Living Ring-Opening Metathesis Polymerization in Aqueous Media Catalyzed by Well-Defined Ruthenium Carbene Complexes

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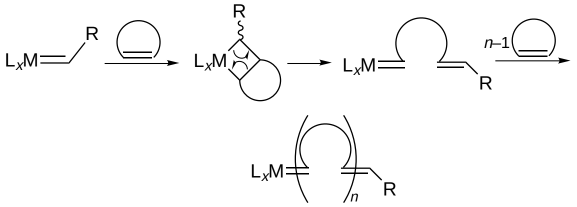
Abstract: In aqueous media, two well-defined ruthenium carbene complexes [$(Cy_3P)_2Cl_2Ru{=}CHCH{=}CPh_2$ (**1**) and $(Cy_3P)_2Cl_2Ru{=}CHPh$ (**2**), Cy = cyclohexyl] catalyzed living ring-opening metathesis polymerization (ROMP) of functionalized norbornenes and 7-oxanorbornenes. Monomers were dispersed in water using a cationic surfactant, and polymerization was initiated by injection of a catalyst solution to yield a polymer latex. The polymerization of hydrophilic 7-oxanorbornene monomer and a hydrophobic norbornene monomer displayed similar behavior in aqueous media, with the resultant polymers having lower molecular weights relative to polymerization in anhydrous organic solution on a similar time scale. The polydispersity indices (PDIs) of polymers prepared from the hydrophilic monomer using catalyst **1** in the presence of water (PDI = 1.20) were narrower than those obtained by solution polymerization (PDI = 2.11), while PDIs for polymers prepared using catalyst **2** remained low in both the presence of water and in anhydrous solution (PDI ≈ 1.13). The linear relationship between molecular weight and monomer/catalyst ratios and the absence of chain transfer and termination processes indicated that these systems are indeed living. Furthermore, this new ROMP technique was shown to be an efficient method for the preparation of well-defined block copolymers.

Introduction

Polymerization reactions which proceed in the absence of termination steps and chain transfer reactions are considered living.[1−3] Living systems in which the rate of polymer chain initiation occurs faster than chain propagation afford polymers with specified molecular weights, narrow polydispersities, and allow the efficient synthesis of block copolymers.[4] Living polymerizations have been achieved via ring-opening metathesis polymerization (ROMP) catalyzed by a variety of well-defined transition metal complexes (eq 1, M = transition metal, L = ligand).[5]



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Although certain molybdenum-based metathesis catalysts can polymerize strained cyclic olefins with polar functional groups,[6−9] their sensitivity to air and protic media severely limits their application as living ROMP catalysts. Industrially useful polymers currently prepared by ROMP contain only olefinic functionality.[10] Tolerance toward functionalized substrates is essential to the practical utilization of these catalyst systems.

Recently developed late transition metal metathesis catalysts exhibit remarkable functional group tolerance compared to early transition metal analogs.[11,12] In fact, the ROMP of functionalized norbornenes and 7-oxanorbornenes in aqueous media has been achieved by simple ruthenium, iridium, and osmium salts;[13−19] however, the catalytically active species in these systems have not been identified. The polymerization of functionalized 7-oxanorbornenes in aqueous media catalyzed by a simple ruthenium(II) complex $[Ru(H_2O)_6(tos)_2$, tos = *p*-toluenesulfonate] has been demonstrated.[15] Although water was shown to increase the rate of initiation in these systems relative to the rate of initiation in anhydrous organic solvents, living polymerization was not achieved.

The environmental and processing benefits of performing industrial polymerizations in aqueous media are numerous.[3,20] A variety of commodity polymers and polymer latexes are

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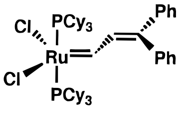
prepared by techniques such as suspension and emulsion polymerization.[3,21] Current efforts include the development of new aqueous systems for the production of functionalized polymers with unique qualities.[22] Recently, Novak reported a nickel allyl initiator ($[(\eta^3\text{-}C_3H_5)Ni(OC(O)CF_3)]_2$) which catalyzes the polymerization of isocyanides in a living fashion. This system remains living upon the exposure of the *propagating* species to air and water.[23]

Two well-defined, ruthenium-based carbene complexes (**1** and **2**) have been shown to induce living polymerization of functionalized norbornenes and 7-oxanorbornenes in solution.[24−27]



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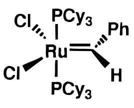

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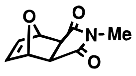
As with other late transition metal metathesis catalysts, they are exceptionally tolerant of polar functionalities and are stable in common organic solvents, even in the presence of alcohol and water. The development of such well-defined, water-tolerant catalysts prompted us to examine the ROMP of strained, cyclic olefins in aqueous media.[28] In this present contribution, we investigated the ROMP of a 7-oxanorbornene derivative (**3**) and two norbornene derivatives (**4**, **5**) initiated by **1** and **2** in an aqueous emulsion. As marked differences in polymerization behavior may be observed for hydrophobic and hydrophilic monomers in such a system, we probed the utility of ROMP in aqueous media with examples taken from both monomer classes. Block copolymerization and the relationship between polymer molecular weight and monomer/catalyst ratios were investigated to determine the living nature of these systems.



