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# Gas Chromatography/Mass Spectrometry Studies of Cationic Polymerization Initiated by Pseudohalide/Lewis Acid Combination. 1. Model Reaction with 2-(Isothiocyanato)-2,4,4-trimethylpentane/Titanium tetrachloride/2,4,4-Trimethylpentene System

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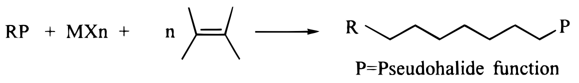
ABSTRACT: Gas chromatography/mass spectrometry (GC/MS) studies of model reactions with 2,4,4-trimethyl-1-pentene (TMP1) initiated by the system 2-isothiocyanato-2,4,4-trimethylpentane (H−TMP−NCS)/titanium tetrachloride ($TiCl_4$) were made in the presence or in the absence of a proton scavenger 4-methyl-2,6-di-*tert*-butylpyridine (MDtBP). The results show the participation of two initiation modes, direct initiation and cocatalytic initiation, with H−TMP−NCS not being an initiator. The exact role of each mode can be separated. In the presence of MDtBP, direct metallation leading to H−TMP−Cl is evidenced upon quenching with MeOD. In particular, this experiment brings some precision about the complexity of the quench reaction. Dimerization of TMP1 leads to a mixture of four main isomers whose structures are specified by charge-exchange MS with $CS_2$ gas and confirmed by a microhydrogenation reaction. This work demonstrates that H−TMP−NCS is not an initiator, and leads to the conclusion that when an isobutene polymerization is carried out in the presence of H−TMP−NCS, the functionalization is obtained by exchange reaction.

## Introduction

Cationic polymerization of olefins has been studied for many years, and the mechanism of polymerization has been deeply investigated. The initiation step has been studied in particular, and three processes have been identified: a cocatalytic process (I)[1]; a coinitiation process (II)[2,3]; and a direct initiation process (III).[4] Process I is always invoked (in conjunction or not with the others) because water at low concentration (moisture remaining in the system) is a cocatalyst for the polymerization of olefin [i.e., isobutene (IB)] and because it is difficult to remove water unless operating with a technique that uses high vacuum with ultradry reactants. Process II is evidenced by the polymer analysis where the fragment R of the initiator is the head-end of the polymer chain (for a monofunctional initiator) or is included in the polymer chain (for a difunctional initiator). In this case, the proton initiation (process I) is suppressed or minimized by the use of a hindered pyridine or an eletron donor. Process III is not always invoked or is sometimes omitted because of the lack of direct evidence. However, authors have mentioned the existence of this initiation process in the polymerization of various olefins (e.g., substituted indenes,[5] isobutylene,[6] styrene[7]).

In the course of our study on the cationic polymerization of olefins, we found that pseudohalide (RP)/Lewis acid ($MX_n$) combinations can induce a cationic functionalizing polymerization of olefins[8,9]:



P=Pseudohalide function

Interestingly, besides the common *tert*-chlorine and the di- and trisubstituted double-bond end groups, the polymer also exhibited the pseudohalide P. Under proper experimental conditions, P can be obtained in a major proportion and even exclusively.

Thus, bis(1-azido-1-methylethyl)-1,4-benzene (a benzylic type azide) (DAMEB)/MXn ($BCl_3$, $TiCl_4$, $AlEt_2Cl$) combinations initiate the polymerization of IB. According to the acidic strength of the Lewis acid (LA), the strong LA-like $BCl_3$ or $TiCl_4$ lead to a poly(isobutene) (PIB) presenting *tert*-chlorine, double bond, *tert*-butyl, and azide terminal ends.[9,10] Obviously, these polymerizations are not living but become living with only an azide end in the presence of an electron donor, (i.e., DMSO[11]). In the case of a weak LA, such as $AlEt_2Cl$, the PIB exhibits exclusively an azide end and the polymerization is living without addition of any electron donor.[12] Moreover, an aliphatic azide, such as 2-azido-2,4,4-trimethylpentane (ATP), led to the same trend (i.e., PIB bearing an azide end), but the living polymerization was not checked.[13] By changing the monomer, such as styrene or isobutylvinylether, the corresponding polymer also exhibits an azide end,[14] indicating that the initiating system can be extended to other olefinic monomers but the polymerization was not living.

When P is the isothiocyanate group (R = 2,4,4-trimethylpentyl, cumyl), the polymerization of IB also leads to a PIB bearing an isothiocyanato or thiocyanato end.[15,16,17] It is interesting to point out that although the pseudohalide function has been changed, the initiating system is still efficient for the polymerization of IB.

However, the following important question arises: Is the pseudohalide the actual initiator in the IB poly-

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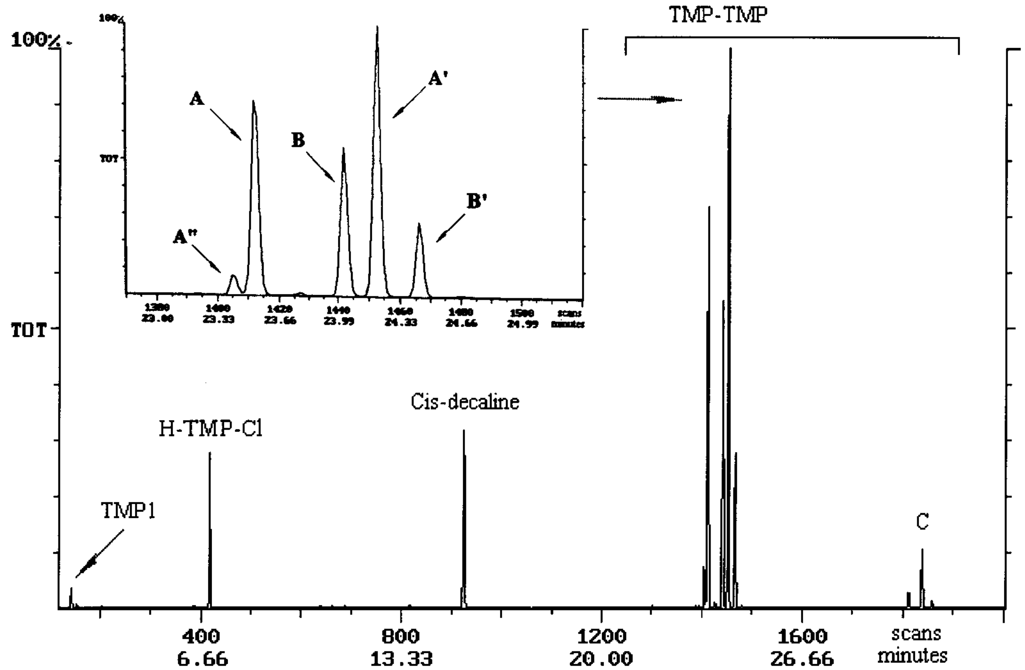


**Figure 1.** Total ion current of TMP1 + $TiCl_4$ reaction (MeOH quench).

merization according to the coinitiation process (II), or does initiation come from the side reaction of water according to process I, followed by an exchange (or transfer) reaction? In the case of a benzylic pseudohalide[15] (or benzylic halide[18]), RP is the true initiator as evidenced by the fact that $^1$H NMR spectra of PIBs show a resonance at 7.3 ppm that is assigned to the aromatic ring. In the case of the aliphatic pseudohalide (i.e., $R = 2,4,4$-trimethylpentyl), a problem appears; that is, the *tert*-butyl end of the PIB can originate either from the pseudohalide itself or from the proton initiation reaction.

