Polymer Bulletin 25, 483–490 (1991)

Polymer Bulletin

Monitoring the $WCl_6/(CH_3)_4Sn$ initiated polymerization of substituted acetylenes by ^{1}H-NMR spectroscopy

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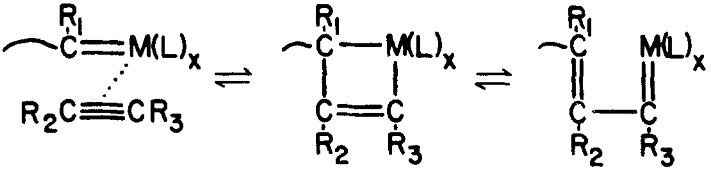
SUMMARY

A study of the $WCl_6/(CH_3)_4Sn/CD_2Cl_2$ initiated polymerization of o-trimethylsilylphenylacetylene and 2-hexyne was completed. This study suggests that generated carbenes initiate the polymerization of mono and disubstituted acetylenes. Evidence was provided which clearly shows the formation of the initiating $[W]=CH_2$ carbene complex and its immediate disappearance upon addition of both the 2-hexyne and o-trimethylsilylphenylacetylene. Under the reaction conditions used in the present study, no spectroscopic evidence of an initiating or propagating chain end or metallocyclobutene intermediate could be provided.

INTRODUCTION

The polymerization of cycloolefins by catalysts consisting of transition metal halides and reducing agents has long been thought to proceed through metal carbene initiating and propagating species (1-5). In the last few years, several research groups were able to prepare well-defined metal carbene complexes which were capable of inducing cycloolefin polymerization. Through this work, the actual mechanism of cycloolefin polymerization has been spectroscopically demonstrated (6-8). This mechanism of polymerization follows a metathesis route, i.e. the [2+2] cycloaddition of a transition metal carbene to a carbon-carbon double bond with the formation of a metallocyclobutane intermediate. These two species are in dynamic equilibrium.

Stable metal carbene complexes, most notably the Fischer, Casey and Rudler carbenes, have also been shown to initiate the polymerization of some acetylenic monomers (9, 10-15). These stable metal carbenes have been shown to effectively initiate the polymerization of a series of mono substituted acetylenes having different substituent sizes, although the overall monomer conversion and polymer yield is low. The polymerization mechanism, as a result of this work, is also believed to follow a metathesis mechanism, i.e., propagation through metal carbenes and cyclometallobutene intermediates.



In addition to the stable metal carbenes, there exists a class of highly reactive unstable metal carbenes that are generated using metal halide based catalysts. The initiation and propagation of acetylenic monomers using metal halide based catalysts is also assumed to proceed through metal carbenes which are in dynamic equilibrium with metallocyclobutenes. Several types of initiation systems are available for the polymerization of acetylenic monomers using metal halide based catalysts. The major difference between these initiation systems is believed to result from the fact that the polymerization of monosubstituted acetylenes can be initiated by transition metal halides only, while that of disubstituted acetylenes requires a transition metal halide and a reducing agent (16-20). It is assumed that for the initiation of monosubstituted acetylenes, the acetylenic proton reacts with and reduces the metal halide to an active carbene complex. The disubstituted acetylene requires the use of a co-initiator (reducing agent) because the disubstituted acetylene can not reduce the metal halide to an initiating metal carbene complex. This initiator-coinitiator system is capable of initiating the polymerization of both mono- and disubstituted acetylenes. One of the most reactive initiator-coinitiator systems for the polymerization of both mono and disubstituted acetylenes is the $WCl_6/(CH_3)_4Sn$ system.

This paper presents our results on the $WCl_6/(CH_3)_4Sn$ initiated polymerization of 2-hexyne and o-trimethylsilylphenylacetylene in an attempt to identify by ^{1}H-NMR spectroscopy the existence of an initiating and propagating metal carbene complex and a cyclometallobutene intermediate.

