Metal-Containing Polymers Synthesized *via* Acyclic Diene Metathesis: Polycarbostannanes

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Received August 28, 1996; Revised Manuscript Received November 21, 1996[⊗]

ABSTRACT: Polycarbostannanes have been successfully synthesized *via* acyclic diene metathesis chemistry utilizing both a well-defined molybdenum akylidene and an aryloxo tungsten "classical" catalyst system. In the case of the well-defined catalyst, the polymerization proceeds smoothly to produce linear polymer which is characterized by proton, carbon, and tin NMR. Molecular weights of about 16 000 g/mol can be produced. The production of a polycarbostannane *via* classical metathesis chemistry is just as facile, producing molecular weights comparable to the well-defined system, and in this case, the monomer performs as both the monomer and the cocatalyst species.

Introduction

In recent years we have shown that acyclic diene metathesis (ADMET) chemistry can be used to synthesize high molecular weight aliphatic[1] and aromatic[2] polymers containing a variety of functionalities.[3] Thus far this research has been done with Schrock's well-defined tungsten and molybdenum alkylidenes and more recently, with Grubbs' ruthenium benzylidene complex.[4,5] In this paper, we report the first metathesis polymerization of a diene containing a tin moiety using either a well-defined molybdenum catalyst or a "classical" catalytic system to produce an unsaturated polycarbostannane. In the latter case *the monomer actually participates in the mechanism as a cocatalyst*. Catalyst structures and the polymerization scheme are presented in Figure 1.

Early experiments in ADMET chemistry performed with Lewis acidic classical catalytic systems demonstrated that vinyl addition chemistry (likely cationic oligomerization) hinders the formation of clean metathesis polymers,[6] and eliminating this competing mechanism is the key to successful ADMET condensation polymerizations. Recently Feldman and co-workers have shown that the aryloxo tungsten complex **2** is capable of producing clean ring closing metathesis (RCM) products when used in the presence of a tetraalkylead cocatalyst species.[7] On the basis of our analogous experiments using tetraalkyltin species as cocatalysts for **2** in ADMET polymerizations[8] and on experiments performed by Nubel and co-workers using alkyltins as cocatalysts for WCl_6 in metathesis polymerizations,[9] we decided to examine more closely the use of classical catalyst systems in ADMET chemistry. Schrock's molybdenum catalyst was used in comparative experiments described in this paper.

Experimental Section

Materials. Schrock's molybdenum alkylidene[10] and W(O)-Cl_2(O-2,6-C_6H_3-Br_2)$_2$[7] were synthesized according to published procedures. Di-*n*-butyltin dichloride was purchased from Acros Organics and used as received. 5-Bromo-1-pentene was obtained from Aldrich Chemical Co., dried over CaH_2, and distilled immediately before use. Diethyl ether was distilled from sodium benzophenone ketyl and stored over 4 Å molecular sieves in an inert atmosphere. Methanol was distilled from magnesium shavings and stored over 4 Å molecular sieves in an inert atmosphere.

^{1}H (300 MHz) and ^{13}C (75 MHz) NMR measurements were performed on either a Varian VXR 300 MHz or a Varian Gemini series 300 MHz superconducting spectrometer system. All peaks are referenced to TMS (0.05% w/w) in $CDCl_3$ unless otherwise noted. Proton-decoupled ^{119}Sn (112 MHz) NMR was performed on a Varian VXR 300 NMR and referenced to an external tetramethyltin standard. Gel permeation chromatography (GPC) was performed on a Waters Associates Model 590 chromatograph using three Phenomenex Phenogel columns (50 000, 5000, and 500 Å) in series with THF as the eluent at a flow rate of 1.0 mL/min. The instrument was calibrated using polystyrene standards. Elemental analysis was performed by Robertson Microlit Laboratories, Inc., Madison, NJ.

