taken into account that up to 30% of the initial radical pairs undergo exit at room temperature in their system. We plotted our values of k_{decay} in the Arrhenius fashion and also found that no curvature was detectable. Thus, failure to take the exit fraction into account may give misleading information regarding the geminate reaction, especially at high temperatures where the escape can be much greater than 30%.

Conclusion

In summary, the geminate and exit rate constants for decay of triplet-derived radical pairs in micelles are strongly influenced by micellar size. Our k_- data suggest that the loss of geminate character by the EO$^\bullet$/BTK$^\bullet$ neutral radical pair is due to exit of the ketyl radical from the micelles into the bulk aqueous environment. The activation energy for this process is around 6–7 kcal/mol and should probably be interpreted as representing the enthalpic barrier due to crossing of the micelle–water interface. In addition, the large negative entropy of activation for exit gives some insight into the nature of the transition state and provides an illustration of the hydrophobic effect, suggesting that entropy plays a significant role in holding the ketyl radical in the micellar environment. Thus, the free energy barrier to ketyl exit also has a large entropic contribution.

The rate constant for geminate reaction, k_{gem}, is also controlled by the micellar size which has been changed by modifying the surfactant's structure, by addition of salts, and by changing the temperature. The values of k_{gem} are interpreted as depending on the product of the degree of singlet character (f_s) and the frequency of reencounter of the geminate radical partners (k_e). While chemical reaction requires singlet character and contact distances, spin evolution requires large separations so that exchange interactions can become comparable or smaller than hfc interactions; as a result, diffusion and spin evolution are coupled processes. The values of k_{gem} are largely dependent on the interplay of these parameters.

Acknowledgment. Thanks are due to Mr. S. E. Sugamori for technical assistance. This work was supported by an operating grant (J.C.S.) from the Natural Sciences and Engineering Research Council of Canada and by a grant (K.U.I.) from the Association for International Cancer Research. We are specially grateful to Professor G. L. Closs for a most valuable discussion during his 1989 visit to Ottawa which led us to propose[24] the model used here.

Registry No. EOH, 59-02-9; EO$^\bullet$, 109954-22-5; SDS, 151-21-3; SDecS, 142-87-0; butyrophenone, 495-40-9; sodium chloride, 7647-14-5.

Living Ring-Opening Metathesis Polymerization of Cyclobutene: The Thermodynamic Effect of a Reversibly Binding Ligand

Zhe Wu, David R. Wheeler, and Robert H. Grubbs*

Contribution No. 8440 from the Arnold and Mabel Beckman Laboratories of Chemical Synthesis, California Institute of Technology, Pasadena, California 91125. Received May 3, 1991

Abstract: Trimethylphosphine, PMe_3, is shown to bind reversibly to the alkylidene complex $W(CH\text{-}t\text{-}Bu)(NAr)(O\text{-}t\text{-}Bu)_2$ (**1**, Ar = 2,6-diisopropylphenyl), and the binding constants at several temperatures are measured ($\Delta H° = -15.7$ kcal/mol, $\Delta S° = -40.7$ eu). In the presence of PMe_3, **1** catalyzes the living ring-opening metathesis polymerization (ROMP) of cyclobutene to yield polybutadiene with a polydispersity index (PDI) as low as 1.03, based on gel permeation chromatography versus polystyrene standards. The polymerization in the presence of PMe_3 is first order in monomer and catalyst concentrations with $\Delta\Delta G^{\ddagger}_{273K} = 19.8$ kcal/mol, $\Delta\Delta H^{\ddagger}_{(p)} = 20.8$ kcal/mol, and $\Delta\Delta S^{\ddagger}_{(p)} = 4$ eu. The observed rate of initiation of the polymerization is much greater than the rate of propagation. In the absence of trimethylphosphine, the polydispersity of the polymer produced with **1** is broader (PDI > 2) due to the rate of propagation being much greater than that of initiation and the existence of chain termination. This difference is attributed to the fact that PMe_3 binds more strongly to the propagating alkylidene complex than to the more sterically bulky initiating neopentylidene.

Introduction

Living polymerizations provide control of polymer properties on a molecular level, thus enabling the facile preparation of block copolymers.[1] The recent syntheses of a number of well-defined transition-metal alkylidene and metallacyclobutane complexes have resulted in the living ring-opening metathesis polymerization (ROMP) of norbornene and some of its derivatives to give essentially monodispersed polymers.[2] Since relief of ring strain is the driving force for these polymerizations,[3] it should be possible to ring open other highly strained olefins, such as cyclobutene, under the proper conditions to obtain polymers of low polydispersity. Perfectly linear, monodispersed polybutadiene (ring-opened polycyclobutene) is needed as a source of linear, monodispersed polyethylene. Presently, polyethylene of low polydispersity is produced by the hydrogenation of 1,4-polybutadiene prepared by the anionic polymerization of 1,3-butadiene. This approach results in branched polyethylene, since the polybutadiene produced by this technique contains C_2 branches as a result of low levels of 1,2-polymerization of the butadiene. Linear, low polydispersity polyethylene is an extremely important synthetic goal and provides the challenge of preparing essentially monodispersed, linear polybutadiene by the ROMP of cyclobutene.

In previous efforts to polymerize cyclobutene using well-defined titanium and tungsten metathesis catalysts, we obtained linear polybutadiene with broad polydispersities and high molecular weights which were much greater than expected from the monomer-to-catalyst ratio.[4] During the polymerization, only a small

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(1) Noshay, A.; McGrath, J. E. *Block Copolymers*; Academic: New York, 1977.

