Transition-Metal-Containing Polymers by ADMET: Polymerization of *cis*-$Mo(CO)_4(Ph_2P(CH_2)_3CH{=}CH_2)_2$

Ginger V. Shultz, Lev N. Zakharov, and David R. Tyler*

Department of Chemistry, University of Oregon, Eugene, Oregon 97403

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ABSTRACT: Polymerization of the *cis*-$Mo(CO)_4(Ph_2P(CH_2)_3CH{=}CH_2)_2$ complex using acyclic diene metathesis (ADMET) polymerization is reported. Ideally, ADMET polymerization is performed in bulk monomer to maximize monomer concentration and favor formation of polymer. The monomer in this case is a solid with a melting temperature of 128 °C, which is well above room temperature and above the range of catalyst stability. The polymerization was carried out therefore in a concentrated solution of toluene. The complex underwent polymerization when catalyzed with Grubbs' second-generation catalyst; neither Grubbs' first-generation catalyst nor Schrock's catalyst was active. Homopolymerization resulted in oligomers of $M_n = 2060$ ($n \approx 3$, GPC relative to polystyrene). At elevated temperatures the coordination core of the polymerized *cis*-$Mo(CO)_4(Ph_2P(CH_2)_3CH{=}CH_2)_2$ complex isomerized to the *trans* geometry. Copolymerization with 1,9-decadiene was also carried out and resulted in an oligomer of slightly higher molecular weight, $M_n = 5800$. It is suggested that ADMET is not an effective method for obtaining high molecular weight polymers in this case because the monomer is neither a liquid nor a low-melting solid, and therefore a high monomer concentration could not be achieved.

Introduction

Synthetic methods for obtaining well-defined transition-metal-containing polymers are sought due to the useful properties of these materials.[1,2] Acyclic diene metathesis polymerization (ADMET) is a potentially attractive method for synthesizing polymers with transition metal complexes in the backbone because the catalysts employed are tolerant of many functional groups, the reactions conditions are mild, and because a wide range of architectures are accessible.[3–8]

Since it was first demonstrated in 1990, Wagener and others have shown the utility of ADMET by synthesizing so-called inorganic/organic hybrid polymers containing main group elements such as polycarbostannanes,[9,10] polycarbogermanes,[11,12] and polycarbosilanes.[13,14] Polyferrocenes[15–17] have also been prepared by ADMET and are the only examples, thus far, of transition-metal-containing polymers prepared by this method. To explore the scope of ADMET in preparing polymers containing transition metals, we studied the ability of ADMET to prepare polymers with molybdenum complexes incorporated into the main chain.

Transition metal complexes can be converted to ADMET monomers by addition of alkene substituents to an appropriate ligand set to obtain the α,ω-diene moiety necessary for polymerization (Figure 1). This strategy is advantageous because ADMET could allow tunability of polymer properties such as solubility or glass transition temperature by simple modifications to the ligand set of the transition-metal complex. Tunability could also be accomplished by copolymerization with appropriate organic dienes or with a second metal-containing diene as shown in Figure 1.[3–7,9] In this paper, we report the ADMET polymerization of an organometallic molybdenum-containing diene and its copolymerization with an organic diene.

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. The starting materials Ph_2PH, $Mo(CO)_6$, bis(tricyclohexylphosphine)benzylidine ruthenium(IV) chloride (Grubbs' first-generation catalyst), 1,3-bis(2,4,6-trimethylphenyl)-2-(imidazolidinylidene)(dichlorophenylmethylene)(tricyclohexylphosphine)ruthenium (Grubbs' second-generation catalyst), and 2,6-diisopropylphenylimidoneophylidene molybdenum bis(hexafluoro-*tert*-butoxide) (Schrock's catalyst) were purchased from commercial vendors and used as received. $Ph_2P(CH_2)_3CH{=}CH_2$[18] and *cis*-$Mo(CO)_4(pip)_2$[19] (pip = piperidine) were prepared according to previously reported literature procedures.

Instrumentation. $^{31}P\{^1H\}$ and ^1H NMR spectra were recorded on a Varian Unity/Inova 300 spectrometer operating at 121.4 and 299.9 MHz, respectively. ^{31}P was referenced to external standard 1% H_3PO_4 in D_2O, and ^1H was referenced to internal standard TMS in $CDCl_3$. Infrared spectra were recorded in CH_2Cl_2 solution using a CaF_2 cell with a Nicolet Magna IR spectrometer. Gel permeation chromatography (GPC) was used to determine 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 410 differential refractometer.

