ROMP Reactivity of *endo*- and *exo*-Dicyclopentadiene

Joseph D. Rule and Jeffrey S. Moore*

The Beckman Institute for Advanced Science and Technology and Department of Chemistry, University of Illinois, Urbana, Illinois 61801

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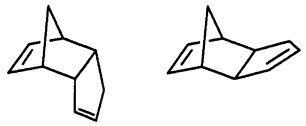
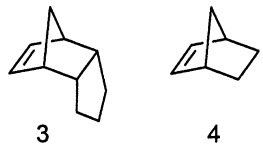
ABSTRACT: The activation parameters for the ring-opening metathesis polymerization (ROMP) of *endo*- (**1**) and *exo*-dicyclopentadiene (**2**), *endo*-1,2-dihydrodicylopentadiene (**3**), and norbornene (**4**) in the presence of Grubbs' catalyst were determined using in situ NMR. The *exo* isomer of DCP was found to be more than an order of magnitude more reactive than the *endo* isomer. *endo*-DCP was found to have reactivity similar to its partially saturated counterpart **3**, suggesting that the cause of the rate difference between the two isomers of DCP is primarily steric in nature. This interaction is shown to be predominantly entropic and is suspected to originate from an interaction of the penultimate repeat unit and the incoming monomer. Additionally, the alkylidene generated during the polymerization of *endo*-DCP was found to form an intramolecular complex, but this complex only affects the rate slightly.

Introduction

In the past few decades, dicyclopentadiene (DCP) has received significant attention as a monomer for ring opening metathesis polymerization (ROMP). Its low cost, high reactivity, and tendency to form tough, highly cross-linked materials have made it a good choice for reaction injection molding (RIM).[1] In the RIM process, the kinetics of the polymerization are critical and, in general, must be very fast. ROMP of DCP was also used in our recently developed self-healing composite material.[2] In this application, as in RIM, cure kinetics play a key role and fast cure times are desirable.

DCP can exist as an *endo* (**1**) or an *exo* (**2**) isomer.





Because commercially available DCP is >95% *endo*, most of the applications of DCP involve the *endo* isomer. Previous studies on the ROMP of other norbornene derivatives have shown that *exo* isomers often react faster than the corresponding *endo* isomers.[3−8] No direct examinations of the difference in ROMP kinetics of *endo*- and *exo*-DCP have previously been reported with a Ru-based catalyst, but a few studies suggest that *exo*-DCP reacts differently than *endo*-DCP.[8−11] Consequently, it seemed likely that *exo*-DCP would have higher ROMP rates than *endo*-DCP using Grubbs' catalyst, and a deeper understanding of this behavior could prove valuable in both the RIM process and the generation of new self-healing materials.

We report the use of in situ NMR to quantify the ROMP kinetics for *exo*- and *endo*-DCP using Grubbs' catalyst ($RuCl_2(CHPh)(PCy_3)_2$). Previous reports have

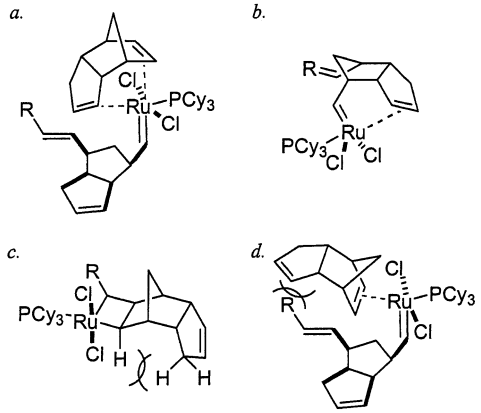


Figure 1. (a) Chelating interaction corresponding to mechanism I. (b) Intramolecular complex corresponding to mechanism II. (c) Steric interaction corresponding to mechanism III. (d) Steric interaction corresponding to mechanism IV.

provided speculative reasons for the differences in reactivity of *exo* and *endo* isomers of norbornene derivatives.[6,7,11] In this work, we examine this issue more deeply by systematically studying reactivity differences between *exo*- and *endo*-DCP and analyze this in the context of mechanistic models. This study involves adapting previously proposed mechanisms to the ROMP of DCP and proposing modifications that could potentially account for the different ROMP rates of the two isomers of DCP. In proposing these mechanisms, it is assumed that the strained norbornene-derived double bond in the bicyclic ring is much more reactive than the cyclopentene-derived double bond in the DCP monomers.[11] It is also assumed that the catalyst attacks the less hindered *exo* face of the monomers.