(2) Gilliom, L. R.; Grubbs, R. H. *J. Am. Chem. Soc.* **1986**, *108*, 733–742. (b) Schrock, R. R. *Acc. Chem. Res.* **1990**, *23*, 158. (c) Grubbs, R. H.; Tumas, W. *Science* **1989**, *243*, 907. (d) Johnson, L. K.; Virgil, S. C.; Grubbs, R. H. *J. Am. Chem. Soc.* **1990**, *112*, 5384. (e) Wallce, K. C.; Schrock, R. R. *Macromolecules* **1987**, *20*, 450–452. (f) Murdzek, J. S.; Schrock, R. R. *Macromolecules* **1987**, *20*, 2640–2642. (g) Schrock, R. R.; Krouse, K.; Feldman, J.; Murdzek, J. S.; Yang, D. C. *J. Mol. Catal.* **1988**, *46*, 243. (h) Bazan, G. C.; Khosravi, E.; Schrock, R. R.; Feast, W. J.; Gibson, V. C.; O'Regan, M. B.; Thomas, J. K.; Davison, W. M. *J. Am. Chem. Soc.* **1990**, *112*, 8378–8387.

(3) Ivin, K. J. *Olefin Metathesis*; Academic Press: London, 1983.

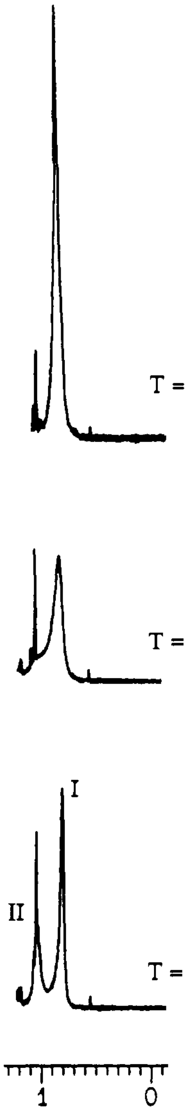


Figure 1. Variable-temperature ^1H NMR spectra in the region of bound and free PMe_3.

amount of catalyst was activated as determined by NMR spectroscopy, indicating that the rate of propagation was much greater than the rate of initiation ($k_p/k_i \approx 10^3$ at -60 °C).[5] In addition, ROMP of simple cyclic olefins, in contrast to bicyclic olefins, results in a significant concentration of cyclic oligomers by "back-biting" reactions. Since polycyclobutene is structurally equivalent to polycyclooctadiene, it is anticipated that cyclic oligomers will also be formed in these systems.

The polymerization of cyclobutene has provided an excellent case for the study of the details of the effect of Lewis bases on ring-opening metathesis polymerizations. This study employs the tungsten alkylidene complex W(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ (**1**, Ar = 2,6-diisopropylphenyl), which was developed by Schrock and Grubbs and their co-workers as an active catalyst for the living ring-opening metathesis polymerization of norbornene.[6a] Attenuation of the rate of polymerizations catalyzed by **1** has been achieved with the addition of strong Lewis bases that reversibly bind and deactivate the propagating alkylidene complexes. Tetrahydrofuran has been used to slow the polymerization of cyclooctatetraene sufficiently for fabrication.[7a] It was also demonstrated that THF modified the reactivity of the propagating species so that less back-biting resulted.[7b] In the polymerization of acetylene catalyzed by **1**, quinuclidene not only bonded to and modified the reactivity of the propagating species but also appeared to change the ratio of the propagation and initiation rates.[7c] Although some phosphine adducts of certain tungsten[7d] and titanium[7e] alkylidene complexes that are metathesis catalysts have been prepared, the effect of bound phosphine on the polymerization of strained cyclic olefins has not been reported. In this paper, we report an investigation of the reversible binding of PMe_3 to catalyst **1**. This investigation has enabled the development of conditions for the living polymerization of cyclobutene, the preparation of polymers with narrow polydispersities and a clarification of the role of Lewis bases in the control of the reactivity of ROMP catalysts.

Table I. Binding Constants of PMe_3 to **1** at Different Temperatures[a]

temp, °C	K_f, M^{-1}	temp, °C	K_f, M^{-1}
−10	16977	18	909
0	5308	25	536
10	1888	40	127

[a] $\Delta H° = -15.7 \pm 1.0$ kcal/mol, $\Delta S° = -40.7 \pm 3.7$ eu.

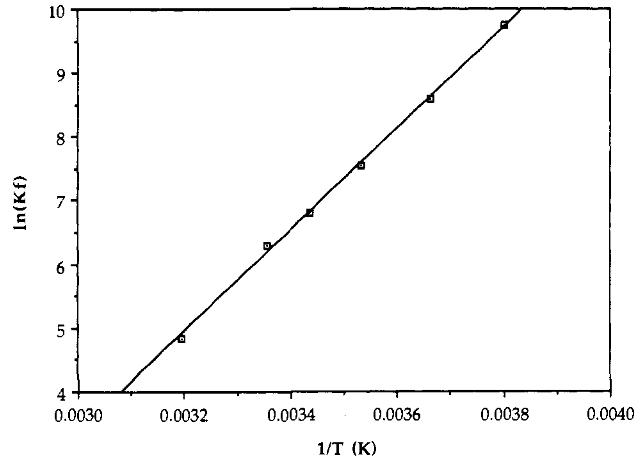
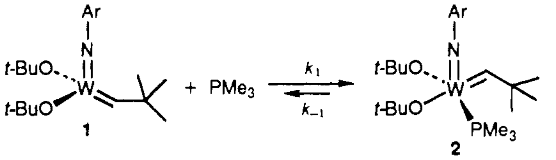


Figure 2. The Arrhenius plot for the binding constants.

Results and Discussion

Weak Lewis Bases. In the absence of Lewis bases, the polymerization of cyclobutene by **1** gave polymers with broad polydispersities (PDI > 2).[4] The polymerization of cyclobutene was slowed in the presence of a number of weak Lewis bases, such as THF, 2-Me-THF, pyridine, diphenylmethylphosphine, and quinuclidine. However, the reaction was not controlled sufficiently to give the desired polydispersity control, as polydispersities greater than 1.5 were obtained.