Synthesis of Bis(4-pentenyl)di-*n*-butylstannane. (3) A clean, dry, 500 mL three-neck reaction flask equipped with a reflux condenser, a 125 mL addition funnel, and a magnetic stir-bar was purged with argon and charged with 4.86 g (0.2 mol) of freshly ground magnesium turnings and 80 mL of anhydrous diethyl ether. 5-Bromo-1-pentene (25 g, 0.167 mol) in 80 mL of dry ether was then added to the reaction mixture in small portions *via* the addition funnel until the reaction began to reflux. The remainder of the solution was then added at a rate that maintained a gentle reflux. The reaction was allowed to stir for 0.5 h and then refluxed for 1 h. The reaction was cooled to room temperature, and 15.15 g (0.049 mol) of di-*n*-butyltin dichloride in 50 mL of ether was added dropwise *via* the addition funnel over a period of 1.5 h. Upon completion of the addition, the reaction was stirred for 3 h and then refluxed for 20 h. The reaction was cooled to room temperature, and the solution was poured into 250 mL of ice cold 1 M aqueous NH_4Cl solution. The organic layer was separated, washed with 300 mL (3 × 100mL) of deionized H_2O, dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The remaining liquid was dried over CaH_2 under Schlenk vacuum for 48 h before being fractionally distilled under full Schlenk vacuum with collection of the fraction boiling at 148−150 °C. Yield: 15.11g (83%). ^{1}H NMR: δ (ppm) = 5.8 (m, 2 H); 4.9 (m, 4 H); 2.1 (q, 4 H); 1.6 (m, 4H); 1.5 (m, 4H); 1.3 (m, 4H); 0.9(m, 14H). ^{13}C NMR: δ (ppm) = 138.7, 114.4, 38.6, 29.3, 27.4, 26.6, 13.7, 8.8, 8.6. ^{119}Sn NMR: δ (ppm) = −13.0. Elemental Anal. Calcd for $C_{18}H_{36}Sn$: C, 58.25; H, 9.78. Found: C, 58.35; H, 9.80.

Polymerization of 3 using Mo(=CHMe$_2$Ph)(N-2,6-C_6H_3-*i*-Pr$_2$)(OCMe(CF$_3$)$_2$)$_2$ (1). All polymerizations were performed using standard Schlenk techniques. Monomer **3**, (1.02 g, 2.75 × 10^{-3} mol, 500 equiv) was charged to a 35 mL round bottom flask equipped with a Teflon Roto-flow valve and a magnetic stir-bar in an argon-purged drybox. Catalyst **1** (5 mg, 6.5 × 10^{-6} mol, 1 equiv) was then charged to the reaction vessel.

[⊗] Abstract published in *Advance ACS Abstracts,* February 1, 1997.

S0024-9297(96)01291-0 CCC: $14.00

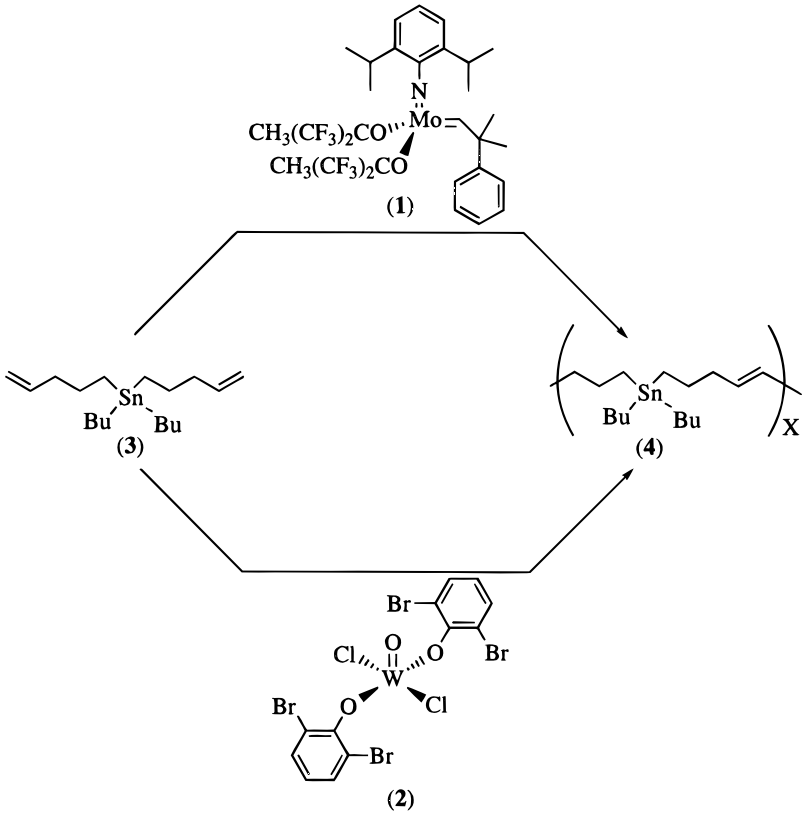

Figure 1. Polymerization of monomer **3** using a well-defined metathesis catalyst (**1**) and a classical metathesis catalyst system (**2**) to produce essentially the same polymer (**4**).

