Articles

Ring-Opening Metathesis Polymerization of Functionalized Low-Strain Monomers with Ruthenium-Based Catalysts

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ABSTRACT: A detailed study of the ring-opening metathesis polymerization of low-strain monomers with ruthenium catalysts is reported. The effects of monomer concentration and catalyst dependence are described for unsubstituted cycloolefins. The ROMP of low-strain olefins with polar substituents is also examined with ruthenium olefin metathesis catalysts, and a predictive model for ROMP feasibility is proposed.

Introduction

Functionalized linear polymers represent an important class of materials. Several methods have been established to prepare functionalized polymers such as ionic and free radical polymerization of vinyl monomers, group transfer polymerization (GTP), and ring-opening metathesis polymerization (ROMP).[1−3] ROMP is an attractive method to synthesize functional polymers as it is robust, produces absolutely linear material, and is amenable to forming various copolymers of controlled architecture.[4,5] Substituted cyclobutenes and cyclooctenes have been used extensively to prepare linear polymers with a wide range of functionality.[6,7] With these monomers it is difficult (and, in the case of monosubstitution, impossible) to control the regioregularity of functionalities along the polymer backbone. Symmetrically substituted five- and seven-membered ring monomers provide access to a range of polymers that are not only regioregular but also provide access to ratios of functionality CHX/CH_2 inaccessible by other means. Few examples, however, are reported in the literature.[8−11] The low ring strains inherent to five-, six-, and seven-membered cycloalkenes[12] make them more challenging substrates for ROMP.

The driving force behind the ROMP of cyclic olefins is the release of strain energy that accompanies ring-opening.[2] For small rings this enthalpic gain is offset by a loss of entropy upon polymerization. As ROMP is typically a thermodynamically governed process, for low-strain systems there will be an equilibrium between monomeric and polymeric forms. The equilibrium monomer concentration can be related to the thermodynamic parameters by eq 1,[13] where any amount of monomer above the equilibrium concentration is converted to polymer (plus a small, finite concentration of cyclic oligomers).[14]

$$\ln[\mathrm{M}]_e = \frac{\Delta H_p}{RT} - \frac{\Delta S^\circ}{R} \tag{1}$$

It is clear from this equation that increasing the strain energy (ΔH_p) or initial monomer concentration will both result in increased polymer yield. Performing the reactions at low temperatures can minimize the unfavorable entropic term and drive the reaction to high molecular weight polymer, but this requires catalysts with high activity and efficient initiation at low temperatures. As a result, ROMP of low-strain monomers has traditionally been performed with highly active early transition metal catalysts.[2,9] Unfortunately, these catalysts are not tolerant of many polar functionalities. It is well-established that ruthenium-based olefin metathesis catalysts demonstrate significantly more tolerance toward polar functionality.[15,16] It was recently demonstrated that catalyst **2** was capable of performing the ROMP of cyclopentene (**4**) at 25 °C.[17] We now report that ruthenium catalysts **1**, **2**, and **3** are all capable of polymerizing low-strain cycloolefins, so that the ROMP of five- and seven-membered cycloalkenes with polar substituents can now be realized.

Experimental Section

Materials. Toluene and CH_2Cl_2 were dried by passage through solvent purification columns.[18] $(PCy_3)_2(Cl)_2Ru{=}CHPh$ (**1**),[19] $(H_2IMes)(PCy_3)(Cl)_2Ru{=}CHPh$ (**2**),[20] $(H_2IMes)(3\text{-Br-py})_2(Cl)_2Ru{=}CHPh$ (**3**),[21] 4-acetoxycyclopentene (**6**),[22,23] 4-*tert*-butyldimethylsilyloxycyclopentene (**7**),[22] 4-cyclohepten-1-one (**9**),[24] and 3-acetoxycyclopentene (**10**)[25] were synthesized according to literature procedures. Cyclopentene (98%) (**4**) (TCI America), 3-cyclopenten-1-one (98%) (**8**) (Astatech), cycloheptene (97%) (**5**) (Pfaltz & Bauer), and *cis*-3,5-diacetoxycyclopentene (98%) (**11**) (Fluka) were used as received.

