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Kinetics of Acyclic Diene Metathesis (ADMET) Polymerization. Influence of the Negative Neighboring Group Effect

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ABSTRACT: The influence of the negative neighboring group has been quantified kinetically using hydrocarbon monomers containing oxygen and sulfur. Rate constants were determined for the ADMET polymerization of bis(4-pentenyl) ether **(3)**, bis(5-hexenyl) ether **(4)**, bis(4-pentenyl) sulfide **(5)**, and bis(5-hexenyl) sulfide **(6)** using both Schrock's catalyst $Mo({=}CHCMe_2Ph)(N\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2)(OCMe(CF_3)_2)_2$ **[Mo]** and Grubbs' phenyl version of the ruthenium metathesis catalyst $RuCl_2({=}CHPh)(PCy_3)_2$ **[Ru]**. Both catalysts experience the effect of functional group presence. Further, a pure hydrocarbon version of the negative neighboring group effect has also been demonstrated using the monomer 1,5-hexadiene. In this case, **[Mo]** catalysis produces linear 1,4-polybutadiene in a reaction that exhibits a typical ADMET rate constant and activation energy. On the other hand, **[Ru]** catalysis leads principally to the formation of cyclic compounds rather than linear polymers. This change in mechanism for **[Ru]** catalysis can be attributed to multiple factors including the dissociation of phosphine ligands, thermodynamic parameters, and π complexation with the adjacent olefin in the monomer, a phenomenon similar to heteroatom nonbonded electron complexation.

Introduction

It is well-known that heteroatoms can be included in ADMET polymerization if sufficient "spacing" separates the active olefin site and the functional group containing the heteroatom itself (Figure 1). Observations in our laboratory and others have shown that close proximity of the functional group slows metathesis chemistry, presumably due to complexation of the heteroatom's nonbonded electrons with the metal center.[1−6] We have called this phenomenon the negative neighboring group effect (NNGE).[3,4] Prior to the establishment of a reliable procedure for measuring ADMET kinetics, it was not possible to measure the effects of these heteroatoms on monomer conversions, regardless of the catalysts chosen for the work. We now have kinetic information quantifying the negative neighboring group effect, data which distinguish between catalysts and which also identify a hydrocarbon manifestation of the effect. While the data are clearcut, the assessment of the meaning of these results is open to question. This paper addresses these issues.

Experimental Section

Characterization. ^{1}H NMR (300 MHz) and ^{13}C NMR (75 MHz) spectra were obtained on a Varian Gemini 300 spectrometer. All NMR spectra were recorded in chloroform-*d* with v/v 1% TMS as an internal reference. Resonances are reported in δ units downfield from TMS at 0.00 ppm. Heteronuclear gated and decoupled quantitative ^{13}C NMR spectra were run for 10−14 h with a pulse delay of 25 s.[7] Carbon relaxation times (T_1) were determined by standard methods. Mass spectra were obtained on a Finnigan MAT 95 Q mass spectrometer. Elemental analyses were performed by Atlantic Microlab, Inc., Norcross, GA.

Materials. Schrock's molybdenum alkylidene $Mo({=}CHCMe_2Ph)(N\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2)(OCMe(CF_3)_2)_2$ **[Mo]** and Grubbs' ruthenium-based catalyst $RuCl_2({=}CHPh)(PCy_3)_2$, **[Ru]** were synthesized according to published procedures.[8−10] 1,9-Decadiene (**1**), 1,5-hexadiene (**2**), and diallyl sulfide (**7**) (from Aldrich Co., Inc.) were dried over calcium hydride. They were then transferred into a potassium-mirrored flask equipped with a high-vacuum Teflon stopcock followed by transfer under vacuum to the reaction flask.

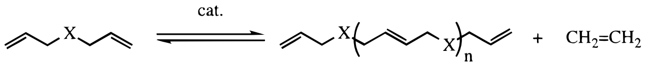

Figure 1. Acyclic diene metathesis (ADMET) polymerization.

Synthesis of Ether and Sulfide Monomers. Bis(4-pentenyl) ether $CH_2{=}CH(CH_2)_3O(CH_2)_3CH{=}CH_2$ (**3**) and bis(5-hexenyl) ether $CH_2{=}CH(CH_2)_4O(CH_2)_4CH{=}CH_2$ (**4**) were synthesized using standard Schlenk techniques. Bis(4-pentenyl) sulfide (**5**) and bis(5-hexenyl) sulfide (**6**) were synthesized as previously reported.[5] These monomers, (**3**−**6**), were purified by stirring over calcium hydride followed by succesive high-vacuum transfers onto potassium-mirrored flasks. The structures of the monomers were confirmed by ^{1}H and ^{13}C NMR spectroscopy, elemental analysis, and mass spectrometry.

Bis(4-pentenyl) Ether (3). 4-Penten-1-ol (18.5 g) was added portionwise to a stirred suspension of 5.15 g of NaH (obtained from 9.45 g of 60% dispersion of sodium hydride in oil washed twice with hexane 20 mL) in 150 mL of absolute THF, and the resulting mixture was refluxed for 2 h with stirring. Reflux was discontinued and 30 mL of hexamethylphosphoramide (HMPA) was added to the warm reaction mixture followed by 5-bromo-1-pentene (32.0 g) at such a rate as to maintain a gentle reflux. Upon addition, the mixture was refluxed for 12 h. The reaction mixture was allowed to cool to room temperature, quenched with 10% aqueous HCl (125 mL), and extracted with pentane (three 50 mL portions). The combined organic fractions were washed with saturated $NaHCO_3$, H_2O, and saturated NaCl and dried over anhydrous $MgSO_4$. Solvent removal by rotary evaporation and fractional distillation of the ether gave pure (99.5%) bis(4-pentenyl) ether in 70% yield. ^{1}H NMR: δ 5.80 (m, 1H), 4.95 (m, 2H), 3.40 (m, 2H), 2.11 (m, 2H), 1.67 (m, 2H). ^{13}C NMR: δ 138.2, 114.5, 70.0, 30.3, 28.9. HRMS (EI): calcd for $C_{10}H_{18}O$ $[M]^+$ 154.1358; found 155.1351. Anal. Calcd: C, 77.92; H, 11.69. Found: C, 77.81; H, 11.73.