EXPERIMENTAL

Materials

2-Hexyne was purchased from Farchan Chemical Co. and distilled from calcium hydride under argon prior to use. Purity by GC was greater than 98%. Tetramethyltin, $(CH_3)_4Sn$, (Aldrich) was stored over activated 4Å molecular sieves prior to use. The WCl_6 (99.9+%), and CD_2Cl_2 (100 atom %) (both from Aldrich Chem. Co.) were used without further purification. All transfers were done in an argon filled glove box. All other solvents and reagents were purified by standard methods. The o-trimethylsilylphenylacetylene and $(^{13}CH_3)_4Sn$ were prepared according to literature procedures (21, 22).

Techniques

The relative molecular weights of polymers were determined by gel permeation chromatography (GPC) with a Perkin-Elmer Series 10 LC equipped with a Nelson Analytical 900 Series data station. The measurements were made using THF as solvent (1ml/minute at 40°C) with a series of PL-gel columns (10^2, $5x10^2$, 10^3, 10^4 and 10^5 Å) and a calibration plot constructed with polystyrene standards. Monomer conversions and purity were determined on a Hewlett-Packard HP 5890 GC using a 6.1m x 0.32cm column of 10% SP-1000 80/100 Supelcoport. Monomer and polymer structures were confirmed by a XL 200 Varian 200 MHz spectrophotometer.

$WCl_6/(CH_3)_4Sn$ initiated polymerization monitoring

In a typical polymerization experiment, 18μl(0.126mmole) of $(CH_3)_4Sn$ was added to an NMR sample tube containing a solution of 25mg(0.063mmole) of WCl_6 in 0.5ml of CD_2Cl_2 and the tube was immediately placed in the NMR spectrometer where proton spectra were recorded every minute. The [W]=CH_2 carbene appeared at approximately 20 minutes following the addition of $(CH_3)_4Sn$ and increased in intensity attaining a maximum concentration approximately 45 minutes following the addition of $(CH_3)_4Sn$. It was at this time that the acetylenic monomer (amount depending on desired monomer to initiator ratio) was added to the reaction tube. The polymerization was monitored to complete acetylene conversion. The solvent peak ($CHDCL_2$, δ 5.35) was used as internal standard. Polymerization monitoring was performed by 200 MHz ^1H-NMR spectroscopy using a XL 200 Varian spectrometer (spectra width 5000Hz, 16 transients with an acquisition time of 2 seconds, time between acquisition of 1 second and 20K FID data points).

RESULTS AND DISCUSSION

The $WCl_6/(CH_3)_4Sn$ system is a well-known initiator for the metathesis of olefins and the metathesis polymerization of cycloolefins (3-4, 23-26). It was speculated by several research groups that the active initiating species in this system is [W]=CH_2 carbene complex. However, it was not until recently that this species was spectroscopically observed (27). The [W]=CH_2 complex was detected by monitoring the reaction of WCl_6 with $(CH_3)_4Sn$ in CD_2Cl_2 using both ^1H and ^{13}C NMR spectroscopy. In addition, it was shown that this complex initiated the polymerization of norbornene and that the CH_2=CH- polymer chain end was spectroscopically observed.

The $WCl_6/(CH_3)_4Sn$ system is an excellent initiator system for the polymerization of some acetylene monomers, particularly 2-hexyne and o-trimethylsilylphenylacetylene. The $WCl_6/(CH_3)_4Sn$ initiated polymerization of 2-hexyne and o-trimethylsilylphenylacetylene was monitored ^1H-NMR spectroscopy in an attempt to substantiate the suggested metathesis mechanism of acetylene polymerization, ie, to spectroscopically observe the carbene-initiation step, the initiating and propagating chain ends and the cyclometallobutene intermediate. The o-trimethylsilylphenylacetylene was selected because: (a) high yields of polymer can be obtained using the $WCl_6/(CH_3)_4Sn$ initiation system and (b) the monomer possesses an acetylenic proton. The acetylenic proton is necessary if a propagating metal carbene complex ([W]=C(H)-) is to be observed by ^1H-NMR spectroscopy. The o-trimethylsilylphenylacetylene will polymerize with both the $WCl_6/(CH_3)_4Sn$ system and WCl_6 alone. The 2-hexyne was selected because: (a) high yields of high molecular weight polymer can also be obtained using the $WCl_6/(CH_3)_4Sn$ initiation system and (b) the initiation of the 2-hexyne polymerization using only WCl_6 does not occur. This is, therefore, a logical route to spectroscopically determine whether a generated metal carbene complex initiates the polymerization of disubstituted acetylene monomers.