Reversible Binding of PMe_3 to 1. Upon addition of 1 equiv of PMe_3 to a 0.021 M toluene solution of **1**, both the bound **2** and free **1** neopentylidene complexes are observed at room temperature by ^1H NMR spectroscopy. Variable-temperature NMR spectra indicate that the rate of phosphine exchange (eq 1) is slow com-



(1)

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(4) (a) Gilliom, L. R. Ph.D. Thesis, California Institute of Technology, 1986. (b) Wu, Z.; Grubbs, R. H. Unpublished results.

(5) Gold, L. *J. Chem. Phys.* **1958**, *28*, 91–99. k_p/k_i can be estimated from monomer and initiator concentrations.

(6) (a) Schrock, R. R.; Feldman, J.; Cannizzo, L. F.; Grubbs, R. H. *Macromolecules* **1987**, *20*, 1169–1172 and references therein. (b) The polydispersity measurement does not include the higher molecular weight shoulder.

(7) (a) Klavetter, F.; Grubbs, R. H. *J. Am. Chem. Soc.* **1988**, *110*, 7807. (b) Klavetter, F.; Grubbs, R. H. Manuscript in preparation. (c) Schlund, R.; Schrock, R. R.; Crowe, W. E. *J. Am. Chem. Soc.* **1989**, *111*, 8004. (d) Schrock, R. R.; Depue, R. T.; Feldman, J.; Schaverien, C. J.; Dewan, J. C.; Liu, A. H. *J. Am. Chem. Soc.* **1988**, 110, 1423–1435. (e) Gilliom, L. R.; Grubbs, R. H. *Organometallics* **1986**, *5*, 721. (f) At higher temperature only two triplets are observed at the above resonances because the exchange rate of phosphine becomes faster.

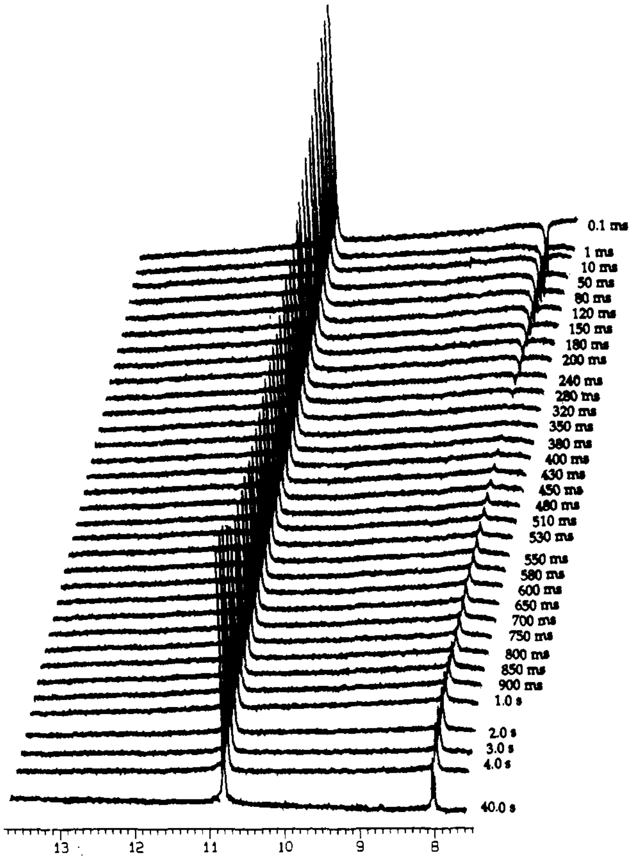

Figure 3. Inversion spin transfer for a mixture of **1** and **2** at 25 °C. Each spectrum consists of 8 scans: delay time τ_2 after selective inversion of the peak of **1** is shown. τ_1 = 0.444 ms. The pulse sequence $\pi/2_x-(\nu_1)-\tau_1-\pi/2_{\pm x}-\tau_2-\pi/2_{\pm x,\pm y}$-acquisition is used.

pared to the NMR time scale at and below room temperature. Figure 1 shows that free phosphine peak I (0.79 ppm) and bound phosphine peak II (1.01 ppm) start to coalesce as the temperature increases from 0 to 60 °C. The binding constant K_f[8] can be determined from

$$K_f = [\mathrm{WP}]/([\mathrm{W}][\mathrm{P}]) \qquad (2)$$

where [WP] = concentration of bound catalyst, [W] = concentration of free catalyst, and [P] =concentration of free phosphine. Binding constants at several temperatures are listed in Table I. The Arrhenius plot for binding of PMe_3 to **1** shows a positive linear slope with excellent correlation (ρ = 0.999, Figure 2). As expected, the binding is exothermic ($\Delta H°$ = −15.8 ± 1 kcal/mol) with a large negative entropy factor ($\Delta S°$ = −40.7 ± 3.7 eu).

At room temperature, the rate of complex formation k_1 and dissociation k_{-1} can be measured by a magnetization transfer experiment (Figure 3)[9] and are determined to be 358.7 $M^{-1}\ s^{-1}$ and 0.595 s^{-1}, respectively. The equilibrium constant (K_f = 603) determined from the ratio of these rate constants is within experimental error of the equilibrium constant (K_f = 536) measured directly by ^1H NMR spectroscopy.

Polymerization of Cyclobutene in the Presence of PMe_3. In the presence of excess PMe_3, **1** catalyzes the polymerization of cyclobutene in toluene or benzene at room temperature. Precipitation in methanol and drying in vacuo affords a sticky polymer in greater than 85% isolated yield. ^{13}C NMR spectroscopy indicates that clean 1,4-polybutadiene is obtained with a blocky distribution of cis and trans double bonds[10] and a cis-to-trans ratio of 3.7:1. There is no evidence of branching by NMR or IR spectroscopy.

