Articles

Synthesis of Polymers Containing Pseudohalide Groups by Cationic Polymerization. 16.† Model Reactions and Oligomerization of Isobutylene with 2-Isothiocyanato-2-phenylpropane/$TiCl_4$ as Initiating System

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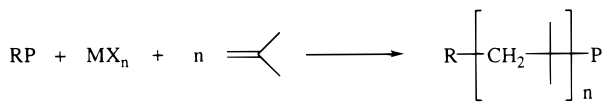
ABSTRACT: Model reactions were carried out with 2-isothiocyanato-2-phenylpropane(Cum-NCS)/$TiCl_4$ combinations as the initiating system and using 2,4,4-trimethyl-1-pentene (TMP1) as nonpolymerizable monomer. The reaction products were characterized by GC/MS, and their presence was interpreted in terms of cationic processes. These results were compared to those obtained by the analysis of oligoisobutylenes synthesized under the same conditions. We showed that the combination of chromatographic techniques (SFC, SEC, and GC) and of mass spectrometry allowed the analysis of such oligomers. This strategy was complementary to the approach using model reactions. Model experiments, such as the reaction Cum-NCS/$TiCl_4$, showed the production of compounds demonstrating the ionization of the initiator, Cum-OMe due to the quench with MeOH. Similarly, the reaction Cum-NCS/TMP1/$TiCl_4$ confirmed the existence of a direct initiation mechanism. The reaction Cum-NCS/TMP1/$TiCl_4$/4-methyl-2,6-ditertiobutylpyridine (MDtBP) indicated that the direct initiation mechanism made use of the whole quantity of $TiCl_4$. The polymerization of isobutylene (IB) in the presence of the system Cum-NCS/$TiCl_4$ indicated that the product of indanic cyclization could be alkylated. The same system in the presence of MDtBP demonstrated that the hindered pyridine favors the elimination reaction so that the polymer did not bear any pseudohalide function. In the presence of DMSO instead of MDtBP, an unexpected side reaction was evidenced, namely the alkylation of the terminal double bonds of the polymer by a cumyl cation, thus producing a polymer having an aromatic nucleus at both ends. This finding also demonstrated that in this system, propagation is faster than initiation. However, an important product was also the expected polymer, i.e., a PIB having a cumyl moiety at one end and an NCS group at the other end.

Introduction

In the course of our study on the cationic functionalizing polymerization of isobutylene (IB), organic pseudohalide (RP)/Lewis acid (MX_n) combinations were developed:[1−3]



We demonstrated that the di(1-azido-1-methylethyl)-1,4-benzene/BCl_3 combination in the presence of an electron donor (DMSO) can give living polymerizations with polymers only functionalized by azide end groups[2].

A similar work, with another pseudohalide group, the isothiocyanate function (−NCS), using 2-isothiocyanate-2,4,4-trimethylpentane (H-TMP-NCS) as initiator has been reported and the corresponding polymerizations of IB also lead to functionalized polyisobutylenes (PIBs) bearing −NCS and/or −SCN functions.[4,5] Yet, the mechanism of initiation was not established because co-initiation and the other mechanisms of initiation lead to the same *tert*-butyl end group. We reported recently the GC/MS study of model reactions, using H-TMP-NCS/$TiCl_4$ as the initiating system and 2,4,4-trimethyl-1-pentene (TMP1) as the nonpolymerizable monomer.[6] These model experiments showed that H-TMP-NCS did not act as an initiator, and it was concluded that the functionalization could come from an exchange process between $-Cl^-$ and $-NCS^-$ moieties at the end of the polymerization.

This unexpected result prompted us to perform experiments with another potential initiator: 2-isothiocyanato-2-phenyl-propane (Cum-NCS), to favor the co-initiation efficiency and thus be able to control the functionalization.

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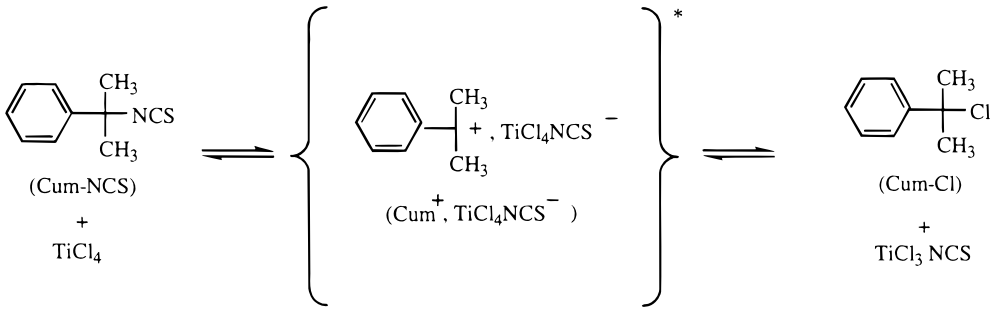
Scheme 1



Our approach in this paper was to perform a preliminary mechanistic study of the initiation reaction with model reactions using TMP1 and to compare these results with subsequent oligomerizations, using $TiCl_4$ in conjunction or not with a proton scavenger, 4-methyl-2,6-di-*tert*-butylpyridine (MDtBP), or an electron donor, dimethyl sulfoxide (DMSO).