Bis(5-hexenyl) Ether (4). Bis(5-hexenyl) ether (**4**) was synthesized in a similar manner as described above in 80% yield. ^{1}H NMR: δ 5.71 (m, 1H), 4.90 (m, 2H), 3.33 (2H), 2.10 (2H), 1.33−1.55 (m, 4H). ^{13}C NMR: δ 138.8, 114.4, 70.8, 33.5, 29.3, and 25.6. HRMS (CI): calcd for $C_{12}H_{23}O$ [M+H] 183.3165; found 183.3159. Anal. Calcd; C, 79.12; H, 12.09. Found: C, 78.96; H, 12.10.

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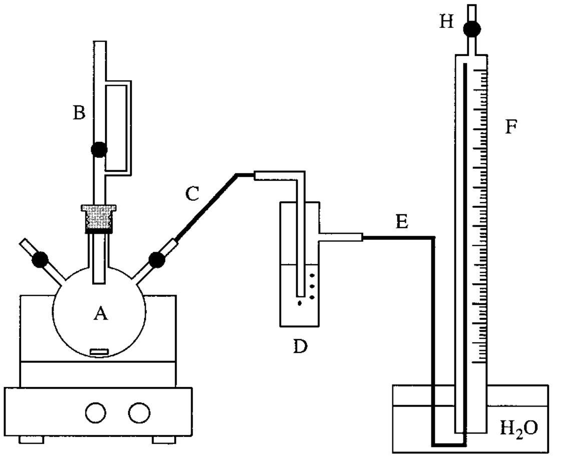


Figure 2. ADMET polymerization apparatus used for kinetic measurements.

Bis(4-pentenyl) Sulfide (5). ^{1}H NMR: δ 5.78 (m, 1H), 4.99 (m, 2H), 2.49 (t, $J = 7.1$ Hz, 2H), 2.15 (m, 2H), 1.66 (m, 2H). ^{13}C NMR: δ 137.6, 114.8, 32.6, 31.2, 28.6. IR (NaCl, thin film): 2928, 1640, 1439, 991, 910 cm^{-1}. HRMS (EI): calcd for $C_{10}H_{18}S$ [M]$^+$ 170.3150; found 170.3146.

Bis(5-hexenyl) Sulfide (6). ^{1}H NMR: δ 5.79 (m, 1H), 4.98 (m, 2H), 2.50 (t, $J = 7.1$ Hz, 2H), 2.10 (m, 2H), 1.70−1.43 (m, 4H). ^{13}C NMR: δ 138.2, 114.4, 33.2, 31.8, 28.9, 27.9. IR (NaCl, thin film): 2927, 1640, 1439, 991, 910 cm^{-1}. HRMS (CI): calcd for $C_{12}H_{23}S$ [M + H] 199.3771; found 199.3765.

Procedure for Kinetics Measurements. The successful polymerization of α,ω-dienes via ADMET continuously generates a volatile molecule, ethylene, which provides a convenient handle for measuring the rate of polymerization. Rate constants (k_p) were determined from kinetic curves obtained by monitoring the volume of ethylene released as a function of time. These measurements were performed in a reaction flask (Figure 2) operating near atmospheric pressure. The reaction flask (A) consisted of a three-port 100 mL glass flask equipped with two Kontes 4 mm glass−Teflon stopcocks bent at 45° angles and an Ace-Thred glass connector. A glass equalization addition funnel (B) was sealed to the reaction flask (A) by means of a teflon bushing and Viton O-ring. A 40 mL glass bubbler (D) filled with mineral oil was joined to the reaction flask by $^1/_4$ in. o.d. FEP tubing (from Savillex Corporation) (C) and $^1/_4$ in. o.d. Swagelok fittings. A section of $^1/_8$ in. o.d. FEP tubing (E) running up through an inverted 100 mL buret (F) connected this buret (F) to the rest of the gas-measurement system. The open end of a 100 mL buret (F) was placed slightly below the surface of a trough of water. The delivery end (H) of the buret (F) was connected to a vacuum source so that the PTFE buret stopcock could be used to control the water level inside the buret (F). Any gas produced in the reaction flask (A) displaced water in the buret (F). This simple system provides a convenient, reproducible means for measuring the volume of ethylene evolved from the ADMET reaction and avoids the hazards associated with handling mercury.

Kinetic Calculations. To determine the order of the reaction with respect to diene through kinetic plots, the $[M_0]/[M_t]$ ratio can be related to the volume of ethylene generated during the ADMET reaction. Here $[M_0]$ is defined as the initial vinyl group concentration (at $t = 0$) and $[M_t]$ is the vinyl group concentration at time t. $[M_0]$ was derived from d, the density of the diene expressed in g/mL, V_1, the volume in mL of the diene employed in the reaction, M_w, the molecular weight of the diene, and V_2, the volume of the vinyl group mixture in L (generally, $V_2 = V_1/1000$ mL), as shown in eq 1.

$$[M_0] = dV_1(2 \text{ mols of vinyl group/1 mol of diene})/(M_wV_2) \tag{1}$$

$[M_t]$ may be related to N_{vg}, the initial moles of vinyl groups present, N_{vc}, the moles of vinyl groups consumed at time t, and V_2, as shown in eq 2.

$$[M_t] = (N_{vg} - N_{vc})/V_2 \tag{2}$$

Since essentially two methylene units must be joined for each molecule of ethylene that is formed, the moles of vinyl groups consumed, N_{vc}, can be determined from the number of moles of ethylene, N_e, as shown in eq 3.