As detailed below, molecular weight analyses and NMR spectroscopic data indicate that the polymerization is living. For example, the molecular weights of polybutadiene (as determined by gel permeation chromatography versus polystyrene standards) obtained from polymerizations with varying equivalents of cyclobutene are given in Table II. In all cases, the molecular weight is proportional to the monomer-to-catalyst ratio and narrow polydispersities are obtained (Figure 4). All samples prepared with

Table II. Molecular Weight Analysis of Polymers

equiv of cyclobutene	M_n(theory)	M_n(GPC)[a]	M_n(GPC)[b]	M_w[a]	PDI
20	1082	3000	1600	3200	1.07[c]
50	2705	6900	3800	7100	1.03[c]
100	8120	12200	6900	16200	1.04[c]
200	10820	23200	12800	23900	1.03[c]
1500	81150	147000	82000	162100	1.1[d]
200	10820	24000	13000	24500	1.02[e]

[a] Based on calibration with polystyrene standards. [b] Based on calibration with polybutadiene standards (from Polyscience). A correction factor of 0.55 was calculated (ref 20). [c] Polymerization was performed in the presence of 10 equiv of trimethylphosphine at room temperature. [d] Polymerization was performed at 0 °C in the presence of 75 equiv of dimethylphenylphosphine. [e] Polymerization was performed by using catalyst **3** in the presence of 10 equiv of PMe_3 at room temperature.

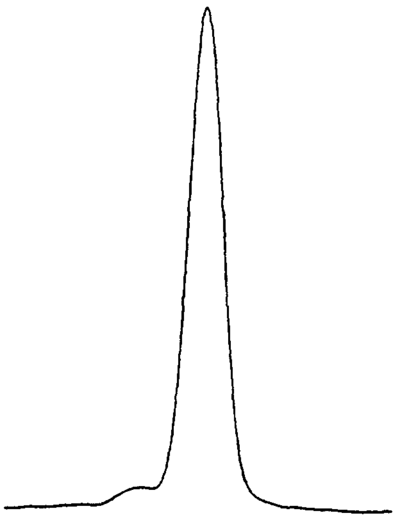

Figure 4. GPC trace of the polymer produced by ROMP of cyclobutene (200 equiv), using catalyst **1** in the presence of PMe_3 (10 equiv).

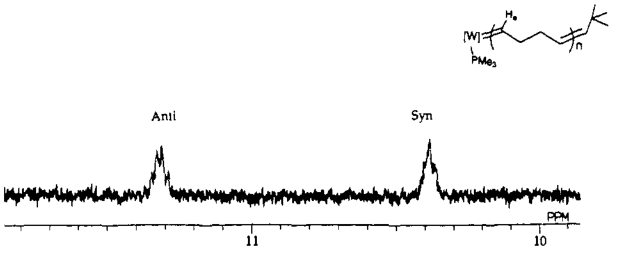

Figure 5. The ^1H NMR spectrum (alkylidene region) of living polybutadiene (20 equiv of cyclobutene).

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[8] The ratio [WP]/[W] can be accurately determined by ^1H NMR integration. Concentration of the unbound phosphine can be calculated using the equation

$$[P] = [P_0] - [C_0]/\{1 + [W]/[WP]\}$$

where $[P_0]$ and $[C_0]$ are the initial phosphine and catalyst concentrations.

[9] (a) Forsen, S.; Hoffman, R. A. *Acta Chem. Scand.* **1963**, *17*, 1787. (b) Oki, M. *Application of Dynamic NMR Spectroscopy to Organic Chemistry*; VCH: Deerfield Beach, FL, 1985. (c) Cowley, A. H.; Mills, J. L. *J. Am. Chem. Soc.* **1985**, *107*, 2670–2682. (d) Doherty, N. M.; Bercaw, J. E. *J. Am. Chem. Soc.* **1985**, *107*, 1670–2682. (e) Robinson, G.; Kuchel, P. W.; Cheynan, B. E. *J. Magn. Reson.* **1985**, *63*, 314–319.

[10] Further analysis of the ^{13}C NMR spectral data shows that $\gamma_t\gamma_c$ = 4.97. Higher cis contents are observed for polybutadiene obtained in the absence of PMe_3 and in the presence of weaker bases, such as THF.

these tungsten complexes show a small, high molecular weight peak, as reported in the first paper in this area.[6]

Reaction of 1 equiv of cyclobutene with **1** in the presence of 5 equiv of PMe_3 resulted in initiation of 66% of the total catalyst.[11] With 20 equiv of cyclobutene, ^1H NMR spectroscopy shows that all of the initial alkylidene is converted to the propagating alkylidene. In the alkylidene region, only two multiplets[7d] at 11.31 and 10.38 ppm are observed throughout the polymerization by ^1H NMR spectroscopy for H_α of the alkylidene ligand (Figure 5) and are attributed to the presence of two isomers (syn and anti) of the propagating species.[7c] The syn isomer (upfield) is observed to form first and a ratio of 1:1 for the two isomers is reached at equilibrium. End-capping of the living polymer chain is accomplished by addition of excess benzaldehyde or acetone at room temperature.[12]

The propagating alkylidene is greatly stabilized by PMe_3. A sealed NMR tube containing 75 equiv of cyclobutene and 5 equiv of PMe_3 was monitored periodically by ^1H NMR spectroscopy. No change in the amount of propagating carbene was evident after storing the reaction mixture for 2 weeks at room temperature. After 2 months at room temperature, only 50% of the propagating carbene had disappeared, which may be due to either the slow decomposition of the catalyst itself or to the reaction of the catalyst with small amounts of impurities that were not detected by ^1H NMR spectroscopy.