In this paper we report the study of a model reaction, using 2-isothiocyanato-2,4,4-trimethylpentane (H−TMP−NCS)/$TiCl_4$ as the initiating system and 2,4,4-trimethyl-1−pentene (TMP1) as a nonpolymerizable monomer, with the intention of elucidating the initiation process by GC/MS. We also deal with the problems of direct initiation and chain functionalization during cationic polymerization.

## Experimental Section

**Reactants.** All reactants were commercially available. $CH_2Cl_2$, 2-isothiocyanato-2,4,4-trimethyl-pentane (H−TMP−NCS), 2-isothiocyanato-2-methyl-propane *tert*-butyl isothiocyanate (Tbu−NCS), 2,4,4-trimethyl-1-pentene (TMP1), and 2,4,4-trimethyl-2-pentene (TMP2) were purified and dried according to our laboratory procedure. $TiCl_4$ in $CH_2Cl_2$ solution (sure seal bottle 1 M, Aldrich), 4-methyl-2,6-di-*tert*-butylpyridine (MDtBP), MeOH, MeOD, butylamine, and *cis*-decaline were used as received.

**General Procedure for Model Reactions.** The reactor was used under vacuum and was fitted with a rubber septum and a magnetic stirrer. The following were introduced in the order mentioned: 0.0018 mol of proton scavenger (MDtBP), 100 mL of $CH_2Cl_2$, 0.036 mol of olefin (TMP1 or TMP2), and 0.0036 mol of initiator (H−TMP−NCS or TBu−NCS). The system was cooled to −50 °C, and 0.072 mol of $TiCl_4$ was added via a syringe. After 30 min, the solution was quenched with MeOH (or MeOD, butylamine) and 0.5 mL of *cis*-decaline as the internal standard was added. The solution was washed several times with water and dried over magnesium sulfate. A small amount of this solution was diluted in pentane before being injected into the GC devices.

**Characterization.** GC/flame ionization detection (FID) analyses were conducted with a gas chromatograph from Hewlett Packard 5880A. The injector temperature was 240 °C. The nitrogen flow was into a 50-m CP-Sil-8CB column adjusted to 1 mL/min. This column was held at 50 °C for 5 min after the sample injection, then ramped to 250 °C at 4 °C/min and held at that temperature for 5 min. The detector temperature was 285 °C.

GC/MS experiments were carried out with a Varian Saturn III quadrupole ion trap mass spectrometer coupled with a gas chromatograph (Varian 7400 CX). Saturn version 5 software was used for data acquisition. The ion trap was maintained at a temperature of 120 °C. The helium flow was adjusted to give a column head pressure of 0.69 bar. A 30-m DB-5 capillary column (0.25 mm i.d. and 0.25 mm film thickness) was used for all analyses. The temperature program was the same as previously used. The transfer line temperature from the gas chromatograph to the quadrupole ion trap was held at 260 °C.

## Results and Discussion

Before studying the initiation mechanism and of the functionalization in the presence of an initiator containing an isothiocyanate function, it was necessary to study the behavior of the system without an initiator.

**GC and GC/MS Study of Initiation in the TMP1/$TiCl_4$ System.** The TMP1/$TiCl_4$ system was investigated under various conditions. In the presence and in the absence of a proton scavenger, three different quenching systems were used (MeOH, MeOD, or butylamine).

**(A) TMP1 + $TiCl_4$ Reaction (MeOH Quench).** The total ion current (TIC) of the TMP1 + $TiCl_4$ reaction in $CH_2Cl_2$ shows a mixture of products (Figure 1) identified as H−TMP−Cl and dimers of TMP (TMP−TMP). The initial reactant molar ratio being TMP1 (10)/$TiCl_4$ (2)/*cis*-decaline (1), the TMP balance of the final adducts is determined by flame ionization detection (FID) and by MS using *cis*-decaline as internal standard, as shown in Table 1. Within experimental error, the quantitative

**Table 1. TMP1 Molar Balance Determined by FID and MS Referenced to *cis*-Decaline (Initial TMP1 Concentration = 10 in Arbitrary Units)**

| detection | TMP1 | H−TMP−Cl | TMP−TMP | total TMP |
|---|---|---|---|---|
| FID | 0.25 | 1.25 | 7.75 | 9.25 |
| MS | 0.3 | 1.25 | 9 | 10.55 |

results given by the two detection methods are in good agreement. Thus, 12.5% of TMP1 is transformed into H−TMP−Cl and 85% into dimers, whereas only 2.5% remained unreacted.

It can be assumed that the TMP−TMP presence (**A, A′, A″, B, B′, C**) is the result of a water cocatalysis dimerization, as shown in Scheme 1a. However, five main unsaturated structures are defined if we take into account *Z*/*E* isomers. The structural assignment of **A, A′, A″, B, B′**, and **C** will be discussed later in a special section. Assuming the peak height of each corresponding species is proportional to its concentration, the percentage of each dimer can be estimated as follows: **A″** = 2%, **A** = 22%; **A′** = 34%; **B** = 20%; **B′** = 18%, and **C** = 4%. The mass spectra of the six dimers, A, A′, A″, B, B′, and C, are shown in Figure 2.

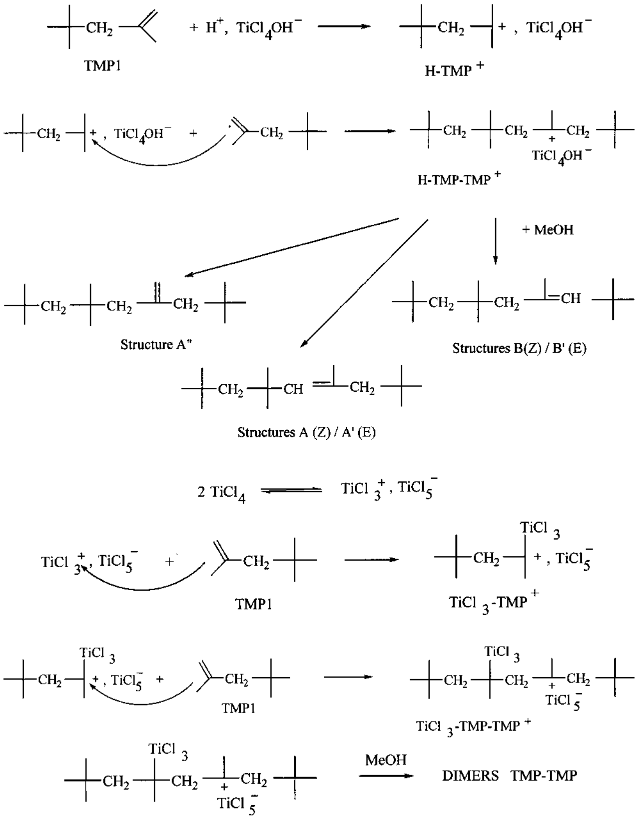
It is worth recalling that it is not necessary to have water and $TiCl_4$ concentrations equal to the dimer concentration because the elimination reaction regenerates the activating proton. However, a direct initiation mechanism can also be invoked because this mechanism leads to the same result (Scheme 1b), with the $TiCl_3$ moiety being removed upon quenching and the elimination reaction playing the same role as already mentioned.

