# Chain Transfer during the Aqueous Ring-Opening Metathesis Polymerization of 7-Oxanorbornene Derivatives

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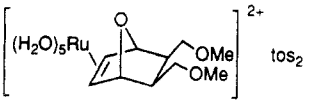
ABSTRACT: Ring-opening metathesis polymerization (ROMP) of *exo,exo*-5,6-bis(methoxymethyl)-7-oxabicyclo[2.2.1]hept-2-ene (3) catalyzed by $Ru^{II}(H_2O)_6(tos)_2$ (tos = *p*-toluenesulfonate) (1) in the presence of terminal acyclic olefins such as 3-buten-1-ol and methyl acrylate affords low molecular weight polymeric materials. Analysis of these oligomer samples by one- and two-dimensional $^1H$ NMR spectroscopy identifies them as resulting from a true metathesis chain transfer mechanism. These data and the identification of the ring-opened monomer units with alkylidene end groups corresponding to the acyclic chain transfer agent by high resolution mass spectrometry confirm this study as the first example of metathesis of an acyclic olefin by 1. A comparison of the chain transfer activities of a series of acyclic esters yields a reactivity order of terminal olefins > deactivated terminal olefins > internal olefins > deactivated internal olefins, consistent with the behavior of well-characterized homogeneous alkylidene complexes.

## Introduction

Group VIII coordination complexes, such as $Ru^{II}(H_2O)_6(tos)_2$ (tos = *p*-toluenesulfonate) (1),[1] have recently been shown to be good catalysts for the ring-opening metathesis polymerization (ROMP) of 7-oxanorbornene derivatives in aqueous media.[2] In light of the growing literature on both metathesis and ROMP,[3] a ruthenium alkylidene complex is postulated to be the propagating species during these polymerizations. However, little is known about the structure and reactivity patterns of this active species or about the initiation mechanism leading to its formation. Ruthenium(II)–olefin adducts of the monomers (*e.g.* **2**)




**2**

have been identified in solution after oxanorbornene polymerizations,[2a] and similar complexes of acyclic, non-polymerizable olefins have been prepared independently.[4] Although these complexes can also initiate polymerization of 7-oxanorbornenes, such species are merely catalyst precursors and not active catalysts.

Previous studies from these laboratories have demonstrated that $Ru^{II}(H_2O)_6(tos)_2$ itself and, more importantly, the ROMP catalyst derived from it are tolerant of a wide range of organic functionality.[2,4-6] This functionality includes alcohols, ketones, and esters which severely disable metathesis catalysts based on the early transition metals. This tolerance for functional groups has allowed the preparation of polymers with different mechanical and chemical properties by varying the functionality along the polymer chain.[5,6] In addition, this functional group tolerance should allow chain transfer reactions with acyclic olefins containing functional groups to produce oligomers and telomers with specific functionalized end groups.[7-12]

In fact, it has recently been reported that ring-opening metathesis polymerization of 7-oxanorbornene derivatives by hydrated $MCl_3$ (M = Ru, Os, Ir) in the presence of acyclic olefins such as *cis*-2-butene-1,4-diol produces low molecular weight oligomers in low yields.[15] Building upon our results from the study of the complexation of functionalized olefins with Ru(II),[4] we have further investigated this chemistry. Higher reactivity and better yields were observed using methyl acrylate, 3-buten-1-ol, methyl 2-pentenoate, methyl 3-pentenoate, methyl 4-pentenoate, and a number of other acyclic olefins with 1 as catalyst precursor.

In contrast to the majority of reports concerning molecular weight regulation by metathesis chain transfer, we have investigated the microstructure of the low molecular weight oligomers using a number of spectroscopic techniques and have identified them as resulting from a true chain transfer mechanism. This is strong evidence for the existence of a ruthenium alkylidene active complex formed from cross-metathesis with an acyclic olefin, which is capable of further productive metathesis. By examining chain transfer activity and the resultant effects on the molecular weight data obtained by gel permeation chromatography (GPC) as a function of the olefin used, we also provide the first experimental evidence, to our knowledge, that the observed reactivity patterns for the ruthenium propagating species are, in fact, analogous to known metal–alkylidene chemistry.

## Results and Discussion

When polymerization of *exo,exo*-5,6-bis(methoxymethyl)-7-oxabicyclo[2.2.1]hept-2-ene (3) catalyzed by 1 is carried out in the presence of acyclic olefins such as methyl acrylate or 3-buten-1-ol, the polymer produced has a molecular weight significantly lower than that of polymer produced in the absence of added chain transfer agent ($M_n$ = (300–1300) × $10^3$, depending on conditions).[2,6] The multimodal GPC trace of the oligomers obtained in this manner with a high concentration of acyclic olefin shows that the product consists of a mixture of oligomeric species

† Contribution No. 8608.
‡ E. I. Du Pont de Nemours and Co. Contribution No. 6409.

