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Homopolymerization of cyclic olefins by a molybdenum olefin metathesis catalyst

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Summary

The cyclic olefins cyclopentene, norbornene, exo- and endo-dicyclopentadiene, exo,exo-norbornadiene dimer, and indene were homopolymerized by $Mo(CO)_5py/C_2H_5AlCl_2/(C_4H_9)_4NCl$. In most cases, the polymers obtained were of the ring-opened type, but also showed ring-retention to varying degrees, depending on the temperature of polymerization. Generally, ring-opening polymerization was favored at lower temperatures. The dicyclopentadiene monomers gave crosslinked materials, showing reaction through both double bonds.

Introduction

In earlier studies, we reported that $Mo(CO)_5py/ C_2H_5AlCl_2/ (C_4H_9)_4NCl$ was an effective catalyst for the metathesis of acyclic olefins (1). In that study, mechanisms were deduced for the formation of the initial metal-carbene complexes in heptane and chlorobenzene solvents. This catalyst system was not applied to the ring-opening metathesis polymerization (ROMP) of cyclic olefins.

More recently, we reported on ROMP of norbornene and norbornadiene dimers by $Re(CO)_5Cl/C_2H_5AlCl_2$, which is also a catalyst for the metathesis of acyclic olefins. However, the polymers obtained, particularly at higher reaction temperatures, were of the ring-retained, rather than ring-opened, type (2,3,4). At intermediate temperatures, polymers were obtained which showed both saturated and unsaturated units in the same chain. These results prompted an investigation of the molybdenum catalyst toward cyclic olefins to learn of the type of polymer produced.

Experimental

Solvents and Starting Materials. Heptane and chlorobenzene, both purchased from Fisher, were distilled over $LiAlH_4$ and CaH_2, respectively. Molybdenum hexacarbonyl was obtained from Climax and used as received. Pyridinepentacarbonylmolybdenum was prepared according to literature methods (5). Cyclic olefins were purchased from Aldrich and distilled over Na, and stored at -10°C under nitrogen. Exo-dicyclopentadiene was prepared according to literature methods (6) as was the exo,exo-norbornadiene dimer (3). Ethylaluminum dichloride (1M in hexanes) was obtained from Aldrich in Sureseal bottles and used as received. Tetrabutylammonium chloride was obtained from Aldrich and dried under vacuum for 24 h at 100°C before used.

Physical Methods. FT infrared spectra were recorded on a Bomem MB-100 laser spectrophotometer. ^1H and ^{13}C NMR spectra were taken on a Varian Gemini 300 MHz spectrophotometer, using $CDCl_3$ as solvent and internal reference. Gel permeation chromatography was conducted on a Waters Associates model 150 C GPC; the sample size was 0.25% in THF, and a microstyryl gel column was used. Molecular weight calibrations were run against a polystyrene standard.

Polymerization of Monomers. All polymerizations were carried out in the same fashion; variations are noted in Table 1. All glassware was dried

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*To whom offprint requests should be sent at Department of Chemistry, UNC-Greensboro, Greensboro, NC 27412, USA in an oven prior to use and assembled with argon flowing through the apparatus. The fully assembled reaction flask was flamed out 3 times under argon before addition of any reagents. Argon released through a Firestone valve was used to protect reactions from moisture and oxygen. The flow of argon was increased when solids were added. Injection of cocatalyst was done with a new, disposable syringe. Temperature control was provided by an electrically heated silicon oil bath.

Polymerization of Norbornene. This is given as a typical example of the polymerization procedure; all others were carried out in a similar fashion. Norbornene (8.17 g, 86.7 mmol), $Mo(CO)_5py$ (0.16 g, 0.50 mmol), 0.07 g (0.25 mmol) of $(C_4H_9)_4NCl$ and 100 ml of heptane were placed into a 250 ml, four-necked, round-bottom flask. The flask was equipped with a condenser, thermometer, thermometer adaptor, gas adaptor, a magnetic stirbar and two septums. To the flask was added 4 ml (4 mmol) of 1 M ethylaluminum dichloride in hexanes. The flask was heated to 100°C and maintained at that temperature for 20 h. The catalyst was deactivated by the addition of 10 ml of methanol. The reaction mixture was added to 400 ml of methanol and the resulting white polymer was obtained by filtration, and dried at 60°C for three days.

Results and Discussion

Table 1 shows some experimental data on the polymerization of cyclic olefins.

