SILOXANE-ACTIVATED CATALYTIC SYSTEMS USED IN THE METATHESIS POLYMERIZATION OF NORBORNENE

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ABSTRACT

The activation of the cycloolefin metathesis polymerization by siloxanes is investigated. The system selected for this purpose is the polymerization of norbornene (NBE) in cyclohexane initiated with the tungsten hexachloride (WCl_6)/tetramethyltin ($SnMe_4$) system. The siloxane activator is hexamethyldisiloxane (HMDS). The formation and stability of the primary active species are followed through ^1H NMR. It is found that such species are generated with the WCl_6/$SnMe_4$, WCl_6/NBE/HMDS and WCl_6/NBE/$SnMe_4$/HMDS systems. The WCl_6/NBE system is inactive. Activation of the polymerization system by HMDS is also followed through a kinetic study. The kinetics of norbornene polymerization initiated with WCl_6/$SnMe_4$ is used as the reference system and is compared with the WCl_6/NBE/HMDS and WCl_6/NBE/$SnMe_4$/HMDS polymerization systems. The latter is found to be the most reactive.

INTRODUCTION

Tungsten based compound are widely used in catalytic systems for the ring opening metathesis polymerization (ROMP) of cycloolefins [1]. Among the latest studies, Verpoort *et al.* [2] have shown that a pretreated silica surface acts as an activator with some tungsten complexes for olefin metathesis reactions. Similar observations have been previously reported [3] with the metathesis reaction of pentene on a silica gel surface using the tungsten hexachloride-tetramethyltin "catalytic" system ($WCl_6/SnMe_4$), which is one of the most widely used initiators for the metathesis polymerization of cycloolefins. More recently, the gas phase metathesis polymerization of cyclopentene onto a glass surface, using $WCl_6/SnMe_4$, has been reported [4]. Verpoort *et al.* [2] found that the metathesis reaction is activated by siloxane bridges, Si-O-Si, on the surface of silica. Along with these studies, it was found that rates of homogeneous ROMP of various cycloolefins, using the $WCl_6/SnMe_4$ system, can be increased by siloxanes and, to a lesser extent, by silazanes [5]. The object of the present work is to investigate through kinetic and NMR studies, the initiation and propagation of this type of polymerization.

For this study, the metathesis polymerization of norbornene initiated with the tungsten hexachloride-tetramethyltin system ($WCl_6/SnMe_4$) in cyclohexane, using hexamethyldisiloxane (HMDS) as an activator, is investigated. Norbornene (NBE) may be considered as a reference monomer in metal-alkylidenic polymerization. Due to its high ring strain, backbiting and side reactions are negligible and consequently, that cycloolefin is very convenient for the type of study to be undertaken. In a previous work [5], many siloxane and silazane compounds were found to be activators for the metathesis polymerization of cycloolefins. Among them, HMDS was one of the most efficient activators and for that reason, it has been selected for the present study.

All measurements have been carried out using cyclohexane as the solvent. It is a relatively good solvent for all the constituents found in the systems under investigation and it is free of any strong interactions which may interfere with the activating processes.

In order to obtain the relevant information, two types of study were undertaken: a study on the nature and the stability of the active centers and the kinetics of polymerization.

EXPERIMENTAL

The procedure used to carry out the reactions of the present study, is fully described elsewhere [6].

Materials

Norbornene (Janssen, 99%) is distilled over sodium at 97°C under pure nitrogen prior to reaction.

Solvents and HMDS (Janssen, 98%) are dried over calcium hydride and cryodistilled just prior to their use.

Tetramethyltin (Aldrich 99.9%) is kept over a molecular sieve and cryo-distilled just prior to its use.

Tungsten hexachloride (Aldrich 99.9%) is used as such without further purification.

NMR and Kinetics Measurements

The nature and stability of the reactants are investigated through proton NMR using deteureted cyclohexane (cyclohexane-d_{12}) as solvent. The measurements are carried out at room temperature using sealed ampoules under vacuum containing a total volume of 2 ml of reacting mixture. Depending upon the systems, the amount of reactant is: WCl_6, 0.12 mol/l; NBE, 1.75 mol/l; HMDS, 0.6 mol/l; $Sn(CH_3)_4$, 0.25 mol/l. The instrument was a Bruker AC 200.