X-ray Diffraction Method. The X-ray diffraction experiment was carried out on a Bruker Smart Apex diffractometer at 173 K using Mo Kα radiation ($\lambda = 0.710\,73$ Å). Absorption corrections were applied by SADABS ($T_{min}/T_{max} = 0.850$). The crystal structure was found by direct methods and refined using a full matrix least-squares method based on F^2. All non-H atoms were refined with anisotropic thermal parameters. H atoms were refined in calculated positions with isotropic thermal parameters in a rigid group model. All calculations were performed by the SHELXTL package. *Crystal data*: $C_{38}H_{38}MoO_4P_2$, $M_r = 716.56$. Colorless plate, $0.35 \times 0.12 \times 0.02$ mm, orthorhombic, space group *Pbca*, $a = 16.961(3)$, $b = 19.876(4)$, $c = 20.621(4)$ Å, $V = 6951(2)$ Å^3, $Z = 8$, $\rho_{calcd} = 1.369$ g cm^{-3}, $\mu = 0.508$ mm^{-1}, $F(000) = 2960$, $2\theta_{max} = 55.0°$, 76296 reflections collected, 7969 unique [$R_{int} = 0.0612$], R factors [$I > 2\sigma(I)$]: $R1 = 0.0481$, $wR2 = 0.0631$, GOF = 1.099.

***cis*-$Mo(CO)_4(Ph_2P(CH_2)_3CH{=}CH_2)_2$ (1).** A solution of $Mo(CO)_4(pip)_2$ (1.53 g, 4.06 mmol) and $Ph_2P(CH_2)_3CH{=}CH_2$ (2.20 g, 8.65 mmol) in CH_2Cl_2 (20 mL) was refluxed for 5 h until the disappearance of reactant was observed in the carbonyl region of the IR spectrum (1844 cm^{-1}). A white powder (1.95 g, 2.71 mmol, 67%) was precipitated by addition of MeOH at 0 °C. Crystals suitable for X-ray analysis were obtained by slow cooling in a mixture of CH_2Cl_2/MeOH. NMR: ^1H δ 7.33−7.49 (Ph, 20H, s); 5.75 ($CH_2{=}CH$, 2H, m); 4.92 ($CH_2{=}CH$, 4H, t); 2.19 (CH_2, 4H, m), 2.08 (CH_2, 4H, m); 1.37 (PCH_2, 4H, m). ^{31}P NMR: δ 27.24

* Corresponding author. E-mail: dtyler@uoregon.edu.

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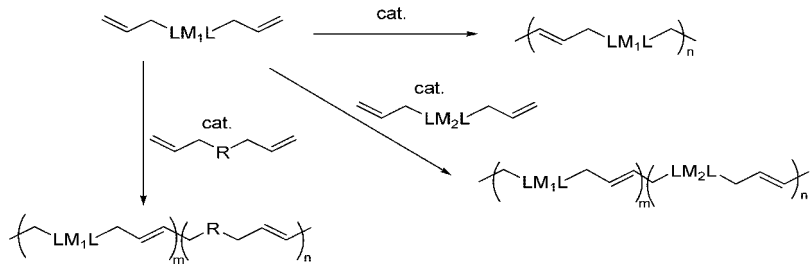


Figure 1. ADMET polymerization of a transition-metal-containing diene, copolymerization with an organic diene, and copolymerization with a second metal-containing diene.

(P, 2P, s). IR: ν(C≡O) 2019 m, 1915 s, 1903 s, 1875 sh cm^{-1}. T_m = 128 °C (DSC).

