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Homopolymerization of norbornene by rhenium olefin metathesis catalysts

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Summary

Norbornene was homopolymerized by $Re(CO)_5Cl/C_2H_5AlCl_2$ and $Re(CO)_5Cl/C_2H_5AlCl_2$/1,7-octadiene. In both cases, the homopolymers were essentially of the ring-retention, rather than ring-opened type, even though $Re(CO)_5Cl/C_2H_5AlCl_2$ is known to promote olefin metathesis of acyclic olefins. Although the homopolymers are nearly completely saturated, they show minor unsaturation. Nmr spectral studies of the nature of the double bonds in the polymer supports a simultaneous insertion-olefin methathesis mechanism.

Introduction

In previous studies, the $Re(CO)_5Cl/C_2H_5AlCl_2$ system was shown to be a long-lived olefin metathesis catalyst for acyclic olefins (1). When the same catalyst system was applied to non-strained, cyclic olefins, ring-opening polymerization did not occur under metathesis conditions (90°C). Instead, when the temperature was raised to 110°C, the catalyst promoted addition polymerization (double bond opening), to give completely saturated oligomers in which the rings of the monomers were retained (2).

A mechanism for the metathesis of acyclic olefins was proposed in which the initiating species of metathesis contained a $Re{=}CHCH_2CH_3$ group (1). The propylidene ligand was proposed to arise from attack on a coordinated CO by the ethyl group of $C_2H_5AlCl_2$, followed by oxygen-for-hydrogen exchange. The hydrogen atom originated at an allylic position on the olefin (1).

In the polymerization of cyclic olefins, the coordinated propylidene was shown to be the initiating species. In the proposed mechanism a metallacyclubutane complex is formed, followed by insertion of a second cyclic olefin into one of the metal-carbon bonds. Thus, a combination of a modified olefin metathesis-Ziegler-Natta process accounted for the production of saturated polymers (2).

We have now carried out the reaction of bicyclo[2,2,1] hept-2-ene (norbornene) in the presence of the $Re(CO)_5Cl/C_2H_5AlCl_2$ catalyst system. Norbornene is a strained, cyclic olefin which readily undergoes ring-opening polymerization with olefin metathesis catalysts. However,

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it has no available allylic hydrogen to complete the formation of the metal-carbene initiator. That is not to say that formation of a coordinated carbene initiator cannot occur; other pathways are known to produce coordinated carbenes on metal carbonyl compounds (3). However, the pathway involving an allylic hydrogen on the olefin is not available.

Experimental

Starting Materials and Solvents. Benzene, tetrahydrofuran (THF) and diethyl ether were distilled over sodium/benzophenone under an atmosphere of argon. Other solvents were purified by distillation over calcium hydride, under argon.

Norbonene and 5-ethylidene-2-norbornene(ENB) were purchased from Aldrich and vacuum distilled from sodium metal. Decacarbonyldirhenium was obtained from Strem Chemicals, and used as received. Chloropentacarbonylrhenium was prepared according to literature methods (4,5) and identified by comparing its IR spectrum with that reported by Abel, et al. (6) Ethylaluminum dichloride in hexane solution was purchased from Aldrich and used as received.

Physical Methods. Infrared spectra (IR) were taken on a Perkin-Elmer Model 597 grating spectrophotometer. The compounds were normally sampled as thin films between CsBr discs. Proton Nuclear Magnetic Resonance (NMR) spectra were determined on Varian EM360 (60 MHz) and Varian XR300 (300 MHz) NMR spectrometers, while ^{13}C NMR spectra were recorded on Varian FT80A and Varian XR300 NMR spectrometers. Normally, $CDCl_3$ was used as the solvent, and tetramethylsilane served as the internal standard for the ^1H spectra.

Polymerization Reactions

Polymerization of Norbornene (Ring Retention). Into a 100 mL, three-necked, round bottom flask, equipped with a thermometer, a magnetic stir bar, a rubber septum and a condenser connected with a gas adaptor to a Firestone valve, was placed 5g (5.3 mmol) of norbornene, 0.19g (0.54 mmol) of $Re(CO)_5Cl$ and 35 mL of chlorobenzene. The mixture was stirred under argon for 15 min, and 1.08 mL (1 mmol) of $C_2H_5AlCl_2$ in hexanes was added. The reaction mixture was stirred at 100°C for 24 h.

