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RING-OPENING METATHESIS POLYMERIZATIONS IN CARBON DIOXIDE

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ABSTRACT

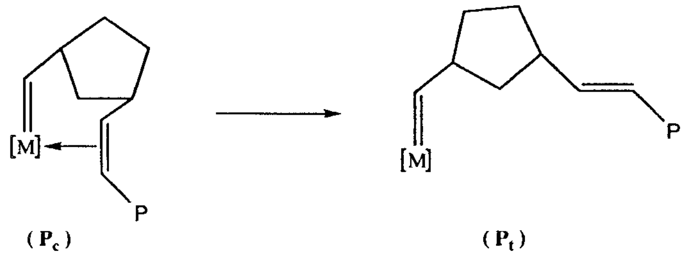
The polymerization of norbornene was successfully initiated with $Ru(H_2O)_6(tos)_2$ in a carbon dioxide medium. The resultant poly(norbornene) was prepared with yields and molecular weights comparable to those obtained in other solvent systems. It was also found that the cis/trans ratio of the polymer microstructure could be controlled by the addition of various amounts of methanol to the reaction mixture. A detailed account of the polymerizations is described and believed to be the first example of a ring-opening metathesis polymerization in carbon dioxide.

INTRODUCTION

Olefin metathesis has been a very important area of research since initial reports nearly 40 years ago [1–4]. Numerous papers and patents have been published in the area [5–10], including some industrial applications for commercial processes [11]. Of particular interest has been the development of functional group tolerant initiator systems that can induce the metathesis of functionalized olefins and also remain active in a broader range of solvent media. If one only considers the ring-opening metathesis polymerization (ROMP) of cyclic olefins, initiator systems most tolerant to functional groups are those based on the late transition metals. The most common are ruthenium complexes as simple salts [12–18] or well-defined ruthenium alkylidene complexes [19–21].

The control of polymer microstructure has also been important regarding the ROMP of cyclic olefins because its affect on the physical properties of the resultant polymer. Controlling polymer microstructure by using different coinitiators with tungsten chlorides [22–24] and also different alkoxide ligands on molybdenum and tungsten alkylidenes [25–28] has been studied. The cis/trans polymer microstructure was also examined using ruthenium halides [10, 29]. The proposed mechanism in this study by Ivin et al. shows that the polymerization involves propagation through two different metal carbene species (Scheme 1). One species has the penultimate polymer vinyl group still coordinated to the metal center (Pc) which leads to *cis*-vinylene formation, and the other species has the free metal center (Pt) which favors *trans*-vinylene formation. Studies by Hamilton et al. [29] supported the idea of two different propagating species by replacing a chloride ion with a trifluoroacetate ligand on $RuCl_3 \cdot 3H_2O$ which showed a marked increase in cis content of the polymers. The more electron-withdrawing trifluoroacetate ligand makes the ruthenium carbene propagating species more polar and more reactive. The more electron-deficient metal center was then postulated to favor structure Pc, leading to the higher *cis*-vinylene content in the polymer. The trifluoroacetate-substituted ruthenium chloride was also found to be more active for the incorporation of cyclopentene in a norbornene copolymer than the unsubstituted ruthenium catalyst. Further studies by Gillian et al. [30] looked at the polymerization of norbornene and several derivatives with catalysts based on ruthenium, osmium, and iridium chlorides. The polymers were completely characterized with respect to microstructure, and it was found that ruthenium and osmium chlorides produced high cis polymer with the addition of a chelating diolefin. This observation was suggested to be the result of the chelating diolefin acting as a permanent ligand on the propagating metal center which resembles Pc in Scheme 1, favoring *cis*-vinylene formation.

In light of the increased concern regarding the dissemination of volatile organic compounds (VOCs), chlorofluorocarbons, and aqueous waste streams into the environment, chemical industries have been prompted to conform to more environmentally sound practices in the manufacture and processing of products. Carbon dioxide offers an environmentally responsible solvent choice and the possi-



SCHEME 1. Two different possible propagating species present in the polymerization of norbornene with $Ru(H_2O)_6(tos)_2$.

bility of developing new polymerization technologies with near zero waste production. It is nontoxic and nonflammable; it is not a VOC as defined by the Environmental Protection Agency; it is inexpensive; it can easily be recycled; and it is effectively inert to a wide range of chemistries [31-37].