Methods and Procedures. Solution NMR spectra were recorded on either a Varian Mercury 300 (299.87 MHz for ^1H and 75.41 MHz ^{13}C) or a Varian Inova 500 (500.62 MHz for ^1H and 125.89 MHz ^{13}C). All solution NMR spectra were recorded in $CDCl_3$ and referenced to residual protio species. Solid-state CP-MAS ^{13}C NMR spectra were recorded on a

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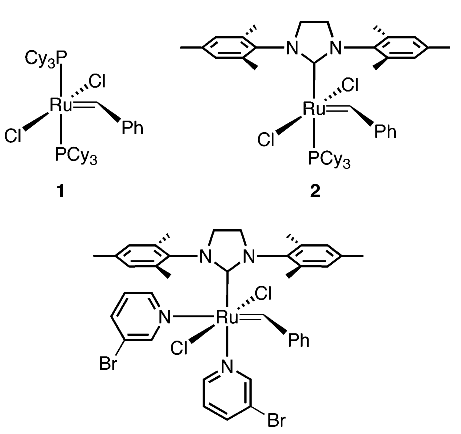


1 **2** **3**

Figure 1. Ruthenium olefin metathesis catalysts.

Bruker 500 MHz spectrometer. Samples were subjected to magic angle spinning at 6.0 kHz. FT-IR spectra were recorded on a Perkin-Elmer Paragon 1000 spectrometer. Gel permeation chromatography (GPC) was carried out in THF on two PLgel 5 μm mixed-C columns (Polymer Labs) connected in series with a DAWN EOS multiangle laser light scattering (MALLS) detector and an Optilab DSP differential refractometer (both from Wyatt Technology). No calibration standards were used, and d*n*/d*c* values were obtained for each injection assuming 100% mass elution from the columns.

Computational Methodology. All calculations were performed using the hybrid DFT functional B3LYP as implemented by the Jaguar 4.0 program package.[26] A 6-31G** basis set was used for all compounds.

Polymerization Procedure: Neat Monomer. In a typical experiment, a small vial was charged with catalyst **1** (11.1 mg, 0.0135 mmol) and a stirbar under a flow of argon. Next, monomer **4** (0.30 mL, 0.231 g, 3.39 mmol, 251 equiv) was added via syringe at room temperature, and the reaction was allowed to stir. The reaction mixture gelled within 1 min. After 24 h, the polymerization was quenched with 0.1 mL of ethyl vinyl ether and then dissolved in 1 mL of dichloromethane. The polymer solution was then precipitated into 75 mL of MeOH at 0 °C. The polymer precipitate was washed several times with MeOH and dried under vacuum overnight; yield 0.185 g (80%).

Polymerization Procedure: Solution. In a typical experiment, a small vial was charged with monomer **5** (0.30 mL, 0.249 g, 2.59 mmol, 259 equiv) and a stirbar under a flow of argon. Next, 0.20 mL (0.01 mmol) of a catalyst **3** stock solution (0.05 M) was added via syringe at room temperature, and the reaction was allowed to stir. The reaction mixture gelled within 1 min. After 30 min, the polymerization was quenched with 0.1 mL of ethyl vinyl ether and then dissolved in 1 mL of dichloromethane. The polymer solution was then precipitated into 75 mL of MeOH at 0 °C. The polymer precipitate was washed several times with MeOH and dried under vacuum overnight; yield 0.180 g (72%).

Polymer Characterization. In all cases, H_a refers to the olefinic protons, H_b refers to the allylic protons, etc. C1 refers to the olefinic carbon, C2 to the adjacent carbon, etc.