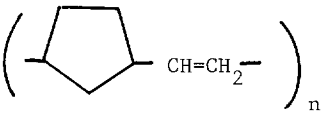
After the mixture had cooled to room temperature, it was poured into 600 mL of rapidly stirred methanol. The polymer precipitated from solution, and the mixture was placed in a refrigerator for 48 h. The polymer was then separated by filtration. The solid was dissolved in a minimum amount of benzene and added to a 50 cm x 5.5 cm Florisil (60-100 mesh) column packed in benzene. The polymer was eluted with chloroform, the solvent was reduced under aspirator vacuum and added to an excess of methanol, precipitating the polymer. The polymer was filtered from solution and dried under high vacuum (yield: 1.34 g, 26.8%). The molecular weight of the polymer as determined by gel permeation chromatography in THF and by osmometry in toluene was: $\overline{Mw}$, 443,000; $\overline{Mn}$, 154,200; polydispersity, 2.14. The polymer softens at 220°C and melts completely at 260°C.

Polymerization of Norbornene (Attempted Ring-opening). A 100 mL flask, equipped as above, contained 0.18 g (0.5 mmol) of $Re(CO)_5Cl$, 10 mL of chlorobenzene and 10 mL (67 mmol) of 1,7-octadiene. The mixture was heated to 90°C, and 4.25 mL (4.25 mmol) of $C_2H_5AlCl_2$ in hexanes was added. The metathesis of 1,7-octadiene to give cyclohexene and ethylene was carried out essentially to completion (20 min) at 90°C. When the evolution of ethylene had essentially ceased, 5 g (53 mmol) of norbornene dissolved in 2.0 mL of chlorobenzene was added through the septum, and the mixture was heated at 90°C for 2 h. The polymer was obtained from the solution and purified as described above. The molecular weight data are as follows: $\overline{Mw}$, 13,300; $\overline{Mn}$, 1,500; polydispersity, 8.79. The polymer melts above 300°C.

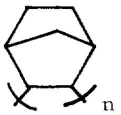
Oligomerization of Norbornene and 5-ethyledene-2-norbornene. These monomers were oligomerized with $C_2H_5AlCl_2$ as the catalyst in a system and under conditions analogous to those described above. The molecular weight data on the oligomers obtained are as follows. For polynorbornene, $\overline{Mw}$ = 7,300; $\overline{Mn}$ = 3,800; polydispersity = 1.92. For poly(ENB), $\overline{Mw}$ = 2,400; $\overline{Mn}$ = 830; polydispersity = 2.9.

Results and Discussion

Polynorbornene, prepared in this work by the $Re(CO)_5Cl/C_2H_5AlCl_2$ catalyst system, is essentially of the ring-retained type (double bond opening) rather than ring opening. The ^1H NMR spectrum shows a broad aliphatic hydrogen signal in the δ0.5-3 range and a minor, broad signal at δ5.2 (olefinic hydrogens). The relative intensities of these signals are about 65 to 1, aliphatic to olefinic hydrogens. Polynorbornene of the ring-opened type would show an integration of 4 to 1, aliphatic to olefinic hydrogens. With relative intensities of 65 to 1, the polymer contains 10 monomers with ring retention for every monomer with a double bond. The structures of the ring-opened and ring-retained polymers are shown below.



Ring-opened Polynorbornene



Ring-retained Polynorbornene

In order to show that the polymer grows on the Re atom, the reaction of norbornene was carried out under the same conditions but without the use of $Re(CO)_5Cl$. The polymer obtained where only $C_2H_5AlCl_2$ was the catalyst is also of the ring-retained type, but the molecular weight is very low (7,200). No evidence was found for any double bonds in the oligomer.

It appears that the polymer obtained from the $Re(CO)_5Cl/C_2H_5AlCl_2$ catalyst system is a single species which contains mainly a saturated chain with an occasional double bond. This conclusion is based on the gel permeation chromatogram which shows a single, rather narrow peak. It is unlikely that two separate polymers, one totally saturated (major product) and one of the ring-opened type (minor product) are present in the final sample, in light of the purification procedures and the gpc results.

The fact that a polymer of the ring-retained type was obtained from the reaction, which was carried out under olefin metathesis conditions, lends support to one of the conditions imposed on the mechanism proposed for the formation of the metallocarbene as the initiator for metathesis of acyclic olefins; an abstractable, allylic hydrogen atom must be present on the olefin.

The question arises whether ring-opening polymerization would occur if a metal carbene species could be made prior to reaction with norbornene. Such an approach is possible with the $Re(CO)_5Cl/C_2H_5AlCl_2$ catalyst system; the metathesis of 1,7-octadiene gives essentially quantitative conversion to cyclohexene, which is inert at 90°C, and ethylene, which is driven off. Therefore, at the end of the metathesis of 1,7-octadiene, two metal alkylidene species will be present: $(CO)_yRe{=}CH_2$ and $(CO)_y\ Re{=}CH(CH_2)_4CH{=}CH_2$.