Kinetics of the polymerizations are followed through gas chromatography analysis of the residual monomer, using toluene as an internal reference.

Aliquots are taken from the reacting mixture in the course of the polymerization at room temperature and deactivated with methanol. Typical concentrations in cyclohexane for the polymerization system are: [NBE], 6.5×10^{-2} mol/l; [HMDS], 6.5×10^{-2} mol/l; [$Sn(CH_3)_4$], 2.5×10^{-3} mol/l; [WCl_6], 1.3×10^{-2} mol/l. The analyses are performed with a Delsi Di 200 chromatograph using a FID detector and a BP1 capillary column of 25 m. The temperature of the injection port and the detector is set at 220°C.
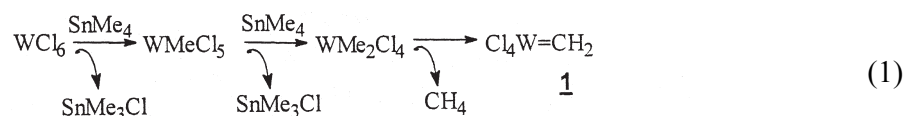
RESULTS AND DISCUSSION

Nature and Stability of the Active Centers

The nuclear magnetic resonance is a very convenient technique for the

identification of the metal-alkylidenic species. Consequently, it has been used to study the nature and stability of the reaction products in the reacting mixtures. Since under polymerization conditions, up to four components are found to take part in the reaction, the investigation is undertaken by taking the reactants first in pairs, and then in threes.
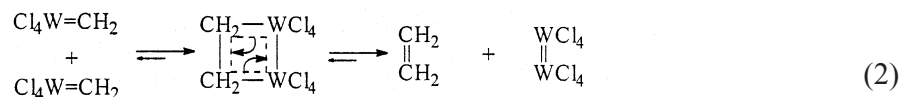
The $WCl_6/SnMe_4$ System

Although the mechanism for generating metal-alkylidenic primary active centers is well known [7], study of the reaction of WCl_6 with $Sn(CH_3)_4$ is carried out in order to optimize the experimental conditions and to define a reference state for the polymerization system.

$$WCl_6 \xrightarrow{SnMe_4} WMeCl_5 \xrightarrow{SnMe_4} WMe_2Cl_4 \longrightarrow Cl_4W=CH_2$$
$$\downarrow \qquad\qquad \downarrow \qquad\qquad \downarrow \qquad\qquad \mathbf{1}$$
$$SnMe_3Cl \qquad SnMe_3Cl \qquad CH_4$$

$$(1)$$

The formation of the metal-alkylidenic species **1** is reputed to be formed according to Equation 1. The ^1H NMR signal characteristic of species **1**, shows at 9.95 ppm (Figure 1). All intermediates shown in Equation 1 are identified in accordance with previous works [7, 8].

The change in concentration of species **1** with time, is followed using cyclohexane ($\delta = 1.34$) contained in cyclohexane-d_{12} as a reference (full line in Figure 2). The concentration of species **1** increased rather slowly at first, then rapidly to reach a maximum after 2 hours before starting decreasing very slowly.

From the results shown in Figure 2, it is not possible to propose a simple kinetic law. However, it is obvious that they represent the result of two simultaneous reactions, one leading to the formation of the alkylidenic species, the other one leading to its consumption. The latter may result from the following reaction which was proposed by Wei *et al*. [8]:

$$\begin{array}{c} Cl_4W=CH_2 \\ + \\ Cl_4W=CH_2 \end{array} \rightleftharpoons \begin{array}{c} CH_2-WCl_4 \\ | \quad | \\ CH_2=WCl_4 \end{array} \rightleftharpoons \begin{array}{c} CH_2 \\ \| \\ CH_2 \end{array} + \begin{array}{c} WCl_4 \\ \| \\ WCl_4 \end{array}$$

$$(2)$$

the presence of ethylene being observed at 5.35 ppm (Figure 1).

