

**An Examination of the Kinetics  
of the  
Ring-Opening Metathesis Polymerization (ROMP)  
of  
a 7-oxanorbornene Derivative with Grubbs' Catalyst**

Thesis by  
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In partial fulfillment of the requirements for  
Honors in Chemistry

Defended on April 29, 1999

Washington and Lee University  
Lexington, Virginia  
1999

*To my family and friends*

*and*

*to Steve and Marcia*

## Acknowledgements

First of all, I would like to thank my research advisors, Dr. Steve Desjardins and Dr. Marcia France. In addition to providing me with a great deal of amusement over the past two years that I have been working on this project, they have also given me a great deal of useful advice regarding the system and experimental setup and provided emotional support when things didn't really go the way they were supposed to, i.e., instruments inexplicably ceased to function when I walked into the room. During the time I have been working with them (when they haven't been fighting/picking on one another, etc.), they have been wonderful mentors and taught me a great deal about the way research really works. I can't thank the two of you enough for helping me to realize how much I truly enjoy research!

I would like to thank Dr. Erich Uffelman, for helping me with the FT NMR portions of this project. Special thanks in the latter department must also be extended to Ashok Krishnaswami of JEOL, who developed the NMR kinetics program, taught us how to do  $^{31}\text{P}$  NMR, and spent many, many hours on the phone with Dr. Uffelman and Dr. Desjardins answering questions and figuring out what was wrong with the NMR at various points. I would also like to thank Dr. Michele Davis for teaching me how to use the kinetics package on the UV-vis spectrometer, spending many hours on the phone with Hewlett Packard, and periodically fixing the UV-vis spectrometer.

I would also like to acknowledge the contributions of two of my fellow students to this thesis. David Cooper and Nicole Johnson provided a great deal of assistance during the preliminary phases of this project. Thanks a lot for the hard work!

The entire chemistry department has been incredibly supportive of me, not only during this project, but throughout the entirety of my five years here at Washington and Lee. I really can't thank you all enough for this. I have never heard of another school where the faculty are as concerned about their students' welfare, both in and out of the classroom, or where they are so willing to help whenever a student is having a problem with the material. I would like to extend extra thanks to Dr. Desjardins, my advisor for the past five years, Dr. Uffelman and Dr. France, both for their friendship and for letting me cry on their shoulders at various points over the last several years.

I must also thank the University, which, through the Robert E. Lee Program, paid my stipend for summer research. Additional thanks go to the W&L Glenn Grant program for covering the cost of chemicals and equipment, to the National Science Foundation – Instrumentation and Laboratory Improvement Grant (NSF-ILI), which provided funds for the purchase of the 400 MHz JEOL Eclipse+ FT NMR and to Hewlett Packard, which provided a grant to purchase the HP Vectra XA UV-vis spectrometer used in these experiments.

Finally, I would like to thank my family and friends for always believing in me.



### Abstract

The study of ring-opening metathesis polymerization (ROMP) has become increasingly important over the past two decades. ROMP is unusual in that it provides a route to polymers with a high degree of unsaturation in the backbone, as it preserves all double bonds found in the monomeric units. Commercially, this process is used in the synthesis of several rubbers used in auto-body parts, such as Metton, Vestenamer and Norsorex. We have been examining the kinetics of a living ROMP reaction between Grubbs' catalyst and a 7-oxanorbornene derivative. These experiments were conducted in two phases. In the first phase, the kinetics of propagation were investigated using a JEOL 400 MHz FT-NMR spectrometer to measure the decrease in monomer concentration over time relative to a ferrocene internal standard. This data was used to calculate the rate constant of propagation,  $k_p$ , by assuming that the system possessed the kinetics typical of living systems. This procedure was repeated over a range of temperatures. The Arrhenius equation was then used to calculate  $E_a$  and  $\Delta S^\ddagger$  for propagation. The second phase was designed to examine initiation kinetics. An HP diode-array UV-visible spectrometer was used to monitor the decrease in the concentration of the uninitiated catalyst over time. This data was then used to calculate the rate constant of initiation,  $k_i$ . As with the propagation studies,  $k_i$  was determined for several temperatures, after which  $E_a$  and  $\Delta S^\ddagger$  of initiation were calculated using the Arrhenius equation. The time scales of initiation and propagation, denoted by  $\tau_i$  and  $\tau_p$ , were also calculated and compared to show that this reaction is in fact a living system.

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## Chapter 1

### Introduction

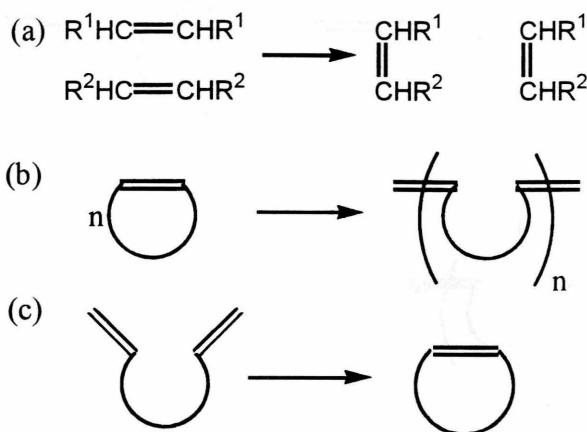
### **A. Background of the Ring-Opening Metathesis Reaction (ROMP)**

Ring-opening metathesis polymerization, or ROMP, is one of a more general class of reactions known as olefin metathesis reactions. This particular type of reaction has become increasingly important since it was first identified by Calderon in 1967.<sup>1, 2</sup> Several well-known industrial processes proceed by the olefin metathesis mechanism, including the Phillips Triolefin Process and the Shell Higher Olefins Process.<sup>3</sup> The ROMP reaction is used to manufacture various commercial polymers such as Norsorex (polynorbornene), a rubber frequently used in engine mountings and shock-proof bumpers, Metton (polydicyclopentadiene), a plastic commonly found in satellite dishes, snowmobiles and car bodies, and Vestenamer (polyoctenamer), a material that is combined with other rubbers to make gaskets and break hoses, among other things.<sup>4</sup> More recently, ROMP has proven useful in the synthesis of electroluminescent and conducting polymers, side chain liquid-crystal polymers, and internally and terminally functionalized polymers.<sup>5</sup> In addition to ROMP, which occurs when cyclic olefins undergo the metathesis reaction, metathesis can occur between acyclic olefins intermolecularly (acyclic olefin metathesis) to give two new olefins or intramolecularly (ring-closing metathesis or RCM) to yield a cyclic olefin. In the last few years, RCM has been widely used in organic syntheses.<sup>1, 6</sup>

One of the reasons the metathesis reaction has proved to be of such great importance is that it allows for the interchange of carbon atoms between a pair of double bonds (Scheme 1). Unlike many other types of polymerization reactions, such as free radical polymerization, metathesis preserves all double bonds found in the monomeric units. This property allows for the synthesis of polymers with a high degree of unsaturation in the backbone. The high degree of unsaturation

available via olefin metathesis can therefore give rise to polymers with properties that are substantially different from those of the saturated polymers synthesized using other methods.<sup>1</sup>

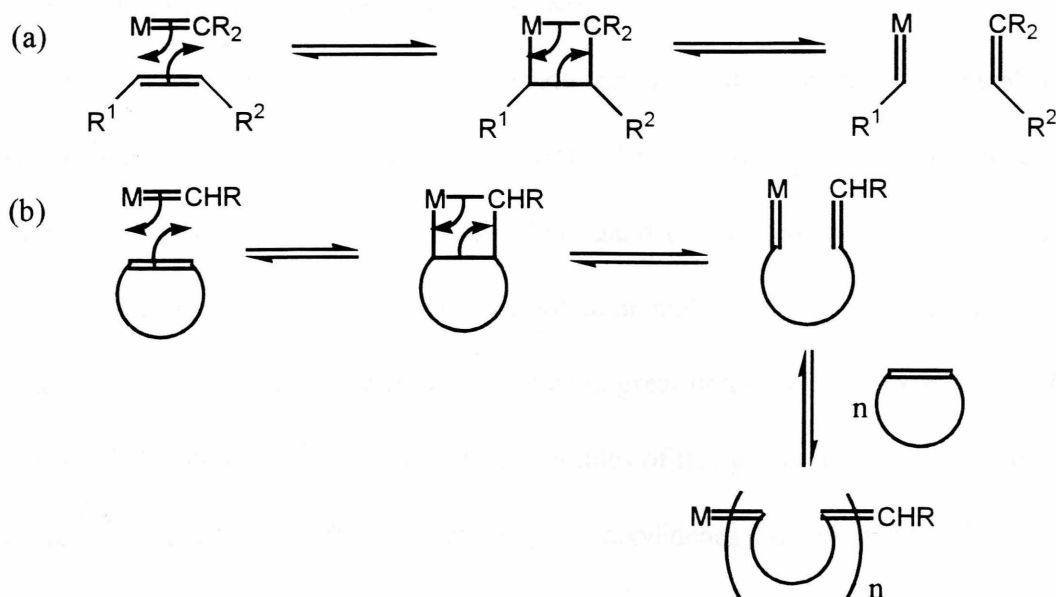
**Scheme 1:** (a) acyclic olefin metathesis; (b) ring-opening metathesis polymerization (ROMP); (c) ring-closing metathesis (RCM)



It is generally agreed that the active species in olefin metathesis is a metal alkylidene (carbene) complex. This metal carbene undergoes a [2+2] cycloaddition with an olefin to form a metallacyclobutane intermediate (Scheme 2). This intermediate either reverts back to the original starting material (non-productive metathesis) or opens in a productive manner to give a new metal alkylidene and a new olefin (productive metathesis). When the olefin is a cyclic alkene, the metallacyclobutane will open to form an olefin which is still tethered to the metal alkylidene. This compound can react with additional cyclic monomers to form a polymer.<sup>1</sup>

Each of the steps in the olefin metathesis mechanism is reversible. Indeed, isotopic labeling studies show that terminal acyclic olefins favor the non-productive metathesis over productive metathesis.<sup>1</sup> In some cases, the metathesis reactions of acyclic compounds can be driven in the