Poly(4), R = H. ^{1}H NMR (500.62 MHz, $CDCl_3$, δ): 5.42−5.33 (m, 2H, H_a), 2.08−1.90 (m, 4H, H_b), 1.39 (quint, J = 7.5 Hz, 2H, H_c). $^{13}C\{^1H\}$ NMR (125.89 MHz, $CDCl_3$, δ): 130.45 (C1 *t*), 129.94 (C1 *c*), 32.51 (C2 *tc*), 32.37 (C2 *tt*), 30.01 (C3 *ct*/*tc*), 29.86 (C3 *tt*), 27.06 (C2 *ct*).

Poly(5), R′ = H. ^{1}H NMR (299.87 MHz, $CDCl_3$, δ): 5.41−5.31 (m, 2H, H_a), 2.08−1.90 (m, 4H, H_b), 1.40−1.22 (m, 6H, H_c/H_d). $^{13}C\{^1H\}$ NMR (75.41 MHz, $CDCl_3$, δ): 130.53 (C1 *t*), 130.07 (C1 *c*), 32.99 (C2 *t*), 30.08 (C3 *cc*), 30.04 (C3 *ct*), 29.97 (C3 *tc*), 29.93 (C3 *tt*), 29.38 (C4 *cc*), 29.26 (C4 *ct*/*tc*), 29.13 (C4 *tt*), 27.60 (C2 *c*).

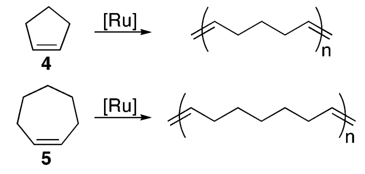
Poly(6), R = OAc. ^{1}H NMR (299.87 MHz, $CDCl_3$, δ): 5.5−5.3 (br m, 2H, H_a), 4.82 (br m, 1H, H_c), 2.3−2.15 (br m, 4H, H_b), 1.99 (s, 3H, OAc). $^{13}C\{^1H\}$ NMR (75.41 MHz, $CDCl_3$, δ): 170.82 (OAc−C=O), 128.68 (C1 *t*), 127.41 (C1 *c*), 73.20 (C3), 73.04 (C3), 37.09 (C2), 31.91 (C2), 21.44 (OAc−CH_3).

Poly(7), R = OTBS. ^{1}H NMR (299.82 MHz, $CDCl_3$, δ): 5.56−5.31 (br m, 2H, H_a), 3.74−3.55 (br m, 1H, H_c), 2.30−1.98 (br m, 4H, H_b), 0.88 (s, 9H, Si-^{t}Bu), 0.03 (s, 6H, Si−Me_2). $^{13}C\{^1H\}$ NMR (75.40 MHz, $CDCl_3$, δ): 129.36 (C1 *t*), 127.87 (C1 *c*), 72.91 (C3), 40.81 (C2), 35.61 (C2), 26.24 (Si−C($\mathbf{C}H_3)_3$), 18.49 (Si−$\mathbf{C}(CH_3)_3$), −4.12 (Si−$(\mathbf{C}H_3)_2$).

Poly(8), R = (=O). ^{13}C NMR (125.78 MHz, CP-MAS 6 kHz, δ): 209.91 (C3), 127.15 (C1), 46.24 (C2 *t*), 41.52 (C2 *c*). FT-IR (KBr pellet, ν_{CO}): 1708 cm^{-1}.

Poly(9), R = (=O). ^{1}H NMR (299.82 MHz, $CDCl_3$, δ): 5.42−5.28 (m, 2H, H_a), 2.48−2.38 (m, 4H, H_c), 2.32−2.18 (m, 4H, H_b). $^{13}C\{^1H\}$ NMR (75.40 MHz, $CDCl_3$, δ): 209.92 (C4), 129.80 (C1 *t*), 129.37 (C1 *c*), 42.80 (C3 *c*), 42.76 (C3 *t*), 26.90 (C2 *t*), 21.81 (C2 *c*).