The WCl_6/NBE System

It is important to check for a possible interaction or even reaction, between WCl_6 and NBE in the absence of $Sn(CH_3)_4$ and HMDS.
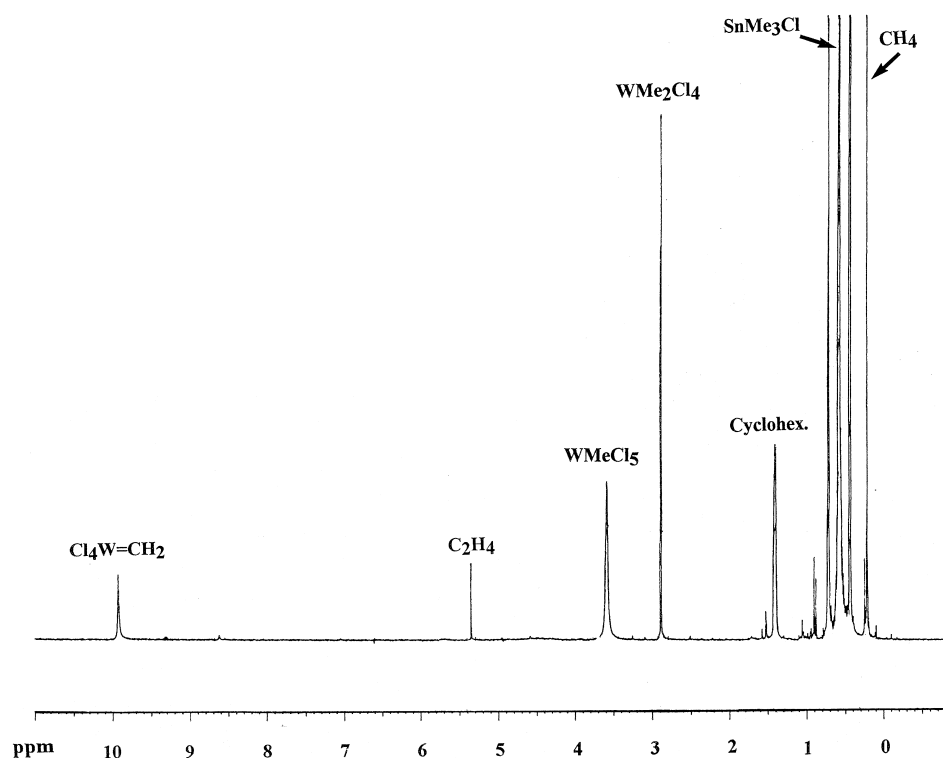
Figure 1. ^{1}H NMR spectrum of $WCl_6/SnMe_4$ in cyclohexane-d_{12} after 20 minutes.