Accordingly, the metathesis of 1,7-octadiene was carried out to completion, and then norbornene was added at 90°C. The polymerization was monitored by NMR, and after 2 h, the olefinic signals at δ6.0 ppm of the norbornene monomer disappeared, and a new olefinic signal at δ5.0-5.5 ppm appeared. However, the relative intensities of the aliphatic to olefinic hydrogen atoms in the purified polymer were 9.5 to 1. Therefore, this polymer is also not of the completely ring-opened type, but indicates a polymeric structure composed of about 50% ring-retained, and 50% ring-opened monomeric units. Once again, the gpc curve of this material shows the existence of a single type of polymer, rather than a mixture of ring-retained and ring-opened species.

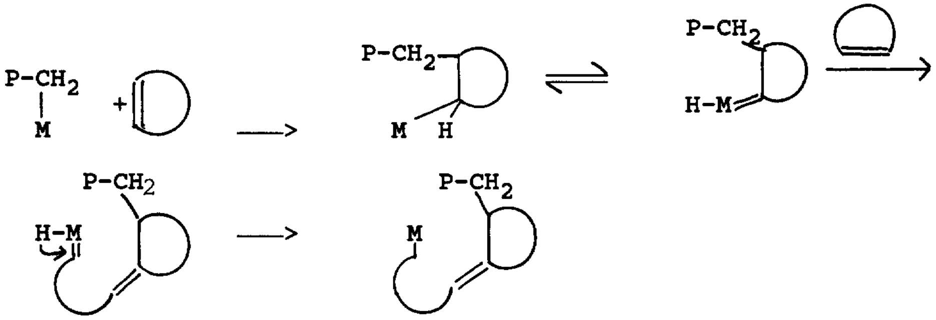
The much lower molecular weight of this polymer, and probably some additional double bonds can probably be attributed to metathesis of the double bonds of the polymer with residual amounts of 1,7-octadiene.

The IR spectra of the purified polymers always show the presence of metal carbonyl bands, and elemental analysis indicates that Re is present in the polymers to the extent of 1-2%. A test was carried out to determine whether the Re atom attached to the final polymer was through a metal-carbene bond, which might constitute a living end. Addition of 1,7-octadiene at 90°C did not remove the Re catalyst, and the polymer was recovered unchanged.

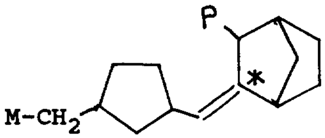
Mechanism

Several cases of polymerizations of cyclic olefins have been reported in which the final polymer contained both double bond-opened (ring-retained) and ring-opened monomer units. For example, a variety of cyclobutenes and cyclobutene derivatives were reported to give polymers containing both ring-opened and ring-retained units (7,8). These results prompted the speculation of the possibility of Ziegler-Natta and ring-opening mechanisms occurring on the same catalyst. The only evidence for this speculation comes from two patents where IR spectra showed that ethylene and cyclopentene could be copolymerized to give an unsaturated polymer containing both ring-retained and ring-opened units (9,10).

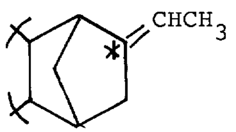
Ivin has proposed a mechanism to account for the possibility of double bond opening and ring opening in the same polymer (11).



If one applies Ivin's proposal to the polymerization of norbornene, then α-hydrogen abstraction followed by an olefin metathesis step to give a ring-opened unit, and migration of hydrogen to give a metal alkyl bond, generates a unique olefinic carbon atom which contains no attached hydrogen. This should be detectable by ^{13}C NMR studies.



As a model compound, oligomeric poly(ENB) was prepared, and the ^{13}C NMR spectrum taken to locate the signal of the unique carbon.



poly(ENB)

A number of signals appear in the δ120-140 ppm (olefinic) region of the ^{13}C NMR spectrum of poly(ENB), but a signal at 138 ppm disappears in the DEPT (distortionless enhancement by polarization transfer) spectrum, showing conclusively that the signal at 138 ppm arises from a carbon without a hydrogen bonded to it. The highly magnified ^{13}C NMR spectrum of polynorbornene also shows an olefinic carbon signal at 138 ppm, which also is absent in the DEPT spectrum of the same compound.

It appears, therefore, 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 then would undergo olefin metathesis to give a ring-opened monomer unit. Any subsequent ring-opening steps that occur before migration of hydrogen would give ring-opened units with a hydrogen on every carbon.

It is interesting that the polynorbornene generated from a metal-carbene initiator is not completely ring-opened. The mechanism to account for ring-retention in a polymer initiated by a metal-carbene species presented by Tsonis and Farona (2), coupled with Ivin's proposal, can account for the structure of this polymer.

Acknowledgement

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