Alternating Copolymerizations of Polar and Nonpolar Cyclic Olefins by Ring-Opening Metathesis Polymerization

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ABSTRACT: The results from copolymerizations of polar 2,3-difunctionalized 7-oxanorbornene derivatives with a series of nonpolar cyclic olefins—cyclooctene, cyclooctadiene, cyclopentene, and norbornene—using catalysts $RuCl_2(=CHPh)(PCy_3)_2$ (**1**) and its mono-1,3-dimesitylimidazolidine-2-ylidene derivative (**2**) are reported. The resulting polymer microstructures have been analyzed by ^1H, ^{13}C, and $^1H-^1H$ COSY NMR spectroscopies. Highly alternating structures were observed for the copolymerizations of *endo*-*N*-ethyl-7-oxanorbornene-2,3-dicarboxylimide (*endo*-**3**), *exo*,*exo*-7-oxanorbornene-2,3-dimethylester (*exo*-**4**), or *exo*-7-oxanorbornene-2,3-dicarboxylic anhydride (*exo*-**5**) with cyclooctene using catalyst **1**. The rates of homopolymerizations of *endo*-**3**, *exo*-**5**, and cyclooctene were determined. Comparison with the rate of the copolymerization of *endo*-**3** with cyclooctene reveals a rate faster than the homopolymerization of *endo*-**3** but slower than the homopolymerization of cyclooctene. The rate of the copolymerization of *exo*-**5** with cyclooctene was observed to be greater than the rate of homopolymerization of either monomer. The use of catalyst **2** resulted in lower levels of alternation with a tendency toward random polymerization.

Introduction

Control over macromolecular architecture and resulting material properties has been a central goal of polymer chemistry. Efforts along these lines have been directed toward developing new synthetic methodologies whereby precise placement of chemical functionality can be achived. Ring-opening metathesis polymerization (ROMP) has attracted considerable research attention recently in large part due to development of well-defined catalyst systems.[1] Highly active metathesis catalysts based on group 6 metals, in particular molybdenum, have been developed by Schrock.[2−4] These catalysts allow for the living ROMP of a variety of monomers and provide control over polymer microstructure such as cis/trans ratios and tacticity. More recently, the ruthenium-based catalyst systems introduced by Grubbs permit metathesis reactions in polar and nonpolar reaction media in addition to being tolerant toward a range of protic and polar functional groups under ambient conditions.[5] As a result of this progress, the ROMP of functionalized norbornene derivatives has facilitated the synthesis of polymers with numerous functional groups, resulting in a range of polymeric structures. Notable examples include block copolymers,[6,7] fluoropolymers,[8] high-temperature polymers,[9] hydrogels,[10] polymers functionalized with biologically relevant side groups,[11−17] polymers with tubular architectures bearing tapered monodendron side groups,[18] polyelectrolytes,[19,20] and side chain liquid crystal polymers.[21] In general, these materials are either homopolymers or block copolymers prepared by a sequential monomer addition. The study of copolymerization by ring-opening metathesis may provide a new route to tune material properties through combinations of various monomers and reaction stoichiometry.

Alternating copolymers can be synthesized by various polymerization methods. However, alternating copolymerization of monomer mixtures by ring-opening metathesis polymerization is very rare. There have been only two reports in the literature. The first report is the alternating copolymerization of the enantiomers of 1-methylnorbornene catalyzed by $ReCl_5$, in which it was not possible to polymerize an optically pure monomer due to steric effects.[22] The low activity of this heterogeneous catalyst and consequently its intolerance toward steric hinderence were presumably key parameters in this alternation mechanism. The second example is the alternating copolymerization of cyclopentene and norbornene, two nonpolar monomers, using $RuCl_3$, $IrCl_3$, or $OsCl_3$ in the presence of phenol as a cocatalyst or solvent. A hydrogen-bonded solvent cage around the catalyst site was invoked to explain rapid cross-propagation relative to homopolymerization. The alternating distribution was obtained under condition of a 1:8 norbornene to cyclopentene feed ratio and was maintained throughout yields ranging from 2 to 20%.[23,24]

The synthetic utility of alternating ring-opening metathesis copolymerization can be expanded considering the recent progress in olefin metathesis that utilize highly active well-defined catalyst systems for polymerizations of various functionalized polar or nonpolar monomers. In this report, we present the first example of alternating ring-opening metathesis copolymerization that incorporates polar and nonpolar monomers, resulting in a series of alternating copolymers with tailorable functionalities.