***trans*-Mo(CO)$_4$(Ph$_2$P(CH$_2$)$_3$CH=CH$_2$)$_2$ (2).** A solution (0.200 g, 0.278 mmol) of **1** in toluene was refluxed for 3−4 h until the appearance of a band at 1892 cm^{-1}, and the disappearance of bands at 1915 and 1903 cm^{-1} was observed in the carbonyl region of the IR spectrum. After cooling, MeOH was added to precipitate a white solid (0.178 g, 0.247 mmol, 89%) from solution that was subsequently washed (3×) with additional MeOH. Residual MeOH was removed in vacuo. NMR: ^{1}H δ 7.33 (Ph, 20H, s); 5.75 (CH$_2$=C*H*, 2H, m); 4.92 (C*H*$_2$=CH, 4H, t); 2.19 (CH2, 4H, m); 2.08 (CH$_2$, 4H, m); 1.37 (PCH$_2$, 4H, m). ^{31}P: δ 38.80 (P, 2P, s). IR: ν(C≡O) 1892 vs cm^{-1}.

Polymerization. A modified synthetic strategy from Wagener was used for the polymerization reactions.[3−5] A 25 mL Schlenk flask was charged with *cis*-Mo(CO)$_4$(Ph$_2$P(CH$_2$)$_3$CH=CH$_2$)$_2$ (0.40 g, 0.51 mmol) and then treated with a solution of Grubbs' second-generation catalyst (5 mol %) in toluene (2 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. After 1 week, monomer conversion had ceased, and the solvent was removed under reduced pressure. Purification was accomplished by cannulating a THF solution of the polymer into cold methanol. NMR: ^{1}H δ 7.33 (Ph, 20H, s); 5.37 (C*H*=C*H*, b); 2.19 (CH$_2$, 4 H, m); 2.08 (CH$_2$, 4H, m); 1.37 (PCH$_2$, 4H, m). ^{31}P NMR: δ 27.24 (P, 2P, s). IR: ν(C≡O) 2019 m, 1915 s, 1903 s, 1975 sh cm^{-1}. M_n = 2080 (GPC relative to polystyrene).

Copolymerization. A 25 mL Schlenk flask was charged with complex **1** (0.40 g, 0.57 mmol) and 5 mol % Grubbs' second-generation catalyst in a drybox. The flask was attached to a Schlenk line, and the solids were dissolved in 2 mL of toluene, and 1 equiv of deoxygenated decadiene (0.08 g, 0.57 mmol) was added via cannula. The flask was opened to vacuum (2 Torr) at periodic intervals (generally every 5−10 min) to remove ethylene gas. Monomer conversion was monitored by GPC and ^{1}H NMR. After 1 week, monomer conversion had ceased, and the solvent was removed under reduced pressure. Purification was accomplished by cannulating a THF solution of the polymer into cold methanol. NMR: ^{1}H δ 7.33 (Ph, s); 5.19 (C*H*=C*H*, b); 5.37 (C*H*=C*H*, b); 2.04−1.78 (CH$_2$, b); 1.62−1.44 (CH$_2$, b); 1.35−0.98 (CH$_2$, b). ^{31}P: δ 27.24 (P, 2P, s). IR: ν(C≡O) 2019 m, 1915 s, 1903 s, 1975 sh cm^{-1}.

Results and Discussion

Organometallic α,ω-dienes for ADMET polymerization were prepared by substituting phosphine ligands containing terminal alkene substituents onto molybdenum carbonyl complexes. Complex **1** was synthesized by refluxing 2 equiv of Ph$_2$P(CH$_2$)$_3$CH=CH$_2$ with Mo(CO)$_4$(pip)$_2$ (pip = piperidine), followed by precipitation with MeOH to afford a white solid (Figure 2). Single crystals of **1** were grown by cooling a mixture of CH$_2$Cl$_2$ and MeOH, and the structure was determined by X-ray crystallography (Figure 3). The X-ray structure indicates the expected octahedral coordination environment around the molybdenum center with *cis* phosphine ligands.

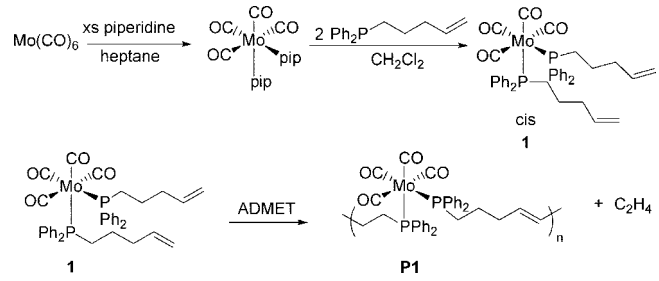


Figure 2. Synthesis of complex **1** followed by ADMET polymerization.