Herein we report the heterogeneous polymerization of bicyclo[2.2.1]hept-2-ene (norbornene) in carbon dioxide (Scheme 2) and carbon dioxide/methanol mixtures using a $Ru(H_2O)_6(tos)_2$ initiator.

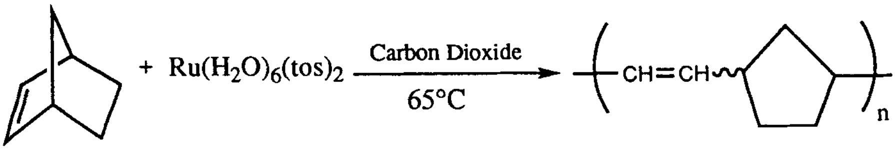
EXPERIMENTAL

Materials

Norbornene was purchased from Aldrich and distilled from sodium before use. $Ru(H_2O)_6(tos)_2$ was prepared following the procedure of Bernhard et al. [38] and stored under argon. Methanol (Baxter B and J Brand) was used as received. Carbon dioxide (Air Products, SFC/SFE grade) was used as received and was delivered to a high pressure view cell via an Isco Model No. 260D automatic syringe pump.

Polymerization Procedure

The high pressure reactions were carried out in a 25-mL cylindrical high pressure reactor constructed of 316 stainless steel with 1 cm thick sapphire windows sealed with Teflon O-rings. The contents were sufficiently mixed with a magnetic stir bar and external stirplate. In a typical experiment, the solid reagents [5 g norbornene and 0.150 g $Ru(H_2O)_6(tos)_2$] were added to the high pressure cell under an argon purge along with a magnetic stir bar prior to sealing the reactor. The methanol was degassed by the freeze-pump-thaw technique or argon purge and added to the high pressure cell via cannula under argon. When all the reagents were in the cell, CO_2 was immediately added at a low enough pressure to allow for thermal expansion as the cell was heated slowly to the reaction temperature (65°C) with a band heater wrapped around the cell. Once the cell was at the desired temperature, the pressure was adjusted by the addition of more CO_2. (Reaction pressures varied from 60 to 345 bar.) At the end of the polymerization the products were easily isolated by venting the CO_2. Yields were determined gravimetrically after purification by dissolving the polymer in toluene or tetrahydrofuran and subsequent precipitation into methanol (with 1% added KOH to remove the initiator).



SCHEME 2. The ring-opening metathesis polymerization of norbornene.

Polymer Characterization

The polymers were characterized by ^1H and ^{13}C NMR using a Bruker 250 MHz NMR and benzene-d_6 as solvent. A Waters 150CV gel permeation chromatograph using a tetrahydrofuran mobile phase fitted with Ultrastyragel columns of 100, 500, 10^3, and 10^4 Å porosities and calibrated with polystyrene standards (Showa Denko) was used for the determination of molar mass and molar mass distribution.

RESULTS AND DISCUSSION

Polymerization in Carbon Dioxide

Norbornene was found to be readily soluble in carbon dioxide under the reaction conditions employed. The $Ru(H_2O)_6(tos)_2$ initiator, however, was not soluble, presumably due to its ionic character. (Carbon dioxide has a very low solvent polarity.) The polymerizations in carbon dioxide initially involved $Ru(H_2O)_6(tos)_2$ dispersed by mechanical stirring in a clear, colorless carbon dioxide/norbornene solution. As the reaction proceeded, the solution turned slightly orange before becoming cloudy and completely opaque due to polymer precipitation. The induction period prior to the onset of precipitation often varied in length, and no clear trend could be found [18]. The polymer had an off-white color and spongy texture except for small sections of discolored material. These sections were presumed to be areas of high catalyst concentration where the solid initiator became trapped in the precipitated polymer and degraded over time. The polymer was slowly dissolved in tetrahydrofuran and precipitated into methanol with 1% KOH to remove the Ru initiator. If the ruthenium was not removed, the polymer would go from white to brown over a period of days, but with removal of the ruthenium, the polymer would remain white for months.