$(CH_3)_4Sn$ was added to a solution of WCl_6 in CD_2Cl_2 at room temperature. Following five minutes of reaction, the intensity of the $(CH_3)_4Sn$ signal (δ 0.03) was reduced 50% with new peaks appearing at δ 0.61, 2.65 and 3.10 which were assigned to $(CH_3)_3SnCl$ (27), $(CH_3)_2WCl_4$ (27) and CH_3WCl_5 (27-28) respectively. Several unassigned peaks also appeared, three in significant concentration at δ 3.15, 3.80 and 3.90. Following twenty minutes of reaction, the $(CH_3)_4Sn$ was completely reacted and a sharp singlet at δ 10.50 assigned to the [W]=CH_2 carbene metal complex was observed (Figure 1a). This assignment was based on the known chemical shifts of tungstencarbene complexes (3, 29-30). A broad less intense signal of unknown origin at δ 4.50 also appeared.

The reaction was allowed to continue. A significant decrease in the singlets at δ 3.80. 3.90 and 4.5 occurred with a corresponding increase in the concentration of the metal carbene complex at δ 10.50 (Figure 1b-d). The metal carbene complex signal reached a maximum intensity with the loss of the 3.80, 3.90 and 4.50 signals. A decrease in the $(CH_3)_2WCl_4$ signal and a significant increase in the $(CH_3)WCl_5$ signal also occurred. A sharp singlet appeared at δ 3.05 which is attributed to CH_3Cl, a by product of the $WCl_6/(CH_3)_4Sn$ reaction (13). At the time of maximum carbene complex concentration (45 minutes from the time of $(CH_3)_4Sn$ addition and 20 minutes following the complete conversion of $(CH_3)_4Sn$), the o-trimethylsilylphenylacetylene (1 equiv.) was added. An immediate complete loss of the carbene metal complex occurred with the simultaneous appearance of signals attributable to the monomer (ArH, δ 7.2-7.5; HC≡, δ 3.10) and unidentified singlets at δ 2.4, 2.8, 5.4 and 5.6 (Figure 2). No evidence of a propagating carbene complex [W]=C(H)-, cyclometallobutene intermediate or vinyl end group was observed. The δ 10.5 carbene complex signal slowly disappeared (within 30 minutes) if acetylene monomer was not added. As the polymerization reaction proceeded, the singlets at δ 2.8 and 2.4 gradually decreased