The [WCl_6/NBE] mixture in solution in cyclohexane-d_{12}, does not lead to any polymerization at room temperature. No change in the ^{1}H NMR spectrum of NBE, even at high WCl_6 concentration, can be detected and the faintest signal in the alkylidenic region cannot be observed. However, formation of very small quantities of primary active centers, too small to be detected through NMR, cannot be ruled out. Amass *et al.* [9] suggested that the polymerization of cyclopentene in chlorobenzene can be initiated with WCl_6. Cyclopentene was also found to undergo a gas phase polymerization when initiated in the bulk with WCl_6 [4]: however, in that case, it is almost certain, the glass surface takes part in the initiation process. Amass *et al.* [9] put forward an explanation based on a particular electronic structure of WCl_6 which would yield an electrophilic feature and induce a direct attack on cyclopentene. In the present case, a similar reaction may take place; however, if it is such, its magnitude is very small and consequently, it can be neglected.
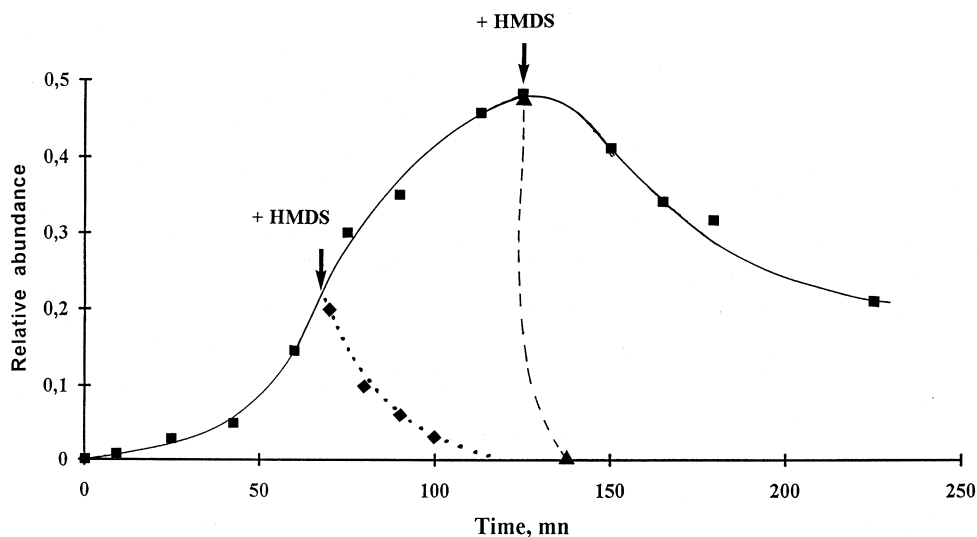
Figure 2. Stability of active centers with time (relative abundance of species1
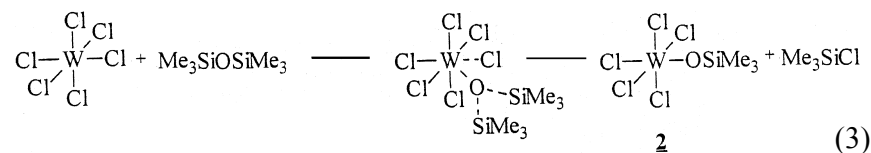   with respect to cyclohexane contained in cyclohexane-d12)
                  _____ WCl$_6$/SnMe$_4$
                  .... upon addition of HMDS 1 hour after initiation
                  ----------- 2 hours after initiation

The WCl$_6$/HMDS System

        No NMR signals associated with alkylidenic species in the 8-12 ppm
region, can be detected. However, it is worth mentioning the showing up of a
new species at 0.37 ppm. This peak is characteristic of Me$_3$SiCl and its intensi-
ty is five times weaker than the methyl groups of HMDS. This observation can
be explained through a partial exchange reaction between chlorines of WCl$_6$ and
a OSiMe$_3$ group. The reaction, similar to the reaction of WCl$_6$ with an alcohol
[10, 11], would be:

$$
\begin{array}{c}
\underset{Cl}{\overset{Cl}{\underset{|}{\overset{|}{Cl-W-Cl}}}}{\overset{Cl}{}} + Me_3SiOSiMe_3 \longrightarrow \quad
\underset{Cl\;\;O--SiMe_3}{\overset{Cl\;\;Cl}{\underset{|}{\overset{|}{Cl-W--Cl}}}} \quad \longrightarrow \quad
\underset{Cl}{\overset{Cl\;\;Cl}{\underset{|}{\overset{|}{Cl-W-OSiMe_3}}}} + Me_3SiCl
\end{array}
$$

$$\underset{}{SiMe_3} \qquad \qquad \qquad \underline{\mathbf{2}} \qquad \qquad (3)$$

        That reaction would be enhanced by the large size of the WCl$_6$ coordi-
nation sphere and by its "oxophilic" character.

It is possible that compound **2** is spontaneously transformed into $Cl_4W=O$ afterwards; however the analytical technics used does not allow for its detection. Recently, the formation of $Cl_4W=O$ from the reaction of WCl_6 with hexamethyldisiloxane, was reported [12] and used as an intermediate for the synthesis of a well-defined initiator for metathesis reactions [13].