Table 1 shows polymerization yield as a function of reaction pressure for the polymerizations conducted in carbon dioxide. A clear decrease in yield was observed for reaction pressures around 140 bar. Further studies are needed to determine the exact nature of the pressure dependence on this polymerization, but the heterogeneous initiator system employed incurs too many variables for accurate analysis. As such, we are actively pursuing an initiator system that will be soluble in carbon dioxide that may eliminate the induction periods.

Polymerization in Carbon Dioxide/Methanol

A more controlled and efficient initiating system was found by adding sufficient quantities of methanol to render the $Ru(H_2O)_6(tos)_2$ soluble in the carbon dioxide medium. Polymerization yields as high as those obtained in carbon dioxide alone were realized in one-third the reaction time (Table 2). The addition of at least 4–5 wt/vol% of methanol was needed to achieve one-phase homogeneous starting conditions. At lower concentrations a second phase rich in methanol and ruthenium initiator was observed. As the mixture was heated to the desired reaction temperature of 65 °C, the solution turned slightly orange before the onset of polymer precipitation. The polymer was usually off-white and found throughout the reaction vessel

TABLE 1. The Polymerization of Norbornene (5 g) with $Ru(H_2O)_6(tos)_2$ (0.15 g) in Carbon Dioxide at Various Pressures. Reactions Were Conducted at 65 °C for 16 hours

Pressure, bar	Yield, %	$M_n \times 10^{-3}$	MWD
68	70	392	3.3
97	48	511	2.0
108	48	335	2.6
141	31	15	2.4
155	76	71	2.2
177	67	101	2.5
207	67	32	2.0
239	70	43	2.2
300	65	162	3.6

as in the pure carbon dioxide medium, but no areas of localized discoloration were seen as in the carbon dioxide polymerizations. Spectroscopic studies are currently underway to examine different cosolvents and their effect on the $Ru(H_2O)_6(tos)_2$ initiator.

TABLE 2. The Polymerization of Norbornene in Carbon Dioxide with Various Amounts of Methanol. Each Polymerization Was Carried Out at 65 °C and 345 bar for 5 hours Using 5 g Norbornene and 0.150 g $Ru(H_2O)_6(tos)_2$

Methanol, wt/vol %	Polymerization yield, %	$M_n \times 10^{-3}$	MWD	*cis*-Vinylene content, %
Neat[a]	77	125	2.3	28
0	6	232	3.6	83
0.07	8	39	2.1	83
0.32	16	22	2.0	87
0.63	5	No[b]	No[b]	65
0.95	26	54	3.4	37
1.6	29	58	3.7	32
3.2	52	86	4.5	31
6.3	49	30	4.1	29
12.7	72	112	2.6	28
15.8	70	44	3.0	33

[a] Control polymerization in methanol under same conditions but under an atmospheric pressure of argon.

[b] No = not obtained.