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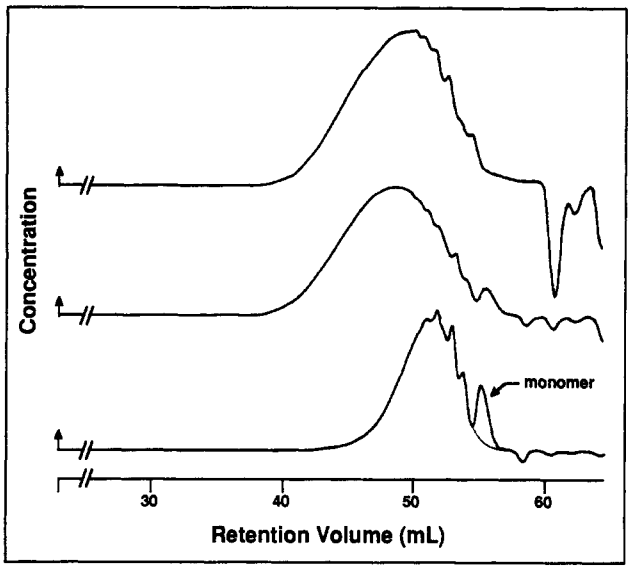



**Figure 1.** GPC traces of samples of poly(3) produced by 1 catalyzed ROMP in the presence of acyclic olefins. Top: [methyl acrylate]:[3] = 1.33. Middle: [3-buten-1-ol]:[3] = 0.18. Bottom: [3-buten-1-ol]:[3] = 0.89.

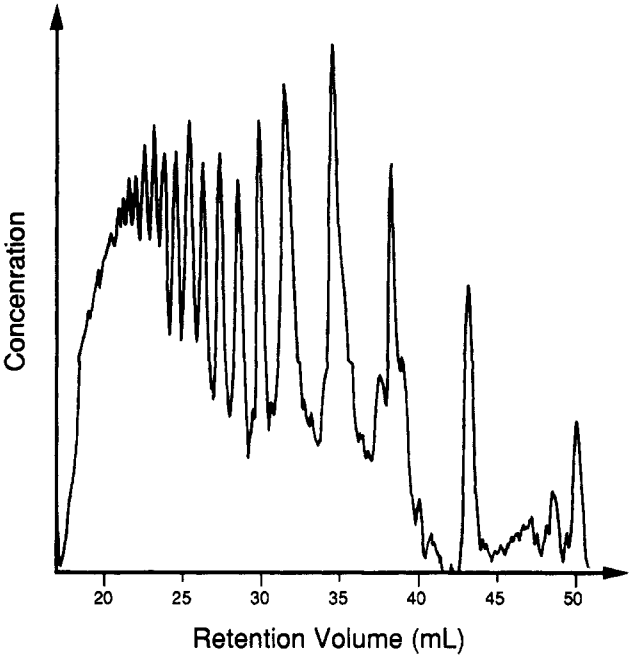
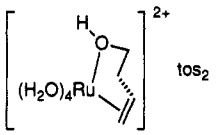



**Figure 2.** High resolution GPC trace of poly(3) regulated with 3-buten-1-ol ([3-buten-1-ol]:[3] = 0.89).

and low molecular weight polymeric material. The $M_n$ of oligomer samples produced with a 0.9:1.0 [3-buten-1-ol]:[3] ratio is extremely low ($1.6 \times 10^3$) and the PDI is 1.5. Distinct peaks can be seen in the GPC trace, but the relatively low resolution precludes assignment of actual structures from the apparent molecular weights of individual peaks (Figure 1). However, it is clear from these data that we have produced a sample dominated by very low molecular weight oligomers. High resolution GPC analysis confirms this conclusion (Figure 2). These initial results suggest that 3-buten-1-ol is a more effective regulator than methyl acrylate: as shown in Figure 1, a 0.18:1.0 [3-buten-1-ol]:[3] ratio produces an oligomer mixture of similar molecular weight as a 1.34:1.0 [methyl acrylate]:[3] ratio.

At low concentrations of methyl acrylate, a lower molecular weight polymer is observed when the acyclic olefin is heated with precatalyst 1 for 15 min prior to addition of monomer 3. If methyl acrylate (10 equiv per ruthenium) and the monomer (56 equiv per ruthenium) are added simultaneously to the reaction mixture, the polymer samples are of higher molecular weight ($M_w \sim 46 \times 10^3$) and polydispersity (PDI $\sim$ 7.1) than when 3 is added after 15-min incubation time ($M_w \sim 29 \times 10^3$, PDI $\sim$ 5.3).[16] As the concentration of methyl acrylate is increased, a saturation effect is observed and the difference in molecular weight values decreases; for a methyl acrylate concentration of 50 equiv to ruthenium, the difference in the values obtained under the two different reaction conditions is insignificant. No significant effect due to incubation time is observed with 3-buten-1-ol, which binds to the ruthenium more strongly than methyl acrylate and thus is a more effective chain transfer agent. For consistency, all experiments were carried out using the 15-min incubation time.

Oligomers of 3 can also be prepared utilizing isolated $Ru^{II}(H_2O)_4(\eta^1(O):\eta^2(C,C')$-$HOCH_2CH_2CH{=}CH_2)(tos)_2$ (4) as the precatalyst in the presence of added 3-buten-1-ol.[4]

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The products are similar to those obtained using 1. Polymerization of 3 by the isolated ruthenium olefin complex 4 in the absence of additional acyclic olefin (*i.e.*, 1 equiv acyclic olefin to catalyst) yielded lower molecular weight ($M_n \sim 125 \times 10^3$) polymer samples than that prepared using 1 ($M_n \sim 300 \times 10^3$) with no added acyclic olefin under the same conditions.