According to the initiation process, the initiating species is either $H{-}TMP^+$ or $TiCl_3{-}TMP^+$. The dimerization efficiency is high but not total, as shown by the presence of H−TMP−Cl (13.5% of initial TMP1), which comes from termination reaction ($TiCl_3-$ or $H{-}TMP^+$ collapses with $Cl^-$ as counterion) or from hydrochlorination of the TMP1 double bond upon quenching (HCl is generated by $TiCl_4$ hydrolysis).

**(B) TMP1 + $TiCl_4$ + MDtBP Reaction (MeOH Quench).** Under the same conditions, but in the presence of MDtBP, the TIC shows a mixture of TMP1, TMP2, H−TMP−Cl, H−TMP−OMe, and the same dimers TMP−TMP in very small amounts [**A** = 23.5%; **A′** = 15.5%; **B** = 22%, and **B′** = 39%; **C** and **A″** (traces)]. Table 2 shows the TMP1 balance determined by FID and MS. The initial reactants molar ratio was TMP1 (10)/$TiCl_4$ (2)/MDtBP (0.5)/*cis*-decaline (1), so it is worth noting that the unreacted TMP1 is very important (71%) because only 2% of initial TMP1 takes part in dimerization and because some isomerization occurs (TMP2, 2%). The reacted TMP1 is in its hydrochlorinated form (H−TMP−Cl, 24%) and, surprisingly, in a methoxide form (H−TMP−OMe, 1%).

Proton initiation being minimized or suppressed by the presence of MDtBP, the TMP−TMP dimers could be the result of a direct initiation process. Thus, the presence of H−TMP−OMe would involve the existence of an ionized $TiCl_3{-}TMP^+$ in equilibrium with its nonionized form $TiCl_3{-}TMP{-}Cl$ (active and dormant species), the quench implying a reaction of $TiCl_3{-}TMP^+$ with methanol. The H−TMP−OMe species could also come from the reaction of HCl with TMP1 during the quenching operation because the MDtBP concentration was less than four times that of $TiCl_4$. However, because the experiment and the quenching operation were carried out in the presence of MDtBP, the H−TMP−OMe species would more likely come from the reaction of MeOH with $TiCl_3{-}TMP^+$, rather than with the $H{-}TMP^+$, followed by methanolysis of the Ti−C bond upon quenching.

**Scheme 1**



It is interesting to notice that by comparison with the TMP1 + $TiCl_4$ reaction, the percentages of **A** and **B** in the mixture of dimers remain constant (within experimental error), whereas **A′** and **B′** are modified.

**(C) TMP1 + $TiCl_4$ Reaction (MeOD Quench).** The TMP1 + $TiCl_4$ experiment was carried out in the absence of MDtBP, with the reactant molar ratio TMP1 (10)/$TiCl_4$ (2)/*cis*-decaline (1), and the reaction was stopped by quenching with MeOD. The TIC and mass spectra gave the following results. First, as in the case of the TMP1 + $TiCl_4$ reaction just reported, TMP1 was mostly consumed; that is, only a small amount remained unreacted and not deuterated. Second, the H−TMP−Cl formed incorporated several deuterium atoms. The mass spectrum of nondeuterated H−TMP−Cl (Figure 3a) does not show any molecular ion, as expected for a tertiary chlorine derivative. We observed only two primary ions, resulting from a simple bond cleavage, at $m/z$ = 113 and $m/z$ = 77, 79 (see Scheme 2). The other ions ($m/z$ = 97, 57, and 55) probably come from $m/z$ = 112 ($M^+$-HCl) by a simple bond cleavage. The ion $m/z$ = 56 results from a McLafferty rearrangement. The average mass spectrum (not shown) of the mixture of deuterated H−TMP−Cl mass spectra shows that several ions ($m/z$ 56, $m/z$ 97, and $m/z$ 113) are shifted by 2 to 4 mass units. The mass spectrum (Figure 3b) shows ions at $m/z$ 56 and 97 that are shifted by 6 mass units to $m/z$ 62 and 103, respectively. This result shows that H−TMP−Cl can insert up to 6 D atoms. Finally, some TMP−TMP dimers are deuterated and some are not. The mass spectra of **A** (Figure 4) and **B′** (Figure 5) show a mixture of dimers presenting one to three deutera-