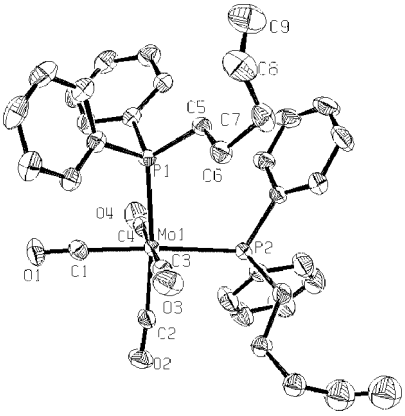


Figure 3. Thermal ellipsoid plot (30% probability level) of complex **1**. The hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Mo(1)−P(1), 2.5371(9); Mo(1)−P(2), 2.5480(9); C(8)−C(9), 1.299(7); C(1)−Mo(1)−C(2), 85.58(13); P(1)−Mo(1)−P(2), 97.87(3).

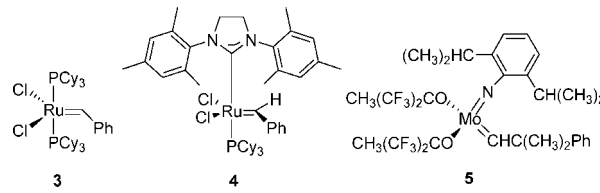


Figure 4. Metathesis catalysts employed: Grubbs' first-generation (**3**), Grubbs' second-generation (**4**), and Schrock's (**5**).

ADMET polymerization of **1** (Figure 2) was carried out under rigorous air-free conditions in a concentrated solution of toluene. Three catalysts (**3** − **5**; Figure 4) were investigated as initiators; however, catalysts **3** and **5** were unreactive after 7 days at room temperature. Polymerization of complex **1** by reaction with catalyst **4** at room temperature afforded an oligomer with M_n = 2060 ($n \approx 3$, GPC relative to polystyrene).

The GPC trace of the product showed a polydisperse oligomer (M_w = 3850 and PDI = 1.86) with multimodal distribution ranging from n = 1 to n = 7. ^{1}H NMR spectroscopy demonstrated the expected changes in the electronic environment

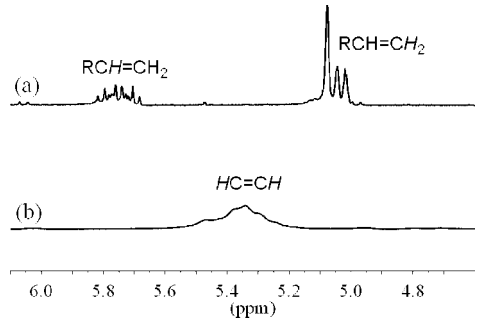


Figure 5. ^{1}H NMR spectra in the olefinic region of (a) complex **1** and (b) polymer **P1**.

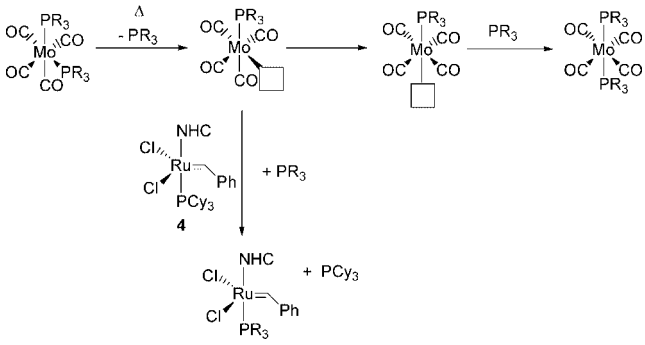


Figure 6. Intermolecular thermally induced isomerization of complexes of the type *cis*-$Mo(CO)_4(PR_3)_2$ may lead to substitution of the labile phosphine ligand on catalyst **4** with a consequent loss of catalytic activity.