Kinetic Data for Cyclobutene Polymerization. The kinetic scheme for the polymerization of cyclobutene in the presence of PMe_3 is shown in Figure 6. In the proposed mechanistic scheme, a rapid equilibrium is first established between the phosphine-ligated and free neopentylidene complexes (eq 5). Cyclobutene reacts with 1 equiv of free neopentylidene to form the propagating alkylidene (eq 6), which is then captured by PMe_3 (eq 7) to form the inactive phosphine adduct. Loss of phosphine regenerates the propagating alkylidene to continue the polymerization (eq 8). By ^1H NMR spectroscopy, it is observed that the initial neopentylidene is completely consumed before the propagating alkylidene begins to react with cyclobutene to form polymer.[13a]

Derivation of the kinetic expressions for the initiation and propagation reactions is possible based upon the following observations and assumptions. First, since the large ring strain of cyclobutene is the driving force for the ring-opening process, the reactions shown in eqs 6 and 8 are irreversible and the rate of backbiting to form cyclooctadiene is negligible compared to the rate of propagation. Second, it is reasonable to assume that all of the propagating alkylidenes have the same reactivity (k_p), irrespective of the polymer chain length. Third, experimental results at room temperature and below show that the association rate of PMe_3 is very large (i.e., $k_1 \gg k_{-1}$ and $k_3 \gg k_{-3}$). Therefore, it is reasonable to assume that the concentration of free catalysts in the system reaches a steady state during the polymerization, yielding the following expression for the propagation rate:

$$-\frac{d[M]}{dt} = \frac{k_p}{K'_f}\frac{[C_0][M]}{[P_0] - [C_0]} = k_{obs(p)}[M] \qquad (3)$$

where K'_f = the binding constant of PMe_3 to the propagating species, [M] = monomer concentration, $k_{obs(p)} = (k_p/K'_f)[C_0]/\{[P_0] - [C_0]\}$, and $[P_0]$ and $[C_0]$ = initial phosphine and catalyst concentrations. The following expression for the initiation rate is derived in a similar manner:

$$-\frac{d[WP]}{dt} = \frac{k_i}{K_f}\frac{[WP][M]}{[P_0] - [C_0]} = k_{obs(i)}[WP] \qquad (4)$$

where K_f = the binding constant of PMe_3 to the initial species and $k_{obs(i)} = (k_i/K_f)[M]/\{[P_0] - [C_0]\}$.

The derived kinetic expressions are consistent with experimental observations. For example, the rates of the polymerization and initiation of cyclobutene were monitored by ^1H NMR spectroscopy at different temperatures and different phosphine concentrations. At low phosphine concentrations, the rate of initiation is too fast to be measured accurately by NMR spectroscopy. The disappearance of the phosphine adduct of the neopentylidene complex can be followed by ^1H NMR spectroscopy at higher PMe_3 concentrations. Plots of ln ($[M]/[M_0]$) versus time are linear throughout the course of the polymerization. The data fit the first-order kinetic rate law (Figure 7a), and $k_{obs(p)}$ can be obtained at different phosphine concentrations and temperatures. Figure 7b shows a linear relationship between $k_{obs(p)}$ and $1/([P_0] - [C_0])$, enabling $k_{app(p)}$ to be obtained from the slope. When the concentration of the catalyst is doubled, the observed propagation rate is also doubled. Variation of the monomer concentration does not change the observed propagation rate constants. Similarly, the rate of disappearance of **2** is first order with respect to the concentration of **2** (Figure 8). Doubling the concentration of the monomer doubles the observed initiation rate. The experimental data are in close agreement with the derived kinetic expressions.

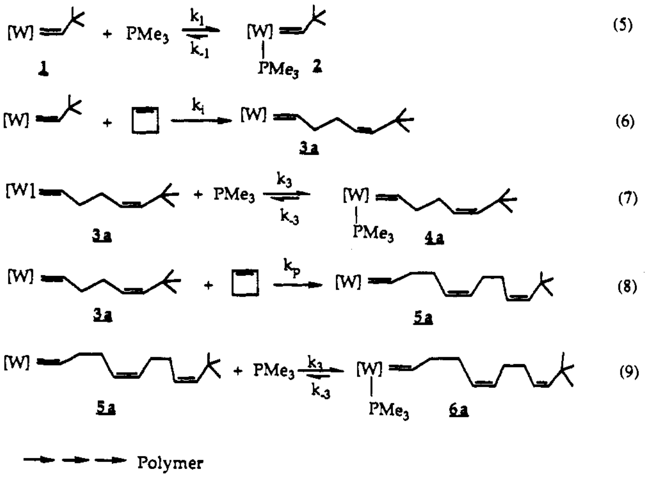
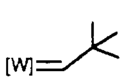


Figure 6. Kinetic scheme for the polymerization of cyclobutene catalyzed by **1**.

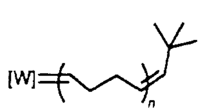
Table III. Kinetic Data for Polymerization and Initiation[a]

temp, °C	$k_{app(p)} = k_p/K'_f$	$k_{app(i)} = k_i/K_f$
−10		0.02532
0	0.05418	0.1014
10	0.1804	0.3280
25	1.159	1.344
40	9.124	

[a] $\Delta\Delta H^\ddagger_{(p)} = 20.9 \pm 2$ kcal/mol, $\Delta\Delta S^\ddagger_{(p)} = 4 \pm 8$ eu, $\Delta\Delta G^\ddagger_{273K} = 19.8 \pm 3$ kcal/mol. $\Delta\Delta H^\ddagger_{(i)} = 17.1 \pm 1$ kcal/mol, $\Delta\Delta S^\ddagger_{(i)} = -8 \pm 4.8$ eu, $\Delta\Delta G^\ddagger_{273K} = 19.4 \pm 2$ kcal/mol.