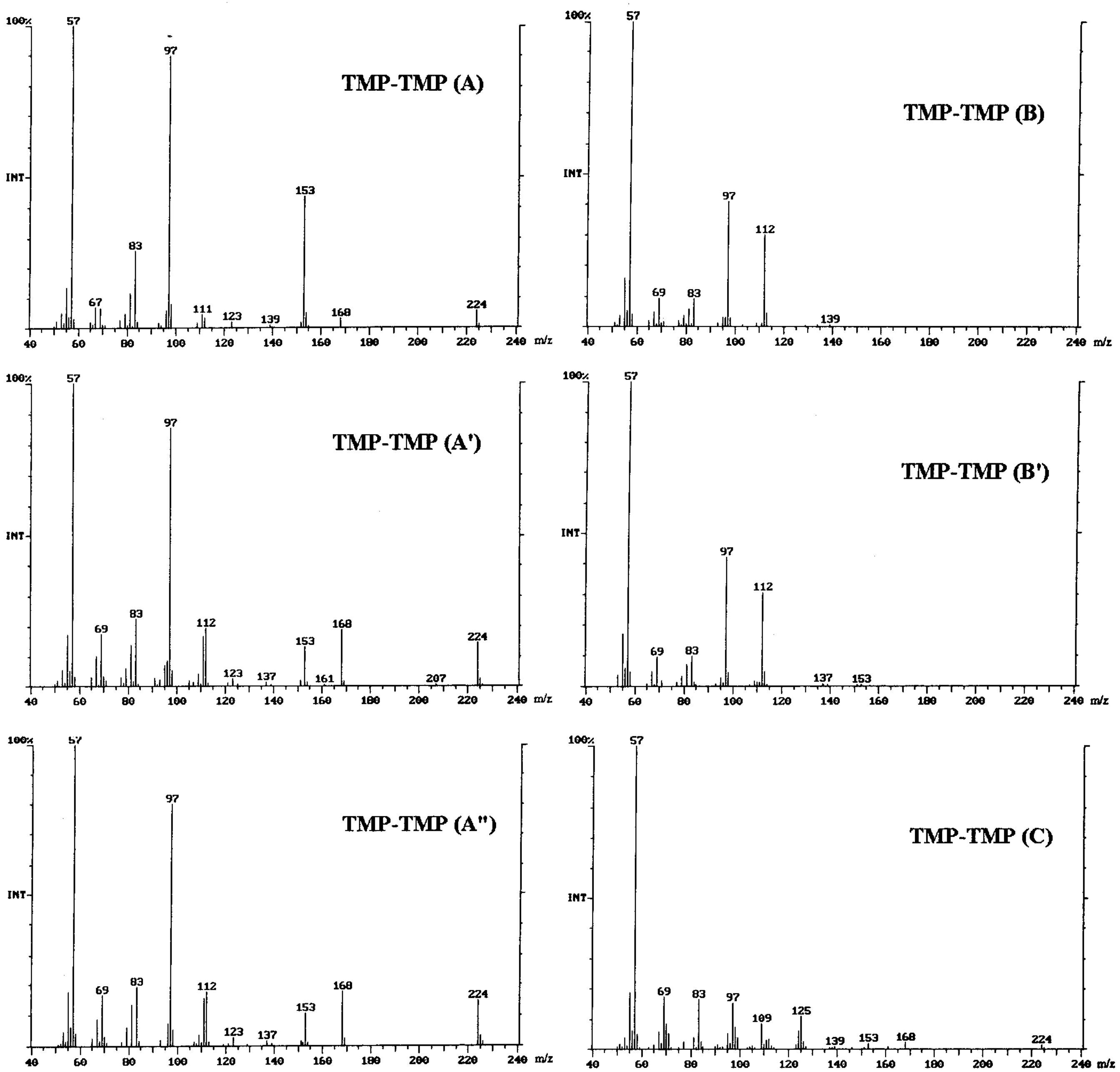


**Figure 2.** Mass spectra of TMP−TMP dimers.

**Table 2. TMP1 Molar Balance Determined by FID and MS**

| detection | TMP1 | TMP2 | H−TMP−OMe | H−TMP−Cl | TMP−TMP | total TMP |
|---|---|---|---|---|---|---|
| FID | 7.45 | 0.15 | 0.1 | 2.65 | 0.15 | 10.5 |
| MS | 7 | 0.3 | 0.1 | 2.4 | 0.2 | 10 |

tions, whereas the spectra of **A′** and **B** remained unchanged (i.e., nondeuterated).

These results show that the quench by MeOH is a very complex process. Reactions of elimination and termination just mentioned occur with a fast H-D exchange depending on the structure of the adducts: for instance, the structures of **A** and **B′** seem more favorable for this exchange compared with those of **A′** and **B**.

**(D) TMP1 + $TiCl_4$ + MDtBP Reaction (MeOD Quench).** The same experiment as already described was carried out in the presence of MDtBP with the reactant ratio TMP1 (10)/$TiCl_4$ (2)/MDtBP (0.5)/*cis*-decaline (1), and the results deduced from the mass spectra are summarized as follows: only 25% of TMP1 reacts with $TiCl_4$ to result in the formation of TMP2 (0.3%), H−TMP−OMe (0.7%), H−TMP−Cl (21%), and dimers (3%); unreacted TMP1 with 15% deuterated 1D; a small amount of TMP2 with 50% deuterated 1D; H−TMP−OMe with 70% deuterated 1D; H−TMP−Cl with 60% deuterated 1D based on the shift of *m*/*z* 97 to *m*/*z* 98; dimers **A** and **B** with 30% deuterated 1D; and dimers **A′** and **B′** not deuterated. Thus, MDtBP hinders the perdeuteration reaction occuring on the adducts. On the other hand, the following question arises: Is methanol appropriate for properly quenching the dimerization (or polymerization) reaction? It seems that methanol is not enough basic, so that a stronger base, such as an amine $RNH_2$, could be needed.

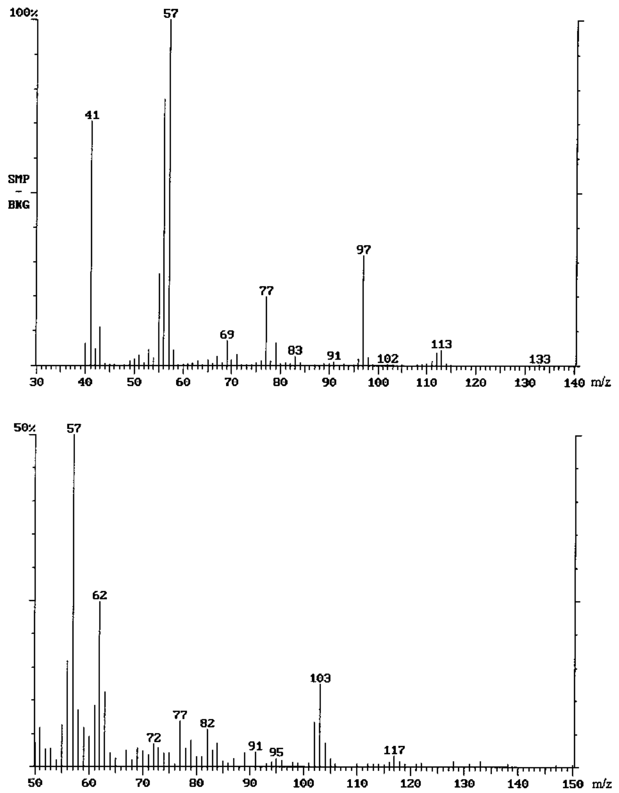
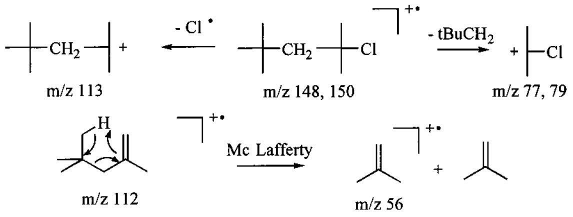


**Figure 3.** (a) Mass spectrum of nondeuterated H−TMP−Cl. (b) Mass spectrum of 6-D deuterated H−TMP−Cl.

**Scheme 2**



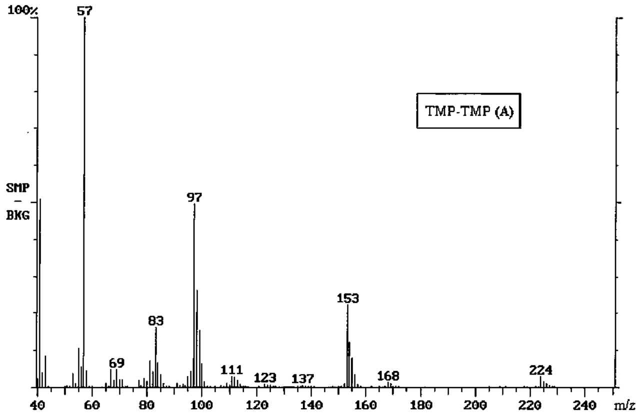


**Figure 4.** Mass spectrum of the mixture of deuterated and nondeteurated TMP−TMP (**A**).

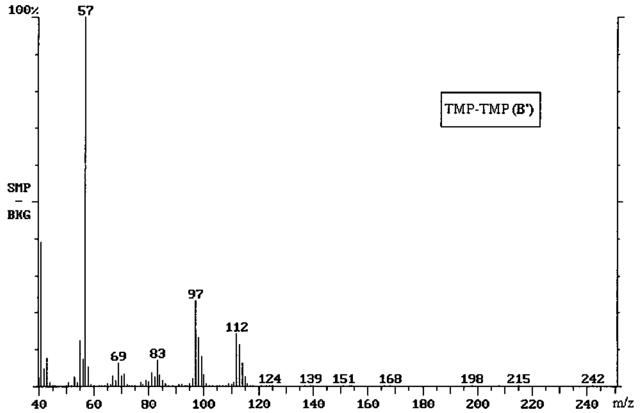


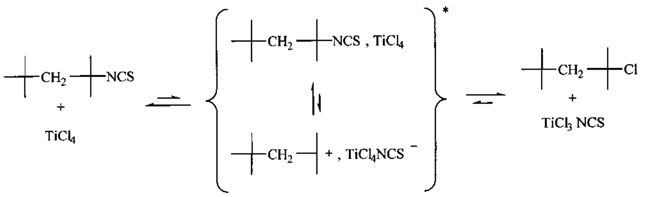
**Figure 5.** Mass spectrum of the mixture of deuterated and nondeteurated TMP−TMP (**B′**).

