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ARTICLE

Preparation of Photoreactive Oligomers by ADMET Polymerization of $[(C_5H_4(CH_2)_8CH{=}CH_2)Mo(CO)_3]_2$

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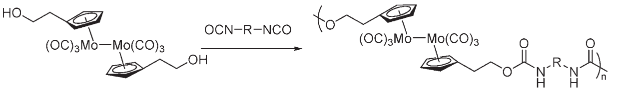
ABSTRACT: Polymerization of the $[(\eta^5\text{-}C_5H_4(CH_2)_8CH{=}CH_2)Mo(CO)_3]_2$ complex by acyclic diene metathesis polymerization (ADMET) is reported. The polymerization reactions were performed using Schrock's catalyst, which resulted in formation of a polydisperse oligomer ($M_n = 2300$ and $M_w/M_n = 4.3$) with Mo−Mo bonds in the oligomer chain. Under dilute solvent conditions, the reaction was shown to favor the formation of the ring-closing metathesis (RCM) product. The ADMET oligomer was photochemically degradable, and irradiation with $\lambda > 520$ nm light in CCl_4 resulted in cleavage of the oligomer backbone and formation of the metal chloride complex $[\mu\text{-}C_5H_4(CH_2)_8CH{=}CH(CH_2)_8C_5H_4\{Mo(CO)_3Cl\}_2]$. The RCM product was also irradiated and the photochemical product is identical to that formed by irradiation of the oligomer. Copolymerization of $[(\eta^5\text{-}C_5H_4(CH_2)_8CH{=}CH_2)Mo(CO)_3]_2$ with 1,9-decadiene using Grubbs' second-generation catalyst resulted in a higher molecular weight oligomer ($M_n = 3400$, $M_w/M_n = 3.9$).

Introduction

A variety of experimental factors, such as light, mechanical stress, and temperature, contribute to polymer degradation.[1,2] A complete examination of these factors is necessary for the preparation of practical commercial materials with predictable lifetimes and for the design of greener plastics that will intentionally degrade after use.[3−6] Photochemical degradation is one of the primary degradation routes for organic polymers in the environment, and it occurs by an intricate oxidation mechanism. Although photooxidation is well understood, due to the complexity of the mechanism it is generally difficult to examine directly the effect of specific factors on the rate and onset of polymer degradation. To circumvent this complexity, we designed polymers with metal−metal bonds in the backbone. The metal−metal bond is cleavable by visible light (Scheme 1) and its disappearance can be conveniently monitored spectroscopically, thereby simplifying studies on polymer degradation. Using these specially designed polymers, our studies previously elucidated the effects of tensile stress,[7,8] time-dependent morphology,[9] and glass transition temperature[10] on the photochemical degradation rates of polymers.

The synthesis of polymers with metal−metal bonds in their backbones is challenging because the M−M bond is relatively weak (e.g., $D_{Mo-Mo} \approx 32$ kcal mol^{-1})[11,12] and will not remain intact under many standard polymerization reaction conditions.[3] A classic step polymerization method was used previously to synthesize polymers, including polyurethanes (eq 1), polyamides, and polyureas, with M−M units in their chains.[3] However, because many of the reagents used in step polymerization reactions will react with the metal−metal bonds, the scope of polymers obtainable by this method is limited, and we are attempting to find more versatile synthetic strategies.