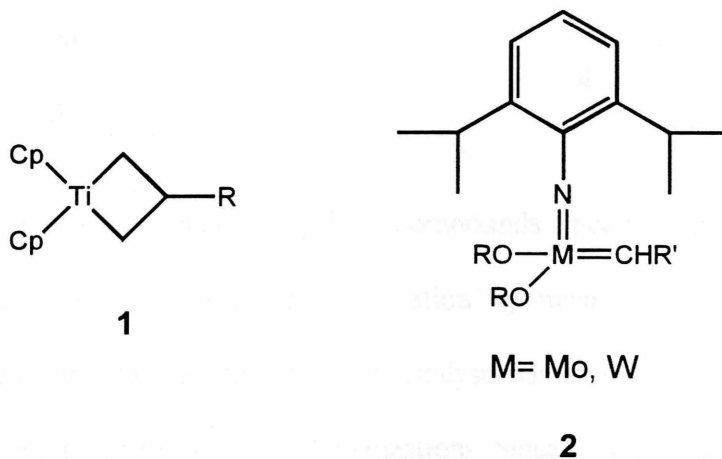
**Scheme 2:** Mechanism of (a) acyclic olefin metathesis and (b) ring opening metathesis polymerization (ROMP).



forward direction through the removal of a volatile component. Ring-opening metathesis polymerization reactions are much less likely to proceed in reverse, since the ring opening step relieves whatever ring strain is present in the system. The driving force of this reaction is the removal of ring strain; this is one reason why less efficient catalysts can only initiate highly strained complexes such as norbornene.<sup>3</sup>

During the past two decades, the greatest advance in the field of olefin metathesis has been the development of well-defined catalysts that show greater versatility. (A well-defined catalyst is one where the structure of both the catalyst and the activated species is known; an ill-defined catalyst is one where the activated species has not been isolated and the mechanism of initiation is unclear.) There are currently a wide variety of metal complexes capable of catalyzing olefin metathesis and ROMP reactions;<sup>1,3,7</sup> these catalysts can be divided into four main classes.<sup>8</sup> Two of the categories consist of catalysts based on early transition-metals such as molybdenum, tungsten, titanium and

rhodium, while the other two categories are based on group VIII transition metals, and usually contain ruthenium, iridium or osmium. The first category of metathesis catalysts is made up of ill-defined catalysts that generally involve a metal halide complex and a non-transition metal co-catalyst. Examples of such systems are  $\text{WCl}_6/\text{SnMe}_4$  and  $\text{MoCl}_5/\text{EtAlCl}_2$ . In these cases, it is believed that an active carbene species is generated from the alkyl ligand on the co-catalyst.<sup>1,3, 7-8</sup> In the 1980s, researchers synthesized well-defined metallacyclobutane and metal alkylidene complexes of these early transition metals. These catalysts were studied in great detail by Schrock et al at MIT<sup>9-10</sup> and by Grubbs et al at Caltech.<sup>11-14</sup> Representative examples of this group include the Grubbs' titanium metallacycle **1**,<sup>11-14</sup> and the molybdenum and tungsten alkylidenes **2** developed by Schrock.<sup>9-10</sup> Both **1** and **2** have been shown to generate living polymerization systems (see part B of Introduction).<sup>7-12</sup>

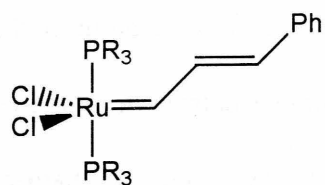


The first catalysts based on group VIII transition metals were ill-defined compounds such as  $\text{Ru}(\text{H}_2\text{O})_6(\text{tos})_2$  (tos = *p*-toluenesulfonate)<sup>14-16</sup> and various hydrated trichlorides of ruthenium, iridium, and osmium.<sup>1, 7, 15-16</sup> The mechanism by which these compounds initiate metathesis is unclear, as the compounds do not have well-defined alkylidene or metallacyclobutane ligands. They also do not require the alkyl-containing co-catalysts that had been necessary for the formation of the active



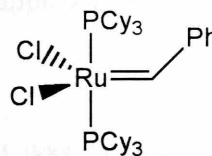
species in reactions utilizing the ill-defined early transition metal catalysts. While the mechanism of initiation with these Group VIII compounds remains a mystery, they are much more tolerant of functional groups on the olefin than their early transition metal predecessors. However, they are also somewhat less reactive overall and are useful only for the polymerization of monomers with a high degree of ring strain, such as norbornene and its derivatives.<sup>1, 8</sup>

The final class of catalysts used for metathesis reactions consists of well-defined group VIII catalysts. The first of these was developed in the early nineties by Grubbs et al;<sup>17</sup> this particular class of catalysts includes compounds **3**<sup>17, 18</sup> and **4**.<sup>19, 20</sup>



R = Ph, Cy

**3**



**4**

Considerable research has been conducted on these compounds since their initial discovery.<sup>5, 18-24</sup> These complexes clearly catalyze olefin polymerization by means of the metallacyclobutane intermediate described earlier. Overall, this group of catalysts has proven to be quite robust; several catalysts within this group give rise to living polymerizations. Since they also have the high functional group tolerance which characterized the ill-defined group VIII catalysts and appear to be less dependent upon the presence of ring strain to initiate the reaction, this group is of great interest today.<sup>1, 5, 8, 18-23</sup>

## **B. Living Polymerizations**

Polymers are primarily of interest due to their highly variable physical and chemical properties. It has long been known that natural polymers, such as wool, silk, cotton and rubber are formed via condensation reactions. These reactions are controlled at the molecular level by the organisms that produce them. This molecular control allows the naturally occurring polymers to be constructed from pre-determined "blocks" of various monomers. Thus, the first segment of a polymer can be composed of one monomer, its second section another monomer, and so on. Since the lengths of these blocks are closely controlled by the organism's enzymes or some other bioregulatory molecule, the resultant molecules of the polymer will all be approximately the same length or have a very low polydispersity (molecular weight distribution).<sup>24</sup>

When man-made polymers were first synthesized, it was through processes such as free radical initiation of vinyl groups or the condensation of small difunctional molecules. The polymers formed by such methods initially consisted of only one monomer type. It was soon realized that by mixing two or more types of monomer into the reaction mixture, random copolymers could be manufactured. However, while these random copolymers greatly expanded the range of useful polymer properties such as elasticity, compressibility, toughness, hardness and strength, there was still a fundamental lack of control over the order in which monomer units bonded to the growing chains and over the length of the final polymer chain. Thus, it was clear that research into new synthetic methods which would allow greater control over the growing polymer at a molecular level was needed if the field of synthetic polymer chemistry was to grow further.<sup>24</sup>

Traditional chain-growth polymerizations such as free-radical polymerization of alkenes consist of four distinct steps: initiation, propagation, chain transfer and termination. However, as

early as 1936 some systems which seemed to proceed without chain transfer or termination had been identified. These systems included the anionic polymerizations of styrene and butadiene. In a transferless polymerization, the number of active chains (growing polymers) remains constant, and since no termination steps occur, the chain ends remain activated even after all the monomer has been polymerized.<sup>24</sup> Szwarc dubbed systems exhibiting these two main characteristics "living polymerizations" since the chain ends remain active until they are "killed" or deactivated by a separate reaction.<sup>25</sup> The fact that the chain ends remain activated in a living system allows for a unique degree of control. For example, it is simple to assemble a regular block copolymer using a living system. First, a catalyst is used to initiate the polymerization reaction in one type of monomer. This polymerization reaction will continue until all of the initial type of monomer has been consumed, at which point the monomeric units which are to form the second block may be added, etc.<sup>24</sup> Many types of living systems are known today, including anionic, cationic, radical, group-transfer, Ziegler-Natta, and ring-opening metathesis polymerization (ROMP), which was discussed in the previous section.<sup>26</sup>

As was stated above, a living system is defined as one that has neither chain-transfer nor termination steps. In addition to these two criteria, a living system must meet one further condition: its initiation step must be faster than or occur at the same rate as the propagation step.<sup>1</sup> These three parts of the definition of a living system combine to give rise to the characteristics which all living systems have in common:<sup>26</sup>

1. Polymerization will proceed until all of the monomer originally present in the reaction mixture has been consumed. Further addition of monomer at a later time will result in continued polymerization.

2. The number average molecular weight,  $M_n$ , is a linear function of conversion, where  $M_n$  equals grams of monomer/moles initiator.
3. The number of polymer chains (and/or activated centers) is a constant.
4. The molecular weight of the final polymer can be controlled by stoichiometry.
5. The polymers produced have a narrow molecular weight distribution (low polydispersity).
6. Block copolymers can be prepared by sequential monomer addition.
7. Chain-end functionalized molecules can be prepared in a quantitative yield.

Due to these unique characteristics, living systems have kinetics quite different from those ordinarily seen in non-living polymerization reactions. This thesis examines the kinetics of a living system that proceeds via ring-opening metathesis polymerization (ROMP), the mechanism of which was discussed in part A.

### C. The Kinetics of Living Systems

In order to understand the kinetics of a living polymerization, it is important to first have a basic understanding of kinetics in general. For any chemical equation which is elementary in nature, elementary meaning that it is a single step in a reaction pathway, a kinetic equation which governs the speed of the reaction can be written using the law of mass action. The rate law, as this equation is called, expresses the rate of a reaction as proportional to the concentration of each reactant raised to a power. For example, for a reaction where



the rate law would be

$$v = k [A][B] \quad (1.1)$$

Here,  $v$  is the velocity (speed) at which the reaction proceeds,  $k$  is the rate constant and  $A$  and  $B$  are the concentrations of the starting materials. The power to which a species is raised in the rate law is known as the order of the reaction with regard to that particular species. Thus, equation 1 is first order in both  $A$  and  $B$ . The overall order of a reaction is determined by the sum of the orders of the individual reactants; therefore, equation 1.1 is second order overall. Rate laws for reactions with more than one elementary step are derived from a combination of the individual rate laws of each elementary step in the reaction pathway.<sup>27</sup>

A typical chain polymerization reaction (for example, free radical polymerization) contains at least three separate elementary steps: initiation, propagation, and termination. Each of these steps possesses its own rate law (eq. 1.2-1.4) where  $I$  refers to the initiating species (in the case of a ROMP reaction, this would be the metal alkylidene catalyst),  $M$  is the monomer, and  $M_n^*$  represents the activated polymer chains.