Table 1. Properties of ADMET Polymers P1 and P2

polymer	M_w	M_n	PDI	T_g (°C)	T_m (°C)
P1	3850	2060	1.9	<−150	55
P2	16400	5800	2.8	<−150	−52

of the olefinic protons (Figure 5). Specifically, the disappearance of terminal proton residues at 5.75 and 4.92 ppm was observed, as was the appearance a new, broad signal at 5.37 ppm corresponding to internal *HC*═C*H* protons.[7] The product is likely a mixture of both linear and cyclic oligomers, the latter of which would form by ring-closing metathesis. This is supported by the disappearance of olefinic protons in the ^{1}H NMR spectrum. Both the ν(C≡O) region in the IR spectrum and the ^{31}P NMR spectrum remained unchanged after polymerization, indicating that at room temperature the coordination core of complex **1** was unaltered in the course of the reaction.

In an attempt to increase the molecular weight, various parameters, including catalyst concentration, solvent, and temperature, were investigated (see Table S1 in the Supporting Information for details of these experiments). Evaluation of these parameters led to the conditions reported in the Experimental Section as the optimal conditions for obtaining the highest molecular weight. It is noted that typical ADMET polymerizations are carried out in neat monomer. However, because the monomer in this case is a solid at the temperatures employed, it was necessary to perform the polymerization in a concentrated solution of toluene. THF was also evaluated, but it is not a favorable solvent for this system: only 20% of the monomer was consumed after 1 week when the polymerization was carried out in a concentrated solution of THF under similar conditions. Catalyst loading and reaction time also affected the molecular weight of the polymers. An increase in catalyst loading resulted in an increase in polymer molecular weight. For example, a catalyst loading of 3 mol % resulted in a lower molecular weight of $M_n = 1400$ compared to $M_n = 2060$ with 5 mol % of catalyst.

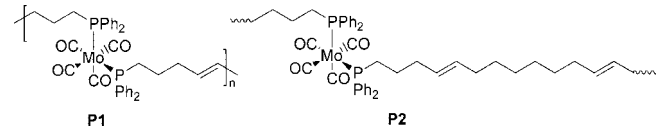
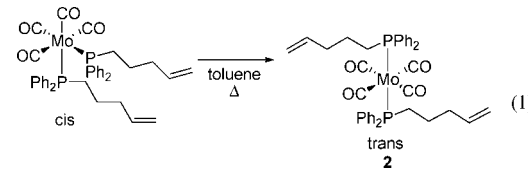


Figure 7. Transition-metal-containing oligomers obtained by ADMET polymerization.

The molecular weight was also increased by longer reaction times, although reaction times longer than a week were nonproductive.

Increased reaction temperature had an unfavorable effect on the polymerization reaction. Reaction of complex **1** with catalyst **4** at 50 °C resulted in thermally induced isomerization of the coordination core of the complex from *cis* to *trans* geometry (eq 1) but did not result in formation of polymer. In fact, no monomer conversion was detected at elevated temperatures, as monitored by ^{1}H NMR spectroscopy and GPC. (The isomerization was observed in the carbonyl region of the IR spectrum by the disappearance of starting material bands at 1915 and 1903 cm^{-1} and the appearance of a strong band at 1892 cm^{-1} (CH_2Cl_2). For comparison, *trans*-$Mo(CO)_4(PPh_3)_2$ has a strong band at 1901 cm^{-1} (C_2Cl_4).[20] Isomerization of *cis*-$Mo(CO)_4(PR_3)_2$ complexes in solution under similar reaction conditions is well documented in the literature.[20–22])



Presumably the failure of complex **1** to polymerize at elevated temperatures is due to the intermolecular nature of the isomerization of the complex.[20] As shown in Figure 6, intermolecular isomerization goes by a pathway involving ligand dissociation. As has been observed in other systems, (uncoordinated) phosphine ligands will substitute onto catalyst **4**, which deactivates the catalyst and inhibits polymerization.[23,24]

The *trans*-$Mo(CO)_4(Ph_2P(CH_2)_3CH{=}CH_2)_2$ complex, **2**, was polymerized in order to compare its polymerizability to that of complex **1**. Complex **2** was prepared by refluxing complex **1** in toluene for 4 h, as evidenced by the appearance of the band for **2** at 1892 cm^{-1} in the carbonyl region and the shift of the ligand signal in the ^{31}P NMR spectrum from 27.2 to 38.8 ppm. Reaction of complex **2** with catalyst **4** at room temperature gave low-molecular-weight oligomers, analogous to the reactivity of complex **1**. The polymerization of complex **2** indicates that the failure of complex **1** to polymerize at elevated temperatures is not due a difference in reactivity between the *cis* and *trans* isomers.