$^1$H NMR of the oligomers established connectivity between the end groups and the polymer chain. We have identified both alkylidene moieties from the 3-buten-1-ol regulator in the $^1$H NMR spectrum of an oligomer sample by utilizing both one- and two-dimensional NMR techniques and find them fully coupled to the bulk polymer proton resonances. A fully assigned two-dimensional $^1$H–$^1$H shift correlation (COSY) NMR spectrum of an oligomer mixture produced from a 3-buten-1-ol-regulated (50 equiv per Ru) polymerization is shown in Figure 3. The resonances for the bulk polymer are assigned in direct comparison with a spectrum of high molecular weight poly-(3). Note that the olefin protons, as well as the allylic protons, of the polymer backbone are split in terms of the *cis* or *trans* configuration of the double bond to which they are attached or adjacent. In addition, the *cis* allylic proton gives rise to two resonances at 4.5 and 4.6 ppm. This inequivalence may be the result of polymer tacticity (meso and racemic dyads).[17] In fact, close examination of the cross peaks of a two-dimensional $^1$H–$^1$H shift correlation (COSY) NMR spectrum of high molecular weight poly(2)[17] (not shown) reveals that both olefin resonances, as well as the *trans* allylic resonance, are also composed of two peaks, but the shift inequivalence is practically undetectable in the 1D spectrum.

The peaks for the alkylidene moieties are essentially the remaining peaks in the spectrum. The vinyl end group is at 6.84 (=CH–), 5.33, and 5.10 ($CH_2$=) ppm, typical for a terminal olefin $^1$H NMR spectrum. It is unclear why the upfield terminal vinyl proton resonance at 5.10 ppm appears as a triplet while the resonance at 5.33 is a doublet, but we note that selective decoupling of the olefin resonance at 6.84 ppm collapses both terminal vinyl resonances to broad singlets. In addition, both resonances appear as doublets in $CD_2Cl_2$ solvent. All three vinyl

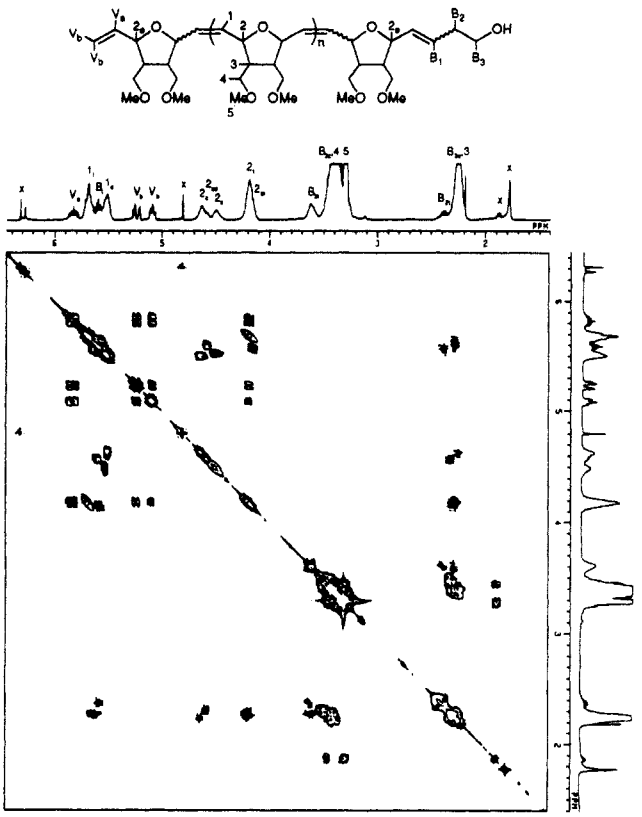
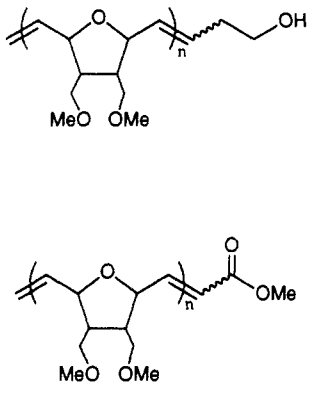


**Figure 3.** Two-dimensional $^1H$–$^1H$ shift correlation (COSY) NMR spectrum of poly(**3**) regulated with 3-buten-1-ol ([3-buten-1-ol]:[**3**] = 0.89) (symmetrized matrix).

protons are coupled to the *trans* allylic proton at 4.2 ppm, but not to the *cis* allylic proton. The small allylic coupling between the terminal vinyl protons and the allylic proton is readily detectable in the COSY spectrum.

The butenol end group is at 5.6 (–CH=), 3.6 ($-CH_2O-$), and 2.4 (=CHC$H_2$–) ppm. The olefin resonance is coupled to both the *trans* allylic proton at 4.2 ppm, as well as the *cis* allylic proton at 4.5–4.6 ppm. This allylic proton which is coupled to the butenol end group actually resonates at a different chemical shift between the bulk polymer *cis* allylic protons at 4.5 and 4.6 ppm. This is clearly seen upon inspection of the cross peaks in the $^1H$–$^1H$ COSY spectrum (Figure 3). In addition, the cross peak for the butenol end group olefin/*trans* allylic proton interaction is slightly upfield of the polymer olefin/*trans* allylic proton interaction. We therefore are able to identify the spectral location of polymer protons which are directly adjacent to the regulator end groups. The resonances at 3.6 ($-CH_2O-$) and 2.4 (=CHC$H_2$–) ppm may arise from only those protons adjacent to *trans* double bonds, with the *cis*-adjacent resonances overlapping with the bulk polymer peaks at 3.4 and 2.3 ppm. This conclusion is drawn from the presence of two cross peaks arising from coupling between the *cis* and *trans* olefin protons of the end group, as identified by their coupling to the *cis* and *trans* allylic protons of the polymer, and the allylic protons of the end group (=CHC$H_2$–) in the region 2.3–2.4 ppm. These resonances, in turn, couple with two separate peaks in the region 3.4–3.7 ppm, separate from bulk polymer cross peaks, allowing us to identify *cis*- and *trans*-adjacent $-CH_2O-$ end group resonances. A similar analysis can be performed on an oligomer sample prepared using methyl acrylate as the regulator.