Mechanism I. The bent shape of *endo*-DCP could facilitate a chelating interaction to form an intermolecular complex between free monomer and the alkylidene. This could inhibit the catalyst and slow the rate (Figure 1a).[7,11]

Mechanism II. A related intramolecular effect could be imagined involving the propagating alkylidene. The geometry of the alkylidene formed from *endo*-DCP could permit coordination between the ruthenium atom and the double bond in the neighboring substituted cyclo-

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pentene ring (Figure 1b).[6] This intramolecular complex could prevent free monomer from coordinating with the catalyst and thus slow the polymerization.

Mechanism III. It has been suggested that the formation of the metallacyclobutane ring may be the rate-determining step in metathesis with first generation Grubbs' catalysts.[12,13] In this case, as the metallacyclobutane is formed, an unfavorable steric interaction may exist between the protons on the newly formed sp^3 center and the cyclopentene ring (Figure 1c).[7]

Mechanism IV. To give the catalyst's bulky tricyclohexylphosphine (PCy_3) group as much space as possible, the propagating species may favor a conformation that places the available coordination site of the ruthenium center over the terminal unit's cyclopentane ring. In this case, there is an unfavorable interaction between the polymer chain's penultimate unit and the *endo* ring of an approaching monomer (Figure 1d).

Mechanism V. The alkylidene formed during the polymerization of *endo*-DCP has all the substituents of the cyclopentane ring in a cis relationship. This creates a rather congested area that could hinder the approach of free monomer.[7]

By gaining a more complete understanding of factors that affect ROMP kinetics in the DCP system, the foundation is laid for being able to rationally design new monomers to have desired kinetic properties.

Experimental Section

^{1}H NMR experiments were performed on a Varian UNITY INOVA 500NB instrument, and ^{31}P experiments were performed on a Varian UNITY 500 instrument. Grubbs' catalyst (Strem), mesitylene (Aldrich), PCy_3 (Aldrich), and toluene-d_8 (Aldrich) were used as received from the suppliers. *exo*-DCP was synthesized according to the procedure described by Nelson and Kuo.[14] GC showed it to contain 1% *endo*-DCP. **3** was prepared through a Diels−Alder reaction of cyclopentene and cyclopentadiene via the literature procedure.[15] *endo*-DCP (Acros), norbornene (Aldrich), and the other monomers were distilled and degassed (consecutive freeze−pump−thaw cycles) before use.

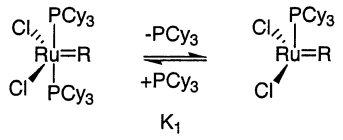
For each series of kinetics experiments, a stock solution of Grubbs' catalyst, PCy_3, and mesitylene (as an internal standard) in toluene-d_8 was prepared in a glovebox. Then, 0.70 g of this stock solution was transferred to each NMR tube. The tubes were capped with septa and wrapped with Parafilm. All samples were used within a few hours of preparation.

For individual kinetics experiments, the instrument and the tube (with only the stock solution) were brought to the desired temperature. Monomer was then added to the tube via syringe (either 50 or 20 μL). The sample was shaken and immediately reinserted into the instrument. Spectra were taken at regular intervals, and the sample was left in the instrument at constant temperature until completion of the experiment.

The monomer concentration was monitored by comparing the signal from the protons attached to the strained double bond in the monomers (5.90−6.02 ppm) to the signal from the ring protons of the mesitylene internal standard (6.67 ppm).

Results and Discussion

The kinetics of ROMP of *endo*- and *exo*-DCP, the *endo*-1,2-dihydro derivative **3**, and norbornene were quantified using in situ ^{1}H NMR. Preliminary experiments gave complex saturation kinetics that were difficult to analyze. Grubbs and co-workers have shown[12,13] that adding PCy_3 to similar metathesis reactions forces a preequilibrium between the inactive five-coordinate form of the catalyst and the active four-coordinate form (eq 1).