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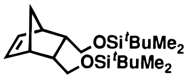

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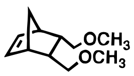

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Results

We first examined the aqueous ROMP of norbornene (NBE) in the presence and absence of a surfactant, using the triphenylphosphine derivative of catalyst **1**. This catalyst polymerized NBE in both systems, although polymer yields were low and PDIs were broad in contrast to polymers of NBE prepared in organic solvent. Additionally, some of the water-insoluble catalyst remained suspended in the aqueous phase during the polymerization. All monomers used in subsequent studies were dispersed in deoxygenated water using an emulsifying agent and the polymerizations were initiated by the injection of the catalyst dissolved in a small amount of organic solvent (5:1 water/organic solvent in a typical polymerization). Dichloromethane and 1,2-dichloroethane (DCE) were found to be the most favorable cosolvents for aqueous systems initiated by **1**, typically yielding more monodisperse polymers than those prepared with benzene or in the absence of cosolvent. Higher yields of polynorbornene were produced with polymerization systems employing **1** and a cationic emulsifying agent, dodecyltrimethylammonium bromide (DTAB, 64%), than with systems employing an anionic surfactant, sodium dodecyl sulfate (SDS, 23%).

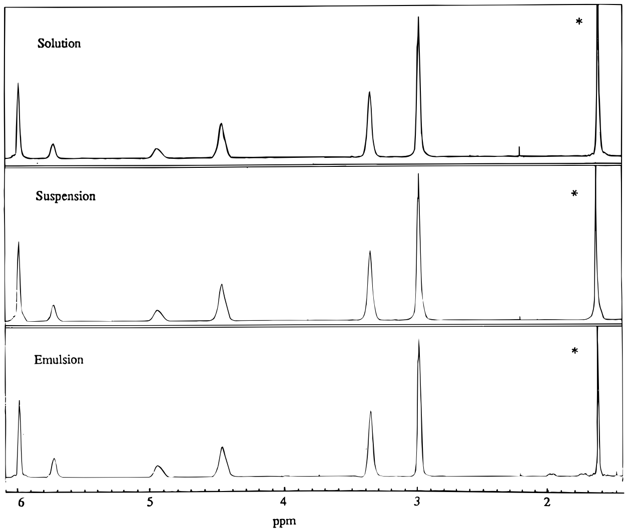


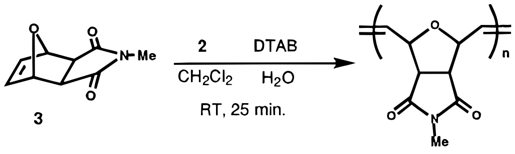
Figure 1. Representative ^1H NMR spectra (in $CDCl_3$) of the polymer obtained from **3** initiated by **2** at room temperature in solution, suspension, and as an aqueous emulsion (* = H_2O).

Table 1. Polymerization of Monomer **3** by Catalysts **1** and **2**

catalyst	polym type[a]	[M]/[C]	yield, %	$10^{-4}M_n$[b]	PDI[b]
1	solution	155	95	8.47	2.11
	suspension	147	82	6.81	1.37
	emulsion	144	85	4.95	1.20
2	solution	100	99	4.41	1.13
	suspension	100	84	2.93	1.12
	emulsion	100	78	2.46	1.07

[a] Polymerizations with **1** were run at 50 °C; polymerizations with **2** were run at room temperature. [b] From GPC data in methylene chloride, relative to polystyrene standards.

ROMP of Hydrophilic Monomer. Catalysts **1** and **2** efficiently polymerized hydrophilic monomer **3** in aqueous media (eq 2).



(2)

Polymerizations in the presence of DTAB (emulsion systems) resulted in a polymer latex, while polymerizations in the absence of emulsifier (suspension systems) phase-separated without vigorous stirring. ^1H NMR spectroscopic data for polymers obtained in aqueous media are consistent with the data previously reported for polymers of **3** prepared via ROMP (Figure 1).[15] Polymer yields and molecular weights for the reactions catalyzed by **2** in the presence of water were typically lower than those obtained under anhydrous conditions on the same reaction time scale, and the PDIs remained low in every case (Table 1). Careful analysis of the aqueous phase after polymerization revealed the presence of unreacted monomer. Increasinging the reaction time for aqueous polymerizations resulted in complete monomer consumption and polymer yields and molecular weights comparable to those for polymers prepared in solution. Molecular weight distributions were bimodal in such cases. When **1** was used to initiate polymer-