**(E) TMP1 + $TiCl_4$ Reaction (Butylamine Quench).** A reaction of TMP1 with $TiCl_4$ quenched with butylamine was carried out. The TIC shows the same mixture of adducts as in the case of the reaction quenched with methanol (Figure 1). This result shows that the dimerization reaction is not affected by the basicity of the quench.

**Discussion of the Mechanism of Initiation in the TMP1/$TiCl_4$ System.** The TMP1 + $TiCl_4$ experiment produces a nonnegligible quantity of H−TMP−Cl (12.5%) in addition to the dimers (85%). Because the TMP1 + $TiCl_4$ experiment quenched with $BuNH_2$ gives approximatively the same result, it can be concluded that the production of H−TMP−Cl is not due to the quench using MeOH. Because the chlorine atom must come from $TiCl_4$, it is clear that it can be produced either through cocatalysis or through direct initiation. The experiment carried out in the presence of the hindered pyridine (MDtBP) even shows a relative increase of H−TMP−Cl (24%) compared with the experiment in its absence (12.5%). This hydrochlorinated product became the main product because the dimer production was strongly decreased (2%).

On the other hand, the H−TMP−Cl content was higher than the initial molar content of $TiCl_4$. This observation can be accounted for by assuming that not only $TiCl_4$ but also the $TiCl_3R$ species are able to experience self-ionization, and finally initiation with TMP1. It is also remarkable that there was practically no dimer production in the presence of MDtBP, although we assume the production of a $TiCl_3-TMP^+,TiCl_5^-$ species, which in principle should be able to propagate dimerization. Two explanations can be proposed to account for this observation. The first one is that the active species is different in the presence and in the absence of MDtBP. Thus, active species solvation by MDtBP prevents the approach of the monomer TMP1 because of steric hindrance. We can also assume that MDtBP reacts with $TiCl_4$ giving rise to a complex MDtBP·$TiCl_4$, whose acidic strength is weaker than that of free $TiCl_4$ so it cannot ionize the halometallated monomer. The complex MDtBP·$TiCl_4$ was evidenced by Masure et al.[19] in the dimerization of 1,1-diphenylethylene initiated by $TiCl_4$. The other explanation points to the fact that when dimerization is initiated by cocatalysis (in the absence of hindered pyridine), the active species $H-TMP^+,TiCl_4OH^-$ is different from the active species given by direct initiation ($TiCl_3-TMP^+,TiCl_5^-$), and this difference could explain the small amount of dimer present in this latter case. In agreement with this last explanation, it has been suggested that HCl is not a cocatalyst in the case of $TiCl_4$ initiation.[20] However, initiation by H−TMP−Cl was used under similar conditions to those used in the present work.[21,22] Consequently, we conclude from this discussion that the species obtained in the case of direct metallation does not easily react with a new molecule of TMP1 to give dimers in the presence of MDtBP. We

**Scheme 3**



also conclude that the main reactions in the system TMP1 (or TMP2)/$TiCl_4$/MDtBP are:

$$2\ TiCl_4 \rightarrow TiCl_3^+,TiCl_5^-$$

$$TiCl_3^+,TiCl_5^- + TMP1 \rightarrow TiCl_3{-}TMP^+,TiCl_5^-$$

$$TiCl_3{-}TMP^+,TiCl_5^- \rightarrow TiCl_3{-}TMP{-}Cl + TiCl_4$$

It is worth noting that chlorinated molecules such as H−TMP−TMP−Cl are never observed at any conditions. We explain this result by the fact that such chlorinated compounds would be highly strained, and elimination is favored. This elimination reaction is probably of zero order versus TMP1 concentration (spontaneous transfer) and the proton is trapped when MDtBP is present, as shown by the low concentration of TMP−TMP under these conditions.

The results obtained by quenching with monodeuterated methanol (MeOD) are more striking. It is possible to account for the deuteration of H−TMP−Cl in the case of the simple experiment TMP1/$TiCl_4$. Indeed, quenching with methanol does not rapidly destroy the LA, and most probably gives rise to new LAs such as $TiCl_n(OMe)_{4-n}$, which can catalyze the reaction sequence of addition−elimination of DCl/HCl, leading to multideuteration of H−TMP−Cl. The reaction giving rise to H−TMP−Cl in the presence of MDtBP must be discussed. This chlorinated molecule is the main product in this experiment and it can be assigned to the metallation reaction (process III). The most important result is that in this case, when the reaction is quenched with MeOD, the H−TMP−Cl is mainly monodeuterated. Considering this monodeuteration, the mechanism involved appears not reversible and seems different than the last one proposed that leads to multideuteration. So, we conclude that the monodeuteration is due to the methanolysis of the carbon−metal bond:

$$MeOD + {-Ti{-}C{-}} \rightarrow MeO{-}Ti{-} + D{-}C{-}$$

From this set of experiments, it is clear that in the presence of a proton scavenger, initiation is mainly due to metallation either through self-ionization of the LA or through direct metallation by the LA in its monomeric form.

**GC/MS Study of Initiation by $TiCl_4$ in the Presence of H−TMP−NCS. (A) H−TMP−NCS + $TiCl_4$ Reaction (MeOH Quench).** The TIC of the H−TMP−NCS + $TiCl_4$ reaction gives a mixture of H−TMP−Cl (3%) and H−TMP−NCS (97%). This reaction leads to an assumed complex (Scheme 3) with a tendency to give only a small quantity of H−TMP−Cl by exchange between $NCS^-$ and $Cl^-$ moieties. It is worth noting that the reaction was clean because no side reaction occured; for instance, the dehydroisothiocyanatation of H−TMP−NCS catalyzed by $TiCl_4$ was not observed.