End group resonances for this sample are also observed in the $^{13}C$ NMR. In the 3-buten-1-ol case, the terminal vinyl carbons resonate at 140.0 (=CH–) and 115.5 ($CH_2$=) ppm. The butenol carbons resonate at 134.5 (–CH=), 129.5 (=CH–), and 62.0 ($-CH_2O-$) ppm. The resonances for the two different end groups are approximately equal in intensity. The $^{13}C$ NMR resonances arising from C3 of poly(**3**) at 47–49 ppm are indicative of the *cis*/*trans* configuration of the double bonds of the polymer backbone.[3c] The peaks at 48.8, 47.9, 47.5, and 47.2 ppm arise from carbons in *cis*–*cis*, *cis*–*trans*, *trans*–*cis*, and *trans*–*trans* dyads, respectively.[6] Unfortunately, complications arising from the end group on these resonances preclude the determination of the *cis*:*trans* ratio of this sample. The appearance of the C2 resonances at 77 and 82 ppm, however, when compared with a spectrum of high molecular weight material, indicates that the microstructure of this low molecular weight sample is similar to poly(**3**) produced in the absence of regulator. In general, acyclic olefin molecular weight regulators have little effect on the *cis* content of the bulk polymer.[3c]



| n | C | MW |
|---|---|---|
| 1 | 14 | 256 |
| 2 | 24 | 440 |
| 3 | 34 | 624 |
| 4 | 44 | 808 |
| 5 | 54 | 992 |



| n | C | MW |
|---|---|---|
| 1 | 14 | 270 |
| 2 | 24 | 454 |
| 3 | 34 | 638 |
| 4 | 44 | 822 |
| 5 | 54 | 1004 |

**Figure 4.** Structures and molecular weights for the first five members of the unsymmetrical telomer series from the 3-buten-1-ol and methyl acrylate regulated polymerizations of *exo*-5,6-bis(methoxymethyl)-7-oxabicyclo[2.2.1]hept-2-ene (**3**).

While the $^1H$ and $^{13}C$ NMR data indicate that there are approximately equal amounts of the two alkylidene end groups in the sample, it does not yield information regarding the end groups of individual telochelomers. If the regulating olefin is represented as $Q_1Q_2$, where $Q_1$ and $Q_2$ are the alkylidene moieties of the unsymmetrical regulating olefin, three structures can be produced: $Q_1(M)_nQ_1$,$Q_1(M)_nQ_2$, and $Q_2(M)_nQ_2$, where $M$ is the ring-opened monomer unit. The unsymmetrical series for both 3-buten-1-ol and methyl acrylate regulated polymerization of **3** are shown in Figure 4. While we have been implying the existence of only this series, we can see in the high resolution GPC trace (Figure 2) that all three series might be present by inspection of the $n$ = 1 peak. Two small shoulders, one at higher and the other at lower retention time, flank this peak and may correspond to the symmetrical series of telomers. The high relative yield of the unsymmetrical series is characteristic for polymerization in the presence of terminal acyclic olefins and results from a preferred orientation of the acyclic olefin in the chain transfer step.[18]

As mentioned earlier, our initial observations indicated that 3-buten-1-ol is a more effective molecular weight regulator than methyl acrylate in this aqueous ruthenium(II) metathesis system. Examination of a range of different concentrations of chain transfer agent leads to plots of molecular weight ($M_n$) versus acyclic olefin concentration (Figure 5).[16] Initially, the molecular weight drops off rapidly with increasing concentration of chain transfer agent but then levels off to a constant, low value. Such behavior would be predicted by a chain transfer mechanism but not by a mechanism involving competitive inhibition