Experimental Section

Materials. $RuCl_2(=CHPh)(PCy_3)_2$ (**1**), (tricyclohexylphosphine)(1,3-dimesitylimidazolidine-2-ylidene)benzylideneruthenium dichloride (**2**), and $Mo(CHCMe_2Ph)(NAr)(OCMe(CF_3)_2)$ were purchased from Strem Chemical. The monomers *exo*-**4** and *exo*-**5** were prepared according to literature procedures.[25] All other reagents were obtained from Aldrich. Cyclooctene, cyclooctadiene, cyclopentene, and deuterated chloroform were passed through columns of basic activated alumina prior to use. Methylene chloride was vacuum-distilled from CaH_2 prior to use. Norbornene was used as received.

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Preparation of *exo*-3. A stirred solution of *N*-ethylmaleimide (50 mmol) and furan (500 mmol) in dry benzene was heated at reflux for 18 h. Benzene and excess furan were evaporated under vacuum at 60 °C. The solid product was recrystallized from diethyl ether and dried under vacuum at room temperature. The product was determined to be pure *exo* isomer by ^{1}H NMR spectroscopy. ^{1}H NMR ($CDCl_3$): δ 1.15 (t, 3 H), 2.82 (s, 2 H), 3.51 (q, 2 H), 5.26 (s, 2 H), 6.50 (s, 2 H).

Preparation of *endo*-3. A solution of *N*-ethylmaleimide (50 mmol) and furan (500 mmol) in dry benzene was allowed to react at room temperature for 4 days. Benzene and excess furan were evaporated under vacuum at 40 °C. The solid product was washed with cold diethyl ether and dried under vacuum at room temperature. The product was determined to be pure *endo* isomer by ^{1}H NMR spectroscopy. ^{1}H NMR ($CDCl_3$): δ 1.03 (t, 3 H), 3.36 (q, 2 H), 3.49 (d, 2 H), 5.31 (d, 2 H), 6.39 (s, 2 H).

Polymer Characterization. ^{1}H, ^{13}C, and ^{1}H−^{1}H COSY NMR spectra were obtained at 300 MHz with a Bruker DPX-300 NMR spectrometer. Gel permeation chromatography (GPC) was performed with a Polymer Lab LC1120 high-performance liquid chromatography (HPLC) pump equipped with a Waters differential refractometer detector. The mobile phase was tetrahydrofuran with a flow rate of 1 mL/min. Separations were performed with 10^5, 10^4, and 10^3 Å Polymer Lab columns. Molecular weights were calibrated vs narrow molecular weight polystyrene standards.

General Copolymerization Procedures. Catalyst **1** or **2** (4 μmol) was dissolved in 1 mL of CH_2Cl_2 and added to a solution of an equimolar mixture of a polar and nonpolar monomer (1 mmol total) in 1 mL of CH_2Cl_2. The reaction mixture was stirred for 12 h at room temperature. The reaction was stopped with injection of 5 mL of CH_2Cl_2 containing a trace amount of ethyl vinyl ether. The polymer was precipitated in 30 mL of methanol, except for the anhydride functionalized polymers which were precipitated in pentane. The polymers were recovered by filtration and dried overnight under vacuum at room temperature. The isolated yields were between 80 and 97% depending on starting monomer combinations.