Normally, chain transfer effects would need to be accounted for here as well; however, since they are ultimately unimportant in living systems, they will be disregarded for now. For living polymerizations such as the ROMP reaction, the initiation step proceeds quickly enough to be kinetically unimportant and the termination step does not occur. Since initiation and termination can therefore be ignored for the purpose of studying the overall reaction rate, the rate of a living system must be controlled by the propagation step:



At first glance, this might appear to be a second order reaction, as the rate law is first order in both the concentration of activated chains ( $[M_n^*]$ ) and in the concentration of monomer ( $[M]$ ). However, since initiation occurs almost immediately upon the addition of the catalyst, or initiating species (I), and there are no termination or transfer steps in living reactions, the concentration of activated chains,  $[M_n^*]$ , will remain constant throughout the reaction. Thus,  $[M_n^*]$  should be equal to the concentration of catalyst ( $[I]$ ) which was originally added to the system, and can therefore be incorporated into the rate law as a constant. By using the following substitution,

$$k' = k[M_n^*] \quad (1.5)$$

the rate law can be written instead as a pseudo-first order equation of the form

$$v = k'[M] \quad (1.6)$$

Since the reaction is now essentially first order, the velocity of the reaction should be linearly

proportional to the amount of monomer present in the system. Of course,  $k'$  will vary as a function of catalyst concentration.<sup>28</sup>

In practice, data is fit to the integrated form of this rate law, where

$$\ln ([M]/[M_0]) = -k't \quad (1.7)$$

Thus, if the initial concentration of the monomer is known and the amount of monomer remaining in the reaction mixture can be tracked over time, it is possible to use the integrated form of the rate law to determine the value of the rate constant  $k'$ . The rate constant  $k$  may then be determined by dividing  $k'$  by the concentration of catalyst.<sup>27</sup>

By calculating  $k$  at different temperatures, it is possible to determine the temperature dependence of  $k$ . Moreover, it is possible to use the Arrhenius equation (1.8) to determine both the energy of activation and the entropy of the reaction.<sup>27</sup>

$$k = Ae^{-E_a/RT} \quad (1.8)$$

Thus, knowledge of  $k$  as a function of  $T$  allows for the determination of the activation parameter,  $E_a$ . The entropy of activation,  $\Delta S^\ddagger$ , can be obtained from the pre-exponential factor  $A$  using activated complex theory as  $A$  can be expressed as:<sup>27, 29</sup>

$$A = Be^2 e^{\Delta S^\ddagger/R} \quad (1.9)$$

The parameter  $B$  represents the quantity

$$kT^2R/hp^0 \quad (1.10)$$

and is a constant, since  $k$  is Boltzman's constant,  $T$  is the temperature in degrees Kelvin,  $R$  is the universal gas constant,  $h$  is Planck's constant and  $p^0$  is the reference pressure.<sup>27, 29</sup>

It should be noted that while initiation can be ignored when studying the overall rate of a living system, the rate of initiation is important in determining if the reaction is, in fact, living. After

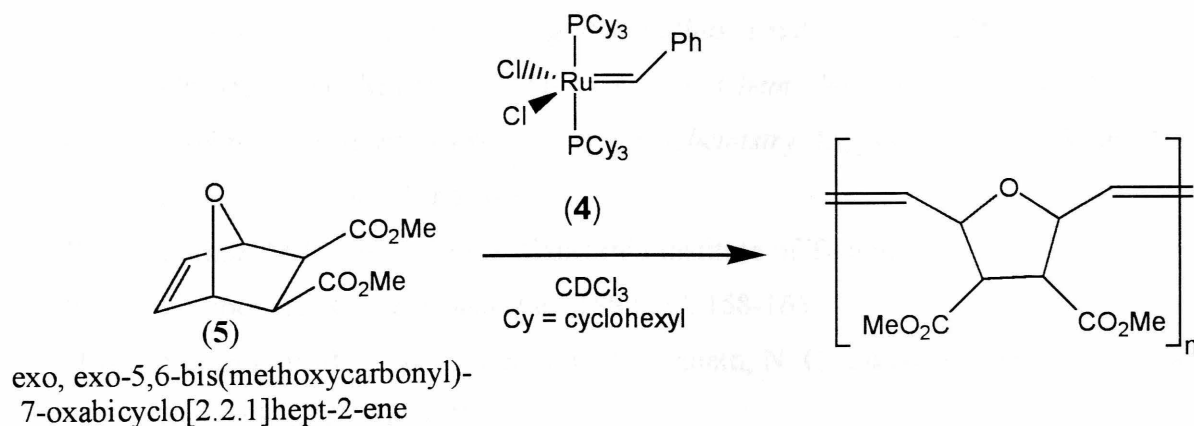
all, the primary requirement for a living system is that the rate of initiation be greater than or equal to the rate of propagation.<sup>1, 24, 26</sup>



## D. Thesis Research

The goal of the research presented here was to examine in detail the kinetics of the ROMP reaction of 7-oxanorbornene derivative **5** with Grubbs' catalyst (**4**)(Scheme 3).<sup>30</sup>

**Scheme 3:** ROMP reaction of Grubbs' catalyst (**4**) with the 7-oxanorbornene derivative **5**.



While there has been some research performed on the kinetics of the reaction of the PPh<sub>3</sub> analogue of Grubbs' catalyst with norbornene,<sup>5, 19</sup> to our knowledge there have been no investigations of the kinetics of its reaction with 7-oxanorbornene or its derivatives. Chapter 2 discusses the determination of the rate constant of propagation,  $k_p$ , and the energy and entropy of activation for propagation using FT NMR. The kinetics of initiation are examined via UV-VIS spectroscopy in Chapter 3. In particular, the rate constant of initiation and the activation parameters are calculated, along with the timescales,  $\tau_i$  and  $\tau_p$ . Some investigations into the structure of the activated species using <sup>1</sup>H and <sup>31</sup>P NMR are discussed as well.

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**Chapter 2**  
**Propagation**

## **A. Introduction**

$^1\text{H}$  NMR was used to study the kinetics of the propagation step of the ROMP reaction between Grubbs' catalyst (4) and 7-oxanorbornene derivative 5. In  $^1\text{H}$  NMR spectroscopy, the area under the peaks in a spectrum is proportional to the concentration of the compounds present in the sample. Thus, if a sample containing a reaction mixture is monitored over the course of the reaction, the peaks associated with the protons on the starting materials decrease while those peaks associated with the protons on the product increase. Since even in single-pulse  $^1\text{H}$  NMR, 2-3 seconds are required for data to be collected and relaxation to occur, this particular technique has limitations when dealing with reactions that occur very quickly, such as initiation of a living polymerization system. However, the propagation step of the reaction being investigated is slow enough (approximately 45 minutes at room temperature) for single-pulse  $^1\text{H}$  NMR to be a viable option.

In order to be investigated using  $^1\text{H}$  NMR, the monomer needed to possess a proton that experienced a measurable change in chemical shift upon polymerization. Further, this shift had to be large enough to avoid overlap between the monomer and the corresponding polymer proton peaks, which is frequently a problem as polymer peaks tend to broaden as the reaction proceeds. In this case, proton *b* experiences a shift of approximately 0.2 ppm (from 2.8 ppm to 3.06 ppm) upon becoming proton *x* when polymerization takes place in  $\text{CDCl}_3$  (Figure 1).