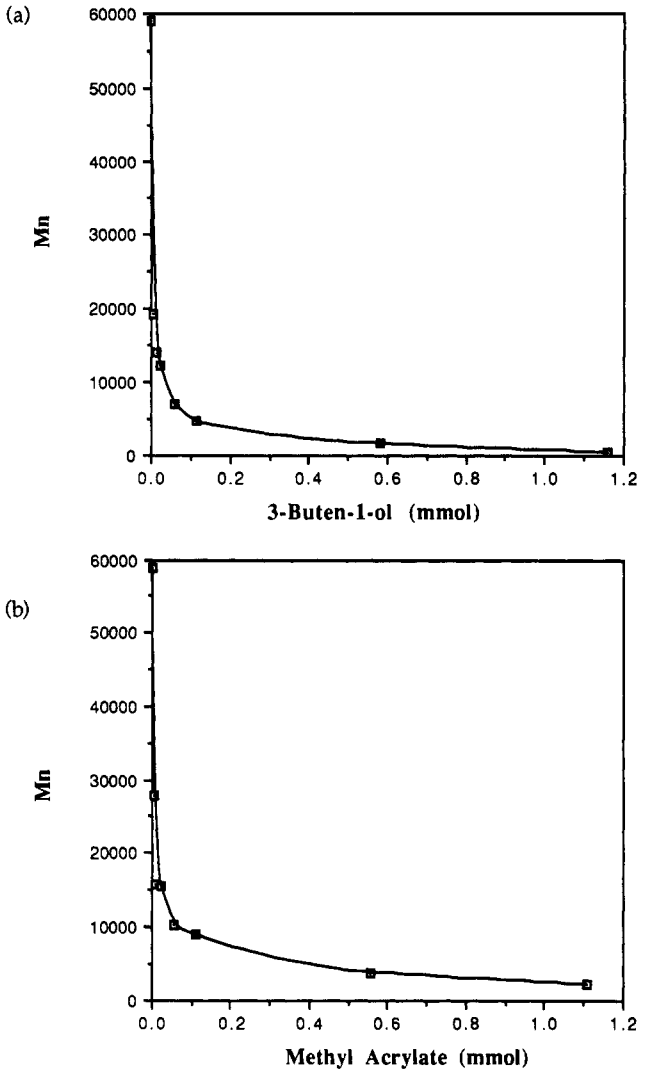



**Figure 5.** Plots of molecular weight ($M_n$) versus concentration of acyclic olefin for **3** polymerized by **1** in the presence of (a) 3-buten-1-ol and (b) methyl acrylate.[16]

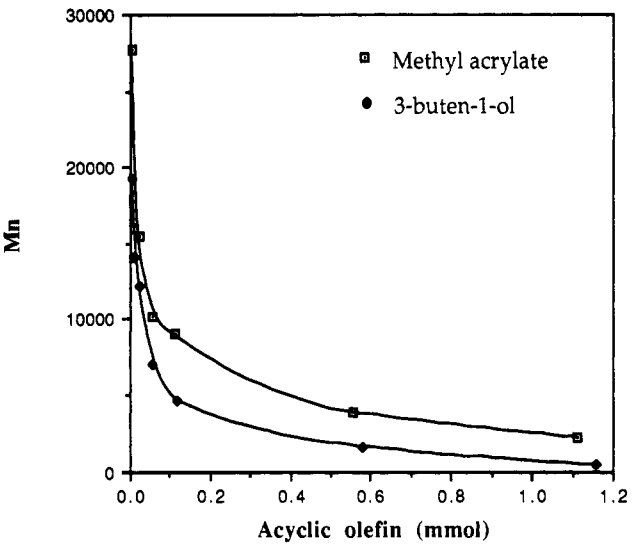
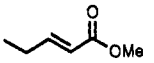
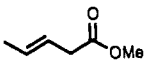
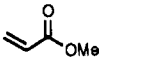
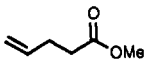



**Figure 6.** Comparison of the plots of molecular weight ($M_n$) versus concentration of acyclic olefin for **3** polymerized by **1** in the presence of 3-buten-1-ol and methyl acrylate. The values for no added olefin have not been included in this plot for clarity.[16]

**Table I. Molecular Weight Regulation by Acyclic Ester Chain Transfer Agents[16]**

| ester[a] | $M_n$ | $M_w$ |
|---|---|---|
|  | 37 700 | 350 000 |
|  | 12 000 | 64 000 |
|  | 3 890 | 13 900 |
|  | 1 100 | 6 610 |

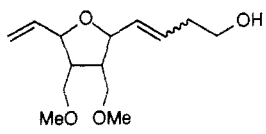
[a] Polymerizations were performed under the conditions indicated in the Experimental Section with [ester]:[1] = 50.

by the acyclic olefin. Chain transfer constants (methyl acrylate = $4.0 \times 10^{-2}$, 3-buten-1-ol = $2.1 \times 10^{-1}$) can be obtained from such data and confirm our initial observations regarding the relative regulating effects of these two olefins. Although the absolute values of chain transfer constants are unreliable, especially when multimodal distributions are involved, comparison of relative values is possible provided that polymerizations are run under similar conditions.[3c] A comparison of the two plots from Figure 5 can be found in Figure 6 and clearly demonstrates the difference in the efficiency of chain transfer for these two regulators.

At a constant concentration of added chain transfer agent, GPC data such as that shown in Table I for a series of acyclic esters are obtained.[16] Interestingly, the reactivity patterns observed with these acyclic olefins parallel that which would be predicted from the reactivity of well-characterized homogeneous alkylidene complexes with olefins. For example, the debilitating effect of an electron withdrawing group on the ability of an olefin to undergo metathetical cleavage has been observed before in both chain transfer reactions[11,19] and acyclic self- and cross-metathesis.[14b,c,20,21] Chain transfer reactivity increases with increasing distance between the olefin and ester functionalities both in classical systems[11,21] and in this study (entries 3 and 4). In addition, the greater steric requirements of internal (entry 1) versus terminal (entry 3) olefins impede their reactivity with well-characterized transition-metal–alkylidene complexes such as W(CH-*t*-Bu)(NAr)(OR)$_2$.[22]

A consideration of both the electronic and steric factors involved in chain transfer efficiency provides a satisfying method for rationalizing the data in Table I for this ruthenium system. The ordering of relative reactivities is predicted to be terminal olefins > deactivated terminal olefins > internal olefins > deactivated internal olefins. While the factors influencing the molecular weight data are admittedly complex,[23] the ruthenium catalyst data follow the predicted trends.