The valve was sealed and the flask was taken from the drybox to a high-vacuum Schlenk line and evacuated while stirring *via* magnetic agitation. The polymerization was allowed to stir at room temperature until the viscosity of the reaction mixture hindered free mixing (approximately 12 h). The temperature was then raised to 45 °C for 24 h and then to 60 °C for 48 h. The polymerization was terminated by exposure of the evacuated vessel to the atmosphere. The polymer mixture was then dissolved in $CDCl_3$ and characterized *via* proton and quantitative carbon NMR. The polymer mixture was then precipitated into vigorously stirring cold methanol from which polymer **4** was isolated in approximately quantitative yield. ^{1}H NMR: δ (ppm) = 5.4 (m, br, 2H); 2.0 (m, br, 4 H); 1.5 (m, 8H); 1.3 (m, 4H); 0.9 (m, 14H). ^{13}C NMR: δ (ppm) = 130.4 (trans); 129.7 (cis); 37.4 (allylic, trans); 32.1 (allylic, cis); 29.3; 27.4; 27.3; 27.2; 13.8; 8.8; 8.7. ^{119}Sn NMR: δ (ppm) = −12.8 (*trans*−*trans*); −13.0 (*trans*−*cis*); −13.2 (*cis*−*cis*). Elemental Anal. Calcd: C, 56.00; H, 9.40. Found: C, 56.23; H, 9.54.

Polymerization of 3 Using $W(O)Cl_2(O\text{-}2,6\text{-}C_6H_3\text{-}Br_2)_2$ (2). Monomer **3**, (1.016 g, 2.737×10^{-3} mol, 250 equiv) was charged in a 50 mL round bottom flask equipped with a Teflon Roto-flow valve and a magnetic stir-bar in an argon-purged drybox. Aryloxo complex **2** (8 mg, 1.035×10^{-5} mol, 1 equiv) was then charged to the reaction vessel and the mixture was stirred for 10 min under argon. The valve was then sealed and the flask was taken from the drybox to a high-vacuum Schlenk line and evacuated while being stirred *via* magnetic agitation. The temperature was slowly raised to 70 °C and vigorous evolution of ethylene was observed during the first 36 h of reaction. The system was then heated to 90 °C and kept at this temperature until the magnetic stirring was no longer possible due to the viscosity of the mixture. The reaction was then allowed to cool to room temperature and dissolved in dry $CDCl_3$. The crude polymer was characterized by tin, proton, and quantitative carbon NMR. Further purification of the polymer was performed by precipitation of the polymer from dry $CDCl_3$ into dry methanol using standard Schlenk techniques. Yield: 75%. ^{1}H NMR: δ (ppm) = 5.4 (m, br, 2H); 1.9 (m, br, 4 H); 1.5 (m, 8H); 1.3 (m, 4H); 0.9 (m, 14H). ^{13}C NMR: δ (ppm) = 130.3 (trans); 129.7 (cis); 37.4 (allylic, trans); 32.2(allylic, cis); 29.3; 27.4; 27.2; 13.7; 8.8; 8.7. ^{119}Sn NMR: δ (ppm) = −12.8 (*trans*−*trans*); −13.0 (*trans*−*cis*); −13.2 (*cis*−*cis*). Elemental Anal. Calcd: C, 56.08; 9.42. Found: C, 55.90; H, 9.47.

Results and Discussion

Metal-containing polymers are well-known materials made by a variety of techniques.[11] Our interest in preparing metal-containing polymers *via* ADMET condensation has led us to explore the behavior of two different catalytic systems in the synthesis of polycarbostannanes.[12]

Schrock's molybdenum catalyst **1** cleanly polymerizes bis(4-pentenyl)di-*n*-butyltin (**3**) to produce polymer **4** as illustrated in Figure 1. Ethylene evolution is evident upon contact of monomer **3** with catalyst **1**, and within 12 h the viscosity of the solution increases to a point at which heat must be applied to facilitate the production of high molecular weight polymer. Examination of the quantitative ^{13}C NMR (Figure 2) illustrates that clean metathesis polymerization to produce an unsaturated polycarbostannane has indeed taken place.

