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Initiation of Ring-Opening Metathesis Polymerization in Protic Media. Extension of $[Ru(H_2O)_6]^{2+}$ Catalyzed Polymerizations to Less-Strained Cyclic Monomers

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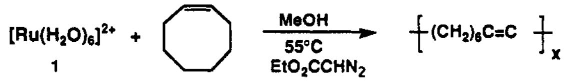
ABSTRACT: $Ru^{II}(H_2O)_6(tos)_2$ (tos = *p*-toluenesulfonate) is an active catalyst for ring-opening metathesis polymerization (ROMP) of norbornene and 7-oxanorbornene derivatives in protic media. The activity of this catalyst can be extended to less reactive monomers, such as cyclooctene and cyclopentene, by the addition of ethyl diazoacetate to serve as an initiator. Due to the polymer/ring equilibrium for this system, the yield of polymer is low. The gel permeation chromatography trace of the product is distinctly bimodal, consisting of a mixture of cyclic oligomers and higher molecular weight polymer. These results show that the difficulty of polymerizing unstrained cyclic olefins in the original ruthenium systems lies in the initiation step and not in the propagation. Although the active catalyst in this system has not been identified, a ruthenium carbene produced from the reaction of ethyl diazoacetate with $(PPh_3)_3RuCl_2$ has been observed.

We recently reported the ring-opening metathesis polymerization (ROMP) of 7-oxanorbornene derivatives in aqueous media using ruthenium salts.[1] A wide variety of group VIII complexes, such as $RuCl_3$ and $Ru^{II}(H_2O)_6(tos)_2$ (tos = *p*-toluenesulfonate) (1),[2] have been shown to be active catalysts.[3] These catalyst systems are of great interest, as they polymerize norbornenes and oxanorbornenes with a variety of functional groups in protic media. However, polymerizations using these ruthenium systems are currently limited to strained, bicyclic monomers.

We[4] and others[5] have recently shown that chain transfer with acyclic olefins occurs during the ROMP of 7-oxanorbornene derivatives by group VIII catalysts. The reaction products indicate that chain-carrying species derived from the acyclic olefin are produced and that the chemistry of these propagating species closely parallels that known for well-characterized alkylidene/metallacyclobutane metathesis systems.[4]

These preliminary mechanistic results suggested that if it is possible to directly generate reactive alkylidene ligands on low-valent ruthenium complexes such as $Ru^{II}(H_2O)_6(tos)_2$, metathesis catalysts of broader activity could be generated. We now report the successful generation of an active ruthenium catalyst system using carbene precursors in protic media and the polymerization of less reactive monomers, such as cyclooctene[6] and cyclopentene,[7] which are not normally polymerized by group VIII ROMP catalysts.[8] This suggests that the bicyclic structure of the "normal" substrates is only important for catalyst generation and is not essential for propagation.

Our strategy involved the reaction of $Ru^{II}(H_2O)_6(tos)_2$ with small molecules that could serve as precursors to alkylidene or vinylidene ligands in the presence of cycloolefins in protic media. Small molecules, such as diiodomethane, propylene oxide, *tert*-butylacetylene, and ethyl diazoacetate (EDA), were screened using cyclooctene (COE) as the substrate. In methanol using $Ru(H_2O)_6(tos)_2$ and ethyl diazoacetate, we were able to observe the ROMP of both cyclooctene, see eq 1, and cyclopentene.[9]



(1)

A ring-opened structure was confirmed by both ^1H and ^{13}C NMR spectroscopy. ^{13}C NMR spectroscopy of the polyoctenamer produced indicated a *cis*:*trans* ratio of approximately 1:1.[10]

Control experiments showed that both $Ru(H_2O)_6(tos)_2$ and ethyl diazoacetate are necessary for polymerization

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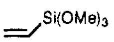
Table I. Polymerization of Low-Strain Cyclic Monomers Using $Ru(H_2O)_6(tos)_2$ under Various Conditions[a]

catalyst condition	none	CH_2I_2		${}^tBu{-}{\equiv}$	EDA	
1/THF/H_2O	–	–	–	–	–	
1/pyridine/THF/H_2O		–	–	–	–	
1/PCy_3/THF/H_2O		–	–	–	–	
1/$PPh_2(PhSO_3Na{\cdot}H_2O)$/THF/$H_2O$		–	–	–	+	
1/$PPh(PhSO_3Na{\cdot}H_2O)_2$/THF/$H_2O$		–	–	–	+	
1/PMe_3/THF/H_2O		–	–	–	–	
1/Et_3N/THF/H_2O		–	–	–	–	
1/MeOH	–	–	–	–	‡	‡
1/$PPh_2(PhSO_3Na{\cdot}H_2O)$/MeOH					‡	
1/$PPh(PhSO_3Na{\cdot}H_2O)_2$/MeOH					‡	

[a] – indicates that no ring-opened product was formed. + indicates that a trace of ring-opened product was observed by ^1H NMR. ‡ indicates that ring-opened product was isolated.

