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Homo- and copolymerization of some norbornadiene dimer monomers

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Summary

The exo-exo- and endo-endo norbornadiene dimers were synthesized and homopolymerized using the $Re(CO)_5Cl/EtAlCl_2$ catalyst system. The exo-exo dimer was copolymerized with norbornene, both as a random polymer and as a diblock. In all cases, the polymers obtained were mainly of the ring-retained, rather than ring-opened type, even though $Re(CO)_5Cl/EtAlCl_2$ is an olefin metathesis catalyst and the monomers are strained ring systems.

Introduction

In a previous paper (1) we reported the homopolymerization of norbornene by the $Re(CO)_5Cl/EtAlCl_2$ catalyst system, which is known to promote the metathesis of acyclic olefins, but polymerize, by double bond opening (ring retention), non-strained cyclic olefins (2). The proposed mechanism for metathesis of acyclic olefins requires the presence of an abstractable, allylic hydrogen on the alkene to form the metallocarbene initiator. Since this is not available on norbornene, ring-opening polymerization was not observed. However, high molecular weight, essentially totally saturated norbornene polymers were obtained. The occasional double bonds occurring in the polynorbornene chain were proposed to arise from an olefin metathesis step, through α-hydrogen abstraction, from an otherwise Ziegler-Natta type insertion mechanism. The polymerization of norbornene by the $Re(CO)_5Cl/EtAlCl_2$ catalyst system served as a model study for the polymerization of the norbornadiene dimers, presented in this work.

Experimental

Solvents and Starting Materials. Benzene, tetrahydrofuran (THF) and diethyl ether were distilled over sodium/benzophenone under an atmosphere of argon. Other solvents were purified by distillation over CaH_2, under argon. Norbornadiene was purchased from Aldrich and distilled through a 2.5 cm Vigreaux column; the middle cut was used in the experiments.

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Decacarbonyldirhenium was obtained from Strem Chemicals and used as received. Chloropentacarbonylrhenium(I) was prepared according to literature methods (3,4) and identified by comparing its infrared spectrum to that reported by Abel, et al (5). Ethylaluminum dichloride in hexanes was purchased from Aldrich and used as received.

Physical Methods. Infrared spectra (IR) were taken on a Perkin-Elmer Model 597 spectrophotometer; the compounds were normally sampled as thin films between CsBr discs. Proton nuclear magnetic resonance (^1H nmr) were recorded on a Varian EM360 spectrometer, while ^{13}C nmr spectra were determined on a Varian FT80A instrument. Normally, $CDCl_3$ was used as the solvent, and tetramethylsilane served as the internal standard for the ^1H spectra.

The hexacyclic exo-exo and endo-endo norbornadiene dimers were prepared from literature methods (3,4,5).

Polymerization of the Exo-exo Norbornadiene Dimer. Into a 100 mL three-necked, round bottom flask equipped with a thermometer, a rubber septum, a magnetic stir bar, and a condenser connected with a gas adaptor to a Firestone valve, was placed 2.0g (10 mmol) of the monomer, 0.04g (0.11 mmol) of $Re(CO)_5Cl$ and 15 mL of dry chlorobenzene. The mixture was stirred under argon and 0.22 mL (0.22 mmol) of $EtAlCl_2$ in hexane was added. The mixture was stirred at 110°C for 24 h, during which time the color changed from yellow to orange to red-brown. The mixture was allowed to cool to room temperature and poured into 180 mL of methanol; a white polymer precipitated from solution. The polymer was filtered from solution, and purified by redissolving it in chloroform, filtering the insoluble material, and adding the chloroform solution dropwise to rapidly stirred methanol (180 mL). The final polymer was isolated by filtration and dried under high vacuum, yielding 0.60g (47.6%). The molecular weight was determined by gpc in THF and by osmometry in toluene: $\overline{Mw}$, 462,300; $\overline{Mn}$, 180,000; polydispersity, 2.57. The polymer softens at 200° and melts above 300° C. Anal.: C, 83.18; H, 8.12; Re, 1.40; Cl, 5.86%.