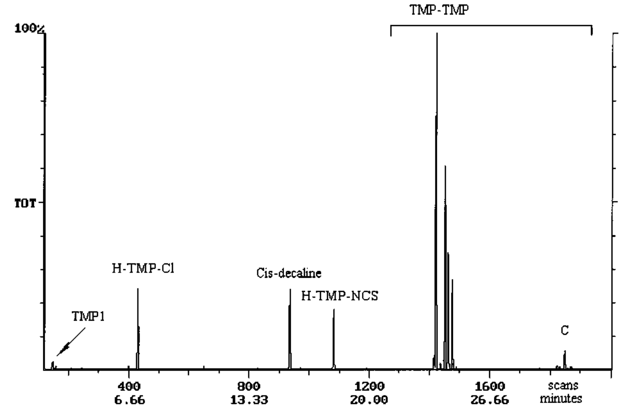
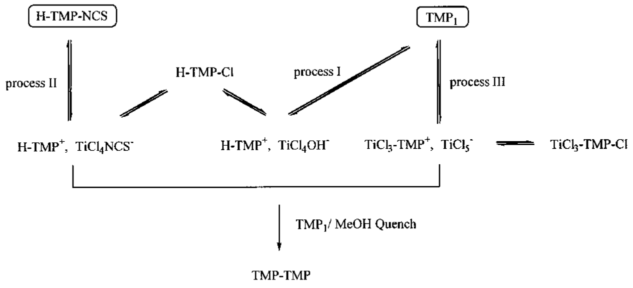


**Figure 6.** Total ion current of H−TMP−NCS + TMP1 + $TiCl_4$ reaction (MeOH quench).

**Table 3. TMP1 Molar Balance Determined by FID and MS**

| detection | TMP1 | H−TMP−NCS | H−TMP−Cl | TMP−TMP | total TMP |
|---|---|---|---|---|---|
| FID | traces | 1 | 1.4 | 8.6 | 10 |
| MS | traces | 1.2 | 1.3 | 9 | 10.3 |

**Scheme 4**



**(B) H−TMP−NCS + TMP1 + $TiCl_4$ Reaction (MeOH Quench).** The TIC of the H−TMP−NCS + TMP1 + $TiCl_4$ reaction (Figure 6) presents a mixture of H−TMP−Cl (8%) and TMP−TMP (92%), and H−TMP−NCS.

Table 3 gives the TMP1 balance determined by FID and MS methods. From the initial reactants molar ratio of H−TMP−NCS (1)/TMP1 (10)/$TiCl_4$ (2)/*cis*-decaline (1), it is clear that H−TMP−NCS remained unchanged and the amount of H−TMP−Cl and TMP−TMP obtained was the same as in the absence of H−TMP−NCS. These results show that H−TMP−NCS is not an initiator for the dimerization of TMP1 and only plays a role in changing the relative percentages of the four major dimers (**A** = 32%; **A′** = 31%; **B** = 28%; **B′** = 15%). The percentages of the **A**, **B** couple are increased and those of **A′**, **B′** couple are decreased.

Scheme 4 presents the possible competitive ways leading to the formation of the final product TMP−TMP in the H−TMP−NCS/TMP1 system in the presence of $TiCl_4$. These ways include: cocatalytic initiation (process I), where in the absence of proton scavenger, TMP1 alone can easily dimerize; H−TMP−NCS initiation (process II), which does not occur through this direct pathway because the H−TMP−NCS concentration remained unchanged; direct initiation (process III), in which TMP1 alone can be ionized into $TiCl_3{-}TMP^+$ followed by dimerization into TMP−TMP (this initiation has been evidenced in the presence of MDtBP, and this pathway can lead to the formation of $TiCl_3$−TMP−Cl, but we already concluded that $TiCl_3$−TMP−Cl is not

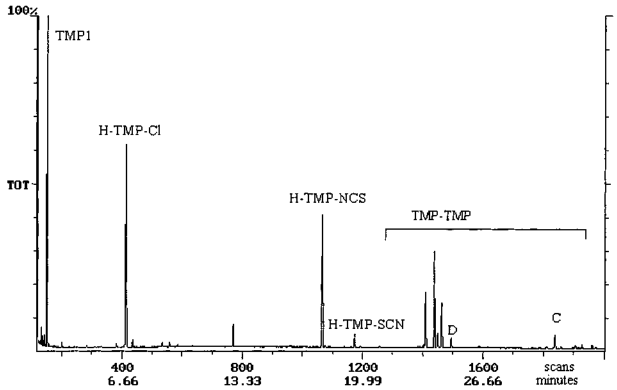
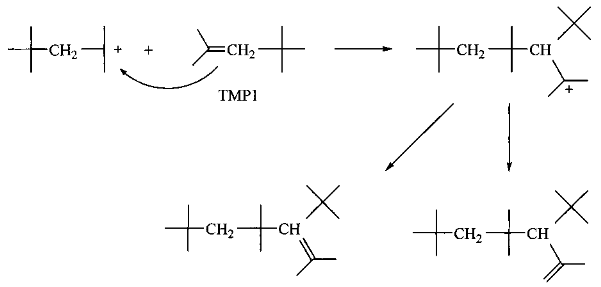


**Figure 7.** Total ion current of H−TMP−NCS + TMP2 + $TiCl_4$ reaction (MeOH quench).

**Scheme 5**



an initiator in the presence of $TiCl_4$); and H−TMP−Cl initiation (an indirect way) in which the presence of H−TMP−Cl can result from either hydrochlorination of the TMP double bond (HCl coming from the hydrolysis of $TiCl_4$ by moisture) or from exchange of nucleophilic moieties $NCS^-$ and $Cl^-$ between H−TMP−NCS and $TiCl_4$ (actually this reaction did not occur because H−TMP−NCS concentration remained unchanged).

The H−TMP−Cl formed during the reaction in the presence of $TiCl_4$ can give also H−TMP$^+$ followed by the dimerization into TMP−TMP. This result is not surprising because, according to Kennedy et al.,[21,22] the initiating systems H−TMP−Cl/$MX_n$ are efficient initiators for the polymerization of IB.

TMP1 can exist under another isomer, a trisubstituted (2,4,4-trimethyl-2-pentene, TMP2) structure, so that in an acidic medium like $TiCl_4$, an isomerization of TMP1 into TMP2 is possible and can play a role in the dimerization of TMP. Thus, an experiment with TMP2 was undertaken.

**(C) H−TMP−NCS + TMP2 + $TiCl_4$ Reaction (MeOH Quench).** Figure 7 displays the TIC of the H−TMP−NCS + TMP2 + $TiCl_4$ reaction. The same unsaturated dimers (**A** = 24%; **A′** = 5.3%; **B** = 43%; **B′** = 19%; **C** = 5.3%) are observed as in the case of TMP1 but with a quantity less important (56%) and also a new dimer **D** (**D** = 3.4%). Dimer **D** is probably one of the two dimers resulting from the reaction of TMP2 with H−TMP$^+$. Because the two isomers give the same carbenium H−TMP$^+$, two others stuctures of dimers are taken into account, as shown in Scheme 5.

The presence of the same dimers **A**, **A′**, **B**, **B′**, and **C** in small amounts is proof that TMP2 isomerizes into TMP1 before dimerization. Because TMP2 is less reactive than TMP1, the amount of H−TMP−Cl formed (44%) is higher than in the case of TMP1.

The results of H−TMP−NCS + TMP1 + $TiCl_4$ and H−TMP−NCS + TMP2 + $TiCl_4$ reactions give a strong argument that H−TMP−NCS is not an initiator in the dimerization of TMP1. To support this conclusion, an experiment was carried out with *tert*-butyl isothiocyanate (TBu−NCS) to obtain an asymetric dimer that would allow the determination of the origin of the *tert*-butyl group in the dimer chain, which can come from either TMP1 or TBu−NCS.