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Alkene metathesis is an extensively investigated method for the formation of C=C bonds due to the versatility, selectivity, and functional group tolerance afforded by the well-defined, commercially available catalysts it employs.[13−15] We reasoned that ADMET, acyclic diene metathesis polymerization (Figure 1a), is a potentially versatile method for synthesizing polymers with metal−metal bonds in the backbone[16,17] because ADMET utilizes the commercially available metathesis catalysts to operate under mild reaction conditions.[18,19] However, there are only a limited number of alkene metathesis reactions reported in the literature that have been performed on transition metal complexes. Consequently, significant room remains for exploration in this burgeoning area of metathesis chemistry.[16,17,20] In order to make metal−metal bonded "monomers" for ADMET polymerization, our strategy was to place the alkene substituents on the cyclopentadienyl ligands of the $Cp_2Mo_2(CO)_6$ molecule (Cp = η^5-C_5H_5).[31−33] (A previous study showed that ADMET was not suitable when the C=C unit is part of a phosphine ligand on the metal dimer complex.[34]) In this paper, we report the synthesis of the $[(\eta^5\text{-}C_5H_4(CH_2)_8CH{=}CH_2)Mo(CO)_3]_2$ complex and the results of ADMET polymerization using this species.

Experimental Section

Materials. All reactions were carried out using Schlenk techniques or in a drybox with a nitrogen atmosphere. All HPLC grade solvents were deoxygenated by passage through columns of alumina and copper oxide under an argon atmosphere. Starting materials 2,5-Diisopropylphenylimidoneophylidene molybdenum bis(hexafluoro-t-butoxide) (Schrock's catalyst), $Mo(CO)_6$, and dicyclopentadiene were purchased from commercial vendors and used as received. The $(C_5H_5)(CH_2)_8CH{=}CH_2$ ligand[32] and $Mo(CO)_3(CH_3CN)_3$[35] complex were prepared according to literature procedures.

Instrumentation. ^{1}H NMR spectra were recorded on a Varian Unity/Inova 300 spectrometer operating at 299.9 MHz and were referenced to internal standard TMS in $CDCl_3$. Infrared spectra were recorded in a CH_2Cl_2 solution using a CaF_2 cell with a Nicolet Magna IR spectrometer. Gel permeation chromatography (GPC) was used to determine the molecular weights of the polymer samples with respect to polystyrene standards. GPC was performed using a Waters 515 HPLC pump with HR3 and HR4 styragel columns and a Waters 4110 differential refractometer.

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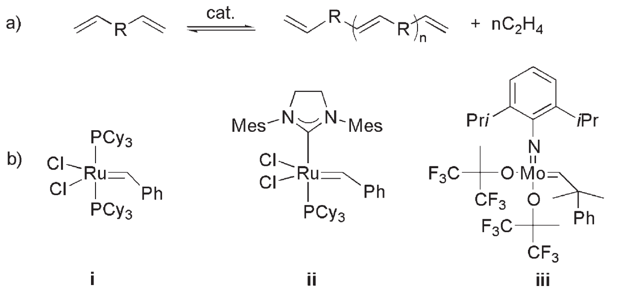
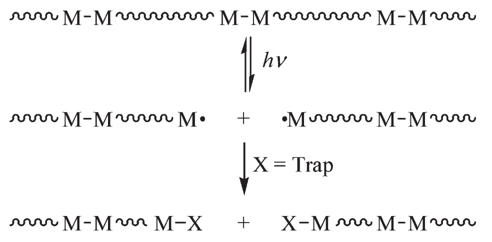


Figure 1. (a) Acyclic diene metathesis (ADMET) polymerization of a generic α,ω-diene using one of three well-defined catalysts (b): (**i**) Grubbs' first generation catalyst, (**ii**) Grubbs' second generation catalyst, and (**iii**) Schrock's catalyst.

Scheme 1. Photochemical Reaction of a Polymer with Metal–Metal Bonds along Its Backbone