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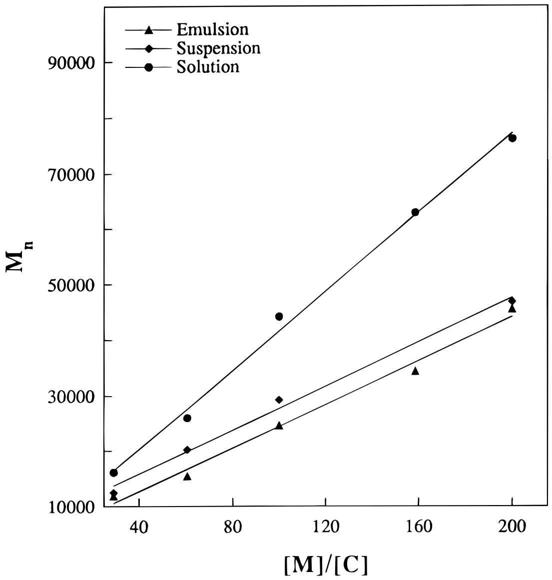


Figure 2. Plot of number average molecular weight (M_n) versus monomer/catalyst ratio ([M]/[C]) for polymers obtained from **3** initiated by **2** at room temperature in solution, suspension, and as an aqueous emulsion. Molecular weights are reported versus polystyrene calibration.

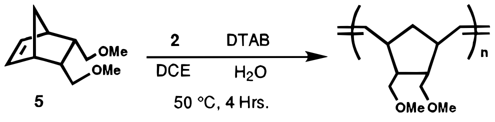
Table 2. Polymerization of Monomer **5** by Catalyst **2**

polym type[a]	[M]/[C]	yield, %	$10^{-4}M_n$[b]	PDI[b]
solution	159	99	2.23	1.18
suspension	159	99	2.34	1.19
emulsion	159	68	1.32	1.10

[a] Polymerizations were run at 50 °C. [b] From GPC data in methylene chloride, relative to polystyrene standards.

ization in the presence of water, PDIs were *narrower* than those obtained by polymerization in anhydrous organic solvent. We investigated the relationship between M_n and [**3**]/[**2**] for polymerization in organic solution, suspension, and aqueous emulsion systems. A linear relationship was observed for the polymerization reactions in the presence of water, as well as for reaction in anhydrous solution (Figure 2).

ROMP of Hydrophobic Monomers. The ROMP of monomers **4** and **5** was also examined in the presence of water (eq 3).



(3)

When **5** was polymerized by **2**, yields and molecular weights for polymers prepared in the presence of DTAB were found to be lower than those prepared in solution or suspension systems on the same time scale, while PDIs remained similar (Table 2). Linear relationships between M_n and [M]/[C] were observed for the polymerization of **5** catalyzed by **2** in solution, suspension, and aqueous emulsion systems (Figure 3). Studies conducted with **4** employing catalyst **2** revealed the polymerization to be living in both solution and suspension systems. Interestingly, the polymerization was not living in the presence of DTAB (Figure 4).

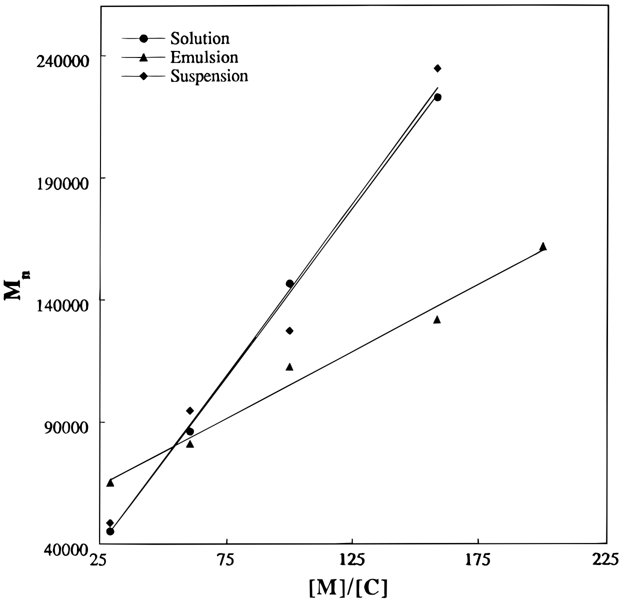
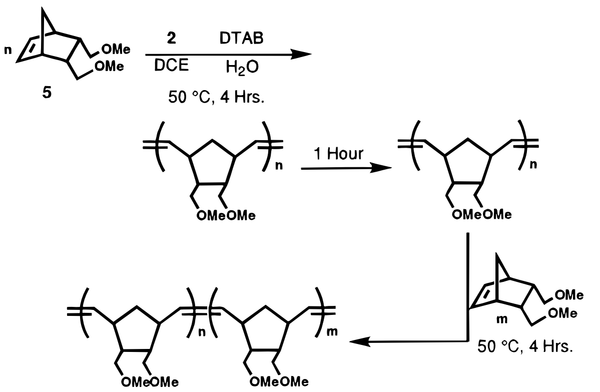