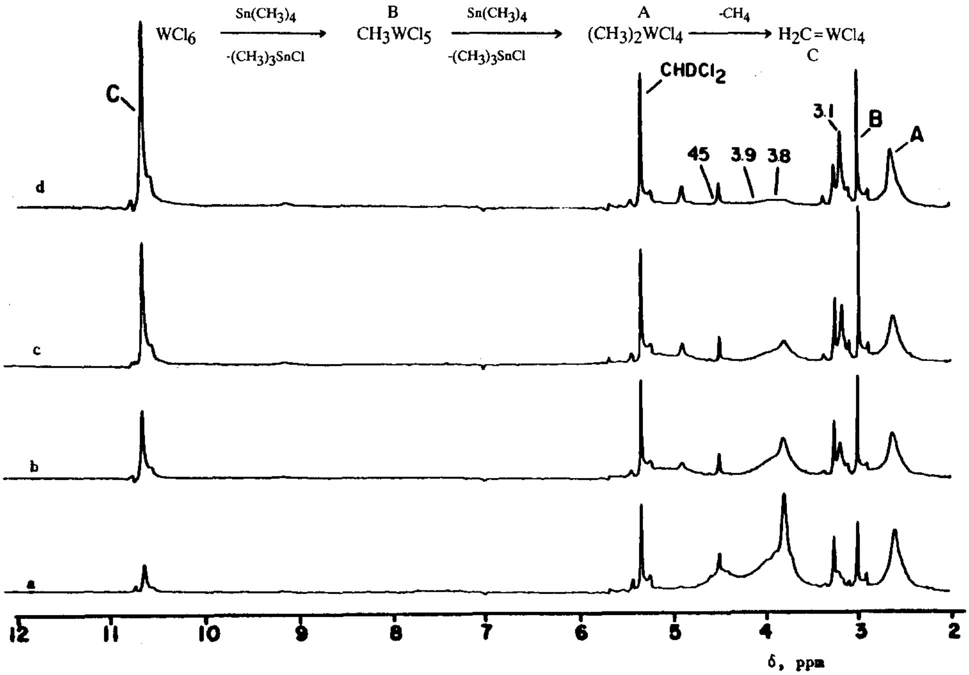


Figure 1. 200 MHz ^{1}H-NMR spectra of the $WCl_6/(CH_3)_4Sn$ reaction mixture (CD_2Cl_2) showing: (a) $[W]=CH_2$ carbene complex (C) at complete conversion of $(CH_3)_4Sn$; (b) 10 minutes following complete conversion of $(CH_3)_4Sn$; (c) 20 minutes following complete conversion of $(CH_3)_4Sn$; (d) 45 minutes following complete conversion of $(CH_3)_4Sn$.

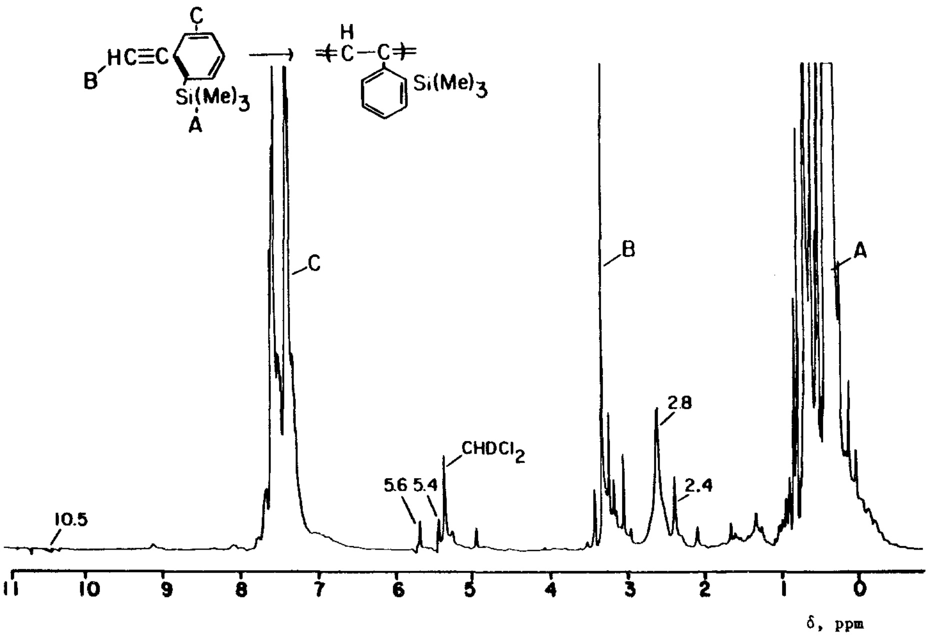


Figure 2. 200 MHz ^{1}H-NMR spectra of the $WCl_6/(CH_3)_4Sn$ reaction mixture immediately following the addition of o-trimethylsilylphenylacetylene.

with the loss of acetylenic proton (δ 3.10) and the formation of poly (o-trimethylsilylphenylacetylene). The polymerization was complete in one hour. Evaluation of the final purified polymer (Mn=20000) by ^{1}H-NMR spectroscopy shows signals typical of a poly (o-trimethylsilylphenylacetylene) (31).