$$N_{vc} = (2 \text{ mol of vinyl group/1 mol of ethylene})N_e \tag{3}$$

Substituting eq 3 into eq 2 relates the moles of ethylene, N_e, to $[M_t]$ and yields eq 4.

$$[M_t] = [N_{vg} - (2 \text{ mol of vinyl group/1 mol of ethylene})N_e]/V_2 \tag{4}$$

Substitution of the ideal gas relationship $PV = nRT$ into eq 4 with subsequent rearrangement yields eq 5, where P is the average pressure maintained in the reaction system ($P \approx 725$ Torr) and V_e is the volume of ethylene produced at time t.

$$[M_t] = N_{vg}/V_2 - [(2PV_e)/(RTV_2)] \tag{5}$$

Since $N_{vg}/V_2 = [M_0]$, eq 5 can be rearranged into eq 6. This expression allows the $[M_0]/[M_t]$ ratio to be determined as ethylene is produced in the ADMET reaction.

$$[M_t] = [M_0] - [(2P)/(RTV_2)]V_e \tag{6}$$

Equation 2 may also be rewritten to express $[M_t]$ as a function of the unreacted vinyl groups, $(1 - p)$, as shown in eq 7.

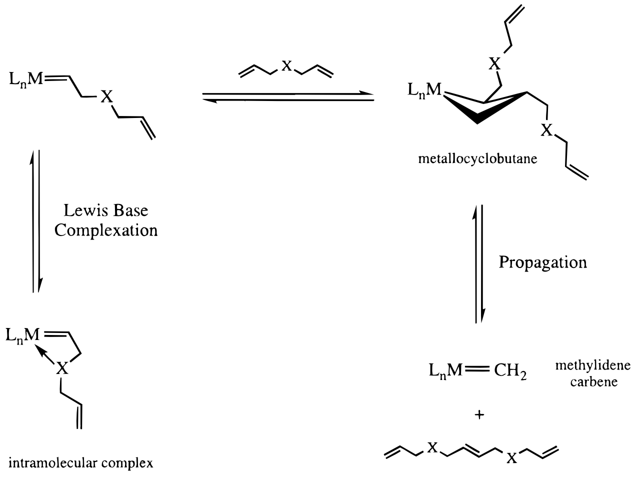
$$[M_t] = [M_0](1 - p) \tag{7}$$

General Polymerization Procedure. All polymerizations are done in the bulk state to maximize the molar concentration of the olefin, and shift equilibria appropriately for the ADMET reaction. The glass reaction flask and additional funnel were charged with **[Mo]** or **[Ru]** catalysts (0.001−0.05 g) and monomers **1**, **2**, **3**, **4**, **5**, or **6** (0.5 mL), respectively, inside an argon-filled drybox. The reaction flask was connected to the system as described above and the system was purged by allowing a stream of argon through one of the stopcock inlets for 30 min. This inlet stopcock was closed and the water level adjusted to a height of 24 in, which corresponds to an initial system pressure of approximately 725 Torr. The reaction vessel was placed in an oil bath at a specific temperature. A monomer (**1**, **2**, **3**, **4**, **5**, or **6**) was then added into the reaction flask and the time monitored by a digital stopwatch. Readings from the burret were taken every 30 s for the first 45−60 min and typically every 5−15 min thereafter. Overall conversions of the monomers **1**−**6** were calculated from ^{1}H NMR spectra by the integration of the internal (at 5.4 ppm) vs external (at 5.8 or 5.0 ppm) vinyl groups. Conversions measured from the evolution of ethylene are equal to calculated values from the ^{1}H NMR spectrum within the limit of experimental error.

Characterization of the ADMET Polymers. Polymerization reactions catalyzed by **[Mo]** were quenched by exposing the reaction mixture to air while **[Ru]** catalyzed reactions were quenced by adding ethyl vinyl ether to the polymerization reaction.[10] The resultant polymers were dissolved in toluene, precipitated into cold methanol, and dried in vacuo at 40 °C overnight. Structure determination of the polymers was done by ^{1}H and ^{13}C NMR spectroscopy in comparison with the known spectra for polyoctenylene and polybutadiene,[11,12] unsaturated polyethers,[2] and unsaturated polysulfides.[5]

Polyoctenylene (Polyoctenamer). ^{1}H NMR: δ 5.4 (CH=CH), 2.0, 1.3 (CH_2). ^{13}C NMR: δ 130.2 (C=C, trans, 80%), 129.6 (C=C, cis, 20%), 32.6 (trans-allyl, 80%), 29.7, 29.2, 27.2 (cis-allyl, 20%). Anal. Calcd for $(C_8H_{14})_n$: C, 87.20; H, 12.73. Found: C, 87.10; H, 12.70.

1,4-Polybutadiene. ^{1}H NMR: δ 5.4 (CH=CH), 2.0. ^{13}C NMR: δ 130.0 (C=C, trans), 129.6 (C=C, cis), 32.7 (trans-allyl)



where X = O, S and M = Mo, Ru

Figure 3. Mechanistic events influencing the kinetics of ADMET chemistry for functionalized olefins.

27.45 (cis-allyl). Anal. Calcd for $(C_4H_6)_n$: C, 88.80; H, 11.20. Found: C, 88.65; H, 11.21.

Poly(oxy-4-octene-1,8-diyl). ^{1}H NMR: δ 5.4, 3.4, 2.0, 1.6. ^{13}C NMR: δ 130.1 (trans C=C, 80%), 129.6 (cis C=C, 20%), 70.2, 29.5 (trans-allyl, 80%), 29.1, 23.8 (cis-allyl, 20%). Anal. Calcd: C, 76.19; H, 11.11; O, 12.70. Found: C, 76.05; H, 11.11; O, 12.84.