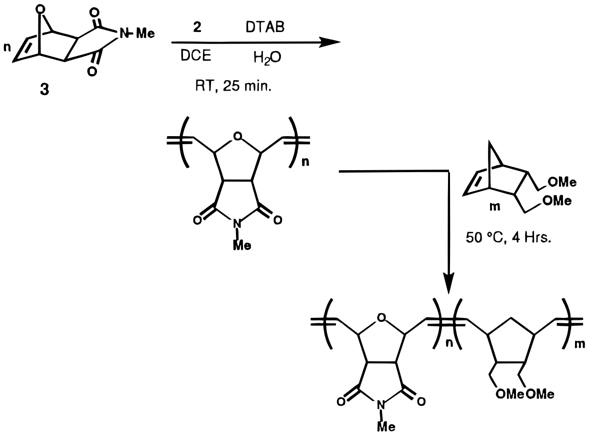
Figure 3. Plot of number average molecular weight (M_n) versus monomer/catalyst ratio ([M]/[C]) for polymers obtained from **5** initiated by **2** at 50 °C in solution, suspension, and as an aqueous emulsion. Molecular weights are reported versus polystyrene calibration.

Block Copolymerizations Using Catalyst 2. A two-step block polymerization of **5** was carried out using **2**. Monomer **5** was polymerized in an aqueous emulsion system until polymerization stopped. The polymerization reaction was allowed to sit for an additional hour after which time a second aliquot of **5** was added to the emulsion, resulting in continued polymerization (eq 4).



(4)

M_n increased from 34 000 for the first block to 126 700 for the final polymer, as determined by GPC (Figure 5). The PDI of the polymer increased from 1.08 to 1.25. A block copolymer of **3** and **5** was synthesized using **2** according to a similar procedure (eq 5). M_n increased from 25 200 for the homopolymer of **3** to 145 300 for the block copolymer after the addition of **5**. The PDI increased from 1.06 to 1.32 (Figure 6).[29]



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Discussion

The results above indicate that the polymerization of functionalized norbornenes and 7-oxanorbornenes by **1** and **2** in

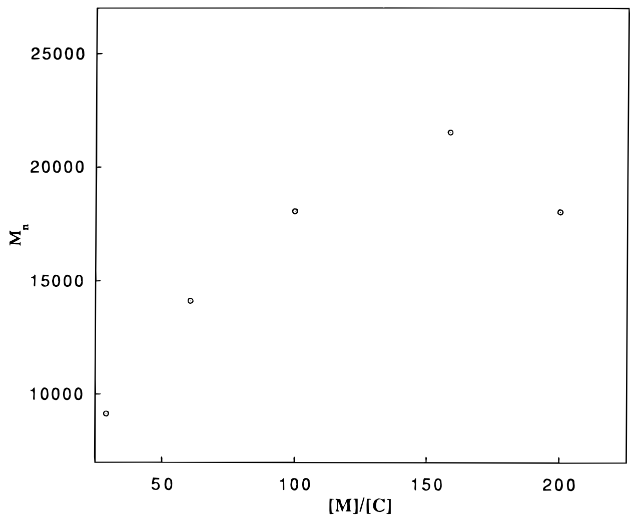

Figure 4. Plot of number average molecular weight (M_n) versus monomer/catalyst ratio ([M]/[C]) for polymers obtained from **4** initiated by **2** at room temperature in an aqueous emulsion. Molecular weights are reported versus polystyrene calibration.

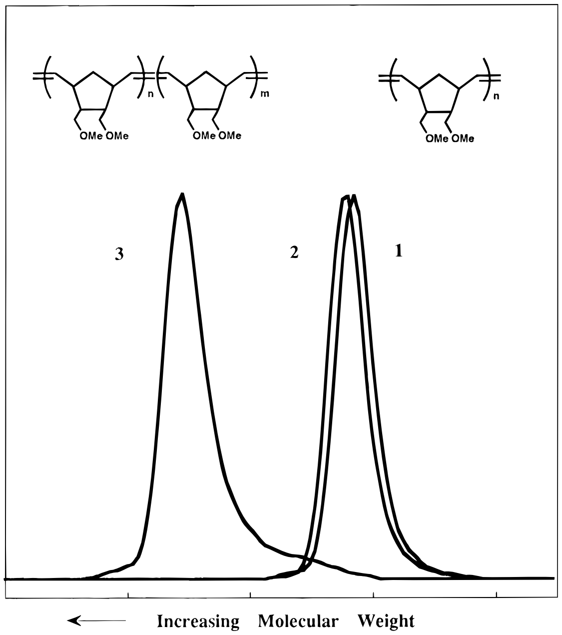

Figure 5. Gel permeation chromatograph traces for polymers obtained from **5** initiated by **2**. The peaks represent (1) polymer after complete incorporation of monomer (M_n = 31 000, PDI = 1.08), (2) polymer after standing an additional 1 h (M_n = 34 000, PDI = 1.08), and (3) the polymer after continued polymerization of additional monomer (M_n = 126 700, PDI = 1.25). Molecular weights are reported versus polystyrene calibration.

aqueous media occurs in living fashion. In the following section, the problem of catalyst solubility is addressed, followed by a detailed analysis of the biphasic nature of the systems and a qualitative view of its impact on polymerization kinetics. The differences in polymerization behavior for aqueous systems employing hydrophilic and hydrophobic monomers are discussed, and several criteria useful for the experimental determination of living polymer systems are addressed.