Characterization of **P1** (Table 1) by DSC indicated a melting temperature at 55 °C and no observable glass transition (T_g) to −150 °C. Subsequent to characterization by DSC, the IR spectrum of the annealed oligomer **P1** indicated isomerization of the coordination core from *cis* to *trans* in the solid state.

Copolymerization of **1** with 1,9-decadiene was also performed and resulted in copolymers with $M_n = 5800$ (Figure 7, **P2**). The GPC trace indicated a polydisperse sample with a PDI = 2.8 ($M_w = 16\,400$). Characterization (Table 1) of copolymer **P2** by DSC indicated a melting temperature of −52 °C and no observable T_g to −150 °C. The ^{1}H NMR spectrum (Figure 8) showed the formation of two new signals in the olefin region at 5.37 and 5.19 ppm corresponding to the internal olefinic protons, C*H*═C*H*, of each subunit and the disappearance of resonances at 5.75 and 4.92 ppm and at 5.52 and 4.83 ppm

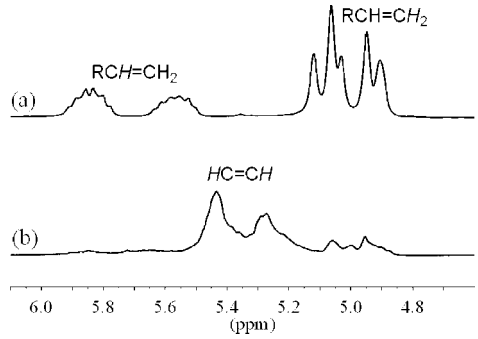


Figure 8. ^{1}H NMR spectra in the olefinic region of (a) a solution of **1** and 1,9-decadiene and (b) copolymer **P2**.

corresponding to the proton residues of complex **1** and the 1,9-decadiene comonomer, respectively.

Conclusions

cis-$Mo(CO)_4(Ph_2P(CH_2)_3CH{=}CH_2)_2$ (**1**) was prepared and oligomerized by the ADMET method using Grubbs' second-generation catalyst. Grubbs' first-generation catalyst and Schrock's catalyst were ineffective in polymerizing the complex. Increased catalyst loading and longer reaction times resulted in higher molecular weights, but even under optimum conditions only oligomers were obtained. Elevated reaction temperatures had an adverse effect on polymerization, presumably because dissociated phosphine poisoned the catalyst. Higher reaction temperatures also caused a thermally induced isomerization of the transition metal complex from *cis* to *trans* geometry. Both the *cis* and *trans* monomers showed similar reactivity toward polymerization at room temperature. In a similar reaction, the polymerized organometallic monomer unit could be isomerized from *cis* to *trans* in solution and in the solid state. The scope of transition-metal-containing ADMET polymers can be increased by copolymerization with organic dienes. Complex **1**, for example, was copolymerized with 1,9-decadiene to afford a copolymer of higher molecular weight.

Conceptually, ADMET is a convenient synthetic method for the preparation of transition-metal-containing polymers because transition-metal complexes can be readily converted to ADMET monomers by substitution with olefin-containing ligands. However, in practice, when the monomer is a solid at room temperature, high-molecular-weight polymers may be difficult to obtain by this method. The melting temperature of the molybdenum complex *cis*-$Mo(CO)_4(Ph_2P(CH_2)_3CH{=}CH_2)_2$ (**1**; 128 °C) is above room temperature and above the range of catalyst stability, and therefore polymerization could not be carried out in bulk liquid monomer. Presumably, lower molecular weights were obtained in the case of monomer **1** because high monomer concentrations could not be obtained.

The *cis*-$Mo(CO)_4(Ph_2P(CH_2)_3CH{=}CH_2)_2$ complex was oligomerized and copolymerized using the ADMET method. The practical limitations of the ADMET method in obtaining high-molecular-weight polymers when the precursor complex is a solid at room temperature are discussed.

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Supporting Information Available: Crystallographic data, including the cif file and tables of angles and bond lengths for complex **1**, and a table describing experimental conditions evaluated to maximize the molecular weight. This material is available free of charge via the Internet at http://pubs.acs.org.

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