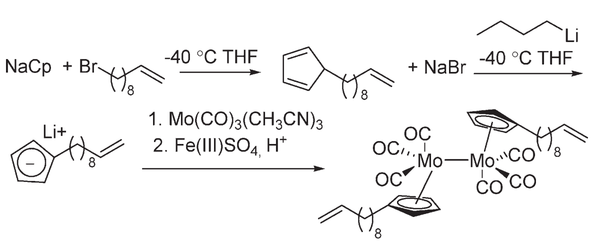


Synthesis of $[(\eta^5\text{-}C_5H_4(CH_2)_8CH{=}CH_2)Mo(CO)_3]_2$ (1). The synthesis of **1** was based on several literature preparations.[35,36] In a 250 mL Schlenk flask, the $C_5H_4(CH_2)_8CH{=}CH_2$ ligand (0.50 g, 3.70 mmol) was dissolved in THF (30 mL), cooled to −40 °C, and deprotonated by addition of butyllithium (2.4 mL, 1.6 M in hexanes). The ligand solution was allowed to warm to room temperature and was then added by cannulation to a separate 250 mL Schlenk flask containing $Mo(CO)_3(CH_3CN)_3$ (1.09 g, 3.61 mmol) in THF (75 mL) and the mixture was left stirring at room temperature. After 48 h, a deoxygenated solution of $Fe^{III}(NO_3)_3\cdot 9H_2O$ (2.30 g, 5.80 mmol) dissolved in 20 mL water with 1 mL acetic acid was added to the mixture. The resulting red solution was washed 3× (in air) with DI water and dried over $NaSO_4$. The solvent was then removed under vacuum to afford a red-purple solid. NMR: ^1H δ 5.81 ($RCH{=}CH_2$, 2H, m); 4.97 ($RCH{=}CH_2$, 4H, t); 5.18, 5.24 (C_5H_4, 8H, s); 2.40 ($C_5H_4CH_2R$, 4H, t); 2.05 ($RCH_2CH{=}CH_2$, 4H, dd); 1.35 (CH_2, 24 H, b). IR: $\nu(C\equiv O)$ 1952 vs, 1909 s cm^{-1}.

Preparation of Oligomer P1. A modified synthetic strategy from Wagener was used for the polymerization reactions.[21,37,38] A 25 mL Schlenk flask was charged with $[(\eta^5\text{-}C_5H_4(CH_2)_8CH{=}CH_2)Mo(CO)_3]_2$ (0.40 g, 0.51 mmol) and then treated with a solution of Schrock's catalyst (5 mol %) in toluene (2 mL) while stirring to form a slurry. The flask was attached to a vacuum line (2 Torr) and opened to vacuum at periodic intervals (generally every 5–10 min) to remove ethylene gas. Monomer conversion was monitored by GPC and ^1H NMR. After about 48 h, monomer conversion had ceased and the solvent was removed under reduced pressure. Purification was accomplished by cannulating a THF solution of the oligomer into cold methanol. NMR: ^1H δ 5.40 ($RCH = CHR$, 2H, b); 5.18, 5.24 (C_5H_4, 8H, s); 2.40 ($C_5H_4CH_2R$, 4H, t); 2.05 ($RCH_2CH{=}CH_2$, 4H, dd); 1.35 (CH_2, 24 H, b). IR: ν $(C\equiv O)$ 1952 vs, 1909 s cm^{-1}. $M_n = 2300$ (GPC relative to polystyrene).

Generation of Complex 2. A 25 mL Schlenk flask was charged with $[(\eta^5\text{-}C_5H_4(CH_2)_8CH{=}CH_2)Mo(CO)_3]_2$ (0.40 g, 0.51 mmol) and then treated with a solution of Schrock's catalyst (5 mol %) in toluene (100 mL) while stirring. The flask was attached to a vacuum line (2 Torr) and opened to vacuum at periodic intervals (generally every 5–10 min) to remove ethylene gas. Monomer conversion was monitored by GPC and ^1H NMR spectroscopy.

Scheme 2. Synthetic Route for the Preparation of $[(\eta^5\text{-}C_5H_4\text{-}(CH_2)_8CH{=}CH_2)Mo(CO)_3]_2$ (1)



NMR: ^1H δ 5.40 ($RCH{=}CHR$, 2H, b); 5.18, 5.24 (C_5H_4, 8H, s); 2.40 ($C_5H_4CH_2R$, 4H, t); 2.05 ($RCH_2CH{=}CH_2$, 4H, dd); 1.35 (CH_2, 24 H, b). IR: $\nu(C\equiv O)$ 1952 vs, 1909 s cm^{-1}. $M_n = 700$ (GPC relative to polystyrene).