Although **1** and **2** are very active and well-behaved metathesis catalysts in organic solvents, they are insoluble in aqueous media. The data observed for aqueous polymerizations of NBE in the absence of organic solvent illustrate the effects of catalyst insolubility in these systems. The higher molecular weights and broader PDIs for these systems relative to polymerization in organic solution are a result of uncontrolled and low initiation efficiency due to the heterogeneity of the reaction. Increased catalyst solubility is required to achieve controlled initiation and well-defined polymers. Accordingly, catalyst was introduced to aqueous dispersions of monomer as a solution using a small amount of organic solvent. In these systems, initiation and propagation occur in the organic phase in a controlled manner, and polymerization behavior and polymer characteristics may be altered by the presence of large amounts of water through choice of monomer and emulsifier concentration. For example, aqueous polymerization in the presence of DTAB resulted in polymer latexes, although the stability of these latexes was limited over time. Polymers precipitated from reaction media within 30 min of termination did not suffer observable degradation.

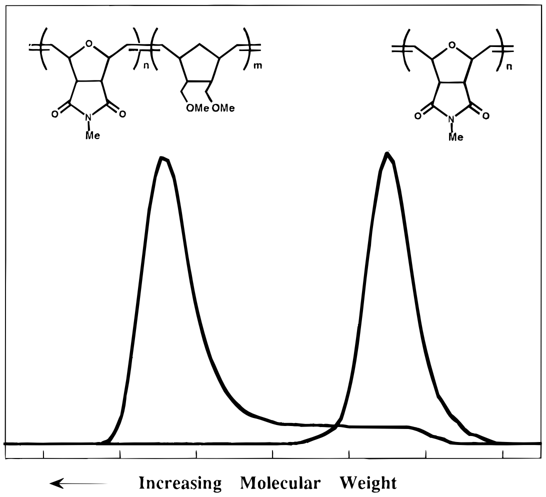

Figure 6. Gel permeation chromatograph traces for polymer obtained from **3** initiated by **2** (M_n = 25 200, PDI = 1.06) and the block copolymer obtained after polymerization of added **5** from the living chain end (M_n = 145 300, PDI = 1.32). Molecular weights are reported versus polystyrene calibration.

Polymer yields and molecular weights for polymerizations of **3** catalyzed by **2** in the presence of water were lower than those obtained under anhydrous conditions on the same reaction time scale, and PDIs remained low (Table 1). Monomer **3** is soluble in both water and organic solvent. During polymerization in aqueous systems, therefore, partitioning of monomer between the aqueous and organic phases results in *decreased* monomer concentration in the organic phase, relative to a solution polymerization employing the same amount of organic solvent. Diffusion of monomer from the aqueous phase into the micelle results in a steady-state concentration of monomer within the micelle during polymerization. However, in the *later* stages of polymerization, monomer concentration should approach zero in the aqueous phase. Accordingly, propagation throughout the polymerization of hydrophilic monomers in the presence of large amounts of water should be slower. The present results are consistent with this scenario, as careful analysis of the aqueous phase after polymerization revealed the presence of unreacted monomer. Increasing the reaction time for the polymerizations in aqueous media resulted in complete monomer consumption, and polymer yields and molecular weights were comparable to those of polymers prepared in solution. Molecular weight distributions were bimodal in such cases, however, indicative of cross-metathesis between polymer chains. In the later stages of polymerization, the rate of monomer diffusion into the monomer-starved organic phase may be sufficiently slow to allow the rate of cross-metathesis to

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(29) The polydispersity of the main peak was 1.08 as seen in Figure 6.

compete with the rate of propagation. It is notable that this cross-metathesis in the late stages of the reaction is not a chain termination step since the number of propagating species does not change and, although the molecular weight distribution changes, the number average molecular weight remains unaffected.

The PDIs obtained with catalyst **1** suggest that the relative rates of initiation and propagation change in aqueous media, resulting in lower PDIs relative to solution polymerization (Table 1). However, it is not clear that this kinetic effect is a direct result of the monomer phase equilibrium mentioned above, as k_i and k_p are both first-order processes with respect to monomer concentration. The relative rates of initiation and propagation would be affected *equally* by a lower monomer concentration within a micelle. However, kinetic data suggest that the dominant mechanism for propagation with **1** and **2** in solution is dissociative in phosphine.[30] Therefore, preferential coordination of water to the propagating species may serve to slow the rate of propagation relative to the rate of initiation. This would result in more monodisperse polymers; however, the experiments conducted in this present study do not unambiguously rule out other possibilities. It has been shown that the ratio of initiation to propagation is much greater for derivatives of **2** ($k_i/k_p = 9$) than for derivatives of **1** ($k_i/k_p = 6 \times 10^{-3}$) for polymerization in solution.[26] For polymerizations employing **2**, therefore, any phenomena which would serve to alter rates of initiation and propagation in the presence of water should be masked by this 1500-fold increase in the relative rates of initiation and propagation. Accordingly, narrower polydispersities in the presence of water are not observed for polymerizations initiated with **2** (Table 1).