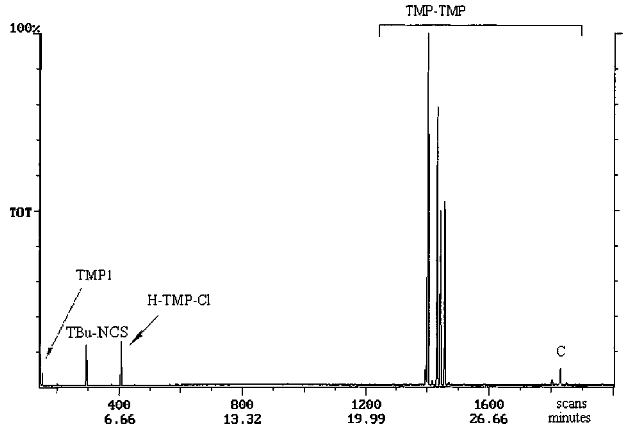


**Figure 8.** Total ion current of TBu−NCS + TMP1 + $TiCl_4$ reaction (MeOH quench).

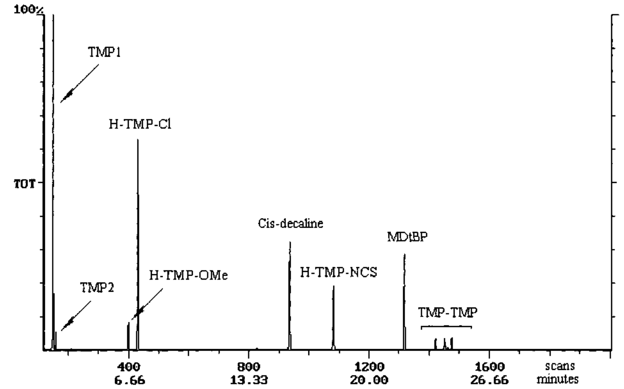


**Figure 9.** Total ion current of H−TMP−NCS + TMP1 + $TiCl_4$ + MDtBP reaction (MeOH quench).

**(D) TBu−NCS + TMP1 + $TiCl_4$ Reaction (MeOH Quench).** The corresponding TIC (Figure 8) shows the same group of dimers (97%) (**A** = 35%; **A′** = 27.5%; **B** = 17.5%; **B′** = 18%, and **C** = 2%) + H−TMP−Cl (3%) as in the case of the TMP1 + $TiCl_4$ reaction and no asymetric dimer. This result supports our conclusion mentioned above and shows the reproducibility of experiments (within experimental error, H−TMP−NCS or TBu−NCS acts as an inert adduct in the dimerization process). The change of the structure of the isocyanato derivative modifies the isomer percentages; that is, **A** is increasing in favor of **B** and **A′** is decreasing in favor of **B′**.

The last model reaction was performed to verify that H−TMP−NCS does not step into the dimerization, especially in the presence of MDtBP.

**(E) H−TMP−NCS + TMP1 + $TiCl_4$ + MDtBP Reaction (MeoH Quench).** The TIC corresponding to this reaction (Figure 9) still shows, in addition to H−TMP−NCS, MDtBP, and *cis*-decaline peaks (unchanged), the same mixture with particularly few change in the percentage of H−TMP−Cl and TMP−TMP dimers (**A**, **A′**, **B**, **B′**) compared with the experiment carried out in the absence of H−TMP−NCS (Figure 2). The initial reactant ratio was TMP1(10)/

**Table 4. TMP Molar Balance Determined by FID and MS**

| detection | TMP1 | TMP2 | H−TMP−OMe | H−TMP−Cl | TMP−TMP | total TMP |
|---|---|---|---|---|---|---|
| FID | 7 | 0.1 | 0.1 | 3.1 | 0.15 | 10.6 |
| MS | 7.5 | 0.1 | 0.15 | 2.6 | 0.1 | 10.45 |

H−TMP−NCS(1)/$TiCl_4$(2)/*cis*-decaline(1)/MDtBP(0.5), and theTMP balance determined by FID and MS is shown in Table 4. These results show that the presence of MDtBP does not favor any coinitiation process.

**(F) H−TMP−NCS + PIB−Cl + $TiCl_4$ Reaction (MeOH Quench).** This experiment was carried out to accurately determine the conditions for an exchange reaction between an aliphatic tertiary chlorine end and an aliphatic tertiary isothiocyanate group. Thus, a PIB chlorinated on the chain end was synthetized in advance in an independent experiment. This polymer ($M_n$ = 2000) was dissolved in $CH_2Cl_2$, mixed with H−TMP−NCS, and brought to −50 °C. Then, $TiCl_4$ was introduced, and the system was allowed to react for 2 h. After quenching with MeOH, the polymer was recovered, cleaned by precipitation, and analyzed by IR spectroscopy. The collected PIB did not contain any NCS function. This finding confirms that with our reaction conditions, no ionization of TIP was observed.

**Discussion of the Mechanism of Initiation in the TMP1/$TiCl_4$ System in the Presence of H−TMP−NCS.** The results just presented support the conclusion that H−TMP−NCS is not an initiator for the TMP1 dimerization. In the presence or in the absence of a hindered pyridine, the system behaves almost as if the H−TMP−NCS molecule is not be present. The results provide evidence for cocatalytic and direct initiations processes. The fact that the following reaction is not observed indicates that this LA is probably not the best choice to initiate IB functionalizing polymerization when an isothiocyante group is involved. It is possible to

$$\text{H−TMP−NCS} + TiCl_4 \rightarrow \text{H−TMP}^+,TiCl_4NCS^-$$

conclude that the exchange reaction between chlorine and the aliphatic isothiocyanate group during IB polymerization initiated by titanium tetrachloride takes place only when polymerizing active species are present.

**Structural Analysis of Dimers.** The dimerization of TMP1 leads to six isomers of molecular formula $C_{16}H_{32}$, in which four are in the majority (**A, A′, B** and **B′**) and two are in the minority (**A″, C**; e.g., TMP1 + $TiCl_4$ reaction). The dimerization of TMP2 via TMP1 also leads to the same six isomers plus an additional dimer, **D** (e.g., H−TMP−NCS + TMP2 + $TiCl_4$ reaction). In the following discussion, we will begin to consider the main dimers from TMP1. Their structural assignment was determined by using MS experiments in combination with chemical reactions.

Unfortunately, 70 eV MS analysis (Figure 2) does not discriminate between *Z* and *E* isomers of the same compound, and the fragmentation patterns rarely show significant differences between the various >C=C< positional isomers for such structures 1, 2, and 3 (Scheme 6). Nevertheless, we observed that the four dimers belong to two groups; that is, those with (**A**, **A′**) and without (**B**, **B′**) a molecular ion $M^{+\bullet}$ at 224 (for the latter group, there was no ion above *m*/*z* = 112).