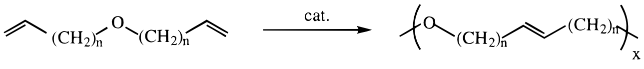
Poly(oxy-5-decene-1,10-diyl). ^{1}H NMR: δ 5.4, 3.4, 2.0, 1.5, 1.4. ^{13}C NMR: δ 130.3 (trans C=C, 80%), 129.8 (cis C=C, 20%), 70.8, 32.4 (trans-allyl, 80%), 29.4, 27.0 (cis-allyl, 20%), 26.2. Anal. Calcd: C, 77.9; H, 11.69; O, 10.41. Found: C, 77.63; H, 11.72; O, 10.65.

Poly(thio-4-octene-1,8-diyl). ^{1}H NMR: δ 5.4, 2.5, 2.1, 1.7. ^{13}C NMR: δ 130.1 (trans C=C, 80%), 129.6 (cis C=C, 20%), 31.5, 31.3 (trans-allyl, 80%), 29.2, 26.3 (cis-allyl, 20%). IR (NaCl, thin film): 2923, 1437, 967 cm^{-1}. Anal. Calcd: C, 67.61; H, 9.86; S, 22.53. Found: C, 67.54; H, 9.86; S, 22.57.

Poly(thio-5-decene-1,10-diyl). ^{1}H NMR: δ 5.4, 2.49, 2.0, 1.48. ^{13}C NMR: δ 130.2 (trans C=C, 80%), 129.7 (cis C=C, 20%), 32.0, 31.9 (trans-allyl, 80%), 29.15, 28.7, 26.7 (cis-allyl, 20%). IR (NaCl, thin film): 2924, 1437, 967 cm^{-1}. Anal. Calcd: C, 70.59; H, 10.59; S, 18.82. Found: C, 70.51; H, 10.60; S, 18.77.

Results and Discussion

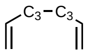
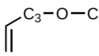
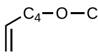
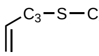
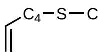
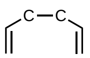
I. Catalyst Influence on the Negative Neighboring Group Effect. The structure/reactivity behavior of functionalized acyclic dienes may be understood by considering how Lewis base atoms might complex with the metathesizing metal center (Figure 3). It is well-known that complexation can occur between Lewis base atoms (i.e., oxygen or sulfur) and metals, thereby hindering metathesis chemistry from occurring either in an ADMET[2,11,13] or a ROMP[14,15] sense.



Monomer	ADMET reactive?
n = 0	No
n = 1	No
n = 2	Sluggish
n = 3	Yes
n = 4	Yes

Figure 4. ADMET reactivity of dienes containing an ether functionality.

Table 1. Structure Reactivity Behavior for Functionalized Acyclic Dienes Containing O and S as Heteroatoms, comparison with ADMET Polymerization of 1,9-Decadiene Using [Mo] and [Ru] as Catalysts[a]

		k_p (L·mol^{-1}·s^{-1})	
monomer	structure	**[Mo]**	**[Ru]**
1		2.4×10^{-3}	1.0×10^{-4}
3		1.2×10^{-3}	6×10^{-6}
4		1.5×10^{-3}	1×10^{-5}
5		2×10^{-4}	0
6		1.3×10^{-3}	0
2		4.1×10^{-3}	cyclization

[a] Catalysts: **[Mo]** = Mo(=CHCMe$_2$Ph)(N-2,6-C$_6$H$_3$-i-Pr$_2$)(OCMe(CF$_3$)$_2$)$_2$, **[Ru]** = RuCl$_2$(=CHPh)(PCy$_3$)$_2$. C = CH$_2$; C$_3$ = (CH$_2$)$_3$; C$_4$ = (CH$_2$)$_4$.

Our first examination to describe this effect was done with dienes containing an ether functionality, as illustrated in Figure 4.[2] Acyclic diene metathesis chemistry generates ethylene immediately if a monomer is reactive; however, if no cyclics or polymer are formed, then the reaction system remains dormant, and consequently, it is easy to monitor the structure/reactivity behavior of a reagent or monomer. Our work has shown that at least two methylene spacers are required in a heteroatom-containing monomer in order for condensation metathesis (ADMET) chemistry to proceed at a reasonable rate.[2] We term the hindrance of ADMET chemistry by the presence of heteroatoms (or, in some cases, the nearby presence of olefins) the negative neighboring group effect (NNGE).[3,4]

This observation has been recorded not only for ethers but also for a large number of other functional groups containing Lewis base atoms and appears to be quite general in scope.[2−6] By applying our new kinetics methodology, we are now able to quantify the NNGE and illustrate how it influences the rate of reaction for different catalysts.

Two well-known metathesis catalysts were used in this study, these being Schrock's molybdenum catalyst Mo(=CHCMe$_2$Ph)(N-2,6-C$_6$H$_3$-i-Pr$_2$)(OCMe(CF$_3$)$_3$)$_2$ **[Mo]** and Grubbs' recent benzylidene ruthenium catalyst RuCl$_2$(=CHPh)(PCy$_3$)$_2$ **[Ru]**. Six monomers were tested in this work, these being 1,9-decadiene, 1,5-hexadiene, bis(4-pentenyl) ether, bis(4-hexenyl ether), bis(4-pentenyl) sulfide, and bis(5-hexenyl) sulfide. Polymerization studies were completed using typical ADMET reaction conditions, and kinetic data were obtained by measuring the rate of ethylene evolution during the polymerizations. The specific rate constants for the polymerization of monomers **1**−**6** at 26 °C are given in Table 1.

A well-established method for determining reaction order of monomers and rate constants in polycondensations consists of plotting $1/(1-p)^x$ vs time (t).[16] Thus $(1-p)$ represents the fraction of unreacted vinyl groups, and $[M_t]$ is the concentration of the vinyl functional groups at time (t). The second-order nature of the ADMET reaction in a diene can be confirmed by a linear relationship in a plot of $1/(1-p)$ against time.

