerization of Norbornene with the Re Catalyst. Norbornene (5.0 g, 53 mmol), $Re(CO)_5Cl$ (0.19 g, 0.54 mmol), and 35 mL of chlorobenzene were placed into a 100-mL, three-neck, round-bottomed flask. The flask was equipped with a condenser, gas inlet, magnetic stir bar, thermometer, and thermometer adaptor. Ethylaluminum dichloride in hexanes (1.08 mL of 1 M, 1 mmol) was injected into the flask by means of a syringe. In separate reactions, the mixtures were heated to the temperatures indicated in Table I for 24 h. The red, homogeneous reaction mixture was treated with 5 mL of methanol, and the resulting solution was dripped slowly into 600 mL of rapidly stirred methanol. The polymer was allowed to settle overnight at 0 °C, collected by filtration, and dried under vacuum for 3 days at 60 °C. The polymer was purified as above. Molecular weight: $M_n = 9000$; $M_w = 13\,000$; $M_z = 17\,600$; PD $(M_w/M_n) = 1.45$. DSC: $T_g = 72$ °C.

Ozonolysis of Polynorbornene. Polynorbornene (1.00 g) was stirred overnight in a solution of ethyl acetate (50 mL) and chloroform (15 mL). After the solution was cooled to −78 °C, the polymer was ozonized by bubbling ozone through the solution. Ozonolysis was stopped when the reaction mixture took on a slight blue coloration. The reaction mixture was added dropwise into a stirred suspension of 0.17 g of Zn and 0.15 g of glacial acetic acid in 60 mL of H_2O. The aqueous solution was extracted with 3 × 50 mL portions of chloroform, and the combined extracts were shaken with saturated NaCl and dried over $MgSO_4$. The solution was filtered, and the solvent was evaporated under reduced pressure, leaving 1.14 g of ozonized polymer.

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Registry No. $Re(CO)_5Cl$, 14099-01-5; $C_2H_5AlCl_2$, 563-43-9; $Mo(CO)_5py$, 14324-76-6; norbornene, 498-66-8; norbornene (homopolymer), 25038-76-0.