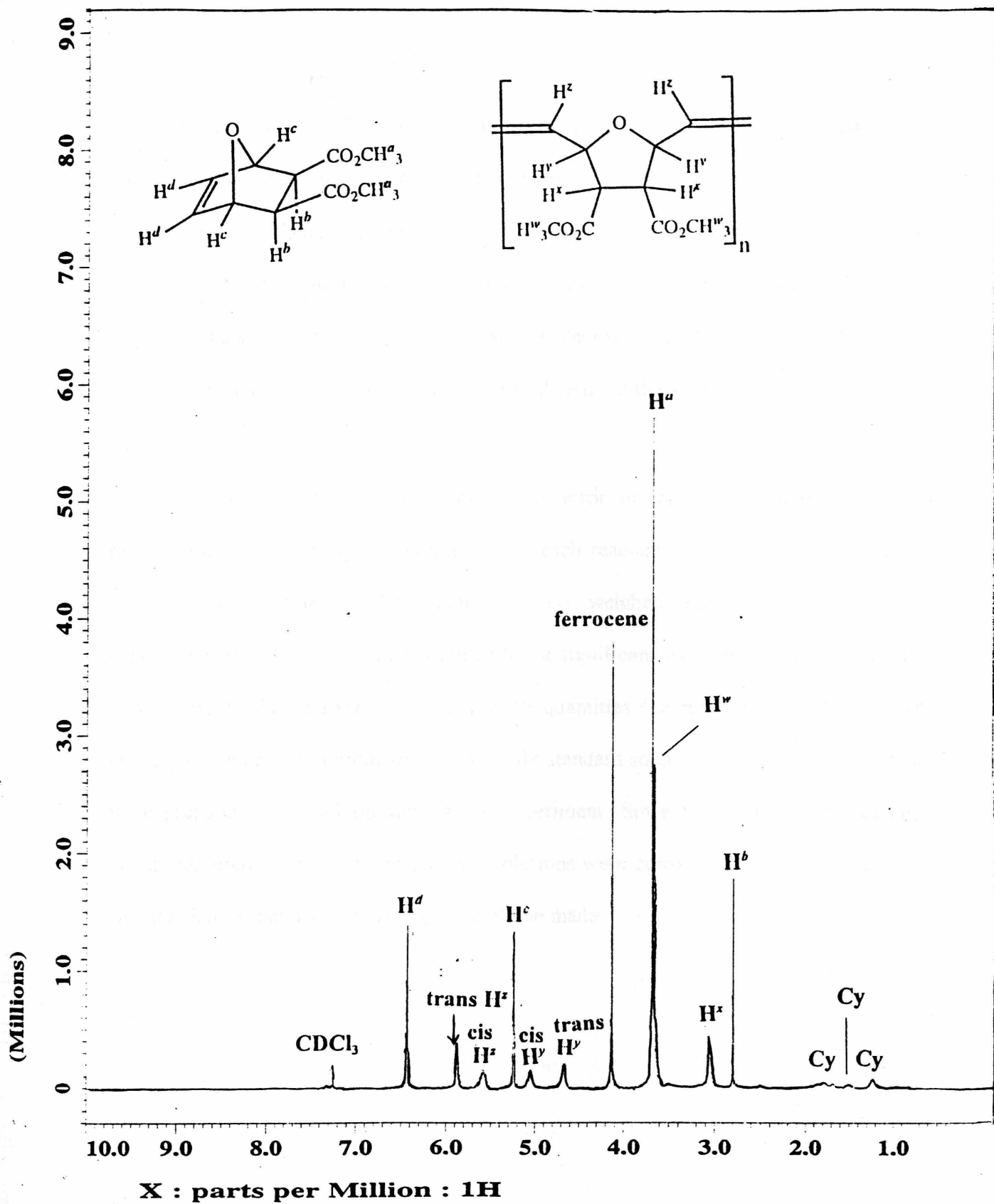


Figure 1:  $^1\text{H}$  NMR spectrum of ROMP reaction, showing monomer and polymer peaks

Single pulse proton spectra were taken at set time intervals. The decrease in monomer concentration over time was tracked by monitoring the decrease in the area of the peak corresponding to proton *b* and comparing this number to an internal standard of ferrocene. A plot of  $-\ln([M]/[M_0])$  vs. time was used to determine the values of  $k'$  and  $k_p$  (eq. 1.7). This procedure was repeated at five degree intervals from  $0^\circ - 45^\circ$  C. The Arrhenius equation (eq. 1.8) was then used to determine the activation parameters  $E_a$  and  $\Delta S^\ddagger$ .

One of the most obvious sources of error in the experimental design was maintaining exact starting concentrations for each reactant over multiple runs. Clearly, there would be variation if the reactants were weighed individually prior to each experiment; the chances of the variations being significant were fairly high, particularly with regard to the catalyst, since such small quantities (on the order of 2.5 mg) were being used. In order to minimize this risk, bulk standard solutions of each of the reactants were prepared and used throughout the experiment. Since the quantities of reactants being measured to make up the standard solutions were considerably larger, there was a smaller chance that a significant error would be made.

## **B. Results/Discussion**

The investigation of the propagation phase of the reaction was designed to determine the rate constant of propagation,  $k_p$ , and the overall kinetics of propagation. The temperature dependence of  $k_p$  was also illustrated and the resulting information used to determine the activation parameters of propagation.

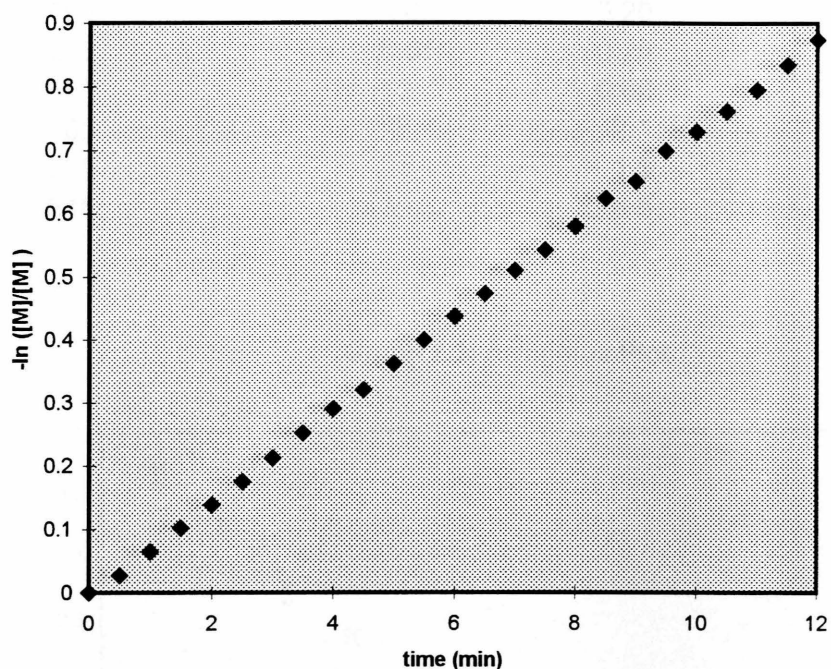
Preliminary experiments to determine the approximate time needed for the reaction to run to completion at various temperatures were carried out in benzene. The rate of the decrease in monomer concentration over time for each experiment was monitored using the kinetics program developed by JEOL (see Section C for details). When temperatures significantly above room temperature were used ( $> 35\text{ }^\circ\text{C}$ ), the decrease in monomer concentration over time became somewhat erratic, a phenomenon not seen at lower temperatures. In some cases, at a temperature of  $45\text{ }^\circ\text{C}$ , the decrease in monomer concentration was erratic and the data was unusable. Thus, only temperatures of  $45\text{ }^\circ\text{C}$  and below were used in the experiment. However, since benzene's melting point is relatively high ( $\text{mp}_{\text{benzene}} = 5.5\text{ }^\circ\text{C}$ ), it was necessary to find another solvent with a lower melting point if data on a wide range of temperatures was to be collected. The reaction was therefore investigated in  $\text{CDCl}_3$ , toluene d-8 and  $\text{CCl}_4$ . The spectra obtained from the reaction mixture in  $\text{CDCl}_3$  had the best separation between the monomer peak of  $\text{H}^b$  and the corresponding polymer peak of  $\text{H}^x$ .  $\text{CDCl}_3$  was therefore selected as the solvent for the kinetics experiments.

The results obtained from  $^1\text{H}$  NMR investigation of the ROMP reaction between Grubbs' catalyst (**4**) and 7-oxanorbornene derivative **5** show that the reaction is clearly first order in nature. When  $-\ln([\text{M}]/[\text{M}_0])$  was plotted vs. time, the graphs were linear



with  $r$  values which were generally equal to or greater than 0.998 (for example, see Graph 2.1).

**Graph 2.1: Determination of the Rate Constant  $k'$  at 40 C**

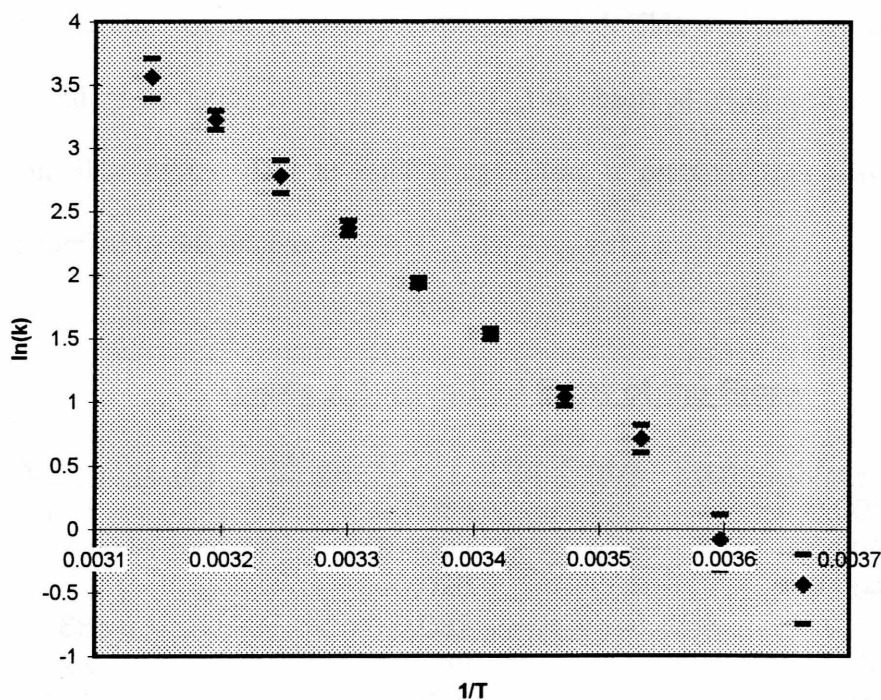


A minimum of 5 replicate measurements were performed at each temperature. The  $k_p$  values thus obtained were averaged, their standard deviations calculated, and the  $k_p$  values tested for outliers. Those  $k_p$  values which were found to be outliers were thrown out, and the average rate constant and standard deviation were recalculated according to the remaining data points. The average rate constants determined at differing temperatures clearly illustrate the temperature-dependent nature of the rate constant, i.e., bimolecular reactions proceed faster at higher temperatures (Table 2.1).

**Table 2.1:**  
**Temperature Dependence of the**  
**Rate Constant,  $k_p$**

Temperature (K)	$k_p$ (L/mol·min)	Standard Deviation
273	0.65	0.17
278	0.92	0.20
283	2.04	0.22
288	2.83	0.20
293	4.63	0.20
298	6.95	0.26
303	10.7	0.62
308	16.1	2.1
313	25.1	1.9
318	35.3	5.6

**Graph 2.2: Arrhenius Plot**



The change in  $k_p$  over 5° intervals is quite regular, as the linearity of  $k_p$  when graphed against  $1/T$  in the Arrhenius plot corresponds to an  $r$  value of 0.998 (Graph 2.2).