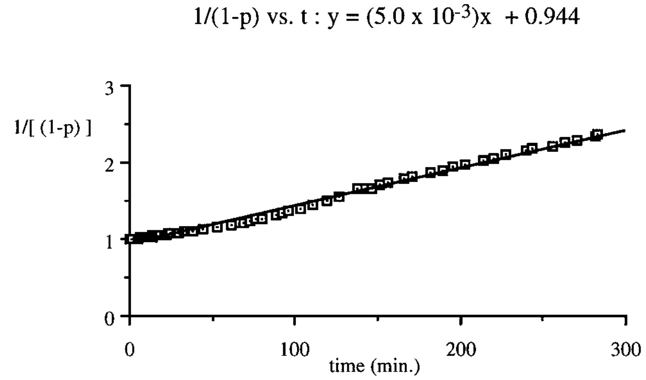


Figure 5. Second-order kinetic plot for the ADMET polymerization of bis(4-pentenyl) ether (**3**) with **[Ru]** as catalyst; $[M_0] = 13.34$ mol·L^{-1}, **[Ru]** = 0.019 mol·L^{-1} at 25 °C.

Table 2. Kinetic Data for the ADMET Polymerization of Ethers 3 and 4 Using [Mo] and [Ru] as Catalysts[a]

monomer[a]	catalyst	temp (°C)	10^3k (L·mol^{-1}·s^{-1})
3	**[Mo]**	26	1.2
3	**[Mo]**	31	2.0
3	**[Ru]**	25	0.006
3	**[Ru]**	37	0.023
3	**[Ru]**	43	0.052
4	**[Mo]**	26	1.5
4	**[Ru]**	26	0.01
4	**[Ru]**	35	0.02
4	**[Ru]**	50	0.05

[a] The concentration of vinyl groups for **3** was [M] = 13.34 mol·L^{-1} and for **4** was [M] = 10.97 mol·L^{-1}. [b] **3** = bis(4-pentenyl) ether, **4** = bis(5-hexenyl) ether.

As illustrated in Figure 5, the second-order plot of 1/(1 − *p*) against time for bis(4-pentenyl) ether yields an excellent fit ($R^2 = 0.994$) over the widest range of percent vinyl group conversion. This linear relationship unequivocally verifies the second-order nature of the ADMET reaction in monomer. The other monomers used in this study gave similar plots displaying linear relationships.

This figure shows that ADMET polymerization of bis(4-pentenyl) ether continues its second-order behavior at least up to 60% conversion. Nonlinearity beyond this point is typical for bulk polycondensation chemistry, usually due to the marked changes in viscosity of the polymerization medium at which point the kinetics of ethylene removal become diffusion controlled. Arrhenius data have also been collected for each of these polymerizations and these data are found in Tables 2 and 3.

The data in Table 1 are particularly revealing—in fact, quite surprising—for it becomes immediately evident that the polymerizations done with the ruthenium catalyst system **[Ru]** are more sensitive to the negative neighboring group effect than are those using the molybdenum catalyst system **[Mo]**. For example, the insertion of an oxygen atom into 1,9-decadiene (monomer **3**) slows the polymerization by a factor of 16 when **[Ru]** catalysis is used; by comparison, the polymerization proceeds only 2 times slower when using **[Mo]** catalysis. Insertion of an extra methylene spacer (monomer **4**) improves the rate in both cases, by 1 order of magnitude when using **[Ru]** catalysis, but only by 25% when using **[Mo]** catalysis. The negative neighboring group effect is clearly illustrated by these results.

The distinctions between the two catalysts are particularly obvious when using sulfur rather than oxygen-containing monomers. Neither of the sulfide monomers polymerize at all when using **[Ru]** catalysis; apparently, the intramolecular complex suggested in Figure 3 is quite stable and prevents propagation from occurring. Such retarded activity has been reported in the ring-closing metathesis (RCM) reactions of sulfur-containing olefins with other ruthenium catalyst systems.[17,18] The nature of this complexation can be explored by monitoring the reaction of diallyl sulfide (**7**) with **[Ru]** by ^{1}H and ^{31}P NMR spectroscopy.[19] The ^{31}P NMR spectrum unequivocally indicates both the formation of a new ruthenium alkylidene and the presence of free tricyclohexylphosphine via resonances at 36.76 and 10.43 ppm, respectively. Examination of the ^{1}H NMR spectrum corroborates this observation by exhibiting resonances corresponding to the new alkylidene (19.36 ppm, a triplet with coupling constant $^3J_{HH} = 5.4$ Hz) and the formation of styrene.

^{31}P NMR spectroscopy also shows that the signal corresponding to free tricyclohexylphosphine increases in intensity as a function of time. These data suggest that intramolecular complexation of the heteroatom to the ruthenium center is responsible for the failure of the sulfur-containing monomers to polymerize. On the other hand, **[Mo]** catalysis, although retarded, does allow the polymerization of these monomers. The sulfur-inserted decadiene analog (monomer **5**) polymerizes at a rate 12 times slower than 1,9-decadiene, whereas the four methylene spacer monomer (monomer **6**) does so at only half the rate of 1,9-decadiene.

The negative neighboring group effect is more pronounced in ruthenium catalysis, and one can speculate that a greater degree of coordination (Figure 2) or perhaps a subtle change in mechanism takes place here. The **[Ru]** catalyst is certainly tolerant of molecular oxygen (in solid form), carbonyl groups, and protonic solvents;[9,10] yet the situation appears to be different when considering both intra- and intermolecular oxygen and sulfur complexation chemistry.

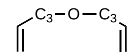
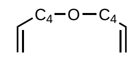
Even more dramatic is the effect of catalyst choice on the polymerization of the monomer, 1,5-hexadiene—i.e., no heteroatoms are present. While our research with 1,9-decadiene shows that catalyst choice (**[Mo]** vs **[Ru]**) influences only the rate of polymerization, in the case of 1,5-hexadiene, we find that *catalyst choice redirects the mechanism*. High molecular weight polymers are formed with **[Mo]** catalysis, whereas with **[Ru]** catalysis, cyclics are formed preferentially. This chemistry is described in the following section.