The alcohol functionality on the butenol end group imparts sufficient nonvolatility to the telomers to preclude extensive characterization of the 3-buten-1-ol regulated polymer sample by gas chromatography (GC). Only two peaks of similar retention times are observed when the sample is run through a capillary GC column (SE-30) at 250 °C. GC-mass spectrometry (GC–MS) analysis by electron ionization (EI) failed to reveal parent ion peaks. Fragmentation upon ionization resulted in high-mass peaks for both GC peaks of only *m/e* 211. Chemical ionization (CI) techniques, however, allowed observation of a parent ion peak by HRMS at *m/e* 257.1753 ($MH^+$). We therefore assign these GC peaks to the two isomers (*cis* and *trans*) of structure **5**. The MS peak at *m/e* 211 presumably arises from loss of a $-CH_2CH_2OH$ fragment, yielding a stable allyl radical, or loss of a methoxymethyl group. In addition, by GC–HRMS the symmetric dimethylene structure **6** has also been identified among the

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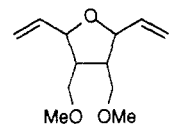


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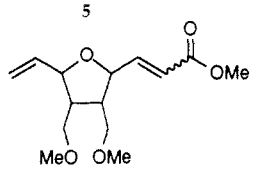


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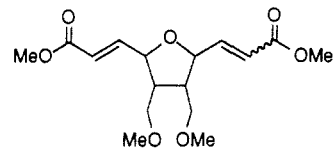


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products of this system ($m/e$ = 213.1470 ($MH^+$)). The asymmetrical structure 7 from the methyl acrylate regulated polymerization of 3 was also identified by GC–HRMS (CI) ($m/e$ = 271.1545 ($MH^+$)) as well as the doubly-ester-capped structure 8 (GC–HRMS (CI) at $m/e$ = 329.1593 ($MH^+$)). Once again, there is a parallel in known alkylidene catalyzed chemistry. The doubly-ester-capped monomer unit analogous to 8 was also characterized by GC–MS in the $WCl_6/SnMe_4$ catalyzed cross-metathesis of norbornene with dimethyl dihydromuconate.[7] Products 5–8 can only be formed from the cross-metathesis of the acyclic olefin with the cyclic monomer. This is the first example of metathesis of an acyclic olefin by 1. Marciniec and co-workers have reported the self-metathesis of tris(alkoxy)vinylsilanes and their cross-metathesis with various terminal olefins catalyzed by $RuCl_3 \cdot nH_2O$ and $RuCl_2(PPh_3)_3$.[24] Marciniec's work represents the only previous example, to our knowledge, of the metathesis of an acyclic olefin using a ruthenium catalyst.[25]

## Conclusion

While the active species in group VIII catalyzed ROMP systems have not yet been directly observed, mounting evidence suggests that they are surprisingly similar to known, well-characterized alkylidene species. We have provided evidence here, including connectivity between end groups derived from the acyclic olefin and the polymer chain, observation of individual telochelomers by mass spectrometry, and relative chain transfer efficiency of various acyclic olefins, that molecular weight regulation with acyclic olefins in the aqueous ruthenium(II) system proceeds by a true chain transfer mechanism. These data support the intermediacy of a ruthenium–alkylidene species which reacts with acyclic as well as cyclic olefins. Since all members of the possible series ($Q_1(M)_nQ_1$,$Q_1(M)_nQ_2$, and $Q_2(M)_nQ_2$) are present, the carbenes resulting from both halves of the olefin ($Ru{=}CH_2$ and Ru=CHR) are active. We are currently investigating the monomeric, dimeric, and trimeric oligomers obtained by GPC fractionation in hopes of identifying an end group structure indicative of the mechanism of initiation of polymerization. Methods of generating alkylidene fragments directly on these aqueous ruthenium centers *in situ* are being explored and have allowed the polymerization of previously unreactive monomers in protic media.[26] In addition, the isolation of a stable ruthenium carbene which polymerizes norbornene in protic media has recently been reported.[27,28]

## Experimental Section

**General Information.** All manipulations involving air- and/or moisture-sensitive compounds were carried out using standard high vacuum or Schlenk techniques. Argon was purified by passage through columns of BASF RS-11 (Chemalog) and Linde 4-Å molecular sieves. Solids were transferred and stored in a $N_2$-filled Vacuum Atmospheres glovebox equipped with a MO-40-1 purification train, a DK-3E Dri-Kool conditioner, and a Dri-Cold freezer.

**Instrumentation.** NMR spectra were recorded on a JEOL GX-400 (399.65 MHz $^1H$, 61.25 MHz $^2H$, 100.40 MHz $^{13}C$). Proton chemical shifts are referenced to internal residual solvent protons. Carbon chemical shifts are referenced to the carbon signal of the deuterated solvents. Gel permeation chromatography (GPC) was performed on either (a) a homemade HPLC instrument employing an Altex model 110A pump, a Rheodyne Model 7125 injector with a 100-μL injection loop, three Shodex Styragel size exclusion columns (KF 803, KF 804, and KF 805), and a Knauer differential refractometer with methylene chloride as the eluent (0.5 wt % solution) at a flow rate of 1.0 mL/min or (b) a Waters Associates instrument employing a Waters syphon pump, a 400-μL injection loop, 4 Microstyragel columns ($10^5$, $10^4$, 500, and 100 in series), and a Waters Model 401 differential refractometer with toluene as the eluent (0.25% solution) at a flow rate of 2.04 mL/min. GPC samples were filtered through a 0.5-μm filter prior to injection. The molecular weights are referenced to narrow dispersity polystyrene samples (Polysciences). High resolution GPC was graciously performed by Prof. Wilhelm Risse of the Phillips Universitat, Marburg, Germany. Gas chromatography (GC) analyses were performed on a Shimadzu GC-Mini-2 flame-ionization instrument equipped with a 50-m capillary column and a Hewlett-Packard Model 3390A integrator. Low resolution mass spectrometry analyses were performed on a Hewlett-Packard Model 5970 mass selective detector in conjunction with a Series 5890 GC equipped with a 15-m SE-30 capillary column or at the Southern California Mass Spectrometry Facility at the University of California, Riverside. High resolution mass spectrometry was performed at the mass spectrometry facilities at E. I. DuPont de Nemours and Co., Wilmington, DE. Infrared spectra were recorded on a Perkin-Elmer 1600 Series FT-IR. Elemental analysis was performed at the analytical facilities of the California Institute of Technology.