(1)

The establishment of this preequilibrium produces much simpler kinetic behavior that can usually be approximated by eq 2.[12,13]

$$-\frac{\mathrm{d[monomer]}}{\mathrm{d}t} = k\frac{[\mathrm{Ru}]_0[\mathrm{monomer}]}{[\mathrm{PCy_3}]_0} \qquad (2)$$

Following this, 1 equiv of PCy_3 with respect to the catalyst was added to the samples, and the resulting kinetics showed a first-order dependence on monomer. The reaction rates were then measured at several temperatures, and an Eyring plot (Figure 2) of the results was used to determine the activation parameters (Table 1). It was observed that *exo*-DCP was nearly 20 times more reactive than *endo*-DCP at 20 °C.

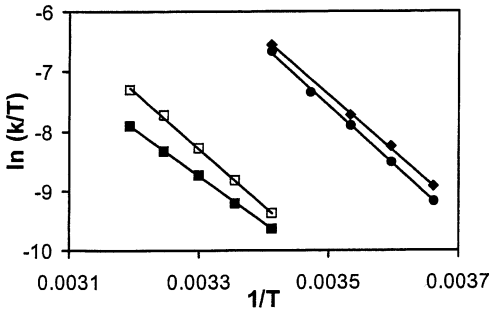


Figure 2. Eyring plots for norbornene (◆), *exo*-DCP (●), **3** (□), and *endo*-DCP (■). The reactions were performed in toluene-d_8. [Ru] = 4 mM and [PCy_3] = 4 mM.

Table 1. ROMP Activation Parameters

monomer	k_{obs}[a] (s^{-1})	$\Delta H^{\ddagger}$ ($kJ\cdot mol^{-1}$)	$\Delta S^{\ddagger}$ ($J\cdot mol^{-1}\cdot K^{-1}$)	$\Delta G^{\ddagger}$[b] ($kJ\cdot mol^{-1}$)
endo-DCP	0.019	66	−52	82
exo-DCP	0.37	82	28	74
norbornene	0.42	79	16	74
3	0.025	80	−2	81

[a] 20 °C in d-8 toluene with 4 mM catalyst and 4 mM Pcy_3. [b] At 20 °C.

As a comparison, the kinetics of neat ROMP (instead of solution ROMP) of the two isomers of DCP were qualitatively examined. In the presence of 0.2 wt % Grubbs' catalyst, *exo*-DCP was found to gel in less than 1 min. When a similar experiment was performed with *endo*-DCP, the monomer required more than 2 h to gel. This shows that the large reactivity difference of *endo*-DCP and *exo*-DCP revealed in the solution polymerization is qualitatively observed in the neat polymerization as well. Also, the activation enthalpy we report for solution ROMP of *endo*-DCP is nearly identical to the activation energy reported for neat ROMP of *endo*-DCP using the same catalyst.[16] On the basis of this, it appears that many of the trends seen in solution ROMP of DCP also apply in neat ROMP.

Insight into the reactivity difference between the two DCP isomers can be gained from the energies of activation listed in Table 1. *exo*-DCP and norbornene have very similar reactivities, suggesting that the cyclopen-

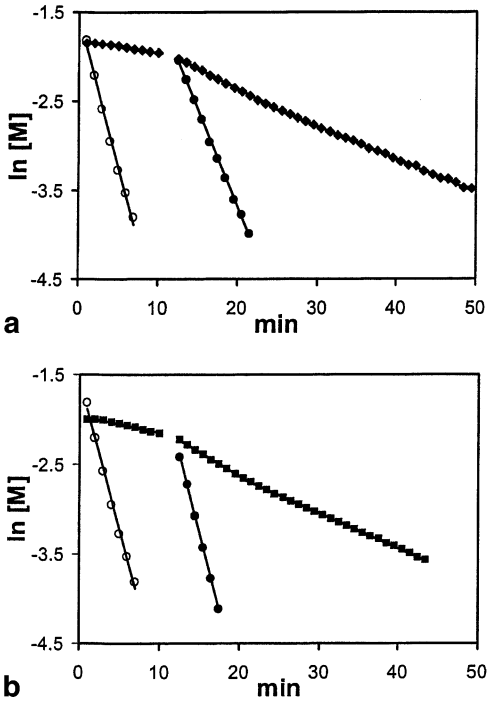


Figure 3. Competition experiments in which 1 equiv of *exo*-DCP (●) was added to a solution of catalyst and (a) *endo*-DCP (◆) or (b) **3** (■) after 10 min. As a reference, a plot of the homopolymerization of *exo*-DCP (○) is included as well. The reactions were conducted in toluene-d_8 at 20 °C. [Ru] = 4 mM, and [PCy_3] = 4 mM.