Monitoring the polymerization of o-trimethylsilylphenylacetylene by ^{1}H-NMR spectroscopy using labelled $(^{13}CH_3)_4Sn$ (protons attached directly to the labelled carbon will now also couple with the carbon atom) was completed in a similar fashion. $(^{13}CH_3)_4Sn$ was added to a solution of WCl_6 in CD_2Cl_2 at room temperature. Following five minutes of reaction, the intensity of the $(^{13}CH_3)_4Sn$ signal (δ -0.1 and 0.5) was reduced by 75%. New peaks assigned to $(^{13}CH_3)_3SnCl$ (δ 0.2 and 0.9), $(^{13}CH_3)_2WCl_4$ (δ 2.2 and 2.9) and $(^{13}CH_3)WCl_5$ (δ 2.6 and 3.3) appeared. Following the complete conversion of $(^{13}CH_3)_4Sn$, a doublet assigned to $[W]={}^{13}CH_2$ (δ 10.2 and 10.9) slowly appeared reaching a maximum concentration at a twenty minute reaction time (Figure 3). The appearance of a doublet at δ 10.2 and 10.9 is strong evidence for the formation of a $[W]={}^{13}CH_2$ carbene complex structure. In addition, an unidentified doublet of doublets appeared at δ 8.8 and 9.4. The singlets at δ 3.75, 3.85 and 4.25, as previously described for the unlabeled monitoring studies, did not appear. Instead, two unidentified strong singlets appeared at δ 4.6 and 4.8. The δ 4.6 and 4.8 singlets and the signals assigned to the metal carbene complex reached a maximum intensity at a 20 minute reaction time (the shorter reaction time to reach a maximum carbene complex concentration compared to the unlabeled monitoring studies is presently unexplained). A broad singlet at δ 2.2 appeared on addition of $(^{13}CH_3)_4Sn$ and did not change in intensity during the course of the reaction. On addition of o-trimethylsilylphenylacetylene (1 equiv.) at a twenty minute reaction time, the $[W]={}^{13}CH_2$ carbene complex, the doublets of doublets at δ 8.8 and 9.4 and the singlets at δ 4.4 and 4.6 disappeared with the immediate appearance of signals attributable to monomer and singlets at δ 5.4 and 5.6. Within 30 minutes, the polymerization reaction was complete resulting in poly (o-trimethylsilylphenylacetylene) of Mn = 17000. The high number average molecular weight despite the low [M]/[I] ratio is due to the low overall efficiency of the initiation process. From the calculated degree of polymerization and the known concentration of WCl_6 and assuming a faster rate of initiation than propagation and a living polymerization process, the overall initiator efficiency was 0.87%. In addition, the actual amount of the observed metal carbene complex responsible for initiation was estimated to be only 20% (assuming complete initiation of the observed carbene complex a poly (o-trimethylsilylphenylacetylene of Mn = 3,300 should have been obtained). This value is typical of the polymerizations described in this report and may be attributed to the presence of impurities present in the reaction mixture. No indication of a $-HC={}^{13}CH_2$ polymer chain end was observed by ^{13}C-NMR spectroscopy. This may be due to either its absence of due to the high molecular weight of the resulting polymer and therefore low concentration of labelled end groups.