**Two-Dimensional $^1H$–$^1H$ Correlated NMR Spectra.** The data were acquired using a JEOL GX-400 NMR spectrometer operating at 399.65-MHz proton frequency. The pulse sequence was 90°–$t_1$–90°–ACQTM–PD and the phases of the pulses and receiver were cycled to provide quadrature detection in $f_1$ and selection of "P-type" peaks. The $^1H$ 90° pulse width was measured on each individual sample by searching for the 180° null and was typically 8.0 μs on the 5-mm $^1H$ probe. The $f_2$ spectral width was chosen at a minimum to accommodate all peaks in the one-dimensional spectrum, and the pulse delay (PD) was minimally 1.0 s. One dummy scan was taken before each slice to eliminate nonequilibrium magnetization. A minimum of eight transients of 1K data points were collected for 256 increments of $t_1$. The data were apodized with a sine-bell window function and Fourier transformed in both dimensions. The absolute value spectrum was calculated and then symmetrized.

**Materials.** Water was either house deionized or purchased from Aldrich (HPLC grade) and degassed prior to use. Chloroform-*d* and benzene-$d_6$ were purchased from Cambridge Isotope Laboratories and used as received. Deuterium oxide was purchased from Aldrich or Cambridge Isotope Laboratories and degassed prior to use. 3-Buten-1-ol was purchased from Aldrich and purified by passage through reagent grade alumina before use. Methyl acrylate was purchased from Aldrich and stored degassed in a dry glass vessel equipped with a Teflon valve closure after being vacuum transferred from calcium hydride. Methyl 2-pentenoate, methyl 3-pentenoate, and methyl 4-pentenoate were prepared from the corresponding carboxylic acids (Aldrich) by standard procedures. Reagent grade ether was used without further purification. 5,6-*exo*-Bis(methoxymethyl)-7-oxabicyclo[2.2.1]hept-2-ene[6] was prepared by literature procedures. Paul Bernhard is gratefully acknowledged for initial samples of $Ru^{II}(H_2O)_6(tos)_2$[1b] and for a modified procedure for its preparation prior to publication.[1a] All samples of $Ru^{II}(H_2O)_6(tos)_2$ prepared in these laboratories were according to the literature procedure.[1a]

**Polymerization of 3 in the Presence of Chain Transfer Agent.** A Schlenk flask charged with 1 (6 mg, 0.011 mmol), acyclic olefin (0.5–200 equiv) and $H_2O$ (1.1 mL) was heated under argon at 55 °C for 15 min during which time the solution turned bright yellow. 7-Oxanorbornene monomer (3) (100 μL, 0.62 mmol, 56 equiv) was added all at once by syringe to the solution, and

the reaction was left at 55 °C for 1–2 h. At very low concentrations of chain transfer agent, polymer precipitated out of the reaction mixture and was washed with water and dried under vacuum. At higher concentrations, the cloudy solution was allowed to cool to room temperature, extracted three times with $Et_2O$ (1 mL), dried over $MgSO_4$, filtered, and concentrated to a clear viscous oil (65–95%). (Longer reaction times may be allowed in order to increase yields when large excesses of regulator are used.) $^1H$ NMR ($CDCl_3$): $\delta$ 5.78 (b), 5.50 (b), 4.55 (b), 4.18 (b), 3.38 (b), 3.25 (b), 2.20 (b).

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## References and Notes

(1) (a) Bernhard, P.; Biner, M.; Ludi, A. *Polyhedron* **1990**, *9*, 1095–1097. (b) Bernhard, P.; Bürgi, H.-B.; Hauser, J.; Lehmann, H.; Ludi, A. *Inorg. Chem.* **1982**, *21*, 3936–3941.

(2) (a) Novak, B. M.; Grubbs, R. H. *J. Am. Chem. Soc.* **1988**, *110*, 7542–7543. (b) Novak, B. M.; Grubbs, R. H. *J. Am. Chem. Soc.* **1988**, *110*, 960–961.

(3) (a) Grubbs, R. H.; Tumas, W. *Science* **1989**, *243*, 907–915. (b) Dragutan, V.; Dimonie, M. *Olefin Metathesis and Ring-Opening Polymerization of Cyclo-Olefins*; Wiley: New York, 1985. (c) Ivin, K. J. *Olefin Metathesis*; Academic Press: London, 1983; pp 399. (d) Grubbs, R. H. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: New York, 1982; Vol. 8, pp 499–551.

(4) (a) McGrath, D. V. Ph.D. Thesis, California Institute of Technology, 1992. (b) McGrath, D. V.; Grubbs, R. H. *J. Am. Chem. Soc.* **1991**, *113*, 3611–3613.

(5) (a) Hillmyer, M. A.; LePetit, C.; McGrath, D. V.; Novak, B. M.; Grubbs, R. H. *Macromolecules* **1992**, *25*, 3345–3350. (b) Hillmyer, M. A.; Lepetit, C.; McGrath, D. V.; Grubbs, R. H. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1990**, *32*, 162–163.