Scheme 1. ROMP of Cyclopentene and Cycloheptene



4 **5**

Table 1. Results for the ROMP of 4 and 5 with Ruthenium Catalysts[a]

entry	monomer ([M])	catalyst	[M]/[cat.]	% yield	M_n ($\times 10^{-3}$) GPC[c]	PDI
1	**4** (11.3)[b]	**1**	250	80	15.2	1.5
2	**4** (11.3)[b]	**1**	500	92	27.1	1.6
3	**4** (11.3)[b]	**1**	1000	84	75.4	1.6
4	**4** (11.3)[b]	**2**	500	87	19.9	1.3
5	**4** (11.3)[b]	**3**	500	38[d]	28.5	1.6
6	**4** (5)	**1**	500	64	22.1	1.5
7	**4** (5)	**2**	500	68	15.7	1.5
8	**4** (5)	**3**	500	67	13.3	1.3
9	**4** (3)	**1**	500	48	13.6	1.5
10	**4** (3)	**2**	500	51	38.4	1.5
11	**4** (3)	**3**	500	41	12.2	1.5
12	**5** (8.6)[b]	**1**	250	88	34.2	1.5
13	**5** (8.6)[b]	**1**	500	89	60.3	1.6
14	**5** (8.6)[b]	**1**	1000	74	117	1.4
15	**5** (8.6)[b]	**2**	250	88	43.3	1.7
16	**5** (8.6)[b]	**3**	250	46[d]	48.7	1.5
17	**5** (5)	**1**	250	89	35.3	1.5
18	**5** (5)	**2**	250	88	37.8	1.8
19	**5** (5)	**3**	250	88	40.5	1.6
20	**5** (2)	**1**	250	82	28.0	1.8
21	**5** (2)	**2**	250	76	40.3	1.6
22	**5** (2)	**3**	250	84	35.6	1.5

[a] Reactions run for 24 h at 25 °C in CH_2Cl_2 solvent. [b] ROMP of neat monomer. [c] Samples run in THF; molecular weight values obtained using MALLS. [d] Catalyst **3** poorly soluble in neat olefin.

Results and Discussion

ROMP of Unsubstituted Monomers. The ROMP of the low-strain monomers cyclopentene (**4**) and cycloheptene (**5**) was investigated with ruthenium catalysts **1**−**3** (Scheme 1).

Polymerization behavior of **4** and **5** was studied with respect to catalyst loading and monomer concentration at room temperature. The experimental strain energy for **4** and **5** are 6.8 and 6.7 kcal/mol, respectively,[12] suggesting they should behave similarly with the olefin metathesis catalysts. Indeed, this appeared to be the case with a few notable exceptions (Table 1).

In agreement with previous reports that utilized early transition metal catalysts, relatively high yields of polymer could be obtained for neat polymerization with the ruthenium catalysts at 25 °C.[9] Entries 1−4 in Table

1 illustrate that yields of 80% and greater are obtained by the neat ROMP of **4** with ruthenium catalysts **1** and **2**; however, a low yield is obtained for neat ROMP of **4** and **5** with catalyst **3**. This is due to the sparing solubility of the bromopyridine catalyst in neat hydrocarbon monomers. The polymer yields are similar for all catalysts in solution studies where catalyst solubility is not a factor. This can be seen in entries 6−8 in Table 1 which all show comparable yields of polymer, with catalyst **3** giving the best molecular weight control. By increasing the monomer-to-catalyst ratio, ([M]/[cat.]), the yields remain constant with a commensurate increase in the molecular weights, M_n, for ROMP of monomers **4** and **5**. The yields for monomer **4** tend to decrease more significantly when run at lower concentrations than polymerizations with **5**. This larger concentration dependence is consistent with **4** having a more unfavorable entropy of polymerization than **5**.