Table 1. Experimental Data on the Polymers from Cyclic Olefins

Monomer	Solvent	T,°C	Yield[1]	O/A	ROMP,%
NBE	Hept	26	46.8	1:6.0	83
NBE	Hept	100	31.7	1:35	24
ENDCP	Hept	26	45.5	1:7.3	--
ENDCP	CBenz	26	36.0	1:3.7	--
ENDCP	CBenz	100	40.0	1:8.6	--
EXDCP	Hept	100	100	1:2.7	--
EXDCP	CBenz	25	54.7	1:4.0	--
EXDCP	CBenz	50	44.7	1:3.8	--
EXDCP	CBenz	100	100	1:5.8	--
XXNBDD	CBenz	26	100	1:15	66
CYPEN	Hept	30	0.5	1:3.6	93
CYPEN	CBenz	26	14.7	1:4.8	82
INDENE	CBenz	30	92.0	1:0.77	66

Notes: [1]Yield of methanol insoluble polymer; NBE = norbornene; ENDCP = endo-dicyclopentadiene; EXDCP = exo-dicyclopentadiene; XXNBDD = exo,exo-norbornadiene dimer; CYPEN = cyclopentene; Hept = heptane; CBenz = chlorobenzene; O/A = olefin/aliphatic proton ratio; all polymerizations were carried out for 20-22 hours.

Table 2 shows some physical properties of the polymers.

Table 2. Molecular Weights, Polydispersities, and Cis/Trans Ratios of the Polymers

Monomer	Solvent	T,°C	Mw x 10^3	PD	%Trans
NBE	Hept	26	262	5.2	76.2
NBE	Hept	100	ND	ND	63.5
ENDCP	Hept	26	2.4	2.2	ND
ENDCP	CBenz	26	1.9	2.0	ND
ENDCP	CBenz	100	121	1.6	ND
EXDCP	CBenz	50	1.1	2.4	ND
EXDCP	CBenz	100	189	2.0	ND
CYPEN	Hept	26	ND	ND	80.3
CYPEN	CBenz	26	ND	ND	73.3

Notes: Abbreviations as in Table 1.; ND = not determined; molecular weights of poly(ENDCP) and -(EXDCP) of the soluble fraction.

It is clear that the $Mo(CO)_5py$ catalyst system promotes metathesis of cyclic olefins, and is active toward ROMP of five-membered rings, as shown in the polymerization of cyclopentene and indene. This is unlike the $Re(CO)_5Cl$ system, also a d^6 metal, which promotes ring retention polymerization with non-strained cyclic olefins (7). The degree of ROMP in polypentenamer is above 80% in both solvents, but the polymer is not completely of the ring-opened type, as determined from the olefinic/aliphatic integrated proton signals. Whereas the $Re(CO)_5Cl$ catalyst system promotes a combination of insertion and ring opening on the same chain with norbornene, the $Mo(CO)_5py$ system apparently does not propagate in that manner. A DEPT ^{13}C NMR spectrum (distortionless enhancement by polarization transfer) of the soluble polymer shows that all carbons have hydrogen atoms attached to them. The mechanism proposed for the Re catalyst requires that a hydrogen atom migrate from an olefinic carbon to create a metallo-carbene complex. Apparently, some branching occurs with the Mo catalyst system, perhaps initiated by the excess ethylaluminum dichloride needed to activate the catalyst.

The polypentenamers made from both solvents are tough, elastomeric materials. The yields for polypentenamer were low, which is typical of results of other researchers. Structural assignments were made according to literature reports on polypentenamer (8,9).

Studies on poly(exo-dicyclopentadiene) and poly(endo-dicyclopentadiene) at various temperatures show that ROMP is much greater at lower temperatures. At higher temperatures, the ratio of the signals is such that it appears that greater than 100% of the polymer is ring-retained. This can be explained again by significant branching occurring from the five-membered rings, in a manner similar to that for polypentenamer.

The major product from the polymerization of exo- and endo-dicyclopentadiene is an insoluble material, a gel from the former, and a white powder from the latter. These polymers, while not studied in detail, are similar in properties to those reported elsewhere (10). Significant crosslinking occurs through metathesis of the norbornene double bond and the five-membered ring.

With norbornene and the exo,exo-norbornadiene dimer, mostly ring-opened polymer was found when the reaction was carried out at low temperatures. However, at 100°C, a polymer was formed which showed that the majority of monomer units were incorporated with ring retention. Apparently, at higher temperatures, insertion, rather than ROMP, is the preferred propagation step. It appears that at higher temperatures, the mechanism of polymerization promoted by the Mo catalyst system is similar to that of the Re system.

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