The WCl_6/NBE/HMDS System

In order to check the occurrence of a reaction between WCl_6, NBE and HMDS in the absence of $Sn(CH_3)_4$, the evolution of the system is followed through NMR.

WCl_6, HMDS and NBE are mixed together in cyclohexane-d_{12} in concentrations given in the Experimental. Polymerization of NBE is observed to take place at room temperature. The formation of an alkylidenic species is observed through ^{1}H NMR. A signal at 10.94 ppm shows up progressively (Figure 3a) and reaches a maximum 15 minutes after NMR measurements has started (t =ε). At the same time, the ethylenic protons of the monomer are replaced by the polymer ones. This is clearly seen in Figure 3b, where the NMR spectrum recorded after 30 minutes (t = ε + 30) is shown. The stability of the active centers with time cannot be studied under these conditions. The reacting mixture becomes very viscous upon the formation of high-molar-mass polymer and the signal precision is lost.

As can be seen from the above, alkylidenic species are not formed with the WCl_6/HMDS system, nor with the WCl_6/NBE system. However, in the presence of HMDS, our results show that WCl_6 reacts with norbornene to form ethylidenic species and polymerization takes place. The lack of experimental precision does not allow us to propose a mechanism in order to explain the results with this system.

The WCl_6/SnMe$_4$/HMDS System

When the 3 components of the system were mixed simultaneously, the ^{1}H NMR spectrum was identical to the one obtained with WCl_6/HMDS system. Over a period of 4 hours, the SnMe$_4$ showed no change with respect to the pure compound. From these results, it seems that reaction (3) occurs first, preventing the reaction of WCl_6 with SnMe$_4$ from taking place.

When HMDS was added posteriorly to the reaction of WCl_6 with SnMe$_4$ the results were found to be quite different. First, HMDS was added when the
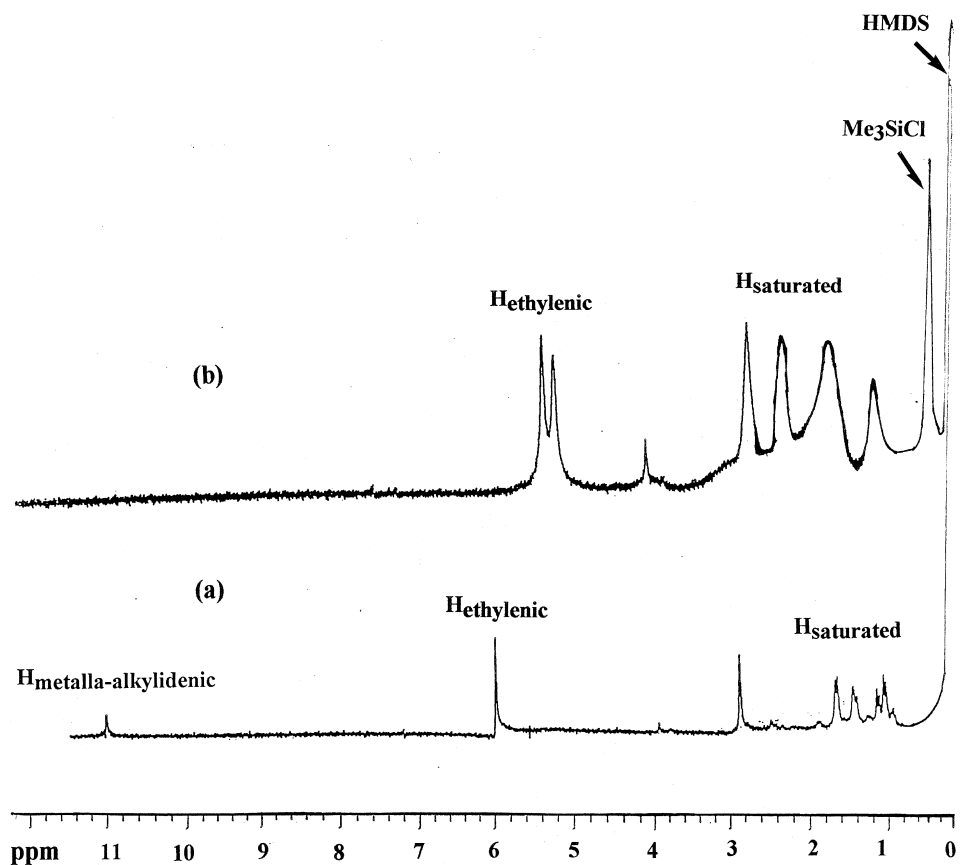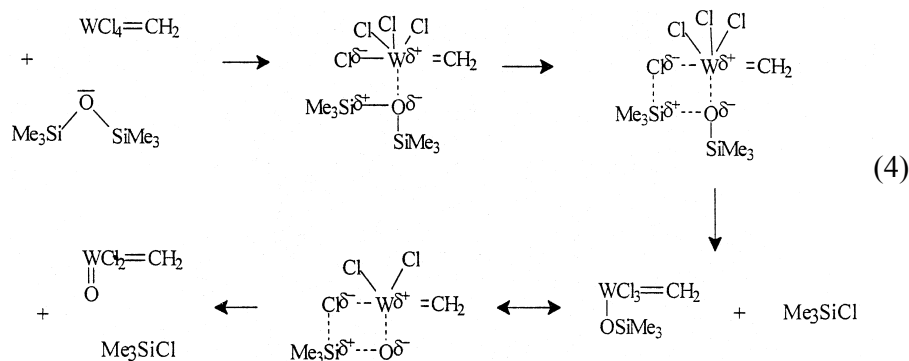
Figure 3. ^{1}NMR spectrum of WCl$_6$/NBE/HMDS in cyclohexane d$_{12}$
    i)   at t =ε (starting time for NMR measurements)
    ii) at t = ε + 30 minutes