To ensure that the thermodynamic ring/chain equilibrium had been established within the 24 h reaction time, the polymerization described by entry 18 in Table 1 was checked at several time intervals. After only 30 min, **poly(5)** was formed in 89% yield, and over 48 h this yield did not improve. In addition, the polymer molecular weight distributions were similar, and the cis/trans ratio of the resultant polymers remained constant over time (cis:trans ~1:5.5 as measured by quantitative ^{13}C NMR spectroscopy). On the basis of these results, we conclude that the ring/chain equilibrium is certainly reached within 24 h and in many cases within 30 min.

ROMP of Substituted Monomers. After successfully demonstrating that catalysts **1**−**3** could ROMP monomers **4** and **5** to high molecular weight polymer, derivatives of these low-strain monomers bearing polar substituents were explored. These functionalities are incompatible with early transition metal catalysts but present no difficulty for the ruthenium systems.[5,16] This would allow for the direct preparation of polar functionalized linear polymers without the need for subsequent polymer modification.[4,15] Furthermore, as we have previously demonstrated, ROMP of a symmetric monomer will ensure an absolutely regioregular polymer,[15,27] thus providing new materials for detailed structure−property studies.

The addition of substituents to monomers **4** and **5** will certainly make the ROMP of these low-strain monomers more challenging.[2] This can be explained by the Thorpe−Ingold effect whereby substituents on a ring serve to stabilize the ring-closed form relative to its linear counterpart.[28] As ROMP is a process governed by thermodynamic equilibrium, this effect results in a higher critical concentration for the monomer reflected in a lower yield of the linear polymer.

The polar monomers employed in this study, and shown in Scheme 2, possess ester, silyl ether, and ketone functionalities. The ROMP of monomers **6**−**9** provide a synthetic route for oxygen containing materials such as ethylene vinyl alcohol (EVOH) and ethylene carbon monoxide (E/CO) copolymers. These materials made using other methods have demonstrated useful properties and many have been commercialized.[15,29,30]

ROMP of the substituted monomers was successfully carried out neat at 25 °C with catalysts **1**−**3**, as illustrated in Table 2.

Scheme 2. ROMP of Substituted Low-Strain Monomers

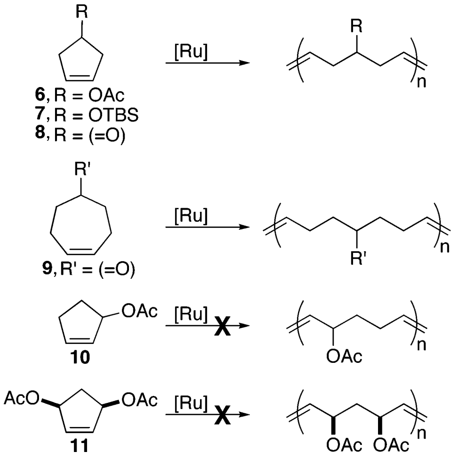


Table 2. Results for the ROMP of 6−11 with Ruthenium Catalysts at 25 °C

entry	monomer ([M])	catalyst	[M]/[cat.]	% yield	M_n ($\times 10^{-3}$) GPC[c]	PDI
1[a]	**6** (8.0)	**1**	500	75	36.9	1.4
2[a]	**6** (8.0)	**2**	500	66	28.9	1.3
3[a]	**6** (8.0)	**3**	500	65	28.0	1.5
5[a]	**7** (4.3)	**1**	150	72	18.7	1.7
6[a]	**7** (4.3)	**2**	150	66	17.0	1.3
7[a]	**7** (4.3)	**3**	150	71	16.6	1.3
8[a]	**8** (12.1)	**1**	250	0		
9[a]	**8** (12.1)	**2**	250	0		
10[a]	**8** (12.1)	**3**	250	24	insol	insol
11[a]	**9** (9.8)	**3**	214	88	66.8[d]	1.2
12[b]	**10** (8.0)	**1**	500	0		
13[b]	**10** (8.0)	**2**	500	0		
14[b]	**10** (8.0)	**3**	500	0		
15[b]	**11** (6.1)	**3**	250	0		

[a] Polymerization time of 24 h. [b] Polymerization time of 30 min. [c] Samples run in THF; molecular weight values obtained using MALLS. [d] Sample run in CH_2Cl_2; MW relative to PS standards.