When k_i/k_p is large and catalyst initiation occurs in a complete manner, living systems can be used to produce monodisperse polymers. The number of polymer molecules produced is then a constant, equal to the number of original initiating species. With ROMP in solution, complete catalyst initiation is typically probed directly by ^{1}H NMR, as carbene signals for the initiating and propagating species are clearly distinguished. In aqueous emulsion systems, however, direct experimental observation of carbene species by ^{1}H NMR is experimentally complicated. The exceptionally narrow PDIs observed for polymerizations in aqueous media are evidence of fast and complete initiation relative to propagation in aqueous systems employing **2**.

The molecular weight of a living polymerization is controlled by the stoichiometry of the reaction,[1] and results in a linear relationship between the number average molecular weight (M_n) of the polymers and the corresponding monomer/catalyst ([M]/[C]) feed ratios. A linear relationship was observed in solution, suspension, and emulsion systems for the polymerization of **3** initiated by **2**, providing experimental support for the living nature of the aqueous systems (Figure 2). As the propagating species for polymers initiated by **1** is identical to the propagating species for polymers initiated by **2**, it is expected that polymerizations initiated by **1** in the presence of water should be living as well. PDIs are broader, however, due to inherent differences in k_i and k_p for this catalyst as discussed above.

Aqueous polymerizations of hydrophobic monomers **4** and **5** were also examined, as any effects resulting from a monomer concentration equilibrium between phases should be negligible. The relationship between M_n and [**5**]/[**2**] was found to be linear for solution, suspension, and aqueous emulsion systems (Figure 3). However, yields and molecular weights for polymers prepared from **5** initiated by **2** in the presence of DTAB were found to be lower than those prepared in solution or suspension systems *on the same time scale*. The fact that the data for polymerizations in suspension and solution systems are nearly identical indicates that the lower molecular weights in the presence of DTAB result from the presence of emulsifier, and not from monomer solubility in the water phase. Although the data do not explicitly exclude the coordination of water to the catalyst during propagation, they indicate that the potential occurrence of coordination is not responsible for lower molecular weights or slower propagation on the time scale of the reaction.

Polymerization of **4** initiated by **2** revealed a linear relationship between M_n and [M]/[C] for reactions in solution and suspension systems. However, the polymerization was not living in the presence of DTAB (Figure 4), and molecular weight data were often inconsistent and irreproducible for identical reactions, particularly at larger [M]/[C] ratios. Previous work with ring-closing metathesis in this group has suggested that **1** and **2** are inactivated over time in the presence of olefinic substrates bearing *tert*-butyldimethylsilyl functional groups.[31] Presumably, the presence of DTAB in reaction media is facilitating the inactivation of the catalyst in this present study.

In living systems, polymerization proceeds until polymerization stops, and further addition of monomer results in continued polymerization,[1] i.e., the polymerization proceeds in the absence of chain termination steps and transfer reactions *on the time scale of the polymerization*. To clearly illustrate this important criterion, a two-step block polymerization of monomer **5** was performed using catalyst **2** (eq 4). The M_n for the final polymer shifted dramatically (to within baseline separation by GPC) relative to the initial block (Figure 5) with a moderate increase of the PDI from 1.08 to 1.25. The PDI of the initial block after sitting for an additional hour remained at 1.08, and no base peaks were observed in the GPC trace after continued polymerization. This indicates the relative absence of chain transfer and termination reactions and attests to the robust nature of the catalyst under aqueous conditions on the time scale of the ROMP reaction.

Block copolymers of **3** and **5** have been efficiently prepared by ROMP in aqueous media (eq 4). M_n for the block copolymer shifted dramatically (Figure 6), and PDI increased from 1.06 to 1.32. The polydispersity of the principal peak remained narrow (1.08) as seen in Figure 6. The low molecular weight material may be due to the observation that these active catalysts can slowly backbite under these extreme conditions to give low molecular weight fragments.[32] In addition, the observed tailing may be attributed to the inefficient manner in which the propagating chain end of polymer **3** serves as an initiating species for the newly-introduced monomer **5**. While the polymerization of monomer **3** is carried out at room temperature, monomer **5** will only polymerize efficiently at 50 °C (see Experimental Section). An aliquot of monomer **5** was added to the polymerized **3** concurrent with the transfer of the reaction medium to a 50 °C sand bath. The time required for the system to reach thermal equilibrium should effect the initiation of the second monomer, and helps explain the broadening observed in the PDI for the block copolymer. Although the monomer feed ratio (**3**/**5**) for the copolymerization was 1:4, the segment ratio of the final copolymer was estimated by ^{1}H NMR to be 1:2.8 (Figure 7). The polymerization was terminated prior to quantitative incorporation of the second monomer as a small amount of polymer precipitation was observed. Repeated attempts to obtain accurate differential scanning calorimetry (DSC) data for the block copolymer were unsuccessful.