Low mass oligomers were synthesized in order to simplify the structural analysis. Their characterizations were not performed by classical techniques such as NMR and IR but by an analytical strategy based on the use of supercritical fluid chromatography (SFC), and the off-line combination of size exclusion chromatography (SEC) with gas chromatography/mass spectrometry (GC/MS) coupling was developed. This technique allows accurate identification of the different oligomers series and byproducts and gives valuable information on the first steps of cationic polymerization.

Experimental Section

Reactants. Reactants were purified and dried according to our laboratory procedure. CH_2Cl_2, TMP1, and IB were commercially available, whereas Cum-NCS was synthesized in two steps:[7] hydrochlorination of α-methylstyrene and nucleophilic substitution reaction with sodium isothiocyanate. $TiCl_4$ in CH_2Cl_2 solution (sure seal bottle 1 M, Aldrich), 4-methyl-2,6-di-*tert*-butylpyridine (MDtBP), dimethyl sulfoxide (DMSO), MeOH, and *cis*-decaline were used as received.

Model Reactions and Polymerization. The general procedures for model reactions and IB polymerizations have been published.[3,6] The reactions were carried out under vacuum at −50 °C in CH_2Cl_2. After 30 min of reaction, the system was quenched with MeOH, 0.5 mL of *cis*-decaline as internal standard was added for the model experiments, or polymer was isolated in the case of polymerization experiments.

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

GC/MS experiments were carried out with a Varian Saturn III quadrupole ion trap mass spectrometer coupled to a gas chromatograph Varian 7400 CX. The 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 6.9×10^4 Pa. 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 that given above. The transfer line from the gas chromatograph to the quadrupole ion trap was held at 260 °C.

Semipreparative SEC was done on a Pye Unicam 4003 system using two Jordi columns (250 mm × 10 mm i.d., 100 Å, and 300 mm × 8 mm i.d., 500 Å) and a Waters styragel column (300 mm × 8 mm i.d., 10^3 Å) with CH_2Cl_2 as the mobile phase (1 mL/min). Both, UV (254 nm) and refractometric detectors were used. The system was calibrated with polystyrene.

Table 1. Relative Molar Content of Cum-NCS(1) + $TiCl_4$(2) Reaction Products Determined by FID and MS Referenced to *cis*-Decaline (*cis*-Decaline = 1 as Internal Reference, Corresponding to 3.1×10^{-2} mol L^{-1})

detection	Cum-OMe	Cum-Cl	Cum-NCS	Cum-αMeSt
FID	0	0.6	0.2	0.01
MS	0.05	0.5	0.2	0.02

SFC experiments were done on a Carlo Erba SFC 3000 system using carbon dioxide as the mobile phase and a DB5 (JW) stationary phase (10m × 100 μm i.d.). A linear pressure gradient from 12 to 28 mPa in 120 min at 130 °C was applied. The detection was by a flame ionization detector (FID).

NMR experiments were carried out with a Bruker 250 MHz spectrometer, with tetramethylsilane as internal reference.

Results and Discussion

The results are reported in two parts, the first one dealing with the initiation reaction through model reactions. In the second one, these results are described and compared to subsequent oligomerizations of IB. Each part contains experiments with $TiCl_4$ alone and in combination with the proton scavenger 4-methyl-2,6-di-*tert*-butylpyridine (MDtBP) and finally with the electron donor dimethyl sulfoxide (DMSO).

I. GC/MS Study of the Initiation with the Cum-NCS/$TiCl_4$ System by Means of Model Reactions. The initiating system Cum-NCS/ $TiCl_4$ was first investigated alone and then in the presence of TMP1.

Cum-NCS + $TiCl_4$ Reaction (MeOH Quench). The molar ratios were [Cum-NCS]:[$TiCl_4$]:[*cis*-decaline] = 1:2:1; the reaction products were determined and quantified by both GC/MS and GC/FID with *cis*-decaline as the internal standard ([*cis*-decaline] = 3.1×10^{-2} mol L^{-1}), as shown in Table 1. For this and all other experiments, the results are the averages of three analysis. Each experiment was done twice.