II. Mechanism Switching in 1,5-Hexadiene Metathesis Reactions. As shown in Figure 6, the ADMET polymerization of 1,5-hexadiene using **[Mo]** as the catalyst produces principally linear polymers. A small quantity of cyclics (≤5%) are formed in this conversion, but no more than is usually observed in a typical polycondensation.[20] However, when **[Ru]** is used as the catalyst, only minor quantities of linear oligomers are formed with the predominant product being the cyclic “dimer”, 1,5-cyclooctadiene (Figure 6).

Evidence for these results includes the GC/MS spectra for the product of 1,5-hexadiene in the presence of **[Mo]** catalysis (the top half of Figure 7), and for the same reaction with **[Ru]** catalysis (the bottom half of Figure 7). As shown, the predominant product is 1,5-cyclooctadiene for the **[Ru]**-catalyzed reaction.

Obviously, a competing mechanism is predominant in **[Ru]** catalysis where the rate constant for “dimerization”, noted as k_c, is greater than the rate constant for propagation, noted as k_p. The size of the hydrocar-

Table 3. Thermodynamic Parameters for the ADMET Polymerization of Bis(4- pentenyl) Ether (3) and Bis(5-hexenyl) Ether (4) with [Mo] and [Ru] as Catalysts

monomer	structure	E_a [kJ·mol^{-1} (kcal·mol^{-1})]	$\Delta H^{\ddagger}$ [kJ·mol^{-1} (kcal·mol^{-1})]	$\Delta S^{\ddagger}$ [J·mol^{-1}·deg^{-1} (cal·mol^{-1}·deg^{-1})]
3		91 ± 2 (21.8 ± 0.5)	−89 ± 3 (−21.3 ± 0.7)	−45.0 ± 1.6[a] (−10.8 ± 0.4)[a]
4		52.6 ± 0.4 (12.6 ± 0.1)	−50.4 ± 0.4 (−12.0 ± 0.1)	−80.9 ± 1.6[b] (−18.6 ± 0.4)[b]

[a] Calculated for $k_p = 6.2 \times 10^{-6}$ L·mol^{-1}·s^{-1} at 25 °C. [b] Calculated for $k_p = 0.98 \times 10^{-5}$ L·mol^{-1}·s^{-1} at 25 °C, and 1 cal = 4.184 J where $C_3 = (CH_2)_3$; $C_4 = (CH_2)_4$.

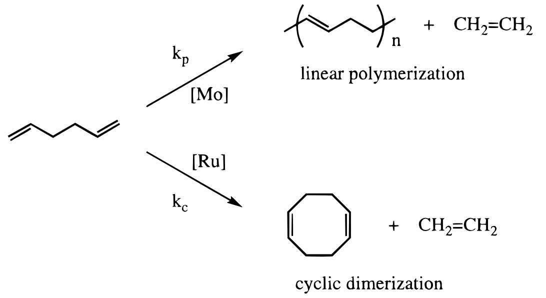


Figure 6. Competition of the ADMET linear polymerization (k_p) with ADMET cyclic dimerization (k_c) of 1,5-hexadiene using **[Mo]** or **[Ru]** as catalyst.

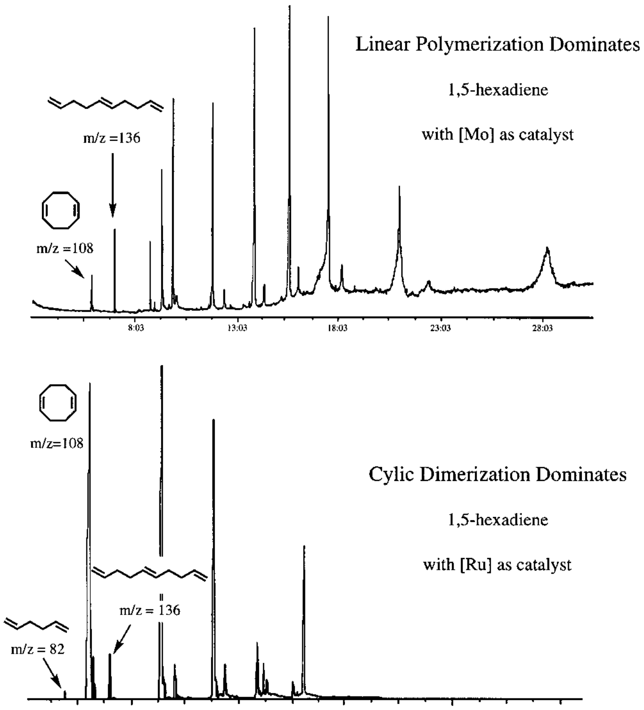


Figure 7. Gas chromatograph with mass-exact labels obtained from the mass spectrum (GC/MS) of the reaction mixture of 1,5-hexadiene (**2**) and **[Mo]** or **[Ru]** as catalyst under bulk conditions, [M] = 16.8 mol·L^{-1}, [catalyst] = 0.01 mol·L^{-1} at 24.5 °C.

bon ring that can be formed during cyclic dimerization plays a role in the relative rates of k_c and k_p. 1,5-Hexadiene is more likely to "dimerize" than is 1,9-decadiene, for example,[20] and when ring formation is entropically favored, as is the case for the 1,7-octadiene to cyclohexene conversion, then catalyst choice is of little consequence. The situation is decidedly different in the reaction of 1,5-hexadiene with **[Ru]**; here catalyst choice, not monomer choice, determines the feasibility of ring formation (Table 4). This result can only be explained in terms of a switch in mechanism.