Copolymerization of 1 with 1,9-decadiene to form P2. A 100 mL Schlenk flask was charged with complex **1** (0.10 g, 0.16 mmol) and 5 mol % of Grubbs' second-generation catalyst in a drybox. The flask was attached to a Schlenk line and the solids were dissolved in 2 mL toluene and the flask was opened to vacuum (2 Torr) at periodic intervals (generally every 5–10 min) to remove ethylene gas. After 8 h, five equivalents of deoxygenated decadiene (0.11 g, 0.80 mmol) were dissolved in toluene (2 mL) and added slowly (over 60 min) via cannula to the reaction flask, which was intermittently opened to vacuum. Monomer conversion was monitored by GPC and ^1H NMR. Purification was accomplished by cannulating a THF solution of the oligomer into cold methanol. The precipitated oligomer was then collected by filtration and dried under vacuum. NMR: ^1H δ 5.40 ($RCH{=}CHR$, b); 5.18, 5.24 (C_5H_4, s); 2.40 ($C_5H_4CH_2R$, t); 2.05 ($RCH_2CH{=}CH_2$, dd); 1.35 (CH_2, b) IR: ν $(C\equiv O)$ 1952 vs, 1909 s cm^{-1}. $M_n = 3400$ (GPC relative to polystyrene).

Photochemical Reactions. Photochemical reactions were carried out with an Oriel 200 W high pressure mercury arc lamp equipped with a Corning CS 3–68 cutoff filter ($\lambda > 520$ nm). The reaction was performed in a CaF_2 cell and monitored using a Nicolet Magna IR spectrometer. Carbon tetrachloride was distilled over P_2O_5 and degassed with N_2 prior to experiments. The following procedure was used for both oligomer **P1** and its ring-closing analog, complex **2**. In the drybox, **P1** (0.03 g, 0.39 mmol) or complex **2** (0.03 g, 0.04 mmol) was weighed and added to a scintillation vial containing 5 mL of THF. A 10-mol excess of CCl_4 was then added to the solution. An aliquot of this solution was then transferred to a 0.1 mm path length CaF_2 sealed IR cell, and an initial spectrum was obtained. The IR cell was then irradiated for 5-min intervals ($\lambda > 520$ nm). The spectrum was obtained after each photolysis interval. NMR: ^1H δ 5.40 ($RCH{=}CHR$, 2H, b); 5.60 (C_5H_4, 8 H, s); 2.40 ($C_5H_4CH_2R$, 4H, t); 2.05 ($RCH_2CH{=}CH_2$, 4H, dd); 1.35 (CH_2, 24 H, b) IR: $\nu(C\equiv O)$ 2048 s, 1972 s cm^{-1}. $M_n = 870$ (GPC relative to polystyrene).

Discussion

Synthesis and Characterization of $[(\eta^5\text{-}C_5H_4(CH_2)_8CH{=}CH_2)Mo(CO)_3]_2$ (1). The synthesis of the $[(\eta^5\text{-}C_5H_4(CH_2)_8\text{-}CH{=}CH_2)Mo(CO)_3]_2$ complex, adapted from several literature procedures,[35,36] was accomplished by the route outlined in Scheme 2. The complex was prepared from the $Mo(CO)_3(CH_3CN)_3$ precursor, which was reacted for 24 h with one equivalent of the deprotonated $LiC_5H_4(CH_2)_8CH{=}CH_2$ ligand, followed by an acidic workup with Fe(III). The complex is soluble in all organic solvents tried, ranging from nonpolar hexanes to polar methanol. The complex was characterized by ^1H NMR and IR spectroscopy (Table 2). Note that the infrared spectrum of complex **1** in the $\nu(C\equiv O)$ region is nearly identical to that of $Cp_2Mo_2(CO)_6$. Noteworthy signals in the ^1H NMR spectrum (Figure 3) include the olefinic proton residues at 5.81 and 4.97 ppm.