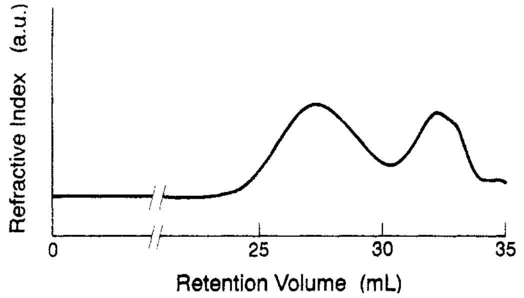


Figure 1. GPC trace of crude polymerization product. ([COE] = 0.6 M, [Ru] = 0.011 M. Total sample, $M_n \sim 2750$, $M_w \sim 12\,500$, PDI ~ 4.5.)[18]

activity in methanol with unstrained cycloolefins. To date, cyclopropanation has not been observed by either capillary GC or ^1H NMR under typical polymerization conditions.[11] Reaction of cyclooctene with ethyl diazoacetate in the presence of complexes such as $[Pd(CH_3CN)_4](BF_4)_2$, $[(COD)RhCl]_2$ or $Rh_2(OAc)_4$, which would be expected to act as carbene coupling and/or cyclopropanation catalysts,[12] yielded no polymer.

To date, $RuCl_3$ has not proven to be an effective polymerization catalyst in the presence of ethyl diazoacetate under the same conditions, nor has diazomethane yielded an effective catalyst system in the presence of $Ru(H_2O)_6(tos)_2$. Polyoctenamer could, however, be obtained using $Ru(H_2O)_6(tos)_2$ and ethyl diazoacetate in methanol in the presence of 1 equiv of $PPh_2(C_6H_4SO_3Na{\cdot}H_2O)$ (*cis*:*trans* ≈ 1.7) or $PPh(C_6H_4SO_3Na{\cdot}H_2O)_2$ (*cis*:*trans* ≈ 1).[13,14] Of the other systems examined, only the vinyltrimethoxysilane[15] initiator produced a small amount of ring-opened product. The presence of the sulfonated triphenylphosphines or other bases, such as pyridine, tricyclohexylphosphine, trimethylphosphine, or triethylamine, did not promote polymerization in conjunction with the remaining potential initiators. These results are summarized in Table I.

During the course of the polymerization using the system $Ru(H_2O)_6(tos)_2/EtO_2CCHN_2$/MeOH, a small amount of high molecular weight polymer, which was clean by ^{13}C and ^1H NMR spectroscopy, precipitated from the solution. The yield of polymer isolated in this manner was quite low (5–10%). This is partially due to the polymer/ring equilibrium for this system,[16] since a homogeneous system in methanol with concentrations of COE high enough to give good polymer yields has proven difficult to achieve.[17] As expected for polymerizations of COE below the critical concentration, a representative GPC trace[18] of the residue after polymerization is distinctly bimodal, consisting of a mixture of cyclic oligomers and higher molecular weight polymer (Figure 1). Similar GPC traces were obtained when the polymerization was carried out using $WCl_6/SnMe_4$ or $Mo(NAr)(OC(CF_3)_2CH_3)_2(CH\text{-}t\text{-}Bu)$ as catalysts. In addition, when the solvent was removed from the remaining polymerization products, which were generally a heterogeneous mixture of precipitated, swollen polymers in a viscous liquid, redissolution of this product (an additional 5–15% yield) has proven difficult, even in halogenated solvents. All other polymer purification techniques attempted to date have failed to isolate the bulk of the product cleanly.[19]

Attempts to observe by ^1H NMR the active species produced by the reaction of ethyl diazoacetate and 1 have failed. However, a ruthenium carbene generated by the reaction of ethyl diazoacetate and $(PPh_3)_3RuCl_2$ has been observed.[20] This species shows a ^1H NMR resonance (triplet) at 17.92 ppm compared with a resonance of 17.94 ppm for the carbene prepared from $(PPh_3)_3RuCl_2$ and diphenylcyclopropene.[21] There is a second alkylidene resonance (doublet) at 13.95 ppm, which may be due to a monophosphine complex. These carbenes are unstable in solution at room temperature and decompose within about 30 min of preparation; however, the downfield carbene has been isolated and appears to be stable in the solid form at −20 °C. Although both of these well-defined ruthenium systems polymerize norbornene, neither is active for the polymerization of unstrained cyclic olefins. Apparently, the ligands present in the isolated systems just stabilize the carbene to the point that only strained rings react. Further investigations of this isolated carbene and of a related system also prepared from ethyl diazoacetate are currently underway and will be the subject of a future communication.

In summary, activation of $Ru(H_2O)_6(tos)_2$ using a carbene transfer reagent in protic media has enabled the polymerization of monomers previously inaccessible with this system. Although the yield of polymer is low, these results demonstrate that the strained ring monomers are essential for initiation in the original $Ru(H_2O)_6(tos)_2$ system but are not necessary for propagation.

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(1) (a) Novak, B. M.; Grubbs, R. H. *J. Am. Chem. Soc.* **1988**, *110*, 7542. (b) Novak, B. M.; Grubbs, R. H. *J. Am. Chem. Soc.* **1988**, *110*, 960.