The results from Table 1 show that approximately 55% of the initial Cum-NCS is transformed into Cum-Cl, 2.5% into Cum-OMe and 1.5% into Cum-αMeSt, 20% remaining intact. The mass spectrum of Cum-Cl presents two molecular ions at *m*/*z* 154 and 156 due to the presence of a chlorine atom and ions coming from simple cleavages: *m*/*z* 119 (Cum^+, loss of $Cl^•$) and *m*/*z* 139 (loss of $Me^•$). The Cum-OMe species was identified without ambiguity from its mass spectrum which does not show any molecular ion but an ion at *m*/*z* 135, corresponding to the loss of $Me^•$. The ions at *m*/*z* 73 $(CH_3)_2C^+ -$ OMe and *m*/*z* 119 (Cum^+) are also diagnostic.

The presence of these products indicates the existence of an ionization/exchange reaction (Scheme 1), as for the H-TMP-NCS + $TiCl_4$ reaction.[6] The stability of the

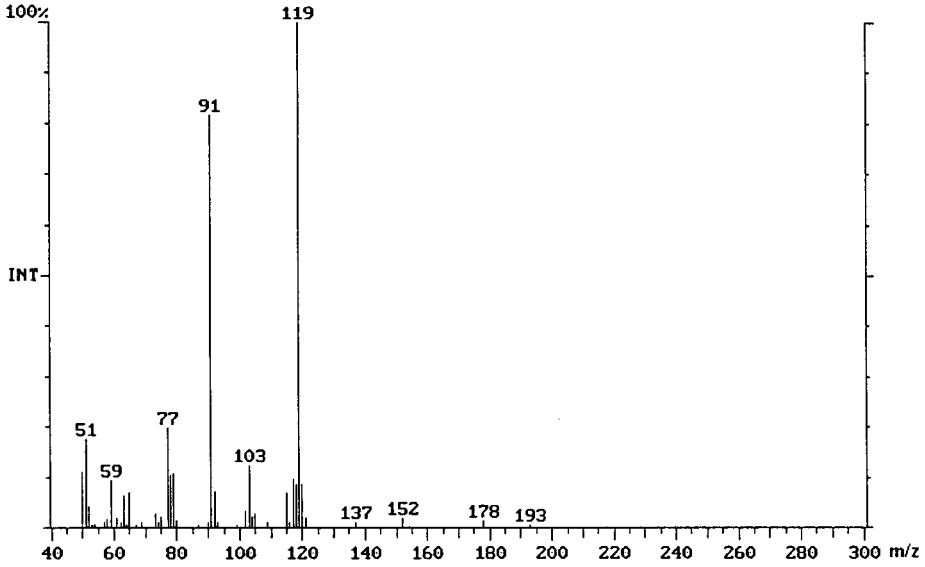


Figure 1. Mass spectrum of Cum-αMeSt **(I)**.