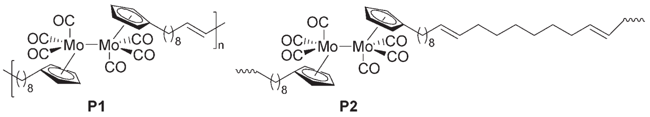


Figure 2. ADMET oligomer **P1** with a Mo−Mo bond in the backbone and co-oligomer **P2** with 1,9-decadiene.

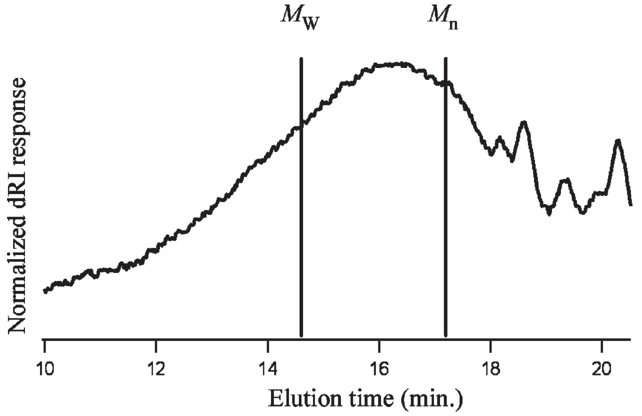


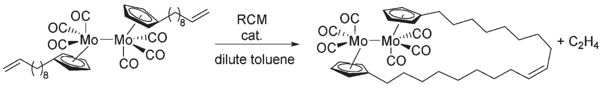
Figure 3. GPC trace (relative to polystyrene) showing the broad molecular weight distribution (PDI ~ 4.3) of the ADMET oligomer **P1**.

Table 1. Properties of ADMET Oligomer P1, Co-Oligomer P2, and Complex 2

product	M_n	M_w	M_w/M_n
P1	2300	10 000	4.3
P2	3400	13 000	3.9
complex **2**	700	n/a	1.0

Polymerization of Complex 1. ADMET polymerization of **1** using Schrock's catalyst afforded an oligomer (Figure 2) with M_n = 2300, which is approximately 3 repeat units (n ~ 3).[37] ADMET polymerization is ideally performed in bulk monomer to maximize monomer concentration and favor formation of polymer.[38,39] However, the monomer in this case is a solid well above room temperatures and above the temperature range of catalyst stability. The polymerization was carried out therefore in a concentrated solution of toluene. The GPC trace (Figure 3) of the oligomer product showed a broad molecular weight distribution with PDI = 4.3 (M_w = 10 000) (Table 1). The low degree of polymerization in this reaction is attributed to the low solubility of the oligomers. A significant portion of the oligomer product was insoluble in all organic solvents utilized, including THF, the eluent used in the GPC instrument. Because the oligomer becomes insoluble in THF at higher molecular weight, the GPC trace is not a true representation of the molecular weight distribution of the product.

Complete monomer conversion was indicated by the ^{1}H NMR spectrum, which showed the expected changes in the electronic environment of the olefinic protons (Figure 4). The disappearance of the terminal proton residues at 5.81 and 4.97 ppm was observed, as was the appearance of a new, broad signal at 5.40 ppm corresponding to internal HC=CH protons. The IR spectrum (Table 2) remained unchanged through the course of the polymerization reaction, indicating that the Mo−Mo unit remained intact



(2)