Entries 1−7 in Table 2 illustrate that the ROMP of symmetric monomers **6** and **7** could be carried out in high yield and with controlled molecular weights with all three ruthenium catalysts. Moreover, no significant difference was observed in the ROMP of **6** and **7** as expected for structurally similar monomers. Monomer **8** does not undergo polymerization with catalysts **1** or **2**, indicating a low ring strain. Catalyst **3**, however, allows for the formation of **poly(8)**, which may be trapped through a kinetic process.[1,31,32] Catalyst **3** is known to initiate much faster than either **1** or **2** and may allow for rapid polymerization of **8** to high molecular weight insoluble polymer. No conditions were found under which monomers **10** and **11** would successfully polymerize. Chelation of the acetate group to ruthenium is a potential complication in the polymerization of **10** and **11**. However, the structurally similar allyl acetate has been shown to be a good substrate in other metathesis reactions with ruthenium-based catalysts; so chelation also is not likely to completely inhibit the polymerization.[33]

Model for Low-Strain ROMP. By varying the placement and nature of the substituents, we observed a marked effect on a monomer's potential to undergo ROMP. It is known that the ease of ROMP is reflected by the strain energy of each monomer.[2,15] In the case of unsubstituted cyclic olefins the strain energies have been experimentally determined.[12] Changing the substitution pattern on a ring is known to affect the strain energy.[28] However, there are an unlimited number of possible substitution patterns on a ring, and it is not

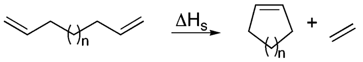


Figure 2. Isodesmic reaction used to calculate the strain energy released by ROMP.

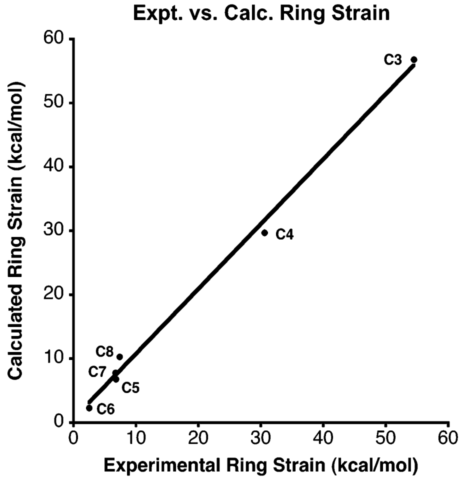


Figure 3. Graph depicting the correlation between calculated (DFT B3LYP/6-31G**) and experimental strain energies.[12]

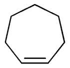
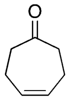
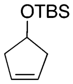
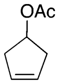
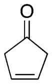
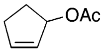
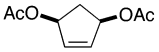
feasible to experimentally determine the strain energy for each molecule. A simple computational method for predicting strain energy of ring systems would provide a predictor for the yield of polymer and guide the design of new monomer systems.

We chose to model the strain energy of a cyclic olefin with the enthalpic terms of a ring-closing metathesis reaction (Figure 2). This model reaction is isodesmic, having the same number and type of bonds in both reactants and products,[34] so that the change in energy is solely due to the strain inherent in the cyclic form. The ring strain for the cyclic olefin is the difference in energy between the products and the reactant. Previous methods for computationally determining strain energy of unsaturated rings have also employed isodesmic reactions but kept the internal double bond.[35] By modeling a ring-closing metathesis reaction, the functionality is maintained internally while placing the double bonds in the terminal positions.