End group analysis of the quantitative ^{13}C NMR spectrum shows a number-average molecular weight of 17 000 g/mol. GPC analysis yields M_n = 36 000, a value which no doubt is in error resulting from the difference in the hydrodynamic volume between the polycarbostannane sample and the polystyrene standard. Nonetheless, the polydispersity ratio of 2.1 as determined by GPC is as expected for any step polymerization polymer, which is the case for ADMET polymerizations.

The use of the aryloxo tungsten complex **2** (monomer: catalyst ratio = 250:1) generates essentially the same ADMET polymer (M_n = 9300 g/mol by ^{1}H NMR, M_n = 16 000 g/mol by GPC) upon contact with monomer **3**,

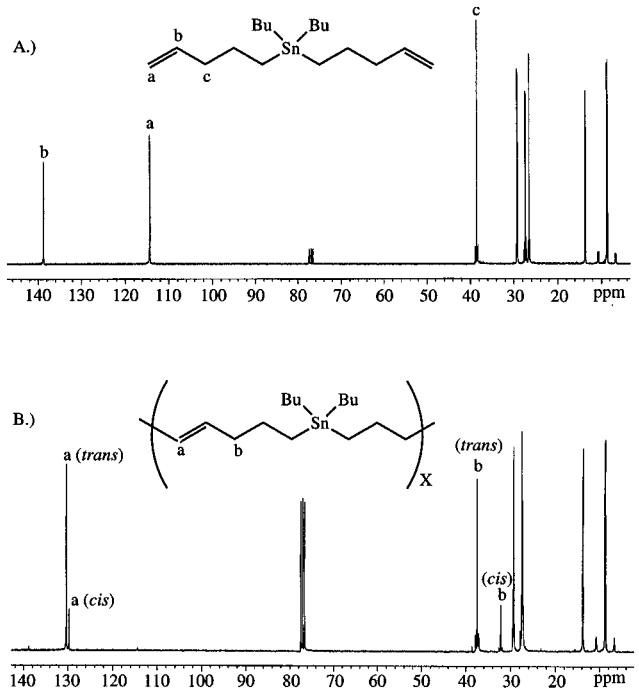

Figure 2. (A) ^{13}C NMR of monomer **3** and (B) quantitative ^{13}C NMR of polymer **4** produced using catalyst **1**.

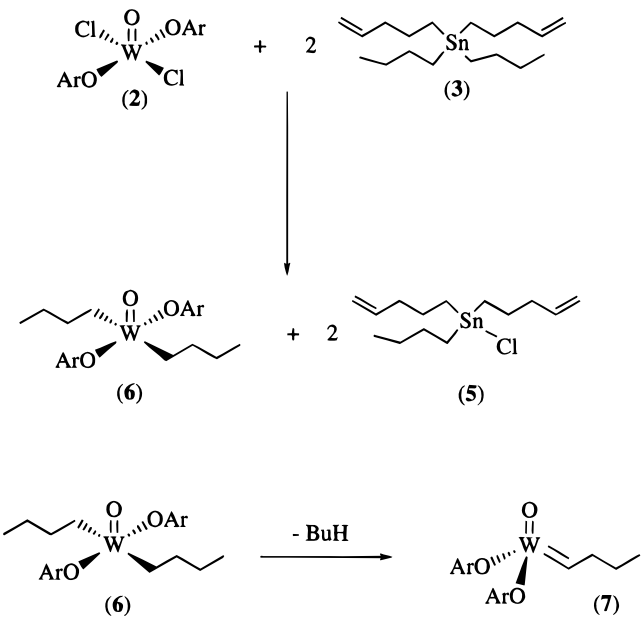

Figure 3. Suggested mechanism for formation of the active metathesis catalyst **7** produced from complex **2**. Alkylation with butyl groups is shown.

and *this polymerization represents the first case where a reagent serves as both the monomer and the cocatalyst in a metathesis polymerization*. The active catalyst is formed *via* the alkylation of 1 equiv of complex **2** by 2 equiv of monomer **3** (Figure 3). This event is followed by the generation of a tungsten alkylidene (**7**) after α-hydride elimination. Basset and co-workers previously described the generation of active metathesis catalysts *via* an alkylation−elimination mechanism of (aryloxo)tungsten complexes with main group organometallic compounds,[13] and the chemistry described herein supports their observations.