Error analysis was performed on this data by examining the standard error of the slope, since  $k_p$  was derived from the slope of a linear regression performed on a graph showing  $-\ln([M]/[M_0])$  vs. time. The standard error of the slope was initially obtained from the linear regression; however, this was not truly the error of  $k_p$ , but of  $k_p'$  (see chapter 1, section C). In order to obtain the error of  $k_p$ , it was necessary to divide the error of  $k_p'$  by the concentration of the catalyst used (the same process used to obtain  $k_p$  from  $k_p'$ ). Once determined, the standard errors were compared both within and across temperature groupings, and their averages and standard deviations calculated (Table 2.2). The error was fairly constant within temperature groupings. When the errors were compared over temperature groupings, however, it was noticed that the error increased as the temperature of the reaction mixture increased. This was also the pattern observed for the standard deviation of  $k_p$  in Table 2.1. The observed trend results from the increasing unreliability of the data at high temperature, a problem that was mentioned in the introduction to this chapter.

**Table 2.2: Standard Error of the Slope**

<u>Temperature (K)</u>	<u>Standard Error of the Slope</u>	<u>Standard Deviation</u>
273	0.0089	0.0015
278	0.0094	0.0026
283	0.020	0.0045
288	0.032	0.010
293	0.049	0.007
298	0.065	0.014
303	0.10	0.026
308	0.19	0.077
313	0.19	0.084
318	0.62	0.23

While, to our knowledge, no investigations of the kinetics of Grubbs' catalyst with 7-oxanorbornene derivatives have been conducted, the kinetics of some other ROMP systems have been explored. One study involved the ROMP reaction between  $(PPh_3)_2Cl_2Ru=CHPh$  and norbornene.<sup>1</sup> This system differs from the one which we have studied in that the catalyst possesses triphenylphosphine ligands in place of the tricyclohexyl ligands found on the Grubbs' catalyst. Also, the unsubstituted norbornene used by Schwab et al contains a carbon at the 7 position instead of the oxygen found in 7-oxanorbornene derivatives. The value of  $k_p$  calculated at room temperature for Schwab's system,  $0.00128 \text{ L/mol}\cdot\text{s}$ ,<sup>1</sup> differs by more than an order of magnitude from our value, which, when translated to the same units, was  $0.07715 \text{ L/mol}\cdot\text{s}$ . This data indicates that the reaction between Grubbs' catalyst and 7-oxanorbornene derivative **5** used in our study occurs at a rate over  $1 \frac{1}{2}$  orders of magnitude greater than the rate of the reaction between  $(PPh_3)_2Cl_2Ru=CHPh$  and norbornene. This result is consistent with data gathered by Nyugen et al showing that the catalyst **3** ( $R=Ph$ ) is considerably less efficient than the tricyclohexylphosphine version.<sup>2</sup>

The values of the energy of activation,  $E_a$ , and the entropy of the reaction,  $\Delta S^\ddagger$ , were obtained using the Arrhenius equation once the temperature dependence of  $k$  had been demonstrated. The value of  $\Delta S^\ddagger$  was found to be  $-28.10 \pm 0.51 \text{ cal/mol}$ ;  $E_a$  was found to be  $13.07 \pm 0.30 \text{ Kcal/mol}$ . The sign for  $\Delta S^\ddagger$  is negative, as is often the case for a bimolecular step. The  $E_a$  value is within reason, as does the  $\Delta S^\ddagger$ , when compared to known values for other types of polymerization reactions. For example,  $E_a$  is between 5-7 Kcal/mol for free radical polymerizations.<sup>3</sup> To our knowledge, these activation

parameters have not been calculated for similar ROMP systems, so no comparisons can be made at this time.

The following table shows the results of the polymerization of styrene in the presence of various amounts of the initiator. The results show that the rate of polymerization increases with increasing initiator concentration. The molecular weight of the polymer also increases with increasing initiator concentration. The results are summarized in the following table.

Initiator Concentration (mol/L)	Polymerization Rate (mol/L·h)	Molecular Weight (g/mol)
0.01	0.02	10000
0.02	0.04	20000
0.03	0.06	30000
0.04	0.08	40000
0.05	0.10	50000

Table 1. Polymerization of Styrene in the Presence of Various Amounts of Initiator

Initiator Concentration (mol/L)	Polymerization Rate (mol/L·h)	Molecular Weight (g/mol)
0.01	0.02	10000
0.02	0.04	20000
0.03	0.06	30000
0.04	0.08	40000
0.05	0.10	50000

The results of the polymerization of styrene in the presence of various amounts of the initiator are shown in Table 1. The results show that the rate of polymerization increases with increasing initiator concentration. The molecular weight of the polymer also increases with increasing initiator concentration. The results are summarized in the following table.

### C. Experimental

**General.** Solids and solutions were transferred and stored in a nitrogen-filled Vacuum Atmospheres Nexus One glove box. All standard solutions were stored at  $-32^{\circ}\text{C}$  in the same nitrogen-filled Vacuum Atmospheres glove box.

**Instrumentation.** NMR spectra were recorded on a JEOL Eclipse+ FT NMR spectrometer operating at 400 MHz. The temperature controller in the JEOL software program was used to set the temperature at  $5^{\circ}$  intervals between  $0^{\circ}$  -  $45^{\circ}\text{C}$ . A program was developed in conjunction with Ashok Krishnaswami at JEOL that took single pulse proton spectra at preset intervals (which corresponded to the different temperatures), ranging from 30 seconds to 10 minutes (Table 2.3).

**Table 2.3 : Time Intervals Between Spectra at Various Temperatures**

<u>Temperature (<math>^{\circ}\text{C}</math>)</u>	<u>Time Interval(min)</u>
0	10
5	10
10	2.5
15	2.5
20	1.5
25	1.5
30	1.0
35	1.0
40	0.5
45	0.5

**Materials.**  $(\text{PCy}_3)_2\text{Cl}_2\text{Ru}=\text{CHPh}$  (**4**) packaged under argon was purchased from Strem and used as received. Ferrocene was purchased from Aldrich and used as received.

Exo,exo-5,6-bis(methoxycarbonyl)-7-oxabicyclo[2.2.1]hept-2-ene (**5**) was prepared by the Chem 242 classes as described by the literature procedure.<sup>4</sup> The purity of the 7-oxanorbornene derivative was checked by <sup>1</sup>H NMR; the compound was recrystallized from methanol when necessary. Anhydrous CDCl<sub>3</sub> packaged under nitrogen was purchased from Aldrich and used as received.

**Preparation of 0.47 M monomer standard solutions.** Exo,exo-5,6-bis(methoxycarbonyl)-7-oxabicyclo[2.2.1]hept-2-ene (1 g) was measured into a 10 mL volumetric flask. The flask was filled to the line with CDCl<sub>3</sub>, capped, and shaken vigorously. The solution was transferred to a capped vial and stored under N<sub>2</sub> at -32 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 6.42 (s, 2H, HC=), 5.22 (s, 2H, CHOCH), 3.66 (s, 6H, OCH<sub>3</sub>), 2.78 (s, 2H, CHCO<sub>2</sub>Me)

**Preparation of 0.27 M ferrocene standard solutions.** Ferrocene (250 mg) was added to a 5 mL volumetric flask, which was filled to the line with CDCl<sub>3</sub>. The solution was transferred to a capped vial and stored under N<sub>2</sub> at -32 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 4.13 (s, C<sub>5</sub>H<sub>5</sub>)

**Preparation of 0.0061 M catalyst standard solutions.** (PCy<sub>3</sub>)<sub>2</sub> Cl<sub>2</sub>Ru=CHPh (50 mg) was added to a 10 mL volumetric flask, which was filled to the line with CDCl<sub>3</sub>. The solution was transferred to a capped vial and stored under N<sub>2</sub> at -32 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 19.99 (s, Ru=CH), 8.44 - 7.33 (m, C<sub>6</sub>H<sub>5</sub>), 2.06 (m, P(C<sub>6</sub>H<sub>11</sub>)<sub>3</sub>), 2.16 (m, P(C<sub>6</sub>H<sub>11</sub>)<sub>3</sub>), 1.77-1.18 (m, P(C<sub>6</sub>H<sub>11</sub>)<sub>3</sub>). <sup>31</sup>P NMR (CDCl<sub>3</sub>): δ 36.32 (s, PCy<sub>3</sub>)

**Preparation of reaction mixture.** The ferrocene standard solution (100  $\mu\text{L}$ , 0.27 M, 0.027 mmoles) and the catalyst standard solution (400  $\mu\text{L}$ , 0.0061M, 0.0031 mmoles) were added to an NMR tube via syringe. The NMR tube was capped with a rubber septum cap. The standard monomer solution (500  $\mu\text{L}$ , 0.47 M, 0.188 mmoles) was added via syringe to the sealed NMR tube just before the tube was inserted into the NMR and the kinetics run begun.



**References**

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- (2) Nguyen, S. T.; Grubbs, R. H.; Ziller, J. W. *J. Am. Chem. Soc.* **1993**, *115*, 9858-9859.
- (3) Carraho, C. E., Jr. *Polymer Chemistry: An Introduction*, 4<sup>th</sup> ed; Marcel Dekkar, Inc.: New York, 1996.
- (4) France, M. B.; Alty, L. T.; Earl, T. M. *J. Chem. Ed.*, **1999**, *76*, 659-660.

## Chapter 3

### Initiation

## A. Introduction

UV-vis spectroscopy was used to study the kinetics of the initiation step of the ROMP reaction between Grubbs' catalyst (**4**) and the 7-oxanorbornene derivative **5** in  $\text{CHCl}_3$ . This form of spectroscopy was chosen to examine the initiation step of the reaction because the time scale was appropriate. Since initiation only takes approximately 5 minutes at room temperature, the spectra need to be taken at intervals of less than 30 seconds in order to obtain a sufficient number of data points for a linear regression. As the UV-vis spectrometer can take spectra every 0.5 seconds, temperatures above room temperature may be examined. The only constraint placed on the system was that the reactants had to have an absorption that decreased significantly as initiation occurred. Preliminary investigations revealed that the system has an absorption at 335 nm which fits these criteria.