(2) For the preparation of this compound, see: Bernhard, P.; Bürgi, H.-B.; Hauser, J.; Lehmann, H.; Ludi, A. *Inorg. Chem.* **1982**, *21*, 3936.

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(6) (*p*-Cymene)$RuCl_2{\cdot}PCy_3$ has been reported to give low yields of polyoctenamer in the presence of ethyl diazoacetate in aromatic solvents. (a) Noels, A. F.; Demonceau, A.; Saive, E.; Hubert, A. J. *Abstracts of the Ninth International Symposium on Olefin Metathesis and Polymerization*, July 21–26, 1991, Ursinus College, Collegeville, PA. (b) Noels, A. F.; Demonceau, A.; Saive, E.; Hubert, A. J. *J. Mol. Catal.* **1992**, *76*, 123.

(7) Copolymerization of cyclopentene with norbornene catalyzed by $Ru(H_2O)_6(tos)_2$ has been observed. Benedicto, A. D.; Grubbs, R. H. Unpublished results.

(8) Inefficient ROMP of cyclooctene and cyclopentene, as well as efficient copolymerization of these monomers with norbornene, using Ir-containing catalysts has been reported. Allylic Ru catalysts were reported inactive with these monomers until treated with H_2, then polypentenamer could be obtained. See: Porri, L.; Rossi, R.; Diversi, P.; Lucherini, A. *Makromol. Chem.* **1974**, *175*, 3097. In a related system, ruthenium catalysts prepared by activation of a variety of precursors with CF_3CO_2H could be used to prepare polypentenamer, see: Porri, L.; Diversi, P.; Lucherini, A.; Rossi, R. *Ibid.* **1975**, *176*, 3121.

(9) To a solution of $Ru^{II}(H_2O)_6(tos)_2$ (6 mg, 0.011 mmol) in methanol (1 mL) under argon was added cyclooctene (80 μL, 0.61 mmol). The reaction mixture was stirred at 55 °C for 15 min to allow formation of the yellow olefin complex and then cooled to room temperature. Ethyl diazoacetate (10 μL, 0.095 mmol) was added all at once. After evolution of N_2 had ceased, the reaction was stirred at 55 °C overnight. The cloudy yellow solution was decanted off the polymer film coating the reaction vessel. This film, consisting of clean oligomer, was dried in vacuo (5–10%). The remaining liquid also contained ring-opened product, as shown by precipitation into water. Isolation was difficult (see text), but small amounts (5–15%) have been purified by removal of ruthenium by passage through silica or alumina, centrifugation, or complexation with EDTA-containing Amberlite resin IRD-718.

(10) See ref 3a, p 202.

(11) Little cyclopropanation would be expected under polymerization conditions because metal catalyzed carbene coupling, using the Pd and Rh species tested, predominates when the ethyl diazoacetate is added quickly, *i.e.*, is present in relatively high concentration. Traces of diethyl maleate and fumarate, the coupling products, have been detected by ^1H NMR in polymerization mixtures. Cyclopropanation conditions reported for $Rh_2(OAc)_4/EtO_2CCHN_2$ were used to prepare an authentic COE cyclopropanation product sample; see: Doyle, M. P.; Dorow, R. L.; Buhro, W. E.; Griffin, J. H.; Tamblyn, W. H.; Trudell, M. L. *Organometallics* **1984**, *3*, 44.

(12) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987.

(13) This system is reminiscent of that reported in ref 6. $Ru(H_2O)_6(tos)_2$ is known to bind aromatic systems to form π-bonded complexes; see: Stebler-Röthlisberger, M.; Salzer, A.; Bürgi, H.-B.; Ludi, A. *Organometallics* **1986**, *5*, 298.

(14) Contrary to the observation for $Ru(H_2O)_6(tos)_2$ catalyzed polymerization, traces of cyclopropanation product were observed when the sulfonated phosphines were present. See refs 6 and 13.

(15) Vinyltriethoxysilane can be cross-metathesized with olefins by ruthenium complexes, such as $RuCl_3{\cdot}nH_2O$ and $RuCl_2(PPh_3)_3$. See: Foltynowicz, Z.; Marciniec, B.; Pietraszuk, C. *J. Mol. Catal.* **1991**, *65*, 113.

(16) (a) Höcker, H.; Reif, L.; Reimann, W.; Riebel, K. *Recl. Trav. Chim. Pays-Bas* **1977**, *96*, M47. (b) Höcker, H.; Reimann, W.; Reif, L., Riebel, K. *J. Mol. Catal.* **1980**, *8*, 191.

(17) At attainable concentrations, *ca.* 0.6 M, a theoretical polymer yield of *ca.* 60% can be estimated at equilibrium; see ref 16b.

(18) GPC traces were obtained with an American Polymer Standards Mixed Bed Linear 10-μm column using CH_2Cl_2 as solvent. All values are referenced to narrow dispersity polystyrene samples.

(19) Poorer solubility due to enhanced crystallinity of polyoctenamer upon drying has been noted previously; however, the extremely poor solubility observed implies cross-linking. We do not yet have data addressing this issue.

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