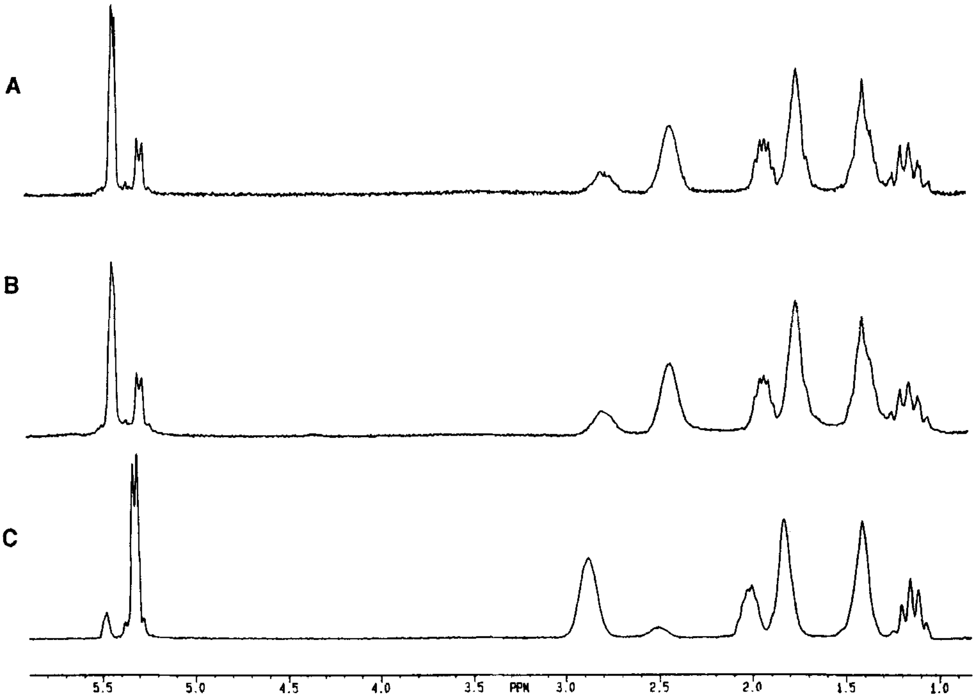


FIG. 1. The ^{1}H NMR of poly(norbornene) prepared in (A) methanol, (B) methanol/carbon dioxide, and (C) carbon dioxide.

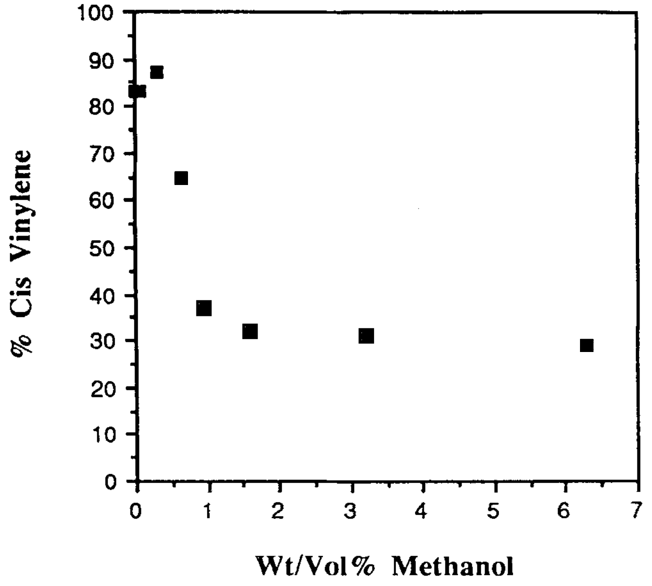


FIG. 2. The change in polymer microstructure with the addition of quantitative amounts of methanol.

cis/trans Polymer Microstructure

When comparing the structures of the polymers prepared in the different polymerization media (Fig. 1), a very interesting variation in polymer microstructure was observed. The polymers prepared in methanol and carbon dioxide/methanol had very high *trans*-vinylene content (vinyl peak at 5.5 ppm), but the poly(norbornene) prepared in neat carbon dioxide had very high *cis*-vinylene content (vinyl peak at 5.3 ppm). Systematic amounts of methanol were then added to the carbon dioxide medium to investigate this effect, and the results are presented in Fig. 2.

As shown in Fig. 2, the microstructure can in fact be controlled by the addition of specific amounts of methanol. Based on results with our system and those discussed in the Introduction, it is plausible that the low polarity carbon dioxide medium favors the Pc propagating species (Scheme 1). The addition of the polar cosolvent may then favor the Pt propagating species (Scheme 1) and therefore increase the trans content of the polymer. Investigations are currently directed toward further elucidation of the observed solvent effect.

CONCLUSIONS

The ring-opening metathesis polymerization of norbornene has been successfully initiated with $Ru(H_2O)_6(tos)_2$ in a carbon dioxide medium with conversions and molecular weights comparable to those in conventional solvent systems. It was found that the cis/trans microstructure of the polymers formed could be manipulated with the addition of methanol. Ongoing investigations are exploring various initiator systems and their compatibility with carbon dioxide in conjunction with the polymerization of different cyclic olefins.

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