tene ring of *exo*-DCP does not significantly affect ROMP. Also, the free energies of activation show that *endo*-DCP is only slightly less reactive than **3**. Because **3** has only one double bond, mechanisms I and II (which involve coordination intermediates) cannot apply. If it is assumed that the steric effects in *endo*-DCP are essentially the same as those in **3**, then the rate depression of *endo*-DCP must be primarily steric in nature.

Because the difference in reactivity of *endo*-DCP and *exo*-DCP is due to steric interactions, the steric dominated mechanisms III, IV, and V were more closely examined. These mechanisms can be subdivided into two classes. Mechanisms III and IV depend on the shape of the monomer that is approaching the catalyst. Mechanism V does not depend on the monomer that approaches the catalyst, but it depends on the configuration of the ring to which the catalyst is attached.

Because mechanism V depends on the ring to which the catalyst is attached instead of the approaching monomer, it would be expected that ROMP of a mixture of *endo* and *exo* isomers would consume both monomers indiscriminately. Therefore, the ROMP rates for both components of the reaction mixture would be almost equal (as opposed to the homopolymerizations that have very different rates). This effect has been observed previously in cases where the reactivity is governed by the propagating center rather than the approaching monomer.[17] In contrast, mechanisms III and IV depend principally on the geometry of the approaching monomer, so the unhindered monomer would be expected to react significantly faster than the hindered monomer. In this case, the rates for each isomer in a mixture of *exo* and *endo* monomers would be expected to be similar to the rates seen in the homopolymerization.

On the basis of this reasoning, competition experiments (Figure 3) were performed to distinguish mechanisms III and IV from mechanism V. Polymerization of *endo*-DCP or **3** was initiated, and the initial reaction rate was monitored. After 10 min, *exo*-DCP was added to the solution and changes in rate were noted. Figure 3a shows that the polymerization of *endo*-DCP accelerated only slightly after the addition of *exo*-DCP. This small change in rate between the homopolymerization and the copolymerization of *endo*-DCP suggests that an interaction specific to the propagating catalyst's configuration (like mechanism V) may be contributing, but only to a small degree. A similar acceleration is seen in the competition experiment involving **3** (Figure 3b). The fact that *endo*-DCP and **3** behave similarly in these competition experiments suggests that this effect is due to sterics and indicates that the terminal unit's stereochemistry does contribute, at least in a minor way, to the reactivity (mechanism V). However, the fact that the *endo* isomers still react significantly slower than *exo*-DCP in the mixture suggests that the consequences of mechanism V are small. Rather, the predominant effect is monomer specific, as in mechanism III or IV.

The activation parameters (Table 1) can be used to determine whether mechanism III or mechanism IV is more significant. Mechanism III generates strain in the developing bonds, so it is largely enthalpic in nature and would be expected to correspond to higher activation enthalpy for *endo*-DCP and **3**. Clearly this is not the case, and in fact, the activation enthalpy for *endo*-DCP is lower than that of the other monomers.

Mechanism IV is more consistent with the activation parameters. Mechanism IV allows a reaction to occur only when the alkylidene is in a conformation that maximizes the distance between the ruthenium center and the other substituents of the cyclopentane ring. Because mechanism IV requires a specific conformation for reaction to occur, its consequences are manifested in activation entropy rather than activation enthalpy. Thus, theoretically mechanism IV would involve lower activation entropy for both *endo*-DCP and **3**, and Table 1 shows that this is the trend that is seen experimentally. Therefore, because mechanism IV is more consistent with the measured activation parameters and the similarity in reactivity between *endo*-DCP and **3**, it appears that interactions between the penultimate repeat unit and the incoming monomer are the primary cause of the reactivity difference between the two DCP isomers. However, the steric effects cannot completely account for the 14 kJ·mol^{-1} difference in activation enthalpy and the 50 J·mol^{-1}·K^{-1} difference in activation entropy between *endo*-DCP and **3** shown in Table 1.