Scheme 2

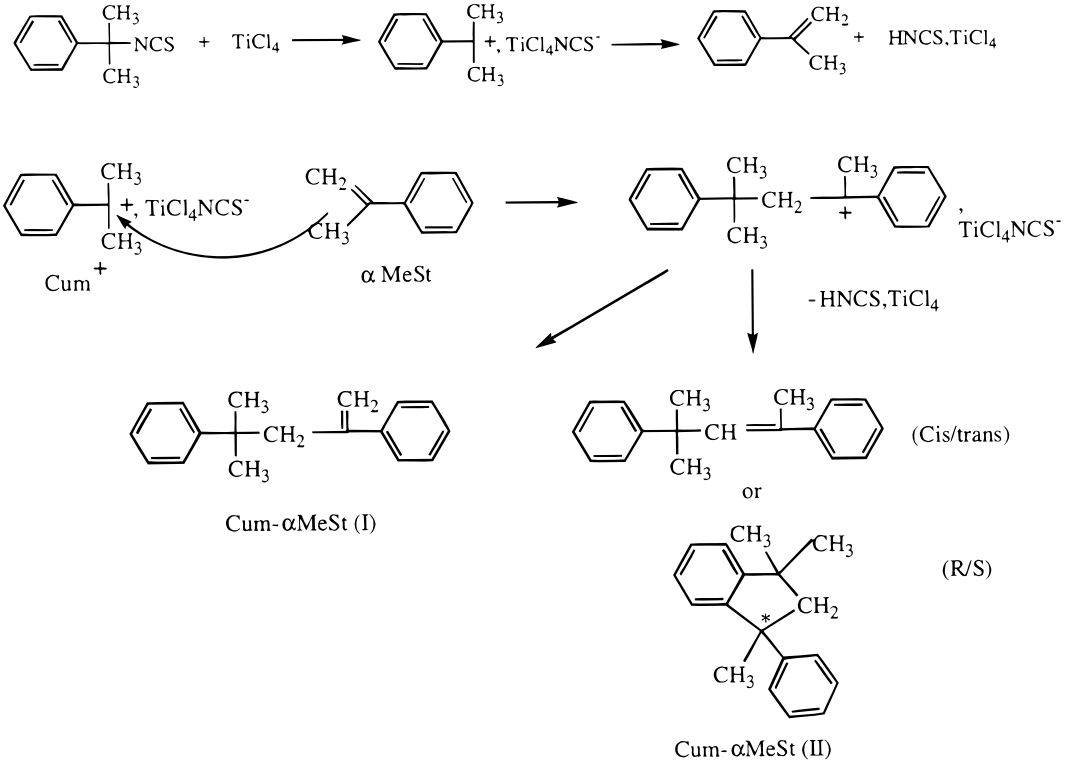


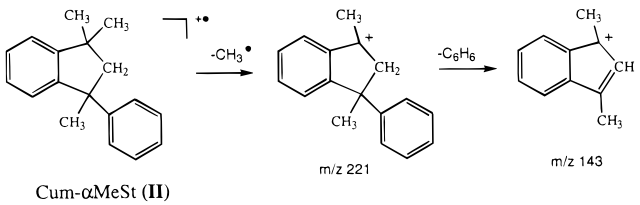
Table 2. Relative Molar Content of the Reaction Products of Cum-NCS(1) + TMP1(10) + $TiCl_4$(2) Reaction in the Absence and in the Presence of MDtBP Determined by FID and MS Referenced to *cis*-Decaline (*cis*-Decaline = 1 as Internal Reference (3.1×10^{-2} mol L^{-1}))

initial MDtBP	detection	TMP1	H-TMP-OMe	H-TMP-Cl	H-TMP-SCN	H-TMP-TMP	Cum-NCS	Cum-TMP^{ind}
0	FID	0.3	trace	1	0.8	2.4	0	1.3
(Figure 3a)	MS	0	trace	0.7	0.7	3.4	0	2.5
0.5	FID	6.65	0.15	2.7	0.55	0.35	0.35	0.9
(Figure 3b)	MS	8	0.15	2.35	0.45	0.34	0.35	1.05

benzylic carbocation (Cum^+) may favor a more pronounced ionic character.

As lifetimes and exchange rates between the various species are not known, this experiment demonstrates only the existence of an interaction between $TiCl_4$ and Cum-NCS leading to the cleavage of the C−N bond. Whereas the presence of Cum-Cl in the reaction prod-