To validate this model, unsubstituted, cyclic olefins ranging from cyclopropene to cyclooctene were calculated and compared with their experimentally determined strain energies. The calculations were carried out using DFT with a B3LYP functional and a 6-31G** basis set. As can be seen by the graph in Figure 3, the correlation of calculated values with experiment is quite good. Slightly larger deviations are observed for cycloheptene and cyclooctene as a result of a natural distribution of several conformers at 298 K for these larger rings that are not reflected in our calculations. Calculations were also carried out at a semiempirical level of theory with AM1, PM3, and PM5 parametrization schemes; however, these all resulted in poor agreement with experimental results.

Satisfied with this method, we proceeded to calculate the strain energies for the substituted monomers described above. The calculated values are shown in Table 3. Again, the experimental results we observe in this study appear to correlate with the model, with lower strain systems giving decreased yields of polymer. Under our polymerization conditions, it appears that the minimal calculated strain energy necessary for successful ROMP lies between 3.4 and 4.4 kcal/mol. This model should allow for the prediction of a new monomer's ability to polymerize via ROMP.

Table 3. Calculated Strain Energies and ROMP Ability for Several Low-Strain Monomers

Monomer	E_s(calc)[a]	ROMP yield(%)[b]
 **5**	7.84	85[c]
 **9**	7.44	88[d]
 **4**	6.84	87[c]
 OTBS **7**	4.99	71[d]
 OAc **6**	4.47	65[d]
 **8**	4.45	24[d]
 OAc **10**	3.36	—
 AcO OAc **11**	2.29	—

[a] Strain energy in kcal/mol, calculated at DFT B3LYP/6-31G**. [b] Neat monomer, rt. [c] Catalyst **2**. [d] Catalyst **3**.

Conclusions

The ROMP of cyclopentene and cycloheptene has been investigated with several ruthenium olefin metathesis catalysts. All of the catalysts employed afforded reasonable to high yields of ROMP polymer and demonstrated molecular weight control. As previously demonstrated, the polymer behavior is extremely dependent on the monomer concentration. This is consistent with the thermodynamic governance of the ROMP process. The use of functional group tolerant ruthenium catalysts has also allowed for the incorporation of polar substituents pendent from the linear polymer backbone. When symmetrically substituted five- and seven-membered ring monomers are polymerized, the resulting materials possess an absolutely linear structure with a perfectly regioregular distribution of functionality. To better understand the relationship between substitution patterns and ring strain of a cyclic olefin monomer, a simple model for predicting ring strains was employed. A high degree of correlation was found between experimental and calculated data for both substituted and unsubstituted cycloolefins. This model could be generally applied as a predictive tool for rational monomer design.