Polymerization of the Endo-endo Norbornadiene Dimer. A procedure analogous to that described above was applied to the polymerization of this monomer. The amount of starting monomer was 2g (10.8 mmol) and the yield of polymer was 1.28g (60%). Molecular weight: $\overline{Mw}$, 55,600; $\overline{Mn}$, 37,300; polydispersity, 1.49. Anal.: C, 85.11; H, 8.28; Re, 0.93; Cl, 5.56; Al, 0.09%.

Copolymerization of the Exo-exo Norbornadiene Dimer and Norbornene. A procedure analogous to that described above was used to carry out the copolymerization of the two monomers. In this reaction 0.095g (0.27 mmol) of $Re(CO)_5Cl$, 2.45g (13 mmol) of the exo-exo dimer, 1.25g (13 mmol) of norbornene and 0.5 mL (0.5 mmol) of $EtAlCl_2$ were used in 35 mL of chlorobenzene solvent. After work-up, 2.0g of the copolymer was obtained (54%), and the polymer melted at

130-160°C. Molecular weight: $\overline{Mw}$ 502,300; $\overline{Mn}$, 325,500; polydispersity, 1.54. Anal.: C, 87.35; H, 8.79; Re, 2.08; Cl, 2.98; Al, 0.1%.

Preparation of a Diblock Copolymer of Norbornene and the Exo-exo Norbornadiene Dimer. Into a reaction vessel equipped identically to that described above was placed 0.095g (0.27 mmol) of $Re(CO)_5Cl$, 1.25g (13.5 mmol) of norbornene, and 20 mL of dry chlorobenzene. The system was purged with argon for 15 min, and 0.5 mL of $EtAlCl_2$/hexanes was added. The mixture was heated at 100°C, and the disappearance of norbornene was monitored by ^1H nmr spectrometry. After 4 h of reaction time, the norbornene had been consumed, and 2.45g (13 mmol) of the exo-exo dimer was added, and the mixture was heated at 100°. The disappearance of the second monomer was also monitored by ^1H nmr spectrometry. When the exo-exo dimer had been consumed (3.5 h), the reaction mixture was allowed to cool to room temperature, and the reaction was worked up as described above. The yield of soluble polymer was 0.58g (15.5%) and showed a melting point of 220-240°C. Molecular weight: $\overline{Mw}$, 262,000; $\overline{Mn}$, 95,300; polydispersity, 2.75. Anal.: C, 84.64; H, 8.45; Re, 4.06; Cl, 3.36; Al, 0.37%.

Fractionation of Polymers and Copolymers. The product was first extracted with heptane; the insoluble portion was then dissolved in a minimum amount of chloroform, heated with a heat gun, and methanol was added dropwise to the stirred solution until complete precipitation was achieved. The polymer was isolated by filtration, washed with methanol, and extracted with acetone for 24 h at room temperature. The materials were dried under high vacuum at room temperature.

Results and Discussion

It is known that transition metals interact with strained carbon-carbon bonds to cause rearrangements in organic molecules. Therefore, it was necessary to establish whether the caged structure of these dimers remained intact during the polymerization process; this was accomplished by ^{13}C spectrometry. The ^{13}C signals for the exo-exo and endo-endo norbornadiene dimers, along with their assignments and carbon numbers are shown below (6).

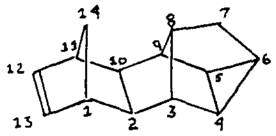
The ^{13}C signals of concern are C(4,5, and 6), i.e., the cyclopropane part of the molecules. After polymerization of the dimers, the ^{13}C nmr spectra are essentially identical to those of the monomers except for the virtual disappearance of the C(12,13) (olefinic C) signals. The high field signals are observed, showing the cage is still intact. The ^1H nmr spectra of the homopolymers of the norbornadiene dimers also show the high field signals (0.7-0.9 ppm region) associated with the hydrogen atoms attached to carbons 4, 5, and 6. Similarly, the copolymers of the exo-exo and endo-endo norbornadiene dimers with norbornene also exhibit ^{13}C

and ^1H signals in their respective nmr spectra indicative of complete retention of the cage.