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[30] Dias, E. L.; Grubbs, R. H. Unpublished results.

[31] Fu, G. C.; Dias, E. L.; Grubbs, R. H. Unpublished results.

[32] Hillmyer, M. A.; Grubbs, R. H. Unpublished results. Backbiting does not result in a decrease in the number of growing chains.

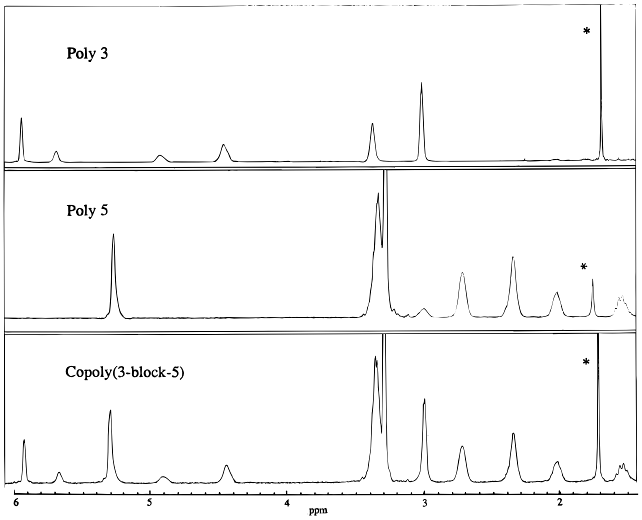

Figure 7. Representative ^{1}H NMR spectra (in $CDCl_3$) of the polymer obtained from **3** (top), the polymer obtained from **5** (middle), and the block copolymer obtained from **3** and **5** (* = H_2O).

Conclusions

Ruthenium alkylidenes **1** and **2** efficiently catalyze the living ring-opening metathesis polymerization of functionalized norbornenes and 7-oxanorbornenes in the presence of water. These systems pass all the tests for living systems.[1] To our knowledge, *this report represents the first example of a living polymerization occurring entirely in the presence of water by any mechanism*. Introduction of a small amount of organic solvent is necessary to achieve controlled initiation. Aqueous polymerizations in the presence of emulsifier yield latexes of nearly monodisperse ROMP product, while suspension polymerizations become ill-defined in the absence of stirring. Block copolymerization and the relationship between polymer molecular weight and monomer/catalyst feed ratios were examined to demonstrate the living nature of the polymerizations in the presence of water. This demonstrates that block copolymers may be efficiently prepared in aqueous media with properly designed catalysts and these living polymerization systems can be used to prepare latexes of nearly monodisperse homopolymers and block copolymers of both water-soluble and water-insoluble monomers. As the properties of polymer latexes make them ideal for the preparation of tacky polymers,[21] we are currently investigating the aqueous ROMP of cyclic olefins such as 1,5-cyclooctadiene. Water-soluble derivatives of **1** and **2** are currently being utilized to expand the scope of these systems.

Experimental Section

General Considerations. Argon was purified by passage through columns of BASF R3-11 catalyst (Chemalog) and 4 Å molecular sieves (Linde). ^{1}H NMR spectra were recorded on a JEOL GX-400 spectrometer (400 MHz) at 25 °C. All chemical shift values are given in ppm and are referenced with respect to residual protons in the solvent. Gel permeation chromatographs (GPC) were obtained using an Altex Model 110A pump, a Rheodyne Model 7125 injector with a 100-μL injection loop, through an American Polymer Standards 10-μm mixed-bed column, and a Knauer differential refractometer; dichloromethane was used as the eluent at a flow rate of 1.0 mL/min. The molecular weights and polydispersities of the polymers are reported relative to monodisperse polystyrene standards.

Materials. Distilled deionized water was used for the polymerizations and was degassed by purging with argon and then stirring under high vacuum prior to use. 1,2-Dichloroethane was vacuum transferred from calcium hydride prior to use. Dichloromethane was purified by passage through solvent purification columns containing activated alumina.[33] Ruthenium carbene complexes **1**[24] and **2**[26] and monomers **3**[15] and **4**[27] were prepared as previously reported. Dodecyltrimethylammonium bromide (DTAB) (Aldrich, purity 99%), sodium dodecylsulfate, ethyl vinyl ether, methanol, and other reagents were used without further purification unless otherwise noted.