active centers concentration reached its maximum, two hours after the initial reaction (see Figure 2). The NMR spectra carried out only 10 minutes after the addition of HMDS, show that the metal-alkylidenic species formed in the first two hours has completely disappeared (Figure 2, broken line).

When HMDS is added to the WCl$_6$/SnMe$_4$ mixture after one hour, before the alkylidenic concentration has reached its maximum, a much slower decrease is observed (Figure 2, dotted line). Moreover, a rapid shielding ($\Delta = 0.2$ ppm) of the metal-alkylidenic proton is detected.

From these results, it seems the addition of HMDS to the WCl$_6$/SnMe$_4$ does not increase the rate of formation of the alkylidenes but rather leads to the formation of a species less stable which, in absence of monomer, would decompose according to Equation 4:

$$
\begin{array}{c}
WCl_4{=}CH_2 \\
+ \\
Me_3Si{\overset{\overline{O}}{}}SiMe_3
\end{array}
\longrightarrow
\begin{array}{c}
Cl{\overset{Cl}{\underset{\;}{\mid}}}Cl \\
Cl^{\delta-}{-}W^{\delta+}{=}CH_2 \\
Me_3Si^{\delta+}{-}O^{\delta-} \\
\mid \\
SiMe_3
\end{array}
\longrightarrow
\begin{array}{c}
Cl{\overset{Cl}{\underset{\;}{\mid}}}Cl \\
Cl^{\delta-}{-}{-}W^{\delta+}{=}CH_2 \\
Me_3Si^{\delta+}{-}{-}{-}O^{\delta-} \\
\mid \\
SiMe_3
\end{array}
\tag{4}
$$

$$
\begin{array}{c}
WCl_2{=}CH_2 \\
\| \\
O \\
+ \\
Me_3SiCl
\end{array}
\longleftarrow
\begin{array}{c}
Cl{\underset{\;}{\diagdown}}Cl \\
Cl^{\delta-}{-}{-}W^{\delta+}{=}CH_2 \\
Me_3Si^{\delta+}{-}{-}{-}O^{\delta-}
\end{array}
\longleftrightarrow
\begin{array}{c}
WCl_3{=}CH_2 \\
\mid \\
OSiMe_3
\end{array}
+ Me_3SiCl
$$

This mechanism is similar to the one proposed by Rappé and Goddard [14], suggesting that an « oxo bond is intimately involved in the catalytic process » in the case of $WCl_6/C_2H_5AlCl_2$ catalytic system. The intermediates are probably very reactive and may be responsible for the activation of the polymerization system.