Data calculated from Arrhenius plots for the ADMET reaction of 1,5-hexadiene suggest that thermodynamic parameters influence the rates of cyclization (k_c) and propagation (k_p). The high tendency toward cyclic dimerization for 1,5-hexadiene with **[Ru]** as catalyst is enhanced due to a favorable entropy factor, which is very low −3.5 ± 0.2 J·mol^{-1}·deg^{-1} (−0.8 ± 0.04 cal·mol^{-1}·deg^{-1}) as compared to the entropy factor from the linear polymerization of 1,5-hexadiene using **[Mo]** catalysis (Table 5). For the polymerization of 1,5-hexadiene with **[Mo]**, the entropy of activation is essentially equal to that found for 1,9-decadiene: −181 ± 9 J·mol^{-1}·deg^{-1} (−43 ± 2) cal·mol^{-1}·deg^{-1} vs −172 ± 8 J·mol^{-1}·deg^{-1} (−41 ± 2) cal·mol^{-1}·deg^{-1} (Table 5). The much larger enthalpy factor found for the **[Ru]** catalyzed metathesis of 1,5-hexadiene also drives the cyclic dimerization reaction (Table 5). Additionally, the cyclic "dimerization" of 1,5-hexadiene with **[Ru]** as the catalyst possesses a higher activation energy (91 ± 2 kJ·mol^{-1} or 22 ± 0.5 kcal·mol^{-1}) than does the linear ADMET polymerization of 1,5-hexadiene with **[Mo]** as the catalyst (46 ± 2 kJ·mol^{-1} or 11 ± 0.5 kcal·mol^{-1}) (see Table 5).

1,5-Hexadiene **(2)** clearly behaves differently from 1,9-decadiene **(1)** when **[Ru]** is used as catalyst in ADMET polymerizations. This observation may be similar to the negative neighboring group effect of heteroatoms (Figure 3) mentioned earlier.[1−6] In this case π-complexation from the neighboring terminal olefin of 1,5-hexadiene's dimer forms the basis for the NNGE (Figure 8), and this may explain the change in mechanism leading to easier formation of cyclic product. For some reason, **[Ru]** catalysis facilitates this change in mechanism. Supporting this analysis is the observation made by Grubbs and co-workers that phosphine ligands are displaced from the metal center via π-complexation in these ruthenium catalyst systems.[21,22]

One might very well question whether or not 1,5-hexadiene is forming cyclics in the case of **[Mo]** catalysis as well. These cyclics might then experience ROMP chemistry with **[Mo]** catalysis leading to the linear polymer that has been characterized. If this were the case, then the molecular weight distribution for the polymer would approximate that of a living chain polymer (i.e., $M_w/M_n \approx 1.0$) rather than a step polymer. In fact, the 1,4-polybutadiene that is formed has a distribution approximating step polymerization chemistry ($M_w/M_n \approx 2.0$).[11] Step polymerization chemistry is responsible for formation of this polymer using **[Mo]** catalysis.

Further evidence for the alternate mechanistic chemistry with the **[Ru]** catalysis of 1,5-hexadiene reactions is found by ^{31}P NMR spectroscopy. Examination of the ^{31}P NMR spectrum of the reaction mixture of 1,5-hexadiene with $RuCl_2({=}CHPh)(PCy_3)_2$ reveals the presence of free tricyclohexylphosphine at 10.47 ppm. A similar observation was previously reported by Grubbs for the reaction of 1,5-hexadiene with the ruthenium catalyst $RuCl_2({=}CHPh)(PPh_3)_2$, in which free triphenylphosphine was found by ^{31}P NMR spectroscopy.[21]

Table 4. Kinetic Data of the ADMET Polymerization and ADMET Cyclic Dimerization of 1,5-Hexadiene (2) Using [Mo] or [Ru] as Catalysts[a]

no.	catalyst	temp. (°C)	catalyst (mol·L^{-1})	$10^{-3}k$ (L·mol^{-1}·s^{-1})	vinyl group conversion (% NMR[b])	vinyl group conversion (% ethyl[c])
1	**[Mo]**	26	0.003	4.2	86.04	88.4
2	**[Mo]**	26	0.023	3.5	89.6	89.6
3	**[Mo]**	26	0.039	4.1	79.7	82.1
4	**[Mo]**	26	0.047	4.3	93.2	92.4
5	**[Mo]**	26	0.065	4.2	93.3	91.5
6	**[Mo]**	35	0.039	9.8	92.7	93.1
7	**[Mo]**	45	0.039	13.0	86.7	90.1
8	**[Ru]**	22	0.010	0.62	95.0	98.0
9	**[Ru]**	24.5	0.005	0.82	89.2	90.0
10	**[Ru]**	24.5	0.013	0.10	87.0	88.2
11	**[Ru]**	24.5	0.038	0.95	88.3	92.1
12	**[Ru]**	33	0.013	2.41	97.8	96.0
13	**[Ru]**	44	0.013	3.27	90.0	95.1

[a] The concentration of the vinyl groups in the monomer in the bulk was [M] = 16.85 mol·L^{-1}. [a] ^{1}H NMR: integration of the internal (at 5.4 ppm) vs external (at 5.8 or 5.0 ppm) vinyl groups. [b] Calculated for the volume of ethylene; see Experimental Section.

Table 5. Thermodynamic Parameters of the ADMET Cyclic Dimerization of 1,5-Hexadiene (2) Using [Mo] or [Ru] as Catalyst[a]

catalyst	E_a [kJ·mol^{-1} (kcal·mol^{-1})]	$\Delta H^{‡}$ [kJ·mol^{-1} (kcal·mol^{-1})]	$\Delta S^{‡}$ [kJ·mol^{-1}·deg^{-1} (kcal·mol^{-1}·deg^{-1})]
[Mo]	46 ± 2 (11 ± 0.5)	−44 ± 2 (−10 ± 0.5)	−181 ± 9[a] (−43. ± 2)[a]
[Ru]	91 ± 2 (22 ± 0.5)	−89 ± 2 (−21 ± 0.5)	−3.5 ± 0.2[b] (−0.8 ± 0.04)[b]

[a] The concentration of the vinyl groups in the monomer in the bulk was [M] = 16.85 mol·L^{-1}. [b] Calculated for $k_p = 4.0 \times 10^{-3}$ L·mol^{-1}·s^{-1} at 25 °C. [c] Calculated for $k_p = 1.07 \times 10^{-3}$ L·mol^{-1}·s^{-1} at 25 °C, and 1 cal = 4.184 J.