Reactivity ratio values were obtained according to the following procedure. Five monomer mixtures with 1/9, 3/7, 5/5, 7/3, and 9/1 cyclooctene to *endo*-**3** ratios were prepared (1 mmol total) and dissolved in 2 mL of CH_2Cl_2. Catalyst **1** (4 μmol) was added to each of these solutions. The polymerizations were stopped at low conversion by precipitation in excess methanol. The polymers were separated from methanol by centrifugation and dried overnight under vacuum at room temperature. The polymer composition values were obtained by ^{1}H NMR. Reactivity ratio values were obtained by nonlinear regression.[26]

Polymerization Monitoring by ^{1}H NMR and Rate Comparison Experiments. The sample solutions were prepared with 0.2 mmol of total monomer in 0.7 mL of $CDCl_3$ in an NMR tube. For copolymerizations equimolar mixtures of monomers were used. Catalyst **1** or **2** (0.8 μmol) was dissolved in 0.1 mL of $CDCl_3$ and added to the monomer solution at room temperature. Rate comparison experiments were conducted by ^{1}H NMR. Data were collected every 2 min using naphthalene as an internal standard. It was not possible to probe the homopolymerization of *exo*-**5** with the above monomer and catalyst concentrations due to precipitation of polymer. Consequently, for these experiments a 1:10 catalyst-to-monomer ratio was used, and the rate constant data were adjusted accordingly.

The preparation of ruthenium−cyclooctene chain end species was performed by addition of cylooctene (60 μmol) to catalyst **1** (12 μmol) in 0.8 mL of $CDCl_3$ and then allowed to react for 20 min at room temperature. The reaction of *endo*-**3** with the resulting chain ends was performed by adding an excess of *endo*-**3** (0.2 mmol) to this solution. The preparation of ruthenium−*endo*-**3** chain end species was performed by addition of *endo*-**3** (36 μmol) to catalyst **1** (12 μmol) in 0.8 mL of $CDCl_3$ and then allowed to react for 20 min at room temperature. The reaction of cyclooctene with these chain ends was performed by adding excess cyclooctene (0.4 mmol) to this solution.

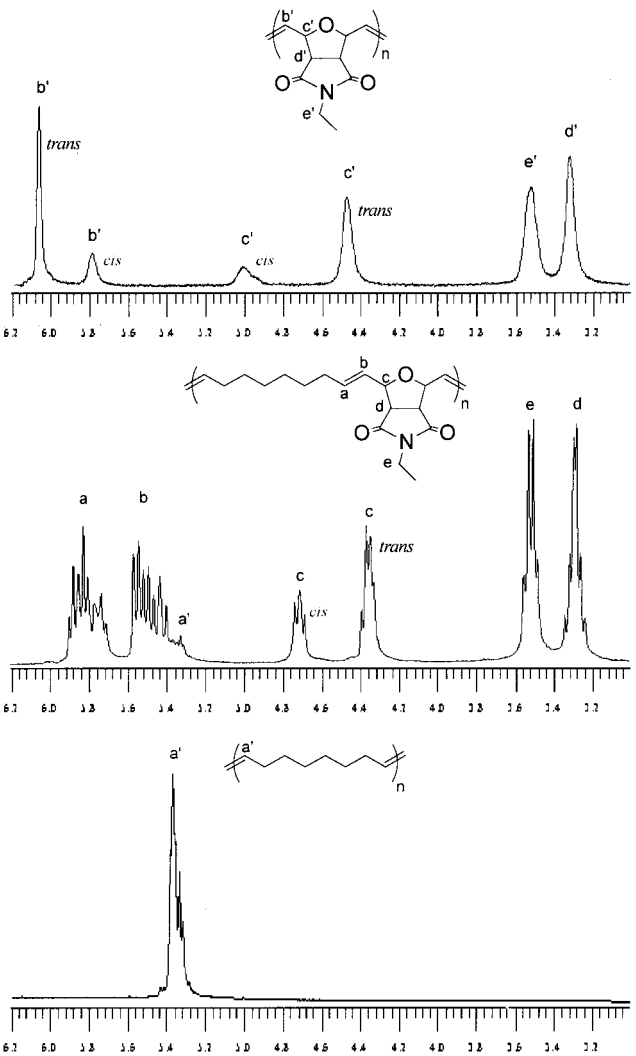


Figure 1. ^{1}H NMR spectra of the homopolymer of *endo*-**3** (top), alternating copolymer of *endo*-**3**, and cyclooctene (middle) and the homopolymer of cyclooctene (bottom) in $CDCl_3$.