Kinetics of Polymerization

In order to check the proposed activation of metathesis polymerization by the siloxanes, kinetics for the NBE polymerization, followed through gas chromatography analyses, is performed for each of the initiator systems described above. Then, it is possible to relate the activation of the polymerization system as measured through kinetic measurements with the NMR results which are more closely associated with the nature of the species responsible for the activation.

The kinetics of the $WCl_6/NBE/SnMe_4$ system is used as the reference. Then, the kinetics for the WCl_6/NBE, $WCl_6/NBE/HMDS$ and $WCl_6/NBE/SnMe_4/HMDS$ systems are compared to the former one. All reactions are carried out in cyclohexane, the experimental conditions being given in the Experimental, and the results are shown in Figure 4.

The $WCl_6/NBE/SnMe_4$ System (Reference System)

The variation of the degree of conversion as a function of time is shown in Figure 4 (curve a). After a 20 minute induction period, the conversion rate increases very rapidly and the reaction reaches completeness after 30 minutes.

The reacting mixture can be separated in two parts through simple filtration. One part is made of a solution containing about 60% of the polymer sample, the other one is made of a swollen gel, totally instable in the usual solvents, representing about 40% of the total polymer.
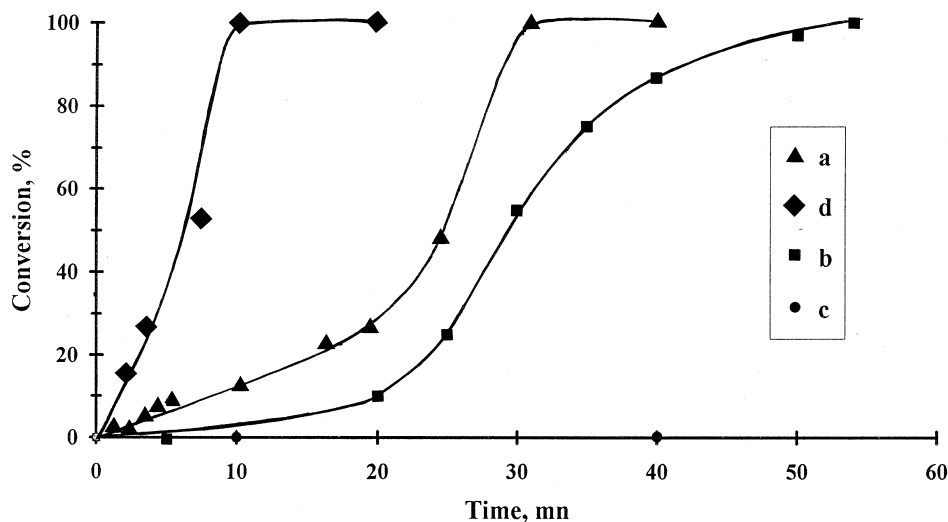
Figure 4.   Kinetics of the NBE polymerization initiated with:
      a) $WCl_6/SnMe_4$ c) WCl_6
      b) $WCl_6/HMDS$ d) $WCl_6/SnMe_4/HMDS$

The soluble polymer can be characterized through Size Exclusion Chromatography (SEC). It has a very broad distribution, the average molar mass being rather small ($M_w = 4100$, $M_n = 1200$, $I = 3,4$).

The structure of the soluble polymer, as determined through ^1H NMR, is in accordance with the one observed for a metal-alkylidenic initiation and corresponds to an unsaturated polymer. The insoluble polymer is probably due to the formation of a very high-molar-mass polymer or to crosslinking following electrophilic reactions with polymer formed.