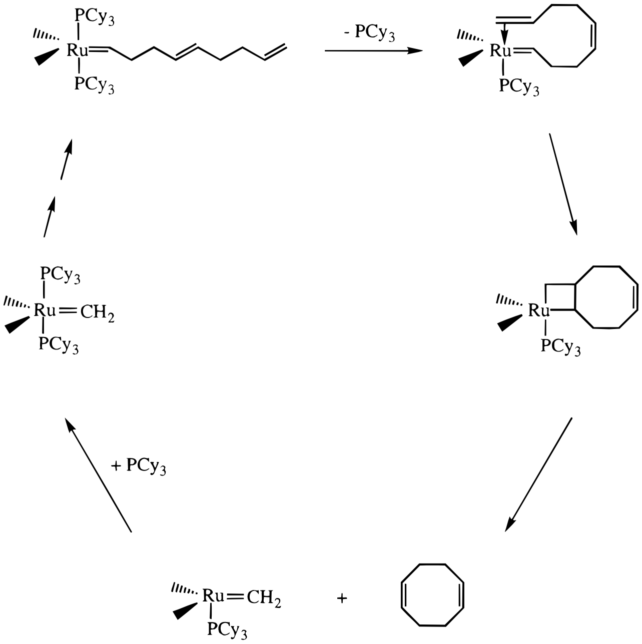


Figure 8. Chelation of the double bond on the dimer adjacent to the metal carbene bond in the ADMET cyclic dimerization of 1,5-hexadiene (**2**) and **[Ru]** as catalyst.

Even when α-olefins such as 1-hexene or 1-octene are reacted with **[Ru]**, free tricyclohexylphosphine is also detected, and so it seems reasonable that phosphine displacement is enhanced as olefin groups π-complex to the metal center.

With a vacant coordination site available through loss of phosphine, chelation of the double bond on the dimer adjacent to the metal carbene bond (Figure 8) may be sterically allowed and favored because of its intramolecular nature and ruthenium's desire to participate in π-back-bonding. The recent isolation by Snapper of a novel ruthenium complex containing an intramolecularly-coordinated alkene in place of one of the phosphine ligands (*which interestingly is a substituted analog of the ruthenium alkylidene from 1,5-hexadiene*) strongly supports the idea of double bond chelation.[23] Such a process leads to formation of a stable 1,5-cyclooctadiene, a new "monomer" that should undergo ROMP chemistry. So why does this not occur?

To understand why the 1,5-cyclooctadiene that is formed does not undergo ROMP, we investigated the reaction of cyclooctadiene with **[Ru]** in the presence and absence of tricyclohexylphosphine. ^{31}P NMR spectroscopy of the reaction between 1,5-cyclooctadiene and **[Ru]** reveals that initially no free PCy_3 is generated and that only a trace amount of free PCy_3 is detected after 24 h.[24] Suppression of π-complexation between cyclooctadiene and the metal center is clearly illustrated by the observation that we cannot ROMP 1,5-cyclooctadiene with **[Ru]** when 1 equiv of free PCy_3 is added to the reaction system.[25] These findings suggest that free tricyclohexylphosphine, generated in the reaction of 1,5-hexadiene with **[Ru]**, inhibits ROMP chemistry of the formed 1,5-cyclooctadiene.

Conclusions

A quantitative measure of the negative neighboring group effect on two metathesis catalysts in ADMET bulk polymerization chemistry has been described using oxygen and sulfur-containing dienes. The rates of polymerization of these monomers (**3**−**6**) vary by as much as 1 order of magnitude depending on which catalyst (**[Mo]** or **[Ru]**) is used, and further, it is evident that the negative neighboring group effect (NNGE) is more pronounced for ruthenium catalysis. We observe second-order rate constants for the ADMET polymerization of monomers, which thereby characterize the step nature of this polymerization. The ADMET polymerization of 1,5-hexadiene with **[Ru]** catalysis is complicated by the occurrence of cyclic dimerization. The high tendency toward cyclic dimerization of 1,5-hexadiene with **[Ru]** is due to both favorable entropy and enthalpy factors (Table 5) and π-complexation from the neighboring olefin. Dissociation and displacement of PCy_3 ligands from $RuCl_2({=}CHPh)(PCy_3)_2$, **[Ru]**, are additional factors in this mechanism. Cyclic dimerization of 1,5-hexadiene with **[Ru]** catalyst proceeds with a considerably smaller decrease in activation entropy than does linear polymerization of 1,5-hexadiene with **[Mo]** as catalyst.

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(19) For this NMR scale reaction, 10 equiv of diallyl sulfide was combined with **[Ru]** in C_6D_6, and the reaction was monitored by ^{1}H and ^{31}P NMR spectroscopy. Most of the starting alkylidene is converted into the new alkylidene, $RuCl_2({=}CHCH_2SCH_2CH{=}CH_2)(PCy_3)_2$ within 15 min. After 30 min, multiple phosphorus resonances are observed, presumably through decomposition of the catalyst system. Note: $CDCl_3$ and CD_2Cl_2 are unsuitable solvents for monitoring this system, as they react with PCy_3.

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(24) For this NMR scale reaction, 10 equiv of 1,5-cyclooctadiene was combined with **[Ru]** in C_6D_6, and the reaction was monitored by ^{1}H and ^{31}P NMR spectroscopy. No free tricyclohexylphosphine was observed after 1 h; however, after 24 h a trace of free PCy_3 was detected at 10.44 ppm via ^{31}P NMR spectroscopy.

(25) 1,5-cyclooctadiene (0.60 mL, 6.3×10^{-3} mol), PCy_3 (0.0030 g, 1.1×10^{-5} mol), and **[Ru]** (0.0080 g, 1.1×10^{-5} mol) were reacted under typical ADMET conditions. No change in color or increase in viscosity was observed for this system after a reaction time of 12 h.

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