Assuming that *endo*-DCP and **3** are sterically equivalent, this difference in activation parameters could result from an electronic effect like mechanism I or II. Coincidentally, *endo*-DCP's activation enthalpy and activation entropy compensate one another to give a free energy of activation that is nearly equal to that of **3** at 20 °C. Therefore, any electronic effect that changes the activation enthalpy and entropy of ROMP of *endo*-DCP does not significantly affect the overall reactivity of *endo*-DCP near ambient temperature. Although this electronic effect only slightly changes the rate, we investigated it further to determine whether it accounts for the unusual activation parameters of *endo*-DCP and whether it affected the reaction in other ways.

It is clear that if an electronic coordination effect like mechanism I or II is present to a significant degree, the PCy_3 that is being displaced must accumulate in solu-

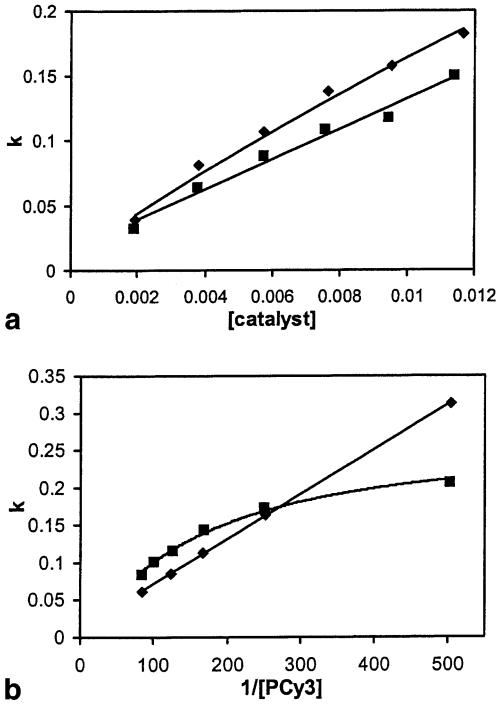


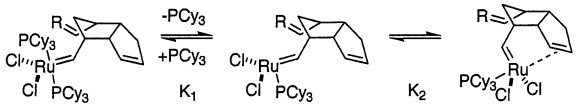
Figure 4. Rate dependence on (a) catalyst concentration and (b) added PCy_3. The observed data for *exo*-DCP (◆) were taken at 15 °C and are shown with a linear fit. The observed data for *endo*-DCP (■) were taken at 40 °C and fit using eq 4. In part a, 8 mM of PCy_3 was added, and in part b, 8 mM of catalyst was added.

tion. To test for this, ^{31}P NMR spectra were taken of *endo*-DCP and **3** during ROMP. The PCy_3 peak (10.5 ppm) was absent before the monomer was added, but clearly appeared during the polymerization of *endo*-DCP. Significantly, it was absent throughout the polymerization of **3**. This confirms that some type of coordination is successfully competing with the coordination with PCy_3, but only in the case where a second double bond (as in *endo*-DCP) is present.

Evidence for this type of interaction is also seen in the competition experiments discussed above. In the presence of *endo*-DCP, the polymerization of *exo*-DCP decelerates slightly (Figure 3a). However, the polymerization of *exo*-DCP does not decelerate noticeably in the presence of **3** (Figure 3b). This is consistent with interactions like mechanisms I and II that lower the concentration of active catalyst by generating a coordinated, inactive form of the catalyst. Because there is less active catalyst in solution, the polymerization of *exo*-DCP is slowed.

There is also evidence to suggest a contribution from mechanism II, which appears to be more likely than mechanism I. Previous reports have confirmed the formation of intramolecular complexes involving the coordination of a ruthenium atom and a nearby double bond to form a five-membered ring.[18,19] These reported systems did not involve norbornene derivatives, but the proposed intramolecular complex in Figure 1b is very similar.