A



B

The Role of PMe_3. The overall role of PMe_3 is that of a competitive inhibitor to the catalytic species, which effectively serves to reverse their relative reactivities by binding more strongly to the propagating alkylidene **B** than to the initiating neopentylidene **A**. Quantitatively, this is illustrated in Table III by a comparison of the apparent rates of initiation and propagation

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[11] During the polymerization of 1.35 equiv of norbornene with catalyst **1** in the absence of a Lewis base, only 31.6% of the total catalyst is initiated. This phenomenon indicates that the apparent k_i/k_p for cyclobutene in the presence of phosphine is larger than k_i/k_p for norbornene in the absence of phosphine.

[12] The ^1H NMR spectrum of the polymer end-capped with benzaldehyde (0.1 M, 10 min, 25 °C) shows two olefinic doublets at 6.42 and 6.31 ppm with H–H coupling constants of 13.18 and 16.11 Hz, corresponding to cis and trans isomers, respectively. When acetone-d_6 is used, the ^2H NMR spectrum of the resulting polymer shows two peaks at 1.65 and 1.57 ppm for the inequivalent perdeuterated methyl end groups.

[13] (a) This is a result of the observation that the rate of trapping of the propagating alkylidene ($k_3[PMe_3]$) by phosphine is much greater than the rate of reaction of cyclobutene ($k_i[M]$) with the initial alkylidene. (b) Schrock, R. R.; Murdzek, J. S.; Bazan, G. C.; Robbins, J.; Dimare, M.; O'Regan, M. *J. Am. Chem. Soc.* **1990**, *112*, 3875–3886.

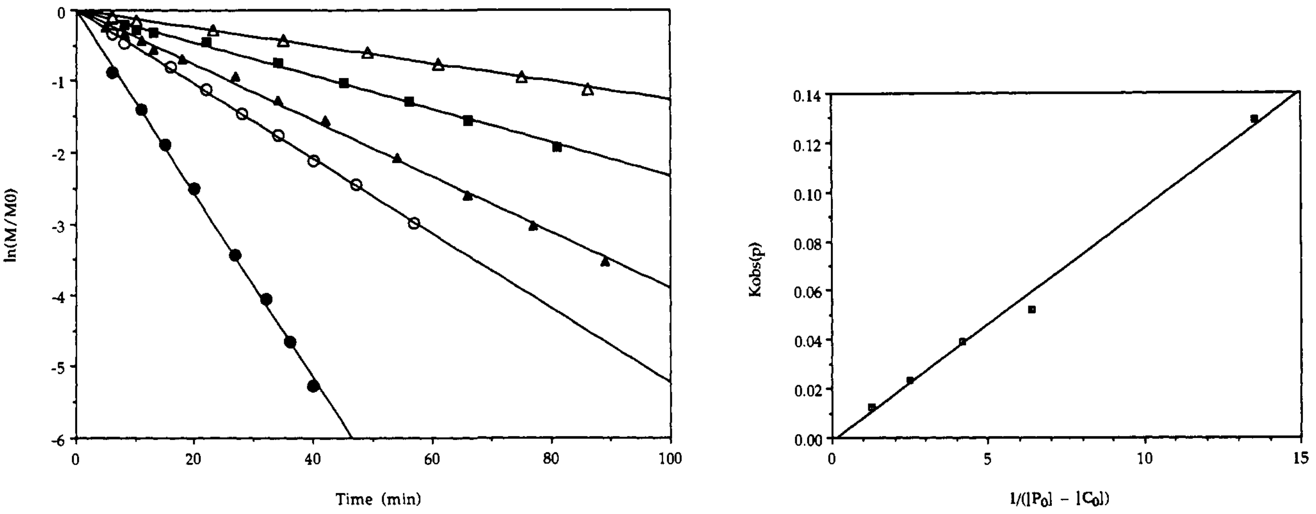

Figure 7. Kinetic data for the polymerization of cyclobutene by **1** at 25 °C. (a, left) $[C_0] = 0.0082$ M; $[M_0] = 0.16$ M. (b, right) The change of observed propagation rates with phosphine concentrations.

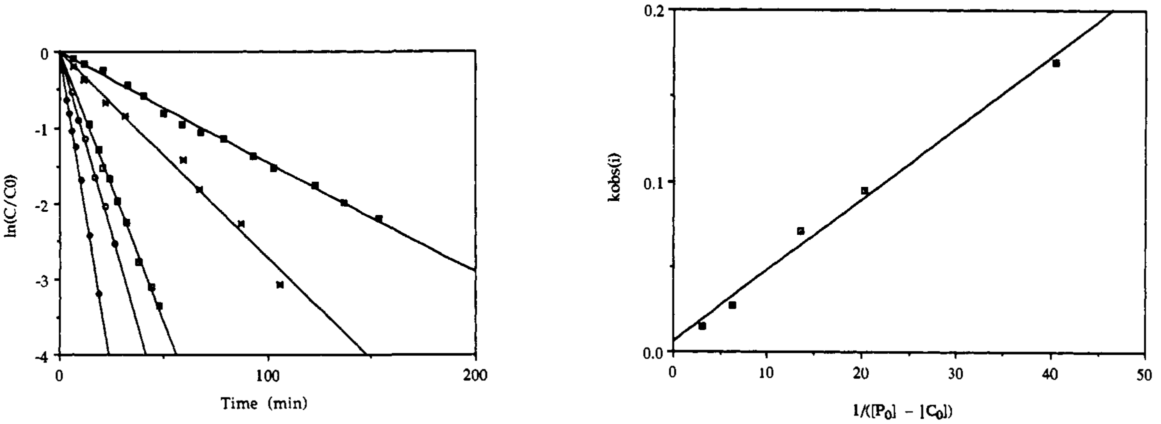

Figure 8. (a, left) Kinetic data for the initiation of cyclobutene by **1** at −10 °C and (b, right) the change of observed initiation rates with phosphine concentrations.