Ring−chain equilibria are common in ADMET polycondensations,[19] and in the case of complex **1**, which contains long flexible alkyl chains, the formation of macrocyclic molecules is likely. Indeed, the GPC trace for oligomer **P1** product is multimodal, with several distinct peaks in the lower molecular weight range, suggesting that cyclic ADMET products are formed along with linear chains. To explore this possibility, the reaction was carried out under dilute solvent conditions. As described next, under these conditions it was found that formation of a single ring-closing metathesis product (eq 2) was favored over formation of linear oligomer chains. To form the ring-closing metathesis (RCM) product, complex **1** (0.40 g, 0.51 mmol) was reacted for 24 h with 5 mol % of Schrock's catalyst at room temperature. The reaction vessel was placed under dynamic vacuum at regular intervals to remove ethylene. The formation of the ring-closed product was evidenced by the ^{1}H NMR spectrum, which showed the disappearance of the terminal proton resonances at 5.81 and 4.97 ppm and the appearance of new internal protons at 5.40 ppm. The ^{1}H NMR spectrum is nearly identical to that of the ADMET oligomer product (Figure 4). However, the presence of the RCM product was supported by the GPC trace (Figure 5), which showed a narrow monomodal peak corresponding to M_n = 700 or one repeat unit (n ~ 1). (The calculated molecular weight of the RCM product is 738.6 g mol^{-1}.) The ring-closing product was isolated by precipitation in MeOH, and the IR spectrum (Table 2) of the product in the ν(C≡O) region is identical to that of complex **1**, $[(\eta^5\text{-}C_5H_5(CH_2)_8\text{-}CH{=}CH_2)Mo(CO)_3]_2$. The polymer end-groups were not detectible by ^{1}H NMR spectroscopy, consistent with the proposed ring structure.[40]

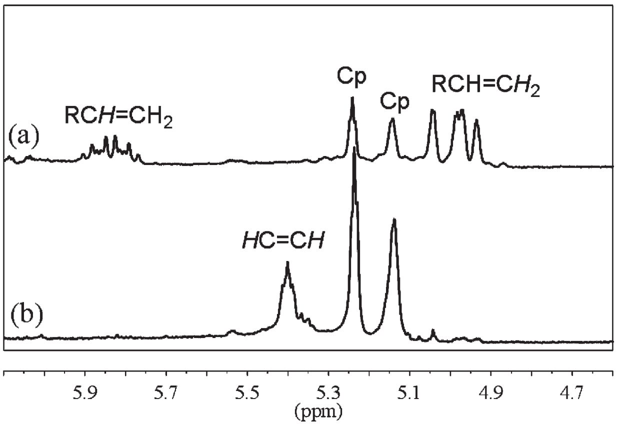
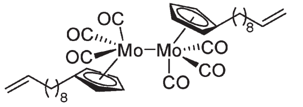
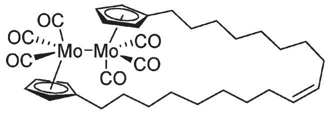
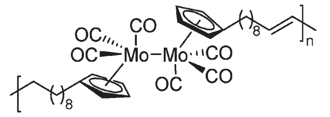
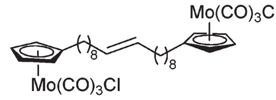
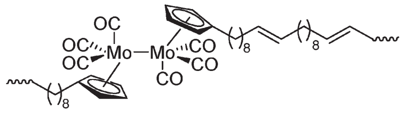
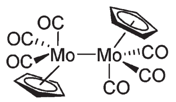


Figure 4. ^{1}H NMR spectra in the olefinic region of (a) complex **1** and (b) oligomer **P1**.