Results and Discussion

Determination of Alternating Microstructure. The ^{1}H and ^{13}C NMR spectra of the polymer resulting from the copolymerization of an equimolar mixture of *endo*-**3** and cyclooctene using catalyst **1** indicated the absence of resonances for either homopolymer. This is most clearly seen by analysis of the olefinic region in the ^{1}H NMR spectrum that reveals resonances from a mixture of *cis* and *trans* isomers of an asymmetric carbon−carbon double bond of a regular alternating structure (Figure 1). Changing the reaction time, catalyst, or total monomer concentrations did not affect the resulting high levels (>98%) of alternation in the copolymer. Molecular weights were tunable from 10 000 to approximately 200 000 g/mol depending on the ratio of catalyst to monomers, from 1/200 to 1/1500, respectively, with polydispersity values near 2. Inspection of the ^{1}H−^{1}H COSY NMR spectrum clearly shows the internal connectivity of a repeat unit that results from an alternating polymerization of *endo*-**3** and cyclooctene (Figure 2).

Alternating Copolymerization of *endo*-3 and Cyclooctene. To quantify the tendency toward alterna-

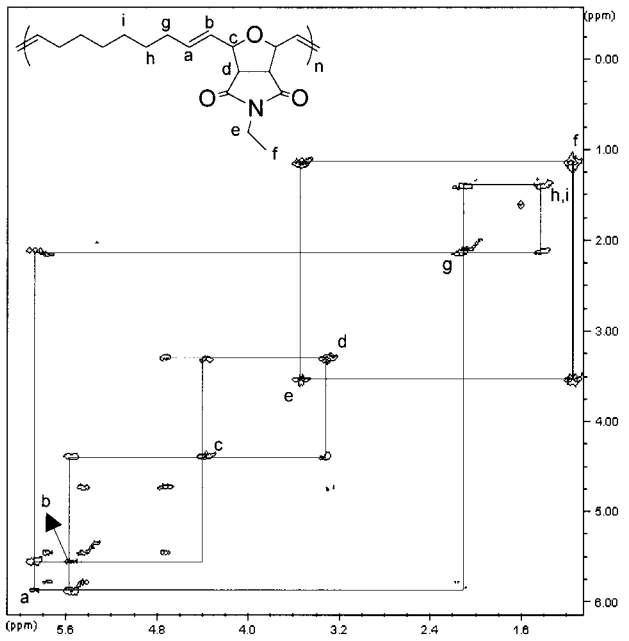


Figure 2. $^1H-^1H$ COSY NMR spectrum of alternating copolymer of *endo*-**3** and cyclooctene. The rectangles show the off-axis peaks establishing the connectivity. Dashed lines represent the cis isomer.

Table 1. Reactivity Ratios for the Copolymerization of Cyclooctene and *endo*-3 Using Catalyst 1 and the Corresponding Reactivity Ratio Product

$r_{\text{cyclooctene}}$	0.08 ± 0.02
r_{endo-3}	0.04 ± 0.02
reactivity ratio product	$0.001 < r_{\text{cyclooctene}} r_{endo-3} < 0.006$

tion, the reactivity ratios for the copolymerization of *endo*-**3** and cyclooctene were calculated using copolymer composition equation.[26] As expected, the reactivity ratios are very small, and the corresponding reactivity ratio product approaches zero (Table 1). In an ideal alternating copolymerization these values become zero, representing the absence of any homopolymerization.

The in situ monitoring of the copolymerization was performed in a series of NMR tube experiments. The rate of disappearance of each monomer was observed to be equal. Furthermore, it was also observed that only an alternating structure appeared from the very onset of polymerization. For comparison, the homopolymerizations of *endo*-**3** and cyclooctene were also monitored by ^1H NMR. The copolymerization of *endo*-**3** with cyclooctene was observed to be faster than homopolymerization of *endo*-**3** but slower than homopolymerization of cyclooctene (Figure 3). When (ln[monomer] − ln[monomer]$_0$) data were plotted vs time, linear functions were obtained for the copolymerization and either of the homopolymerizations. From these calculations the rate constants were found to be 2.3×10^{-3} s^{-1} for cyclooctene homopolymerization, 4×10^{-5} s^{-1} for *endo*-**3** homopolymerization, and 4×10^{-4} s^{-1} for their copolymerization. Although only an alternating structure is observed from an equimolar monomer mixture, the rate of copolymerization is slower than cyclooctene homopolymerization.