**Scheme 6**

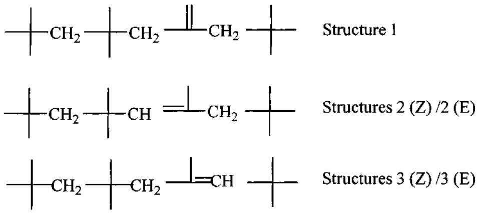
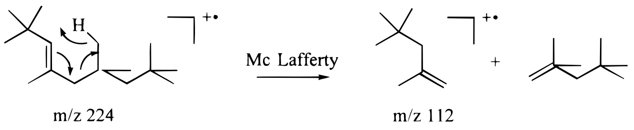


**Table 5. Charge Exchange (CS2) Mass Spectra of A, A′, B, B′ Dimers**

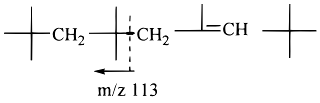
| dimer | *m*/*z* 97 | *m*/*z* 112 | *m*/*z* 113 | *m*/*z* 153 | *m*/*z* 168 | *m*/*z* 224 |
|---|---|---|---|---|---|---|
| **A** | 5 | 0 | 0 | 100 | 12 | 25 |
| **A′** | 5 | 0 | 0 | 20 | 70 | 100 |
| **B** | 5 | 72 | 100 | 5 | 5 | 5 |
| **B′** | 5 | 100 | 27 | 25 | 0 | 3 |

To obtain more information about the structure of these dimers, we performed ionization by charge exchange, which is a softer ionization method than that with electron impact. The internal energy of $M^{+\bullet}$ is determined by the difference in ionization energy of the gas reactant ions and the simple molecules M. A commonly used reagent gas, $CS_2$, has an ionization energy (10.06 eV) that is slightly higher than those of olefins (8−9 eV). The internal energy of $M^{+\bullet}$ dimers will therefore be 1−2 only eV. Table 5 presents the charge exchange mass spectra of the dimers **A**, **A′**, **B**, and **B′**. With these conditions, all dimers present a molecular ion $M^{+\bullet}$ at 224, and show distinct fragmentation patterns that can be related to one of the structures **1**−**3**. Thus, **B′** is the only dimer that does not present an ion at *m*/*z* = 168 [$(M-C_4H_8)^{+\bullet}$]. The only structure compatible with this feature is isomer **3** (*Z* or *E*), which undergoes a McLafferty rearrangement to give the base peak at *m*/*z* = 112. According to the hindrance effect, the structure **3***E* can follow more easily than a McLafferty rearrangement:



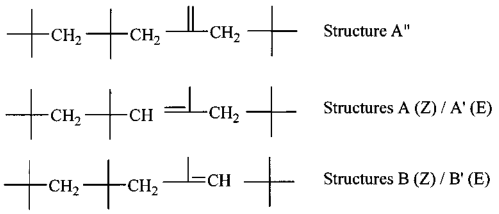
The mass spectra of dimers **A** and **A′** display the same fragmentations. They differ from one another only in abundances of the ions. The dimer **A′** exhibits a base peak at *m*/*z* = 153, corresponding to the elimination of the $C_5H_{11}$ radical by a cleavage, whereas the base peak of dimer **A** is the molecular ion. Both dimers show an ion at *m*/*z* = 168, which is the result of a $C_4H_8$ loss by McLafferty rearrangement. These two spectra are compatible with the structures 2*Z* and 2*E*.

The last major dimer **B**, which does not present a molecular ion with electron impact method, could correspond to the structure 3*Z*, which is able to give an important ion at *m*/*z* = 113 by allylic cleavage.



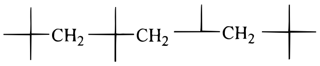
For thermodynamic reasons, the charge is retained by the $C_8H_{17}$ ion rather than the allylic counterpart $C_8H_{15}$. The comparison of $DH_f$ between $C_4H_9^+$ and $C_4H_7^+$ ions shows that the former is 45 kcal/mol more

**Scheme 7**



stable.[23] A similar difference is expected between $C_8H_{17}$ and $C_8H_{15}$ ions. The structure 3*Z* is also compatible with the intense peak at $m/z = 112$, which can be formed directly via a McLafferty rearrangement.

To confirm these structures, a microhydrogenation ($H_2/PtO_2$) of the isomers mixture was carried out, and GC analysis showed the formation of a main compound associated with the simultaneous disappearance of the four main products. The MS analysis of this product is compatible with the following structure:



This result confirms the structures of **1**, **2*Z*/2*E***, **3*Z*/3*E*** (e.g., TMP1 + $TiCl_4$ reaction), which give the same saturated hydrocarbon by hydrogenation.

The structures **A″** and **C** are not well defined. The amount of **A″** is too low to give results by charge exchange; however, the corresponding 70 eV mass spectrum (Figure 2) is compatible with the last unassigned structure **1**. Compound **C** seems to be significantly different from the olefinic dimers. It could be a chlorinated dimer if we consider the difference of retention times, but the mass spectrum does not give further information confirming the presence of chlorine. Nevertheless, the carbon skeleton seems to be unique; that is, the loss of $C_7H_{15}^{\bullet}$, which gives an ion at $m/z = 125$, is incompatible with the expected H−TMP−TMP−Cl.

The results of these different experiments carried out for the identification of dimers are compatible with the structures proposed, as indicated in Scheme 7. The results show that when H−TMP−NCS is present, the percentage of the **A**, **B** couple is increased and that of the **A′**, **B′** couple is decreased. It is worth noting that structural determination provides an explanation of this observation, because isomers **A** and **B** are *Z* isomers, showing that the elimination favors the formation of the *Z* isomers. This conclusion is understandable if it is assumed that H−TMP−NCS is interacting with the ions, thus favoring *Z* placement upon elimination. Consequently, it can be deduced that the role of H−TMP−NCS is only to be a weak electron donor interacting with the cations. This deduction is a clear demonstration that the electron donors are interacting not only with the LAs, but also with the active species of cationic polymerization.

## Conclusion

The results of these experiments indicate that H−TMP−NCS is not an initiator for the dimerization of TMP1. Although initiation via H−TMP−Cl formed in situ (by exchange reaction) is possible, its level is low so that it can be neglected in our reaction conditions. The results also show that two mechanisms are involved in the dimerization of TMP; they are, $H_2O$ (protonic) initiation and direct initiation followed by spontaneous transfer. The structure of the initiator RP is important in the mechanism of the initiation reaction. An aliphatic RP, such as H−TMP−NCS, seems not to be an initiator for the dimerization of TMP1. Thus, the functionalization by an NCS or a SCN group observed in IB polymerization initiated by $TiCl_4$ in the presence of H−TMP−NCS could be due to an exchange reaction and not due to initiation from H−TMP−NCS. The functionalization would occur only on the active species that is generated independently. In the case of an aromatic RP, such as 2-isocyanato-2-phenylpropane, the ion generation reaction most probably occurs and then polymerization proceeds. This sequence has been evidenced by $^1H$ NMR analysis of polymers (peak at 7.3 ppm assigned to aromatic ring).[15]

In conclusion, this study gives a better understanding of the mechanism of olefin dimerization (and by extension polymerization) initiated by $TiCl_4$ alone or in combination with R-NCS.

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