General Polymerization Procedure. Typical polymerization reactions were conducted in the following manner. Deviations from this general procedure are indicated below for specific cases. In a nitrogen-filled drybox, monomer (0.558 mmol) was added to a 4-dram vial equipped with a Teflon-coated stirbar. For emulsion-type polymerizations, DTAB (0.516 g, 1.67 mmol) was added. The vial was capped with a rubber septum and secured with copper wire. Catalyst was added to a 1-dram vial and capped with a rubber septum, and organic solvent (0.8 mL) was added to the catalyst via syringe. Outside the drybox, water (4 mL) was added to the vial containing the monomer (for emulsion and suspension polymerizations only), and the contents were stirred vigorously (1300 rpm) at room temperature for 0.5 h. The catalyst solution was sonicated briefly to ensure complete dissolution of the catalyst, and the polymerization reaction was initiated by adding the catalyst solution to the vial containing the monomer via a gas-tight syringe. Polymerization was terminated by adding an excess of ethyl vinyl ether (2 mL) to inactivate the catalyst and a small amount of methylene chloride to prevent precipitation. Stirring was continued for 0.5 h after termination. Polymers were typically purified by precipitation from methanol and were dried under dynamic vacuum overnight at room temperature prior to analysis. Reactions used to study the living nature of the polymerizations were not purified; water and organic solvent were removed *in vacuo* after catalyst termination, and the crude polymer samples were analyzed directly by GPC.

Synthesis of *endo*-5,6-Bis(methoxymethyl)bicyclo[2.2.1]hept-2-ene (5). An oven-dried 500-mL, 3-necked flask was equipped with a Teflon-coated stirbar, a pressure-equalizing addition funnel, and a Vigreux condenser. Under argon purge, the reaction vessel was charged with NaH (3.50 g, 0.146 mol) in dry THF (100 mL). *endo*-5,6-dicarbinolbicyclo[2.2.1]hept-2-ene[27] (9.00 g, 58.36 mmol) was dissolved in dry THF (30 mL) and added dropwise through the addition funnel. After complete addition, the reaction was stirred for an additional 0.5 h. CH_3I (39.80 g, 0.280 mol) was added slowly through the addition funnel. An exotherm was observed during the addition of the CH_3I, and the reaction was placed in an ice bath and allowed to stir for 2 h after complete addition. Water was added dropwise to quench the remaining NaH. The reaction mixture was poured into diethyl ether (500 mL) and filtered. The filtrate was washed four times with water (200 mL), dried over Na_2SO_4, and filtered, and volatiles were removed *in vacuo* to yield the crude product as a yellow oil (8.87 g, 83.36%). The product was purified by Kugelrohr distillation (55 °C, 4 mTorr) to yield the product as a clear oil in 76% yield. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.37 (dd, 2H, $J = 8.3$ Hz), 2.43 (m, 2H), 2.88 (br s, 2H), 2.97 (t, 2H, $J = 9.0$ Hz), 3.15 (dd, 2H, $J = 7.5$ Hz), 3.27 (s, 6H), 6.10 (m, 2H) ppm. ^{13}C NMR (proton decoupled, $CDCl_3$, 400 MHz) 135.30, 72.82, 58.68, 49.11, 45.59, 41.47 ppm. IR (neat) 3057 (m), 2978 (s), 2919 (s), 2870 (s), 2870 (s), 2828 (s), 2807 (s), 2755 (w), 1480 (m), 1459 (m), 1389 (m), 1347 (m), 1245 (w), 1199 (m), 1168 (m), 1133 (s), 1102 (s), 970 (m), 958 (m), 911 (m), 892 (w), 826 (w) cm^{-1}. Anal. Calcd for $C_{11}H_{18}O_2$: C, 72.49; H, 9.95. Found: C, 72.02; H, 9.97.

Polymerization of 3 and 4. The general polymerization procedure outlined above was followed. Dichloromethane was used to dissolve the catalyst. Reactions were run at room temperature and terminated 25 min after initiation.

Polymerization of 5. The general polymerization procedure outlined above was followed. DCE, a higher boiling solvent, was used to dissolve the catalyst since polymerization conditions required heating at 50 °C for 4 h before termination. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.42 (br s), 1.95 (br s), 2.27 (br s), 2.67 (br s), 2.97 (br s), 3.28 (s), 3.35 (br s), 5.39 (br s) ppm. ^{13}C NMR (proton decoupled, $CDCl_3$, 400 MHz) 132.15, 71.42, 58.68, 45.88, 44.12, 38.23 ppm.

Two-Step Polymerization of 5. Monomer **5** was polymerized according to the procedure outlined above. After 4 h, an aliquot (0.2 mL) was removed and precipitated into methanol for analysis by GPC.

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(33) Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, in press.

The reaction was allowed to proceed for an additional hour at 50 °C, and another aliquot (0.2 mL) was removed. Additional monomer **5** (0.408 g) was added neat via a gas-tight syringe and the reaction was stirred for an additional 4 h. The polymerization was terminated and purified as outlined above.

Synthesis of Copoly(3-block-5). Monomer **3** was polymerized according to the procedure outlined above. After 25 min, an aliquot (0.2 mL) was removed from the reaction with a gas-tight syringe and precipitated into methanol for analysis by GPC. Simultaneously, the reaction was transferred to a 50 °C sand bath, monomer **5** (0.408 g) was added neat via a gas-tight syringe, and vigorous stirring was continued. Four hours after monomer **5** was added, a small amount of polymer precipitate was observed, and the polymerization was terminated and purified as outlined above.

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