An alternating copolymerization includes two different propagation reactions. In this particular case, one step is the addition of *endo*-**3** to a ruthenium−cyclooctene chain end, and the other is the addition of cyclooctene to a ruthenium−*endo*-**3** chain end. To resolve these two propagation rates, both propagating

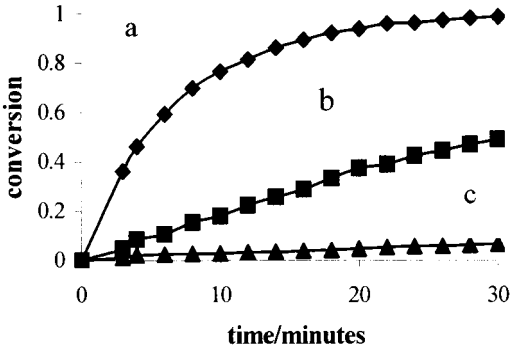
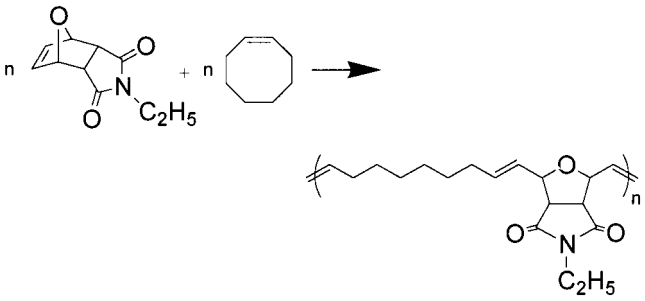


Figure 3. Comparison of the rates of cyclooctene homopolymerization (a), copolymerization of equimolar mixture of cyclooctene and *endo*-**3** (b), and homopoymerization of *endo*-**3** (c) using catalyst **1**.

Scheme 1. Alternating Copolymerization of *endo*-3 and Cyclooctene



species were independently generated and then allowed to react with the other monomer. Addition of excess cyclooctene to catalyst **1** in $CDCl_3$ consumed all cyclooctene and initial catalyst in less than 20 min, generating ruthenium carbene species at the chain ends of cyclooctene oligomers as observed by ^1H NMR. An excess of *endo*-**3** was added to this solution. The reaction rate was observed from the disappearance of the resonance for the ruthenium carbene proton of the ruthenium−cyclooctene chain end (19.3 ppm) and appearance of a resonance for the ruthenium−*endo*-**3** chain end (18.6 ppm). In a similar fashion, the ruthenium−*endo*-**3** chain ends were generated in an NMR tube; an excess of cyclooctene was added to this solution. The comparison of the rates for the different propagating steps is presented in Scheme 2. The observation that R_a is approximately 2 times faster then R_b would result in a preference for an alternating structure. On the other hand, the observation that R_c is more than 10 times slower than R_b explains why the overall rate for copolymerization of cyclooctene and *endo*-**3** is slower than cyclooctene homopolymerization.

Alternating Copolymerization of *exo*-5 and Cyclooctene. The conversion vs time data for the copolymerization of *exo*-**5** with cyclooctene and their homopolymerizations were obtained in a similar manner. The comparison of the plots revealed that the copolymerization of *exo*-**5** with cyclooctene is faster than homopolymerization of either monomer (Figure 4). This result is consistent with the resulting alternating distribution. The rate constant was 5×10^{-4} s^{-1} for *exo*-**5** homopolymerization, 2.3×10^{-3} s^{-1} for cyclooctene homopolymerization, and 2.2×10^{-2} s^{-1} for their copolymerization. The value for the copolymerization rate constant is presumably a lower limit as the first data point of the polymerization was at very high conversion. Unlike the homopolymer of *exo*-**5**, this alternating copolymer