The rates' dependence on catalyst and PCy_3 (Figure 4) also suggest that mechanism II affects the reaction. As expected, the rate of ROMP of *exo*-DCP is directly proportional to both the catalyst concentration and the reciprocal of the phosphine concentration as predicted by eq 2. However, *endo*-DCP shows much more complex behavior, and its dependence on PCy_3 is dramatically different. To examine this interesting difference in dependence on PCy_3, the theoretical effects of mechanism II were compared to the observed dependences on phosphine and catalyst. With mechanism II, there are no longer only two forms of the catalyst as described by eq 1, but there are three forms, and each of the species should exist in equilibrium (eq 3). Only the four-



(3)

coordinate catalyst species is ROMP active, so the rate should depend on the concentration of this four coordinate species at equilibrium. On the basis of eq 3 and the fact that the total concentration of ruthenium and PCy_3 in the system must remain constant, the steady-state concentration of the active species at equilibrium can be calculated. This leads to the rate expression

$$\frac{-\mathrm{d}[\textit{endo}\text{-DCPD}]}{\mathrm{d}t} = b(-[\mathrm{PCy_3}]_0 - c + \sqrt{[\mathrm{PCy_3}]_0^2 + 2c[\mathrm{PCy_3}]_0 + 4c[\mathrm{Ru}]_0 + c^2})[\textit{endo}\text{-DCPD}] \quad (4)$$

where $b = k_3/[2(K_2 - 1)]$, $c = K_1(K_2 - 1)$, and k_3 is the second-order rate constant describing the addition of monomer to the active catalyst. Stoichiometric concentrations $[PCy_3]_0$ and $[Ru]_0$ represent the amounts of PCy_3 and catalyst that were added to the solution, and they do not represent steady-state concentrations. This equation was used to fit the *endo*-DCP data in Figure 4, and it was found to correspond very well to the observed dependence on phosphine and catalyst. This provides even more support to the hypothesis that the intramolecular complex in Figure 1b is formed.

Mechanism II is also consistent with the lower activation entropy of *endo*-DCP relative to the other monomers. The dissociation of PCy_3 shown in eq 1 generates two free molecules and would be expected to involve a significant increase in translational entropy. This step occurs before the rate-determining step of the reaction (which must be during or after the coordination of monomer), so it would translate to relatively high activation entropy.

The complexes involved in mechanisms I and II would also have to dissociate for reaction to occur. Like the dissociation of phosphine, the dissociation of the complex involved in mechanism I (Figure 1a) would give two molecules and a large increase in entropy. However, because the complex involved in mechanism II (Figure 1b) is intramolecular, it dissociates into only one molecule, and no translational entropy would be gained. Consequently, this step results in a lower activation entropy. Thus, the 50 $J \cdot mol^{-1} \cdot K^{-1}$ difference in activation entropy between *endo*-DCP and **3** is consistent with the intramolecular complex shown in Figure 1b, but it is not consistent with the interaction shown in Figure 1a. The 14 $kJ \cdot mol^{-1}$ difference in activation enthalpy for these two monomers could correspond to the bond energy between PCy_3 and ruthenium being greater than that of the pi-coordination of the olefin and ruthenium that is depicted in Figure 1b.

Conclusion

It has been shown that the ROMP of *exo*-DCP is much faster than that of *endo*-DCP both in bulk and in

solution. Steric interactions appear to be the primary cause of this reactivity difference. It was shown that this steric effect must result from an interaction specific to the approaching monomer, and it is mostly entropic in nature. This is most consistent with an interaction between the *endo* substituents of the approaching monomer and the substituents of the cyclopentane ring to which the propagating center is bound. The ROMP of *endo*-DCP also appears to involve the formation of an intramolecular complex between the ruthenium center and the adjacent cyclopentenyl double bond. While this interaction affects the rate only slightly at ambient temperatures, it significantly affects the reaction's dependence on temperature and added PCy_3. By understanding the origin of the rate differences in norbornene based systems like the one studied here, monomers or catalysts can be specifically designed to tune the rates. This, in turn, creates the possibility to refine applications like RIM in which kinetic control is critical.

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Supporting Information Available: Figure containing ^{31}P NMR spectra showing the presence of free PCy_3 during the ROMP of *endo*-DCP. This material is available free of charge via the Internet at http://pubs.acs.org.

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