at several temperatures. The ratio of the observed rates for initiation and propagation is proportional to the ratio of the apparent rate constants, and hence, the observed initiation rate is larger than the observed propagation rate. Since the apparent rate constant is inversely proportional to the binding constant, PMe_3 binds more strongly to the propagating species than to the initiating species, thus reducing the propagation rate constant more than the initiation rate constant. The stronger binding of PMe_3 to the propagating alkylidene **B** ($K'_f \approx 10^5$ at 25 °C) than to the initiating neopentylidene **A** ($K_f \approx 500$) results from the steric bulkiness of the neopentylidene ligand disfavoring phosphine association. Further evidence for the importance of steric factors in regulating the polymerization is provided by the molybdenum neopentylidene complex Mo(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ (**3**, Ar = 2,6-diisopropylphenyl).[13b] Complex **3** is electronically different from its tungsten analogue **1**, but should show the same relative difference in steric bulk of the propagating alkylidene and initiating neopentylidene. This complex also gives narrow polydispersity polybutadiene from the polymerization of cyclobutene in the presence of PMe_3.[14]

In the case of cyclobutene, the addition of strongly donating Lewis bases (PMe_3, PMe_2Ph, or PEt_3) is necessary to reverse the relative magnitudes of the observed rates of initiation and propagation. For example, the polymerization of cyclobutene catalyzed by **1** yields polymer with high polydispersity index in the presence of THF or 2-Me-THF, probably because the ligands bind not much differently to initiating and propagating species. There is no evidence for the cyclic oligomers that should be in equilibrium with polycyclobutene or polycyclooctadiene. The bound phosphine completely suppresses back-biting reactions, as was found with THF in the COT polymerization reactions.[7b]

Summary. The polymerization of cyclobutene catalyzed by **1** in the presence of PMe_3 exhibits the five characteristics[15a] of an ideal living polymerization: (i) well-defined kinetics, (ii) linear increase of molecular weight with percent monomer conversion, (iii) irreversible propagation steps, (iv) the absence of chain termination and transfer steps, and (v) complete and rapid initiation.[15b] This living polymerization results in near-monodispersed and predetermined molecular weights. The polymerization of cyclobutene by **1** clearly indicates that the large ring-strain energy of the monomer is a necessary, but not sufficient, condition for achieving nearly monodispersed polymer. The large ring strain only ensures that the polymerization is irreversible but does not determine the relative magnitude of the propagation and initiation rates. In this study, control of these rates is enabled by the addition of reversibly bound Lewis bases, which alter the amount of active species in the system without varying their intrinsic reactivities. As demonstrated by the related studies with other monomers and Lewis bases, the reactivity of the monomer and the complexing ability of the base must be matched. The rate of ROMP in the presence of a Lewis base is the product of a rate constant and equilibrium constant. For a reasonably unreactive monomer, a

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(14) A typical polymerization was conducted in a 0.01 M toluene solution of **3** in the presence of 10 equiv of PMe_3 for half an hour at room temperature. The product was precipitated into methanol and dried in vacuo.

(15) (a) Flory, P. J. *J. Am. Chem. Soc.* **1940**, *62*, 1561. (b) Although it is still possible for a polymerization to have all the other living characteristics in spite of $k_p \gg k_i$ as pointed out in ref 5, complete and rapid initiation is a common feature for an ideal living polymerization. Near monodispersed polymer (especially using the techniques in normal use) can result if any one of the five characteristics is relaxed.

weak ligand is sufficient to have a major effect. As the monomer becomes more reactive, a stronger base is needed to lead to the required balancing of the rate constants. This living system has resulted in the preparation of perfectly linear and essentially monodispersed polybutadiene, which upon hydrogenation gives linear, nearly monodispersed polyethylene. These results provide a quantitative basis for the use of this technique in controlling the living polymerization of other strained, cyclic olefins.

Experimental Section

General Procedures. All manipulations of air- and/or moisture-sensitive compounds were carried out using standard Schlenk or vacuum-line techniques or in a N_2-filled drybox. Argon was purified by passage through a column of BASF RS-11 (Chemlog) and Linde 4Å molecular sieves. ^1H NMR spectra were recorded on a JEOL GX 400-MHz (399.65 MHz ^1H; 100.4 MHz ^{13}C; 61.25 MHz ^2H) spectrometer. Magnetization transfer experiments were performed according to published procedures.[16] Gel permeation chromatography (GPC) utilized Shodex KF-803, KF-804, and KF-805 columns and a Knauer differential refractometer. All GPC analyses were performed on a 0.5% w/v solution of polymer in dichloromethane. An injection volume of 0.1 mL and a flow rate of 1.5 mL/min were used. Calibration was based on narrow dispersity polystyrene standards (Polyscience) ranging from M_n = 3550 to 600000.

Materials. Cyclobutene,[17] $P(CD_3)_3$,[18] and W(CH-*t*-Bu)(O-*t*-Bu)$_2$(NAr)[6a,19b] (Ar = 2,6-diisopropylphenyl) were prepared according to literature procedures. Mo(CH-*t*-Bu)(O-*t*-Bu)$_2$(NAr)[13b] was kindly provided by Dr. Franz Stelzer. Dichloromethane-d_2 was dried over CaH_2. Benzene and toluene were distilled from sodium benzophenone ketyl. PMe_3 was distilled from Na. Acetone-d_6 was stirred over 4 Å molecular sieves. Benzaldehyde was washed with 10% Na_2CO_3 and saturated Na_2SO_3, dried over $MgSO_4$, and distilled under reduced pressure. Methanol was used without further purification. All of the purified solvents were stored under Ar in a flask with a Teflon valve.