Another advantage of using UV-vis spectroscopy was the ease with which the catalyst concentration could be determined at each time step. In UV-vis spectroscopy, the measurement of the absorbance at a given wavelength is proportional to the concentration of the compound according to the Beer-Lambert law

$$A = \epsilon cl \quad (3.1)$$

where  $A$  is the absorbance at a given wavelength,  $\epsilon$  is the molar extinction coefficient,  $c$  is the concentration of the compound, and  $l$  is the path length of the cell.<sup>1</sup> The molar extinction coefficient,  $\epsilon$ , can easily be calculated by taking a spectrum of a solution with a known concentration. For our system,  $\epsilon$  was calculated to be  $583 \pm 3 \text{ L}/(\text{mol}\cdot\text{cm})$ . Once  $\epsilon$  is known, the absorbance value can easily be used to track the decrease in monomer concentration over time. A program was designed using the kinetics portion of the HP

biochemical analysis package which measured the absorbance at 335 nm periodically for reactions run at 10 °C, 15 °C and 20 °C. Three replicate measurements were taken for the reaction at each temperature.

Since the initiation step of the polymerization is bimolecular in nature



the rate law for the initiation step must be second order, as was shown in part C of the introduction:

$$v = k[M][I] \quad (1.2)$$

The integrated form of this rate law is given by

$$kt = \frac{1}{[M]_o - [I]_o} \left\{ \ln \left( \frac{[I]_o}{[I]_o - x} \right) - \ln \left( \frac{[M]_o}{[M]_o - x} \right) \right\} \quad (3.2)$$

where  $M_0$  is the initial concentration of monomer,  $I_0$  is the initial concentration of unactivated catalyst and  $x$  is the extent of reaction, i. e., the difference between  $I_t$  and  $I_0$ .<sup>2</sup> A plot of the right side of equation 3.2 vs. time was used to calculate  $k_i$  for each run. The rate constants were then averaged for each temperature, and the Arrhenius equation (eq. 1.8) was used to determine the activation parameters  $E_a$  and  $\Delta S^\ddagger$  for initiation.

As with the examination of the rate constant of propagation, an obvious source of error was how to maintain consistent starting concentrations for each reactant over multiple runs. Indeed, this problem was amplified during the examination of the initiation, since, while the ratio of reactants was kept the same as in the propagation studies, the actual amounts of catalyst (0.25 mg) and monomer **5** (4.03 mg) had to be dramatically decreased in order to place the value of the absorbance at 335 nm within the

range the instrument could measure accurately. Thus, bulk standard solutions of each reactant were prepared and used throughout the kinetics experiments.

Although the main focus of these experiments was to determine the rate constants of initiation, an investigation into the mechanism of initiation was also conducted. Interest in the mechanism of the initiation was piqued when  $^1\text{H}$  NMR spectra taken after the reaction had run to completion revealed that the initial carbene peak at 19.99 ppm had turned into two peaks, one at 18.75 ppm and one at 18.2 ppm. This result was very much at odds with what had been reported in the literature. In the two cases where studies of the kinetics of polymerization by bisphosphine ruthenium catalysts **3** (R=Ph) and  $(\text{PPh}_3)_2\text{Cl}_2\text{Ru}=\text{CHPh}$  (**6**) had been conducted, only one carbene peak had been reported for the propagating alkylidene.<sup>3,4</sup> One possible explanation might be that the propagating species is a mixture of *cis* and *trans* forms, as Nguyen et al reported seeing two carbene peaks in a spectrum of a mixture of the *cis* and *trans* forms of **3** (R=Ph).<sup>5</sup> (In this context, *cis* refers to the conformation where one phosphine is equatorial and the other axial; in a *trans* conformation, both phosphines are axial). However, this is unlikely because catalyst **4** is in a pure *trans* form.<sup>4</sup> Another more likely explanation for this result was that one of the phosphines was dissociating from the catalyst to give two different active species, a monophosphine complex and a bisphosphine complex. Indeed, it has been contended that bisphosphine-Ru catalysts proceed along two different pathways in olefin metathesis reactions. It is thought that two activated species are created, one species where the monomer has displaced one of the phosphines, giving rise to a monophosphine 6-coordinate complex and a species where both phosphines remain attached.<sup>6, 7, 8</sup> This hypothesis was tested using  $^{31}\text{P}$  NMR, since, if the proposed two-pathway mechanism

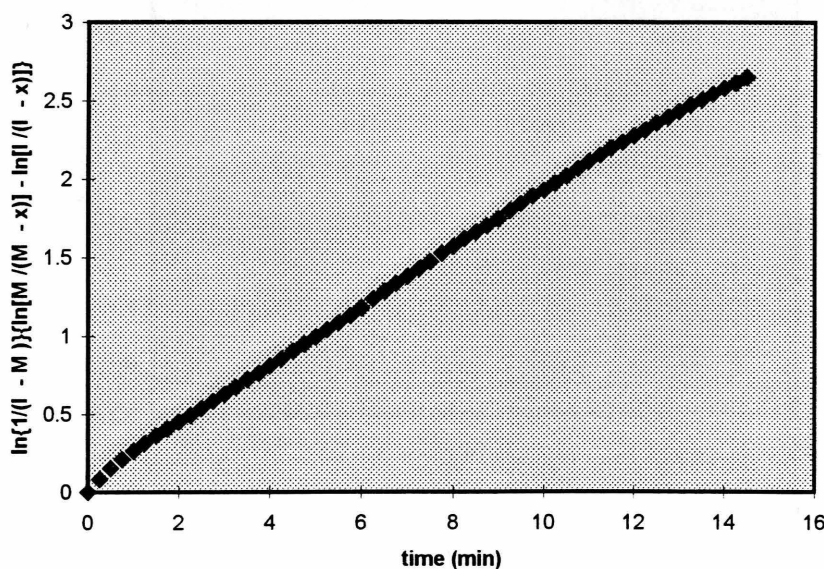
was operating in our system, three peaks might be expected – one for the bisphosphine complex, corresponding to the propagating carbene derived from the original catalyst, a monophosphine peak representing the catalyst/monomer complex, and a free tricyclohexyl phosphine peak at 11.81 ppm, arising from the dissociation of a phosphine from the bisphosphine species.

## B. Results /Discussion

The investigation of the initiation phase of the reaction was designed to determine the rate constant  $k_i$  and the overall kinetics of initiation. The temperature dependence of  $k_i$  was also illustrated and the resulting information used to determine the activation parameters of initiation. In addition, the relationship between  $k_i$  and  $k_p$  was examined to show that this system is in fact a living system.

The results obtained from the UV-vis investigation of the ROMP reaction between Grubbs' catalyst (4) and 7-oxanorbornene derivative 5 show that the initiation step of the reaction is second order in nature. When the right side of the integrated rate law (eq. 3.2) was plotted vs. time, the graphs were linear, with correlation coefficients greater than or equal to 0.998 (for example, see Graph 3.1).

**Graph 3.1: Determination of the Rate Constant  $k$  at 10 C**



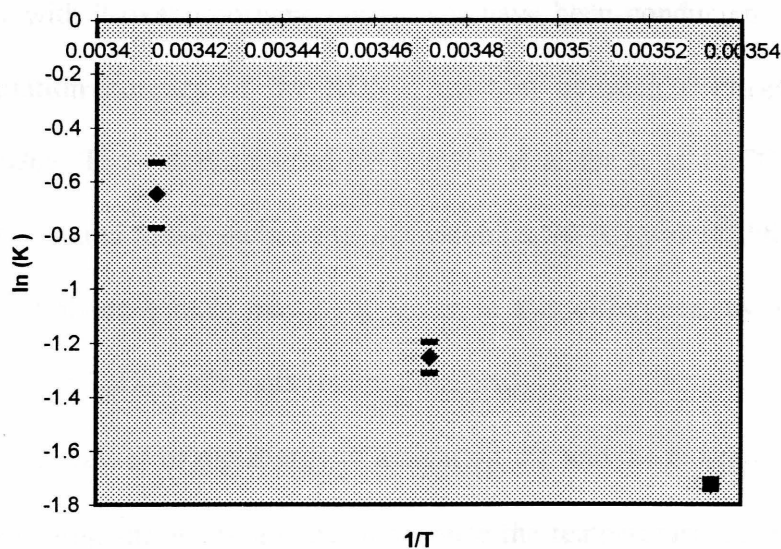
Three replicate measurements were performed at each of the three temperatures. The  $k$  values were averaged and standard deviations calculated. None of the measurements were found to be outliers when tested. The average rate constants that were thus obtained clearly demonstrate the temperature dependence of  $k_i$  as expected, since bimolecular reactions proceed faster at higher temperatures.

**Table 3.1:**  
**Temperature Dependence of the**  
**Rate Constant,  $k_i$**

<u>Temperature (K)</u>	<u><math>k_i</math> (mol/L·min)</u>	<u>Standard Deviation</u>
283	0.178	0.0033
288	0.29	0.016
293	0.52	0.064

While only three data points were obtained, the change over 5° intervals the linearity of  $k_i$  when graphed against  $1/T$  in the Arrhenius plot corresponds to an R value of 0.997.

**Graph 3.2: Arrhenius Plot**





Error analysis was performed on this data by examining the standard error of  $k$ , as given by the linear regression data. The standard errors were compared both within and across temperatures, and their averages and standard deviations calculated (Table 3.2). The error was fairly constant within temperature groupings. There was a slight increase of approximately 0.5% for each five degree interval, but the errors remained small; the largest, at 20°C, was only 1.44%. This pattern of increases in the standard error was also seen during investigations of propagation (see Chapter 2).

**Table 3.2: Standard Error of the Slope**

<u>Temperature (K)</u>	<u>Standard Error of the Slope</u>	<u>Standard Deviation</u>
283	0.0008	0.0003
288	0.0027	0.0002
293	0.0076	0.0001

To our knowledge, no investigations on the kinetics of initiation of Grubbs' catalyst with 7-oxanorbornene derivatives have been conducted. Data was gathered on the initiation kinetics of the ROMP reaction between  $(PPh_3)_2Cl_2Ru=CHPh$  (**6**) and norbornene. The value obtained by Schwab et al for  $k_i$  at 17 °C was 0.0115 L/mol·s.<sup>4</sup> When translated to the same units, our value (at 20 °C) was slightly smaller, at 0.008731 L/mol·s. Solvent effects may be a factor in this difference, as Schwab's reaction was conducted in  $C_6D_6$  while ours was run in  $CHCl_3$ .