Copolymerization with 1,9-Decadiene. In order to obtain a higher molecular weight polymer, complex **1** was copolymerized with 5 equiv of 1,9-decadiene. Although complex **1** is soluble in 1,9-decadiene, polymerization in neat 1,9-decadiene resulted in unreacted complex **1** embedded in polymerized 1,9-decadiene. To circumvent the reactivity differences between the two monomers, complex **1** was first reacted in a concentrated solution of toluene for eight hours after which time 1,9-decadiene was added slowly dropwise over a 1 h time period. The reaction afforded a co-oligomer (Figure 2) of M_n = 3400 and PDI = 3.9 (Table 1). The polydispersity is somewhat higher than expected for a step polymerization, but slightly improved from the oligomer **P1**. Characterization by ^{1}H NMR spectroscopy showed the disappearance of terminal olefinic proton residues at 5.81 and 4.97 ppm and the appearance of a new resonance at 5.40 ppm corresponding to the internal protons of the C=C bond. As expected,

Table 2. Infrared and ^{1}H NMR Spectroscopic Data for all Relevant Complexes and Metathesis Products

Compound	IR (CH_2Cl_2) ν(C≡O) cm^{-1}	^{1}H NMR ($CDCl_3$)
	1952 vs, 1909 s	δ 5.81 (RCH=CH$_2$, m) 5.18, 5.24 (C$_5H_4$, s) 4.97 (RCH=CH_2, t)
	1952 vs, 1909 s	δ 5.40 (RCH=CHR, b) 5.18, 5.24 (C$_5H_4$, s)
	1952 vs, 1909 s	δ 5.40 (RCH=CHR, b) 5.18, 5.24 (C$_5H_4$, s)
	2048 s, 1972 s	δ5.60 (C$_5H_4$)
	1952 vs, 1909 s	δ 5.40 (RCH=CHR, b) 5.18, 5.24 (C$_5H_4$, s)
	1960, 1920 ($CHCl_3$)[41]	δ 5.33 (C$_5H_5$)[41]
	2035, 1985 ($CHCl_3$)[41]	δ 5.63 (C$_5H_5$)[41]

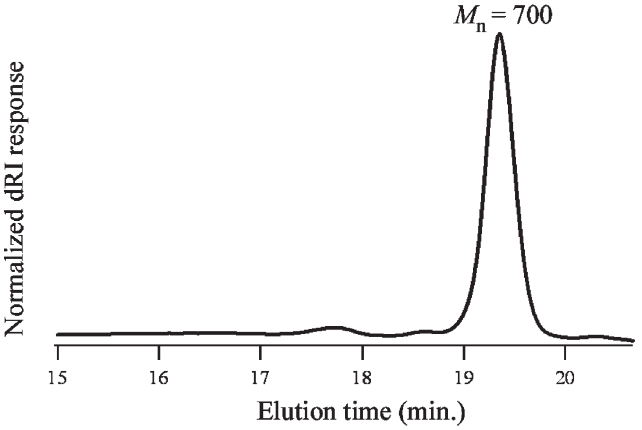
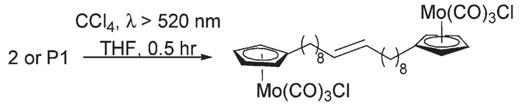


Figure 5. GPC trace (relative to polystyrene) showing a monomodal peak with narrow molecular weight distribution representing the ring-closing metathesis product, **2**, with M_n = 700.

the carbonyl region of the infrared spectrum was unchanged from that of complex **1**, indicating no electronic changes to the Mo−Mo unit.

Photoreactivity of Oligomer P1 and the RCM product. Oligomer **P1**, and the ring-closing product, complex **2**, were found to be photoreactive. When irradiated with $\lambda > 520$ nm in the presence of CCl_4, both **P1** and **2** formed a product that is assigned as the metal halide complex shown in eq 3. The carbonyl region in the infrared spectrum of the photoproduct contains bands at 2048 s, 1972 s cm^{-1} (CH_2Cl_2), which compare closely to that of the CpMoCO$_3$Cl complex, which has ν(C≡O) bands at 2035 and 1985 cm^{-1} (in chloroform) (Table 2).[41] As expected, the photoreaction of the oligomer resulted in cleavage of the oligomer backbone, as indicated by GPC, which showed that the molecular weight after irradiation was reduced to $M_n \sim 870$ ($n \approx 1$). (The calculated molecular weight of the photochemical product is 809.5 g mol^{-1}.) The mechanism of these photochemical reactions likely follows the well established pathway involving photochemical homolytic cleavage of the Mo−Mo bond, followed by trapping of the Mo radicals with CCl_4 (Scheme 3). Note that, according to this mechanism, both **P1** and **2** will give the same product, which was indeed found to be the case.