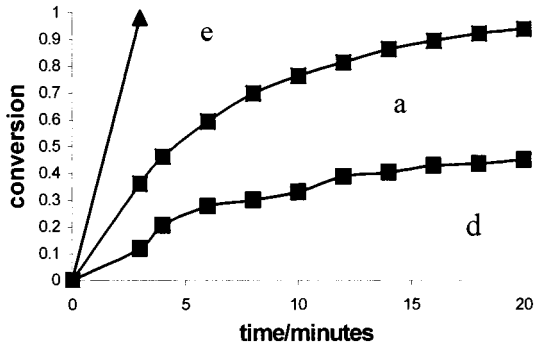
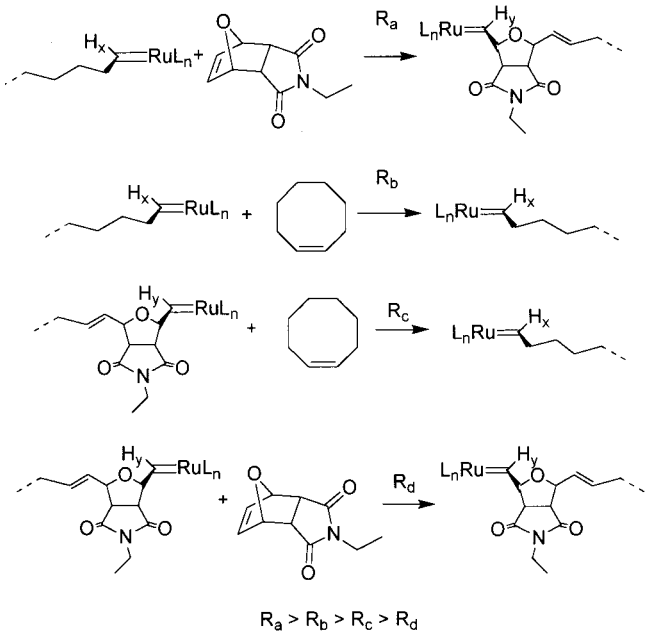


Figure 4. Comparison of the rates of homopolymerization of cyclooctene (a), *exo*-**5** (d), and their copolymerization from equimolar mixture (e) using catalyst **1**.

Scheme 2. Comparison of the Rates for *endo*-3 Addition to a Ruthenium−Cyclooctene Chain End (R_a), Cyclooctene Addition to a Ruthenium−Cyclooctene Chain End (R_b), Cyclooctene Addition to a Ruthenium−*endo*-3 Chain End (R_c), and *endo*-3 Addition to a Ruthenium−*endo*-3 Chain End (R_d); Both Chain Ends Were Derived from Catalyst 1



is soluble in common organic solvents. An importance of this alternating copolymer is the precisely separated anhydride functionalities which provide the opportunity for further functionalization.

Generality of Alternating Copolymerization. Oxanorbornenes are known to be more reactive than cyclooctene in ring-opening metathesis homopolymerization due to their higher ring strain. Rather than obtaining a block copolymer structure that would have resulted from preferential consumption of one monomer prior to consumption of the other, we have observed alternating structures for the copolymerization of cyclooctene with either *endo*-**3**, *exo*-**4**, or *exo*-**5** (Table 2). The change from the *endo* to *exo* isomer of **3** decreases the tendency toward alternation. This result can be understood if the approach of a propagating metal center to an oxanorbornene derivative to form a metallocyclobutane intermediate is accepted to be from the *endo* face of the carbon−carbon double bond. Thus, the more hindered *endo* isomer of **3** undergoes a slower homopropagation relative to the cross-propagation with cyclooctene. After cyclooctene has ring-opened, the chain

Table 2. Percentage of Alternating Diads[a] Resulting from the Copolymerizations of Different Monomer Combinations for Catalysts 1 and 2

Monomers[b]	1	2
endo **3**	98	85
exo **3**	80	70
exo **4**	91[d]	60[d]
exo **5**	96	75[d]
exo **5**	92[d]	[c]
exo **5**	85	70[d]
exo **5**	40	[c]