The chemistry shown in Figure 3 suggests that alkenyltin chlorides **5** are produced as comonomers, which indeed is the case. Evidence for the existence of the Sn−Cl bond in the polymer backbone is supported by the formation of an insoluble gel when a sample of the polymer synthesized from a 100:1 monomer to catalyst ratio is exposed to water.[14] On the other hand, samples of the same polymer handled in the absence of moisture remain soluble in common organic solvents. Thus when water is present, gelation (cross-linking) is a direct result of hydrolysis of the Sn−Cl bond followed by nucleophilic attack of the new Sn-OH bond on another Sn−Cl site.

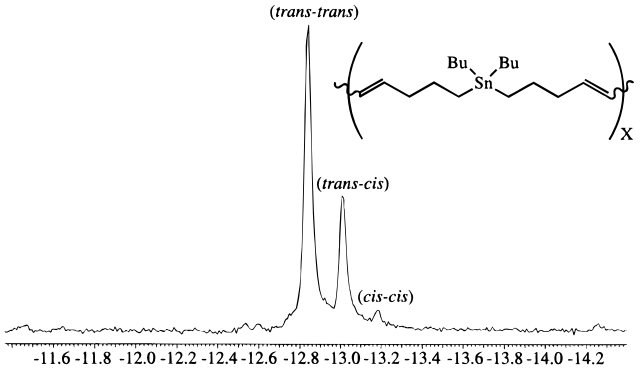

Figure 4. ^{119}Sn NMR of polymer **4** synthesized using catalyst **1** illustrating the three possible olefin environments in the ratio of 65:30:5.

Gelation is not observed when moisture is present in the workup of the polymer synthesized with the well-defined catalyst (**1**), since no Sn−Cl bonds are formed. Further, complex **2** can be used with a conventional cocatalyst (e.g. Bu_4Sn) in the polymerization of pure hydrocarbon monomers like 1,9-decadiene, and no cross-linking is observed.[8] Completely soluble, high molecular weight ADMET polymers are the result, regardless of whether moisture is present in the workup procedure.

The ^{13}C NMR spectrum of the polymer synthesized using complex **2** is essentially the same as that for the polymer made with catalyst **1**, both having approximately the equilibrium distribution of *cis* and *trans* isomers in the typical 80:20 ratio observed for ADMET chemistry. Only the solubility differences in the presence of moisture distinguish these two polymers. Thus while the Sn−Cl repeat unit is present in the polymer when using the (aryloxo)tungsten complex **2**, its concentration is sufficiently low, as would be expected, such that it cannot be observed by ^{13}C NMR. Further, the ^{119}Sn NMR spectra of both polymer samples display three distinctive peaks which correspond to the statistical distribution of the three possible olefin environments around each tin moiety. Each tin atom resides between two olefin linkages, thus the *trans*−*trans*, *trans*−*cis*, and *cis*−*cis* geometries connecting each repeat unit can be observed by the differences in chemical shift, as displayed in Figure 4. Integration of the resonances yields a ratio of 65:30:5, a value in good agreement with the calculated distribution of 64:32:4.[15] No other resonances could be identified.

Conclusions

ADMET polymerization of bis(4-pentenyl)di-*n*-butyltin (**3**) can be accomplished with either Schrock's alkylidene **1** or with the tungsten aryloxo complex **2**, where in the latter case the monomer also serves as a cocatalyst. The polymerization of metal-containing monomers broadens the scope of the ADMET polycondensation reaction to include the formation of polymers containing metals within their primary structure. The synthesis

of metal-containing polymers *via* ADMET chemistry is an active field of study for our research group.

Acknowledgment We wish to thank the National Science Foundation (DMR-9520803) for financial support. Helpful suggestions by Dr. Jerry Feldman at Dupont's Experimental Station and Dr. Andrew Bell of B F Goodrich are appreciated. We also thank Dr. Ion Ghiviriga for his valuable help with ^{119}Sn NMR spectroscopy.

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(14) The gelation is a direct effect of the concentration of Sn−Cl bonds. This was verified by examining the different behaviors of polymer samples synthesized using different monomer to catalyst ratios (250:1 and 100:1). Workup of a polymer sample (250:1) in the presence of moisture did not form insoluble material whereas the polymer produced from a 100:1 ratio yielded an insoluble gel under the same conditions. We acknowledge the reviewer for bringing this to our attention.

(15) The distribution was calculated based on the cis:trans (21:79) ratio determined by quantitative ^{13}C NMR.

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