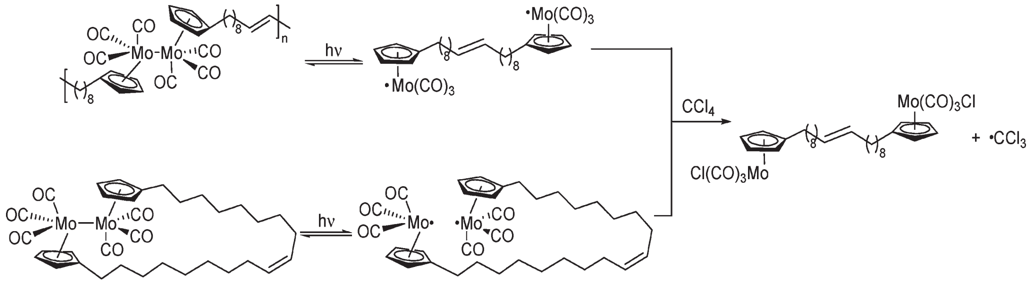


(3)

Summary and Conclusions

A photoreactive oligomer with Mo−Mo bonds in the main chain was prepared using the ADMET method. Specifically, complex **1**, [(η^5-C$_5$H$_4$(CH$_2$)$_8$CH=CH$_2$)Mo(CO)$_3$]$_2$, was reacted with Schrock's catalyst under concentrated solvent conditions to afford an oligomer, **P1**. Under dilute conditions, a ring-closing metathesis product, **2**, was formed. The ADMET oligomer was of low molecular weight, as determined by GPC, a result attributed to the low solubility of the oligomers formed in the ADMET reaction. Slightly higher molecular weight was achieved by copolymerization of **1** with 1,9-decadiene. Both the

Scheme 3. Stepwise Photochemical Pathway of Oligomer P1 and Complex 2 When Irradiated with Visible Light (λ > 520 nm) in the Presence of a Radical Trap (CCl_4) To Form Complex 3



homo-oligomer **P1** and the ring-closing metathesis product **2** were irradiated with λ > 520 nm in the presence of CCl_4 to form $[\mu\text{-}C_5H_4(CH_2)_8CH{=}CH(CH_2)_8C_5H_4\{Mo(CO)_3Cl\}_2]$, **3**. The photochemical reaction resulted in net cleavage of the oligomer backbone and a reduction in molecular weight, as indicated by GPC.

As discussed in the Introduction, a key concern in any polymerization involving a monomer with a metal−metal bond is that the polymerization conditions will be too harsh for the weak metal−metal bond, with consequent degradation of the metal−metal bonded molecule. The results reported here demonstrate the successful occurrence of olefin metathesis in the coordination sphere of a reactive dimeric transition metal complex. Specifically, the reaction conditions afforded by the use of Schrock's catalyst were sufficiently mild that the weak Mo−Mo bond remained intact during the course of the reactions reported herein. The method is limited, however, due to the reduced solubility of the oligomers that form and to the inability to achieve sufficiently high monomer concentrations when in solution.[30] ADMET, as a condensation polymerization, is ideally performed in neat monomer to maximize monomer concentration and favor formation of polymer. Presumably higher molecular weights could be obtained if it were possible to perform the polymerization in the bulk. Slightly higher molecular weights were achieved when copolymerization with a liquid organic diene was carried out, but even in this case the molecular weights were not impressive.

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Supporting Information Available: Infrared spectrum of **P1** after photochemical degradation. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

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