[a] Based on ^{1}H NMR spectra. [b] Equimolar mixtures of monomers. [c] Not determined. [d] %5 error margin due to poor resolution of the peaks.

end becomes less sterically hindered and preferentially propagates by the addition of the higher ring strain *endo*-**3**. In comparison, *exo*-**3** has a less hindered carbon−carbon double bond and consequently undergoes faster homopropagation in the presence of cyclooctene, leading to a less precisely alternating structure. The copolymers prepared from cyclooctene and *endo*-**3** or *exo*-***5*** are observed to be the closest to perfectly alternating copolymers. In their ^{1}H NMR spectra, a small peak arising from a homopolymer of only one of the comonomers (e.g., a′ in Figure 1, middle) indicates a possible stoichiometric mismatch in the reaction feed rather than a tolerance to random monomer addition in which case the presence of both types of homopolymers would be observed.

When cyclooctene is replaced by cyclooctadiene, cyclopentene, or norbornene, the alternating copolymer structure begins to have more irregularities, indicating the effect of different ring strains. In the copolymerization of norbornene and *exo*-**5** the tendency toward alternation is lost. Overall, these results indicate that in the ruthenium-catalyzed ring-opening metathesis copolymerization a balance of ring strain and steric hinderence of the comonomers are crucial factors for achieving alternation.

To probe the generality of alternating copolymerization with different catalysts, the copolymerizations were performed using **2**. A decrease in the tendency toward alternation was observed in all cases (Table 2). For example, the ^{1}H NMR of the copolymer obtained from

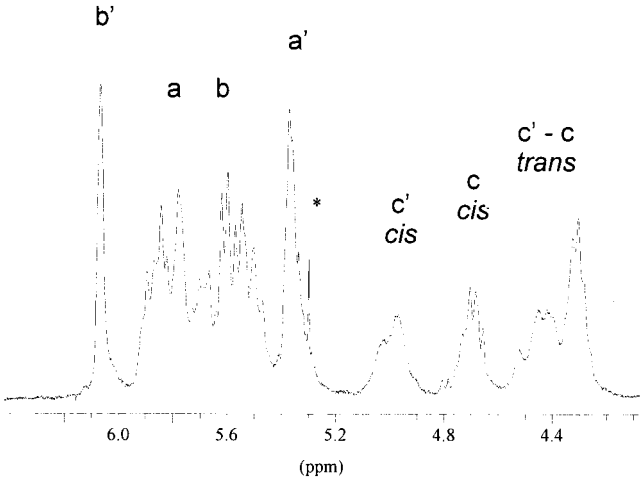


Figure 5. ^{1}H NMR spectrum of the copolymer of *endo*-**3** and cyclooctene made from an equimolar mixture using catalyst **2**. The peak assignments are the same as in Figures 1 and 2 (* = CH_2Cl_2).

the copolymerization of an equimolar mixture of *endo*-**3** and cyclooctene is shown in Figure 5. The resonances labeled as a′, b′, and c′ show the presence of symmetric unsaturations resulted from homopropagation; a, b, and c are asymmetric units which result from cross-propagation. This can be explained by the known higher activity and greater steric tolerance of this catalyst, which results in less selectivity during copolymerization.[27] The attempted copolymerization of *exo*-**4** and cyclooctene using Mo(CHCMe$_2$Ph)(NAr)(OCMe(CF$_3$)$_2$)[28] resulted in a copolymer structure with ^{1}H NMR resonances arising predominantly from homopolymer sequences. Although a significant amount of asymmetric unsaturations that result from cross-propagation was also observed, the resulting polymer is most likely a tapered-block copolymer.

Conclusion

In summary, the alternating copolymerization of 2,3-difunctionalized 7-oxanorbornene derivatives with nonpolar cyclic olefins via ring-opening metathesis has been demonstrated. This new synthetic method holds promise for preparing well-defined copolymers with tailorable polar functionalities separated by nonpolar spacers. The presence of anhydrides on the alternating polymer provides a precursor for attaching a range of functionalities. Furthermore, we envisage using ring-opening metathesis copolymerization as a general strategy for introducing varying levels of polar functionalities into polyalkenamers.

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