(6) Novak, B. M. Ph.D. Thesis, California Institute of Technology, 1989.

(7) Cramail, H.; Fontanille, M.; Soum, A. *J. Mol. Catal.* **1991**, *65*, 193–203.

(8) Amass, A. J.; Dale, A. L.; Tighe, B. J. *Makromol. Chem.* **1988**, *189*, 515–522.

(9) Reyx, D.; Campistron, I.; Heiling, P. *Makromol. Chem.* **1982**, *183*, 173–183.

(10) Pinazzi, C. P.; Campistron, I.; Croissandeau, M. C.; Reyx, D. *J. Mol. Catal.* **1980**, *8*, 325–328.

(11) Otton, J.; Colleuille, Y.; Varagnat, J. *J. Mol. Catal.* **1980**, *8*, 313–324.

(12) Such materials are useful for the production of larger polymeric materials and block copolymers,[9,10,13] and cross-metathesis of functionalized, terminal olefins would be an important synthetic route to $\alpha,\gamma$-disubstituted olefins.[14]

(13) Nguyen, H. A.; Maréchal, E. *J. Macromol. Sci., Rev. Macromol. Chem. Phys.* **1988**, *C28*, 187–291.

(14) (a) Banks, R. L.; Banasiak, D. S.; Hudson, P. S.; Norell, J. R. *J. Mol. Catal.* **1982**, *15*, 21–33. (b) Mol, J. C. *J. Mol. Catal.* **1982**, *15*, 35–45. (c) For a brief survey of the area of metathesis of functionalized olefins, see: Mol, J. C. *J. Mol. Catal.* **1991**, *65*, 145–162.

(15) Feast, W. J.; Harrison, D. B. *J. Mol. Catal.* **1991**, *65*, 63–72.

(16) These GPC values were obtained in toluene, and although they are internally consistent, they are not directly comparable to other values reported in the text, which were obtained in methylene chloride. The relative response factors of the 7-oxanorbornene polymer and polystyrene may not be the same in different solvents due to differences in the behavior of the two polymers (such as polymer folding) on changing from toluene to methylene chloride.

(17) Benedicto, A. D.; Novak, B. M.; Grubbs, R. H., *Macromolecules* **1992**, *25*, 5893.

(18) (a) Hérisson, J.-L.; Chauvin, Y. *Makromol. Chem.* **1970**, *141*, 161–176. (b) Rossi, R.; Diversi, P.; Lucherini, A.; Porri, L. *Tetrahedron Lett.* **1974**, 879–882. (c) Kelly, W. J.; Calderon, N. *J. Macromol. Sci., Chem.* **1975**, *A9*, 911–929. (d) Lal, J.; Smith, R. R. *J. Org. Chem.* **1975**, *40*, 775–779.

(19) Porri, L.; Rossi, R.; Diversi, P.; Lucherini, A. *Makromol. Chem.* **1974**, *175*, 3097–3115.

(20) Bosma, R. H. A.; Aardweg, G. C. N. v. d.; Mol, J. C. *J. Organomet. Chem.* **1983**, *255*, 159–171.

(21) Verkuijlen, E.; Dirks, R. J.; Boelhouwer, C. *Recl. Trav. Chim. Pays-Bas* **1977**, *96*, M86–90.

(22) For example, see: Schrock, R. R.; DePue, R. T.; Feldman, J.; Schaverien, C. J.; Dewan, J. C.; Liu, A. H. *J. Am. Chem. Soc.* **1988**, *110*, 1423–1435.

(23) Assuming an alkylidene intermediate, the molecular weight data should be heavily influenced by the reactivity of the acyclic olefin with the growing polymer chain, the reactivity of the monomer with the alkylidenes produced from the acyclic olefin, the reactivity of the monomer with the growing polymer chain, and the reactivity of the acyclic olefin with the alkylidenes produced from the acyclic olefin. Our analysis relies on the monomer reactivity being much higher than that of the chain transfer reagent, thus reducing the amount of unproductive chemistry. For example, to date we have not observed self-metathesis products from the acyclic olefin.

(24) (a) Foltynowicz, Z.; Marciniec, B.; Pietraszuk, C. *J. Mol. Catal.* **1991**, *65*, 113–125. (b) Foltynowicz, Z.; Marciniec, B. *J. Organomet. Chem.* **1989**, *376*, 15–20. (c) Marciniec, B.; Maciejewski, H.; Gulinski, J.; Rzejak, L. *J. Organomet. Chem.* **1989**, *362*, 273–279. (d) Marciniec, B.; Rzejak, L.; Gulinski, J.; Foltynowicz, Z.; Urbaniak, W. *J. Mol. Catal.* **1988**, *46*, 329–340. (e) Marciniec, B.; Gulinski, J. *J. Organomet. Chem.* **1984**, *266*, C19–C21.

(25) More recently, a well-defined ruthenium carbene, $(PCy_3)_2Cl_2Ru(=CHCH=CPh_2)$, has been observed to catalyze the metathesis of acyclic olefins. Nguyen, S. T.; Grubbs, R. H. Unpublished results.

(26) France, M. B.; Paciello, R. A.; Grubbs, R. H. *Macromolecules*, in press.

(27) Nguyen, S. T.; Johnson, L. K.; Grubbs, R. H. *J. Am. Chem. Soc.* **1992**, *114*, 3974–3975.

(28) Gagné, M. R.; Grubbs, R. H.; Feldman, J.; Ziller, J. W. *Organometallics* **1992**, *11*, 3933.