The values of the energy of activation,  $E_a$ , and the entropy of initiation,  $\Delta S^\ddagger$ , were obtained using the Arrhenius equation once the temperature dependence of  $k_i$  had been shown. The value of  $\Delta S^\ddagger$  was found to be -53.95 cal/mol;  $E_a$  was found to be 4.92 Kcal/mol. More data points are needed if a reliable error value for these parameters is to

be obtained.  $\Delta S^\ddagger$  is in the appropriate range and has the correct sign, as  $\Delta S^\ddagger$  is typically negative for a bimolecular system. As with the  $E_a$  for propagation, the  $E_a$  for initiation is quite close to values cited for the initiation of free radical polymerizations, which have been reported as ranging from 4-10 Kcal/mol.<sup>9</sup>

After  $k_i$  had been calculated, an analysis of the rate constants was conducted to show that the ROMP reaction of Grubbs' catalyst with 7-oxanorbornene derivative **5** is, in fact, a living system. As has been previously mentioned, for a system to be considered living, the rate of initiation must be greater than or equal to the rate of propagation. It is necessary to understand that it is the rates that must have this relationship, not the rate constants. The rates are given by equations 1.2 and 1.3. For purposes of comparison, the time scales of initiation and propagation, denoted  $\tau_i$  and  $\tau_p$ , were determined. Roughly, the time scale is the length of time it takes for the concentrations of initiating species (starting alkylidene **4**) and monomer, respectively, to drop to 37% of their initial value. The time scales were calculated using the rate constants at 20 °C ( $k_i = 0.524$  mol/L·min;  $k_p = 2.83$  mol/L·min) and assuming polymerization conditions where the concentration of monomer is far greater than the concentration of catalyst. This assumption is reasonable because, for our system, the initial concentration of monomer,  $[M]_0$ , was 0.47 M and the initial concentration of catalyst,  $[I]$ , was 0.0061 M. Under these conditions, the initiation step may be presumed to be pseudo-first order since even the complete initiation of the catalyst leaves the monomer concentration unchanged, since the catalyst concentration is so much smaller than the monomer concentration. Thus,  $\tau_i$  and  $\tau_p$  may be derived in the following way.

If initiation is presumed to be first order, then the rate law for initiation becomes

$$v_i = -\frac{d[I]}{dt} = k_i[I][M] \approx k_i[I][M]_0$$

which integrates to

$$[I] = [I]_0 e^{-k_i[M]_0 t} = [I]_0 e^{-t/\tau_i}$$

where  $\tau_i$  is  $1/k_i[M]_0$ . A similar analysis may be conducted for the pseudo-first order propagation step. This leads to

$$v_p = -\frac{d[M]}{dt} = k_p[M_n][M] \approx k_p[I]_0[M]$$

assuming that the concentration of growing chains ( $M_n$ ) is equal to the initial concentration of catalyst. This equation integrates to

$$[M] = [M]_0 e^{-k_p[I]_0 t} = [M]_0 e^{-t/\tau_p}$$

where  $\tau_p$  is  $1/k_p[M]_0$ . Using the concentrations and rate constants specified above,  $\tau_i = 4.1$  minutes and  $\tau_p = 57.8$  minutes. Thus, under polymerization conditions, the initiation step is much faster than the propagation step, despite the relative values of the rate constants  $k_i$  and  $k_p$ . Therefore, the ROMP reaction of Grubbs' catalyst with the 7-oxanorbornene derivative **5** is clearly a living system.

The  $^{31}\text{P}$  studies, conducted to investigate the reason for the two carbene peaks in the  $^1\text{H}$  NMR spectra, were inconclusive as to whether or not phosphine dissociation was occurring during the reaction. Upon activation, the single  $^{31}\text{P}$  peak at 36.32 ppm (Figure 1) was shifted downfield slightly and appeared as three major peaks at 37.18 ppm, 37.65 ppm, and 38.12 ppm, and one minor peak at 38.68 ppm (Figure 2). These peaks appeared in spectra taken at 15, 30 and 45 minutes after activation, prior to the cessation of propagation. It is possible that the three major peaks represent catalyst-monomer