The WCl_6/NBE/HMDS System

The behavior of that system (Figure 4, curve b) is kinetically comparable to the reference system with a slower reaction (55 minutes for 100% conversion against 30 minutes for the reference system). The polymer is completely soluble and shows a very broad distribution with average molar masses and structures similar to the ones obtained with the soluble polymer fraction of the reference system.

This system seems to be free from crosslinking but sizeable amount of very low-molar-mass polymer, whose structure has not been determined, is present in the sample.

The WCl$_6$/NBE System

As can be seen from curve c of Figure 4, there is no consumption of monomer in this system. This observation goes along with the NMR results and it confirms the system is inactive under the present conditions of polymerization.

### The WCl$_6$/NBE/SnMe4/HMDS System

This system is marked off from others by the absence of an induction period and a very fast consumption of monomer (total conversion is slightly more than 10 minutes), as can be seen from curve d in Figure 4.

The polymer is completely soluble, with a very broad distribution (M_w = 28000, M_n = 2600, I = 10) and a structure corresponding to a metathesis process.

CONCLUSION

Kinetics and NMR measurements show that the WCl$_6$/NBE system, through various combinations with SnMe$_4$ and HMDS, can generate different active species, all capable to initiate polymerization of NBE with different kinetics, the fastest kinetics being obtained with the WCl$_6$/NBE/SnMe$_4$/HMDS system.

The NMR results shows that HMDS can react with WCl$_6$ to yield compound **2** (Equation 3) which is able to lead to the initiation of the polym-erization (Figure 4). If WCl$_6$, HMDS and SnMe$_4$ are mixed together, NMR shows that the reaction of WCl$_6$ with HMDS occurs first. On the other hand, if the reaction of WCl$_6$ with SnMe$_4$ is allowed to proceed (Equation 1) to a certain extent and then HMDS added, HMDS reacts very quickly (Figure 2) according to Equation 4 to yield a complex of the form suggested by Scheme 5. In this case, the available doublet of the oxygen of HMDS is assumed to form a coordination bond through the vacant orbital of tungsten.

$$WCl_4 = CH_2 \longrightarrow Cl_3\,W = CH_2 + Me_3SiCl$$

(5)
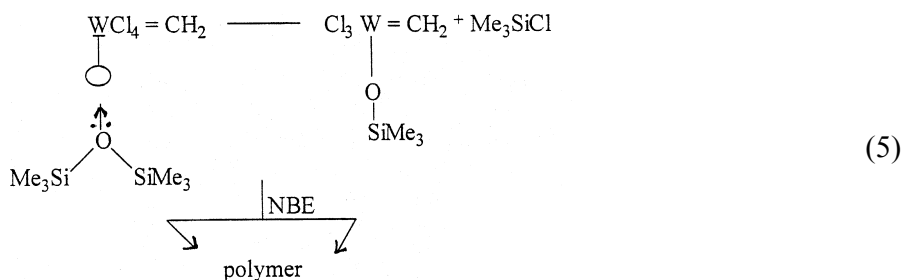
It is reasonable to think that the polymerization initiated through Equation 5 is mainly responsible for the activation of the polymerization system, that is a rapid acceleration of the polymerization rate upon the addition of HMDS (Figure 4).

From the present set of results, it is quite obvious that, using the Wcl_6 - $SnMe_4$ - HMDS mixture, initiation and propagation for the polymerization of NBE may take place in several ways, notably: a) from the reaction of Wcl_6 with $Sn(CH_3)_4$, the slow formation of $WCl_4=CH_2$ is followed by a slow propagation; b) from the reaction of Wcl_6 with HMDS, the rapid formation of a complex (Equation 3) is followed by a rapid propagation (Figure 4); c) from the reaction of $WCl_4=CH_2$ with HMDS, the very rapid formation of a complex (Figure 2) is followed by a very rapid propagation (Figure 4).

With the $WCl_6/SnMe_4/HMDS/NBE$ system, reaction b) occurs first and a small amount of $WCl_4=CH_2$ is formed, which reacts immediately with HMDS. The latter reaction is followed by a very rapid propagation so that the overall rate polymerization rests on a very small concentration of active chains.

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