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References and Notes

(1) Grubbs, R. H., Ed. *Handbook of Metathesis*; Wiley-VCH: Weinheim, 2003.
(2) Ivin, K. J.; Mol, J. C. *Olefin Metathesis and Metathesis Polymerization*; Academic Press: London, 1997.
(3) Odian, G. *Principles of Polymerization*, 3rd ed.; Wiley & Sons: New York, 1991.
(4) Lynn, D. M.; Kanaoka, S.; Grubbs, R. H. *J. Am. Chem. Soc.* **1996**, *118*, 784−790.
(5) Choi, T.-L.; Grubbs, R. H. *Angew. Chem., Int. Ed.* **2003**, *42*, 1743−1746.
(6) Maughon, B. R.; Grubbs, R. H. *Macromolecules* **1997**, *30*, 3459−3469.
(7) Hillmyer, M. A.; Laredo, W. R.; Grubbs, R. H. *Macromolecules* **1995**, *28*, 6311−6316.
(8) Dounis, P.; Feast, W. J.; Kenwright, A. M. *Polymer* **1995**, *36*, 2787−2796.
(9) Schrock, R. R.; Yap, K. B.; Yang, D. C.; Sitzmann, H.; Sita, L. R.; Bazan, G. C. *Macromolecules* **1989**, *22*, 3191−3200.
(10) Trzaska, S. T.; Lee, L.-B. W.; Register, R. A. *Macromolecules* **2000**, *33*, 9215−9221.
(11) Patton, P. A.; Lillya, C. P.; McCarthy, T. J. *Macromolecules* **1986**, *19*, 1266−1268.
(12) Schleyer, P. v. R.; Williams, J. E.; Blanchard, K. R. *J. Am. Chem. Soc.* **1970**, *92*, 2377−2386.
(13) Ofstead, E. A.; Calderon, N. *Makromol. Chem.* **1972**, *154*, 21−34.
(14) Chen, Z.-R.; Claverie, J. P.; Grubbs, R. H.; Kornfield, J. A. *Macromolecules* **1995**, *28*, 2147−2154.
(15) Scherman, O. A.; Kim, H. M.; Grubbs, R. H. *Macromolecules* **2002**, *35*, 5366−5371.
(16) Hillmyer, M. A.; Lepetit, C.; McGrath, D. V.; Novak, B. M.; Grubbs, R. H. *Macromolecules* **1992**, *25*, 3345−3350.
(17) Bielawski, C. W.; Grubbs, R. H. *Angew. Chem., Int. Ed.* **2000**, *39*, 2903−2906.
(18) Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518−1520.
(19) Schwab, P.; Grubbs, R. H.; Ziller, J. W. *J. Am. Chem. Soc.* **1996**, *118*, 100−110.
(20) Sanford, M. S.; Ulman, M.; Grubbs, R. H. *J. Am. Chem. Soc.* **2001**, *123*, 749−750.
(21) Sanford, M. S.; Love, J. A.; Grubbs, R. H. *Organometallics* **2001**, *20*, 5314−5318.
(22) Buckley, S. L. J.; Drew, M. G. B.; Harwood, L. M.; Macias-Sanchez, A. J. *Tetrahedron Lett.* **2002**, *43*, 3593−3596.
(23) Goering, H. L.; Seitz, E. P.; Tseng, C. C. *J. Org. Chem.* **1981**, *46*, 5304−5308.
(24) Marshall, J. A.; Royce, R. D. *J. Org. Chem.* **1982**, *47*, 693−698.
(25) Goering, H. L.; Kantner, S. S.; Seitz, E. P. *J. Org. Chem.* **1985**, *50*, 5495−5499.
(26) Jaguar 4.0, Schrodinger, Inc., Portland, OR, 2000.
(27) Wagener, K. B.; Patton, J. T.; Forbes, M. D. E.; Myers, T. L.; Maynard, H. D. *Polym. Int.* **1993**, *32*, 411−415.
(28) Allinger, N. L.; Zalkow, V. *J. Org. Chem.* **1960**, *25*, 701−704.
(29) Drent, E.; van Broekhoven, J. A. M.; Budzelaar, P. H. M. *Recl. Trav. Chim. Pays-Bas* **1996**, *115*, 263−270.
(30) Sen, A. *CHEMTECH* **1986**, *16*, 48−51.
(31) Scherman, O. A.; Rutenberg, I. M.; Grubbs, R. H. *J. Am. Chem. Soc.* **2003**, *125*, 8515−8522.
(32) Scherman, O. A.; Grubbs, R. H. *Synth. Met.* **2001**, *124*, 431−434.
(33) Blackwell, H. E.; O'Leary, D. J.; Chatterjee, A. K.; Washenfelder, R. A.; Bussmann, D. A.; Grubbs, R. H. *J. Am. Chem. Soc.* **2000**, *122*, 58−71.
(34) Lewis, L. L.; Turner, L. L.; Salter, E. A.; Magers, D. H. *J. Mol. Struct.: THEOCHEM* **2002**, *592*, 161−171.
(35) Khoury, P. R.; Goddard, J. D.; Tam, W. *Tetrahedron* **2004**, *60*, 8103−8112.

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