Polymerization of Cyclobutene. A typical experiment was done in a small flask with a Teflon valve. The flask was charged with ~3 to 5 mg of catalyst dissolved in ~0.5 to 1.0 mL of benzene or toluene and ~5 to 10 equiv of phosphine in the drybox. The mixture was then degassed at liquid nitrogen temperature and cyclobutene was vacuum-transferred onto it. After being mixed well at −78 °C, the reactants were warmed up to room temperature and stirred for about an hour. The resulting polymer solution was added dropwise into rapidly stirring methanol containing a small amount of BHT. The precipitated polymer was collected and dried in vacuo overnight (87% yield).

Kinetics of the Polymerization with 1. A typical kinetic run consisted of the following: Stock solutions of 1.6 M cyclobutene, 4.112 M $P(CD_3)_3$, and 0.0907 M catalyst in toluene-d_8 were prepared. NMR tubes were charged with aliquots of the stock solutions, diluted with additional toluene-d_8 to provide 0.5 mL total volume. The tubes were kept at −78 °C before being rapidly transferred into the NMR probe. The spectra were recorded at the desired temperatures during certain time intervals. The disappearance of the olefinic protons of cyclobutene at 5.9 ppm was monitored with respect to the mesitylene internal standard at different phosphine and catalyst concentrations for over 3 half-lives ($\rho \geq 0.998$). Similarly, the disappearance of the bound-catalyst alkylidene proton resonance at 10.85 ppm was monitored at different phosphine and monomer concentrations over 3 half-lives. The first-order plots have $\rho \geq 0.996$. Least-squares analyses of first-order plots of ln ([M]/[M$_0$]) vs time and ln ([C]/[C$_0$]) vs time yielded $k_{obs(p)}$'s and $k_{obs(i)}$'s. Linear Erying plots for both propagation and inition have ρ = 0.996 and 0.997. Activation parameters were obtained from least-squares analyses of ln ($k_{app(p\ or\ i)}/T$) vs $1/T$ plots.

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[16] Robinson, G.; Kuchel, P. W.; Chapman, B. E. *J. Magn. Reson.* **1985**, *63*, 314.

[17] Salaun, J.; Fadel, A. *Org. Synth.* **1986**, *64*, 50.

[18] Bryndza, H. E.; Domaille, P. E.; Paciello, R. A.; Bercaw, J. E. *Organometallics* **1989**, *8*, 379–385.

[19] (a) Reference 5. (b) Schrock, R. R.; DePue, R. T.; Feldman, J.; Schaverien, C. J.; Dewan, J. C.; Liu, A. H. *J. Am. Chem. Soc.* **1988**, *110*, 1423–1435.

[20] (a) Lee, S. J.; McGinnis, J.; Katz, T. J. *J. Am. Chem. Soc.* **1976**, *98*, 7818. (b) Katz, T. J.; Lee, S. J.; Acton, N. *Tetrahedron Lett.* **1976**, *47*, 4247.

A Model for Homogeneous Hydrodesulfurization. The Importance of η^2-Coordination and Sulfur Coordination in C–H and C–S Bond Cleavage Reactions of Thiophene

Lingzhen Dong, Simon B. Duckett, Kristine F. Ohman, and William D. Jones*

Contribution from the Department of Chemistry, University of Rochester,
Rochester, New York 14627. *Received May 15, 1991*

Abstract: The reaction of $(C_5Me_5)Rh(PMe_3)PhH$ with thiophene at 60 °C produces the C–S cleavage adduct $(C_5Me_5)\overline{Rh(PMe_3)(SCH{=}CHCH{=}C}H)$ in high yield. Irradiation of $(C_5Me_5)Rh(PMe_3)H_2$ at −20 °C in the presence of thiophene results in the formation of both the C–S insertion product and the new C–H addition adduct $(C_5Me_5)Rh(PMe_3)$(2-thienyl)H. The latter can be independently prepared by the reaction of $(C_5Me_5)Rh(PMe_3)Cl_2$ with 2-thienyllithium, followed by $LiHBEt_3$. The 2-thienyl hydride rearranges intramolecularly to the C–S insertion adduct with activation parameters $\Delta H^{\ddagger}$ = 25.15 (45) kcal/mol and $\Delta S^{\ddagger}$ = 3.0 (2) eu. Preparation with $LiDBEt_3$ generates $(C_5Me_5)Rh(PMe_3)$(2-thienyl)D, which rearranges to the C–S insertion product in which the deuterium is scrambled over both carbons that were originally adjacent to the sulfur atom. Similarly, the complex $(C_5Me_5)Rh(PMe_3)$(3-thienyl)H was prepared and observed to isomerize intramolecularly to the 2-thienyl derivative at 23 °C with a rate constant of 1.2 (1) × 10^{-3} s^{-1}. The corresponding deuteride complex $(C_5Me_5)Rh(PMe_3)$(3-thienyl)D was observed to rearrange selectively first to $(C_5Me_5)Rh(PMe_3)$[2-(3-deuteriothienyl)]H and then to a mixture of the C–S insertion adducts with deuterium attached to either the 3 or 4 carbon. The rearrangements of several methyl derivatives have also been studied and found to occur with similar regiospecificity. Heating of $(C_5Me_5)Rh(PMe_3)PhH$ in the presence of tetramethylthiophene results in the formation of the S-bound complex, $(C_5Me_5)Rh(PMe_3)(SC_4Me_4)$. The chloro derivative $(C_5Me_5)Rh(PMe_3)$(2-thienyl)Cl was found to crystallize in the monoclinic space group $P2_1/c$ with a = 8.992 (7) Å, b = 11.324 (10) Å, c = 18.480 (8) Å, β = 91.52 (6)°, V = 1881.0 (2.3), and Z = 4.

Introduction

The hydroprocessing of oil is a procedure in which a complex combination of chemical reactions are used to remove sulfur, nitrogen, and metals by reaction with hydrogen over a heterogeneous catalyst. In particular, the removal of sulfur (commonly referred to as hydrodesulfurization or HDS) from the less reactive aromatic sulfur-containing residues such as thiophene has been the subject of many studies.[1] While this process has been carried

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