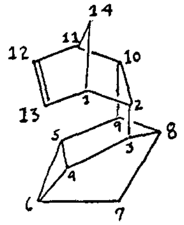
Table 1.
^{13}C Chemical Shifts of
Hexacyclo$[9.2.1.0^{2,10}.0^{3,8}.0^{4,6}.0^{5,9}]$tetradec-12-enes.

δppm (TMS,$CDCl^3$)

C(1,11)	C(2,10)	C(3,9)	C(4,5)	C(6)	C(7)	C(8)	C(12,13)	C(14)
49.30	45.12	44.77	18.16	14.30	33.77	39.07	138.50	43.39
47.25	45.38	45.38	14.13	20.11	27.31	48.68	133.16	57.48



exo-exo



endo-endo

Although the homopolymers are both of the ring-retained type (double bond opening rather than ring opening) a minor olefinic signal appears in the ^1H nmr spectrum of each. The nmr integration is 1 to 32, olefinic to aliphatic hydrogens, in the homopolymer of the exo-exo dimer. A completely ring-opened structure would show an integration of 1 to 7 for the same hydrogens. This is analogous to the structure of polynorborene, the model compound, and the ^{13}C signal at 138 ppm in polynorbornene, which was shown not to contain an attached hydrogen atom, also occurs in the ^{13}C nmr spectrum of the homopolymer of the exo-exo dimer. Consequently, the mechanism of polymerization is essentially that of Ziegler-Natta insertion, with an occasional olefin metathesis step occurring from time to time. The fact that a ring-opening mechanism does not occur lends support to the mechanism proposed for the formation of the initiator for olefin metathesis with the $Re(CO)^5/EtAlCl_2$ catalyst: an abstractable, allylic hydrogen is required for the formation of a metal-carbene species.

The ^1H nmr spectrum of the random copolymer of norbornene and the exo-exo norbornadiene dimer reveals the disappearance of the olefinic signals at 6.0 ppm corresponding to the monomers. The somewhat broad signal at 0.7-0.9 ppm arises from the protons of the cyclopropane ring, which means that the exo-exo cage has not opened during polymerization. The rest of the aliphatic signals can be attributed to the two monomers in the chain, by comparison with the nmr spectra of the two homopolymers. Clearly, both monomers are incorporated in the polymer with ring-retention.

A block copolymer of the ring-retention type, composed of norbornene and the exo-exo norbornadiene dimer monomers, was also synthesized. The diblock was prepared by sequential addition of the monomers, and monitored by observing the disappearance of the olefinic protons by ^1H nmr spectrometry. The gpc evidence for a diblock is predictable. At the time of additon of the second monomer, some of the catalytic centers are inactive. Therefore, the diblock will show a higher molecular weight than the dead polymers and also show a narrower polydispersity than the homopolymer. These predictions were confirmed by the gpc data of the diblock copolymer. In addition, the nmr spectra of the random and diblock copolymers are significantly different in the aliphatic region.

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References

1. M. A. Alonso, K. E. Bower, J. A. Johnston, and M. F. Farona, J. Polym. Sci, Polym. Chem. Ed., submitted for publication.

2. W. S. Greenlee and M. F. Farona, Inorg. Chem., 15, 2129 (1976).

3. J. R. Thomas, U.S. Patent 4,094,917 (1978).

4. G. Suld, A. Schneider, and H. K. Myers, U.S. Patent 4,207,080 (1980).

5. J. R. Thomas, U.S. Patent 4,094,916 (1978).

6. R. I. Khusnutdinov, V. A. Dokichev, A. A. Panasenko, L. M. Khaliov, and U. M. Dzhemilev, Izv. Akad. Nank. SSR., Ser Khim, 11, 2492 (1984).

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