Monitoring of the $WCl_6/(CH_3)_4Sn/CD_2CL_2$ reaction using 2-hexyne was completed in a similar fashion. The generation of the $[W]=CH_2$ metal carbene complex occurred exactly as described above. At the time of maximum metal carbene complex concentration, 2-hexyne (2 equiv.) was added. The immediate loss of the signal at δ 10.5 of the carbene complex occurred! The monomer was consumed in one hour and poly-

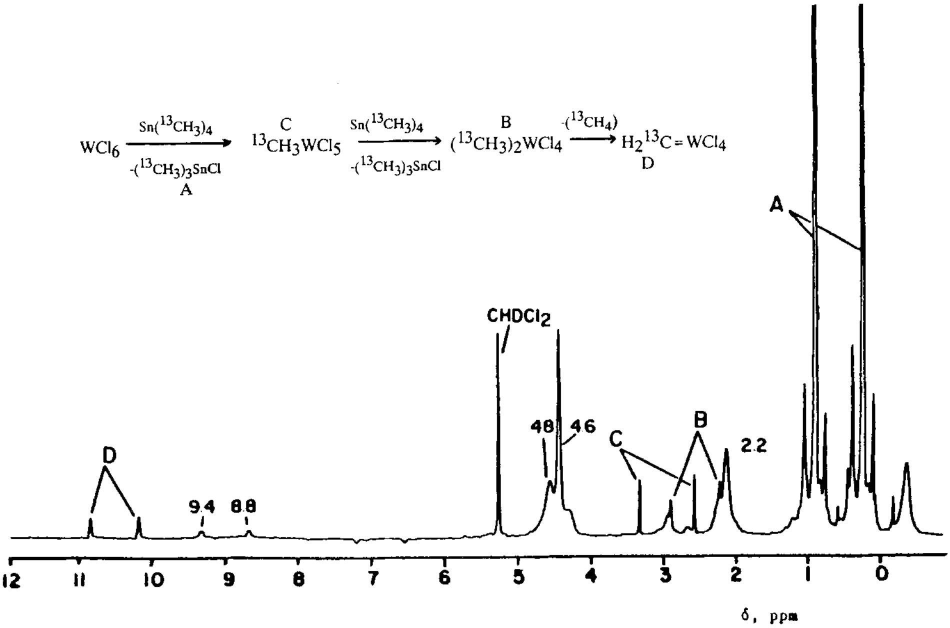


Figure 3. 200 MHz ^1H-NMR spectra of the $WCl_6/{}^{13}CH_3)_4Sn$ reaction mixture at the time of maximum carbene concentration (CD_2Cl_2, 25°C).

(2-hexyne) resulted. This is spectroscopic evidence for the existence of an initiating carbene metal complex in the $WCl_6/(CH_3)_4Sn$ initiated polymerization of disubstituted acetylenes. No indication of signals attributable to a cyclometallobutene intermediate or vinyl end groups were detected under these reaction conditions.

The rapid and complete disappearance of the $[W]=CH_2$ carbene complex on addition of o-trimethylsilylphenylacetylene and 2-hexyne is a strong indication that generated carbenes initiate the polymerization of acetylene monomers through a carbene mechanism. However, alternative initiation mechanisms are possible. Under the reaction conditions used in the present study, no evidence of a propagating carbene complex or cyclometallocyclobutene intermediate was observed. In addition, no evidence of a vinyl end group was observed immediately after the addition of acetylene monomer to the carbene complex (5-10% conversion). This implies that the first step of the polymerization may not result in the formation of a $[W]=C(R)\text{-}C(R)=CH_2$ carbene complex. The absence of signals assignable to the propagating carbene complex and vinyl end groups may also be a result of the concentration of carbene complex actually involved in the initiation process. As stated previously, the concentration of initiation complex was estimated to be 20% of that observed and in fact, could be much lower. The concentration of the end groups would then be too low to be detected by NMR spectroscopy.

The complete polymerization mechanism of acetylene derivatives using generated metal carbenes still remains unelucidated. The $[W]=CH_2$ carbene is too reactive to study the mechanism of polymerization under the reaction conditions used. The high reactivity of the initiating carbene limits our ability to observe these groups. As of today we cannot provide enough evidence to elucidate the metathesis mechanism of polymerization of acetylenes. Spectroscopic monitoring of these reactions by ^{1}H-NMR using a stable carbene complex of suitable reactivity as initiator should provide an understanding of this mechanism. However, these additional experiments require a suitable stable metal carbene complex to become available.

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Accepted December 10, 1990 K