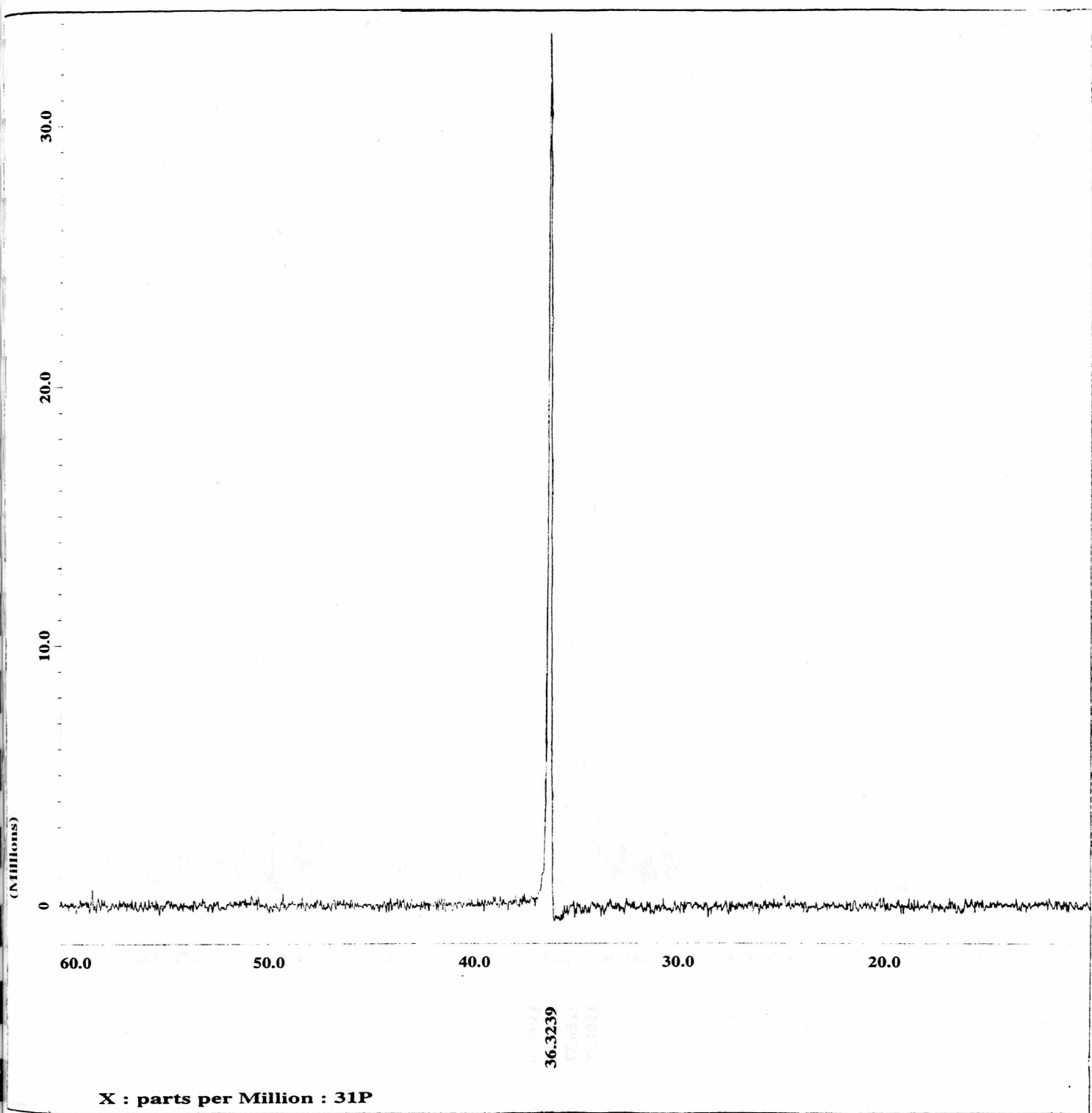


Figure 1:  $^{31}\text{P}$  NMR spectrum of Grubbs' catalyst prior to initiation

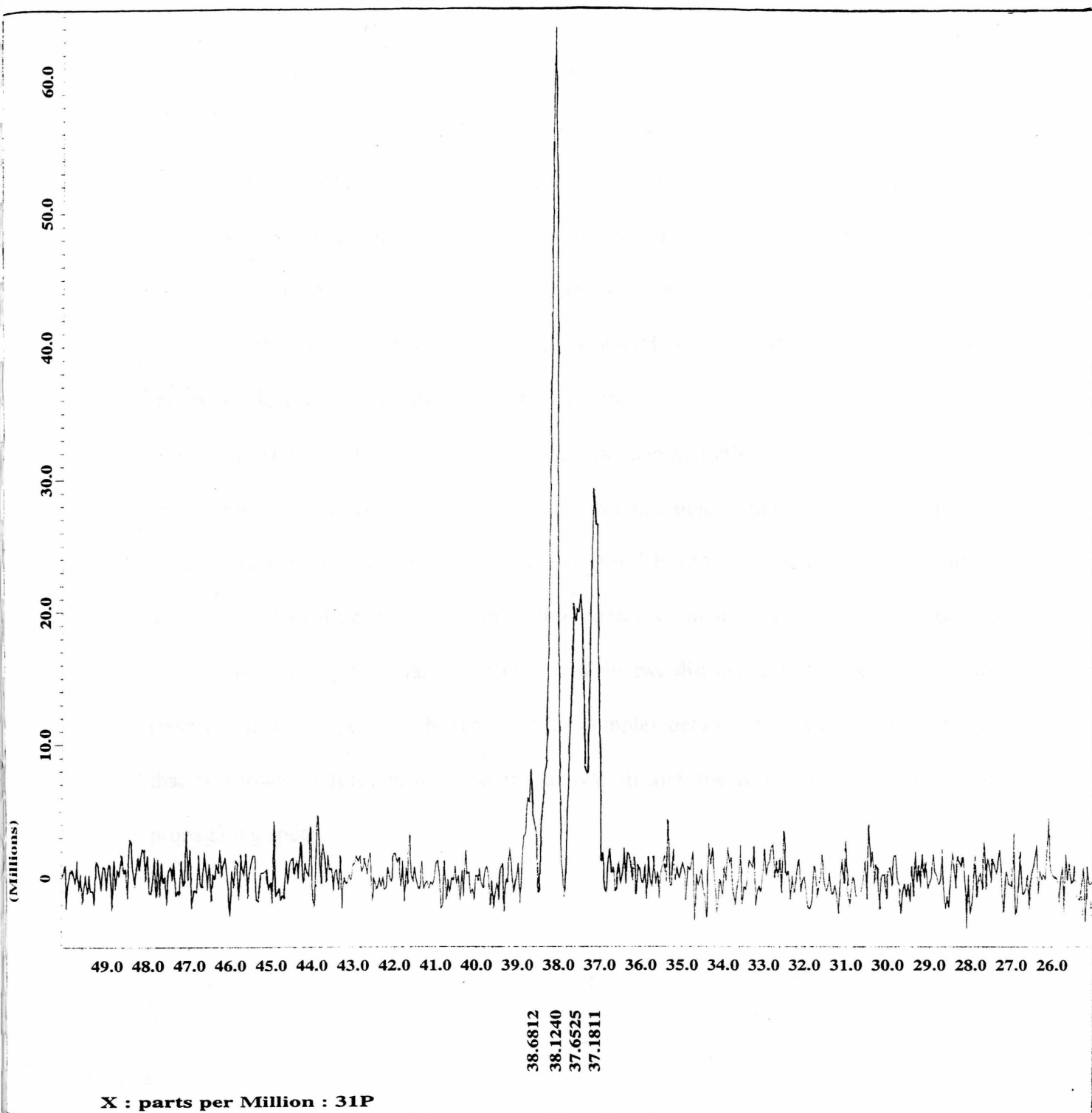


Figure 2:  $^{31}\text{P}$  NMR spectrum of Grubbs' catalyst at 45 minutes after initiation

complexes, although it is impossible to determine if all three complexes are active or not. No free phosphine was observed, which would suggest that no phosphine dissociation occurred. However, one theory advanced by Dias et al, whose  $^{31}\text{P}$  NMR spectra of olefin metathesis reactions using catalysts **3** and **4** also failed to show free phosphine, is that the dissociation might be occurring in only a very small percentage of the catalyst (no more than 5%). If this is the case, free phosphine would not be visible via  $^{31}\text{P}$  NMR. This theory would explain the observation by Dias that the addition of free phosphine to the reaction mixture slows the rate of the reaction considerably.<sup>7</sup> One problem with this theory, however, is that if the free phosphine the monophosphine complex were present in such small amounts that they were not visible in  $^{31}\text{P}$  NMR, one would not expect to see a peak corresponding to a monophosphine complex in the  $^1\text{H}$  NMR either. Another explanation that might explain the presence of the two distinct carbene peaks in  $^1\text{H}$  NMR spectra is that one peak might represent the complex between the catalyst and monomer that is known to form prior to actual activation and the other represents the actual propagating species.

### C. Future Work

There are several areas of the ROMP reaction between Grubbs' catalyst and the 7-oxanorbornene derivative **5** which need further investigation. First of all, it would be desirable to determine the  $k_i$  at additional temperatures. However, the Peltier temperature controller has proven unable to cool the reaction below 10 °C, preventing expansion of the temperature range in that direction. It may be possible to determine  $k_i$  at 25 °C and 30 °C, although the speed of initiation at such temperatures may be too fast for even the UV-vis to track reliably. If this is the case, additional  $k_i$  values for intermediate temperatures between 10 °C and 20 °C, such as 12.5 °C, 17.5 °C and 22.5 °C should be obtained. While this would not provide a larger range of temperatures for comparison between  $k_i$  and  $k_p$ , it would allow for the refinement of the Arrhenius plot and a more accurate determination of the energy of activation,  $E_a$ , and the entropy of initiation,  $\Delta S^\ddagger$ .

Another area for continued investigation is the presence of the two carbene peaks in the  $^1\text{H}$  NMR, as there are some observations pertaining to other systems discussed in the literature that could be investigated on our own reaction. For example, the carbene region in polymerizations of norbornene with Grubbs' catalyst, a system which has been well characterized, might be observed.<sup>4</sup> Also, the peaks could be observed across a range of temperatures; if they merge at higher temperatures, it might be a sign that they result from a mixture of *trans* and *cis* isomers of the active species being present in the reaction mixture (the merging resulting from rapid equilibration of the two species at higher temperatures).

Finally, as we believe that the ROMP of Grubbs' catalyst with the 7-oxanorbornene derivative used in this study is an example of a living polymerization, the

molecular weight (MW) and polydispersity index should be determined using gel permeation chromatography (GPC). Since one of the criteria for living systems is that they give rise to low polydispersities, information that our system fulfills this requirement would serve to further corroborate the results of the kinetic investigations.



## **D. Experimental**

**General.** Solids and solutions were transferred and stored in a nitrogen-filled Vacuum Atmospheres Nexus One glove box. All standard solutions were stored at  $-32^{\circ}\text{C}$  in the same nitrogen-filled Vacuum Atmospheres glove box.

**Instrumentation.** UV-vis spectra were recorded on a Hewlett Packard Vectra XA with an HP biochemical analysis package and an HP Peltier temperature controller. A kinetics program was created that measured the absorbance of the solution at 335 nm at preset intervals ranging from 5 to 15 seconds corresponding to  $10^{\circ}\text{C}$ ,  $15^{\circ}\text{C}$ , and  $20^{\circ}\text{C}$ . (Table 3).  $^{31}\text{P}$  and  $^1\text{H}$  NMR spectra were recorded on a JEOL Eclipse + NMR spectrometer operating at 400 MHz.

**Table 3.3: Time Intervals Between Spectra at Various Temperatures**

<u>Temperature (<math>^{\circ}\text{C}</math>)</u>	<u>Time Interval (min)</u>
10	15
15	10
20	5

**Materials.**  $(\text{PCy}_3)_2\text{Cl}_2\text{Ru}=\text{CHPh}$  (**4**) packaged under argon was purchased from Strem and used as received. Exo, exo-5,6-bis(methoxycarbonyl)-7-oxabicyclo[2.2.1]hept-2-ene was prepared by the Chem 242 classes as described by the literature procedure.<sup>10</sup> The purity of 7-oxanorbornene derivative **5** was checked by  $^1\text{H}$  NMR; the compound was recrystallized from methanol when necessary. Anhydrous  $\text{CDCl}_3$  packaged under

nitrogen was purchased from Aldrich and used as received. Anhydrous  $\text{CHCl}_3$  packaged under nitrogen was purchased from Aldrich and used as received.

**Preparation of 0.47 M monomer standard solutions.** Exo, exo-5,6,-bis(methoxycarbonyl)-7-oxabicyclo[2.2.1]hept-2-ene (1 g) was measured into a 10 mL volumetric flask. The flask was filled to the line with  $\text{CHCl}_3$ , capped, and shaken vigorously. The solution was transferred to a capped vial and stored under  $\text{N}_2$  at  $-32\text{ }^\circ\text{C}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  6.42 (s, 2H,  $\text{HC}=\text{}$ ), 5.22 (s, 2H,  $\text{CHOCH}$ ), 3.66 (s, 6H,  $\text{OCH}_3$ ), 2.78 (s, 2H,  $\text{CHCO}_2\text{Me}$ )

**Preparation of 0.0061 M catalyst standard solutions.**  $(\text{PCy}_3)_2\text{Cl}_2\text{Ru}=\text{CHPh}$  (50 mg) was added to a 10 mL volumetric flask, which was filled to the line with  $\text{CHCl}_3$ . The solution was transferred to a capped vial and stored under  $\text{N}_2$  at  $-32\text{ }^\circ\text{C}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  19.99 (s,  $\text{Ru}=\text{CH}$ ), 8.44-7.33 (m,  $\text{C}_6\text{H}_5$ ), 2.06 (m,  $\text{P}(\text{C}_6\text{H}_{11})_3$ ), 2.16 (m,  $\text{P}(\text{C}_6\text{H}_{11})_3$ ), 1.77-1.18 (m,  $\text{P}(\text{C}_6\text{H}_{11})_3$ ).  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  36.32 (s,  $\text{PCy}_3$ )

**Preparation of reaction mixture for UV-vis spectroscopy.** The catalyst standard solution (50  $\mu\text{L}$ , 0.0061M,  $3.05\text{E-}4$  mmol) was added to a quartz cell ( $l = 0.2$  cm) and diluted with 0.69 mL  $\text{CHCl}_3$ . The cell was capped with a septum top. The standard monomer solution (40  $\mu\text{L}$ , 0.47M, 0.188 mmol) was added via syringe to the sealed cell just before it was inserted into the UV-vis spectrometer and the kinetics run begun.

**Preparation of reaction mixture for  $^{31}\text{P}$  NMR.**  $(\text{PCy}_3)_2\text{Cl}_2\text{Ru}=\text{CHPh}$  (15 mg, 0.018 mmol) was measured into an NMR tube and dissolved in 0.5 mL  $\text{CHCl}_3$ . The 7-oxanorbornene derivative **5** (240 mg, 1.12 mmol) was measured into a vial and dissolved in 0.5 mL  $\text{CHCl}_3$ . After an initial  $^{31}\text{P}$  NMR spectrum of the catalyst solution had been obtained, the 7-oxanorbornene derivative **5** was added to the catalyst solution via syringe.  $^{31}\text{P}$  NMR spectra were then taken at 15, 30 and 45 minutes after the start of the reaction.  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  38.68, 38.12, 37.65, 37.18.

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