Scheme 3



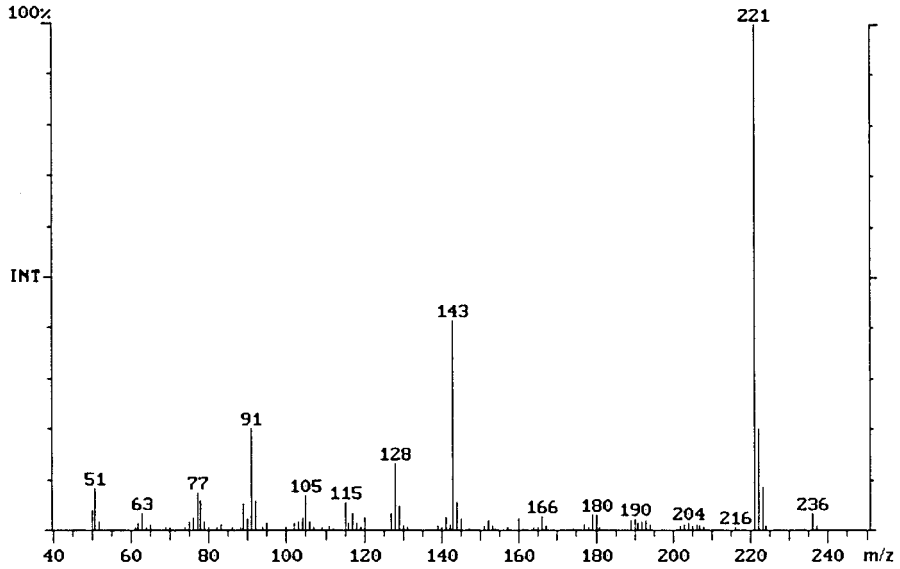
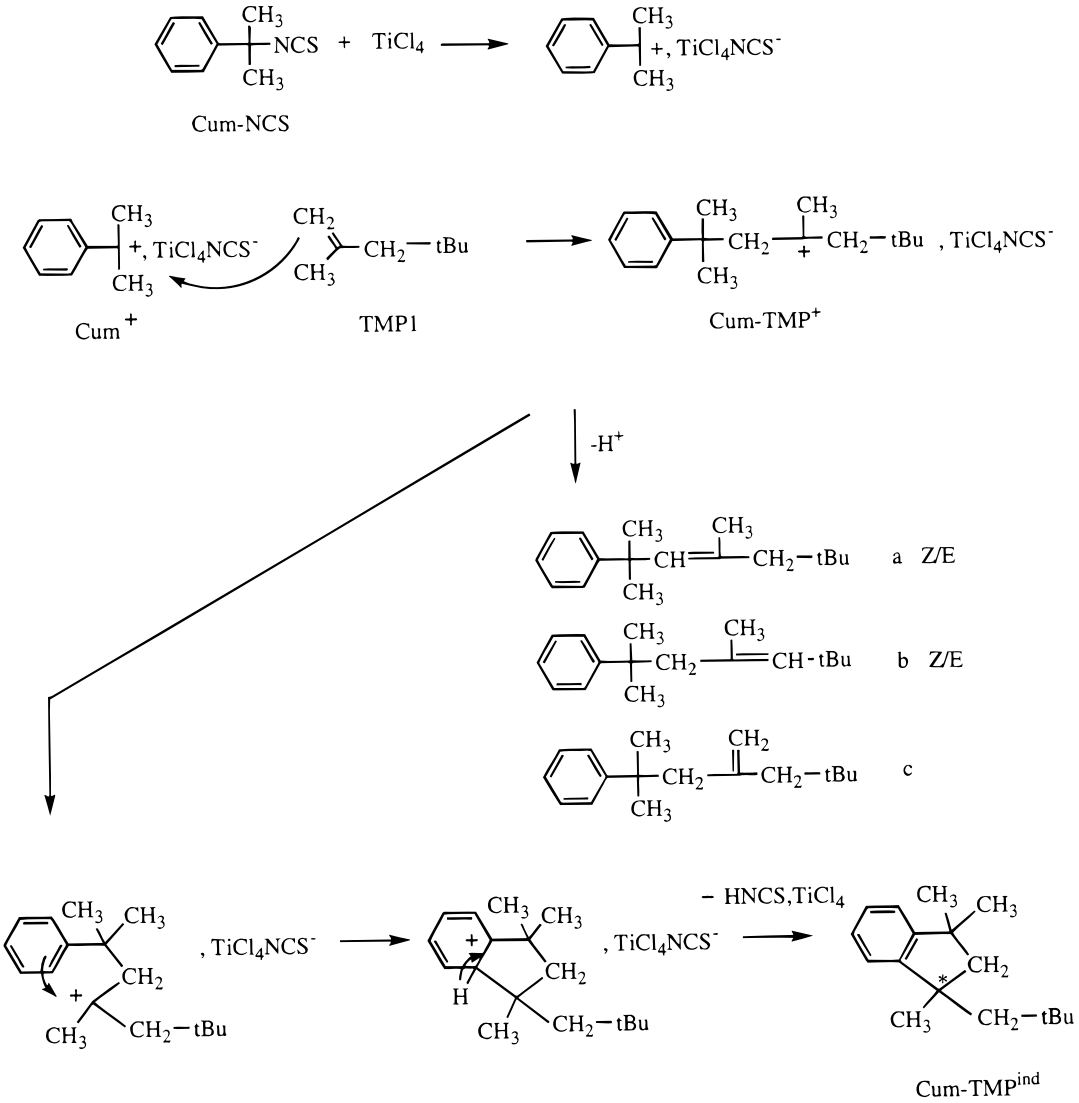


Figure 2. Mass spectrum of Cum-αMeSt **(II)**.

Scheme 4



ucts can be interpreted as arising from exchanges between NCS^- and Cl^- during the reaction, Cum-OMe is formed only from the carbenium ions during the addition of MeOH. A small amount (1.5%) of the two isomeric compounds Cum-αMeSt (**I**) and (**II**) is also formed, implying that a loss of HNCS can lead to the formation of α-methylstyrene (αMeSt) which reacts with Cum^+ as shown in Scheme 2.

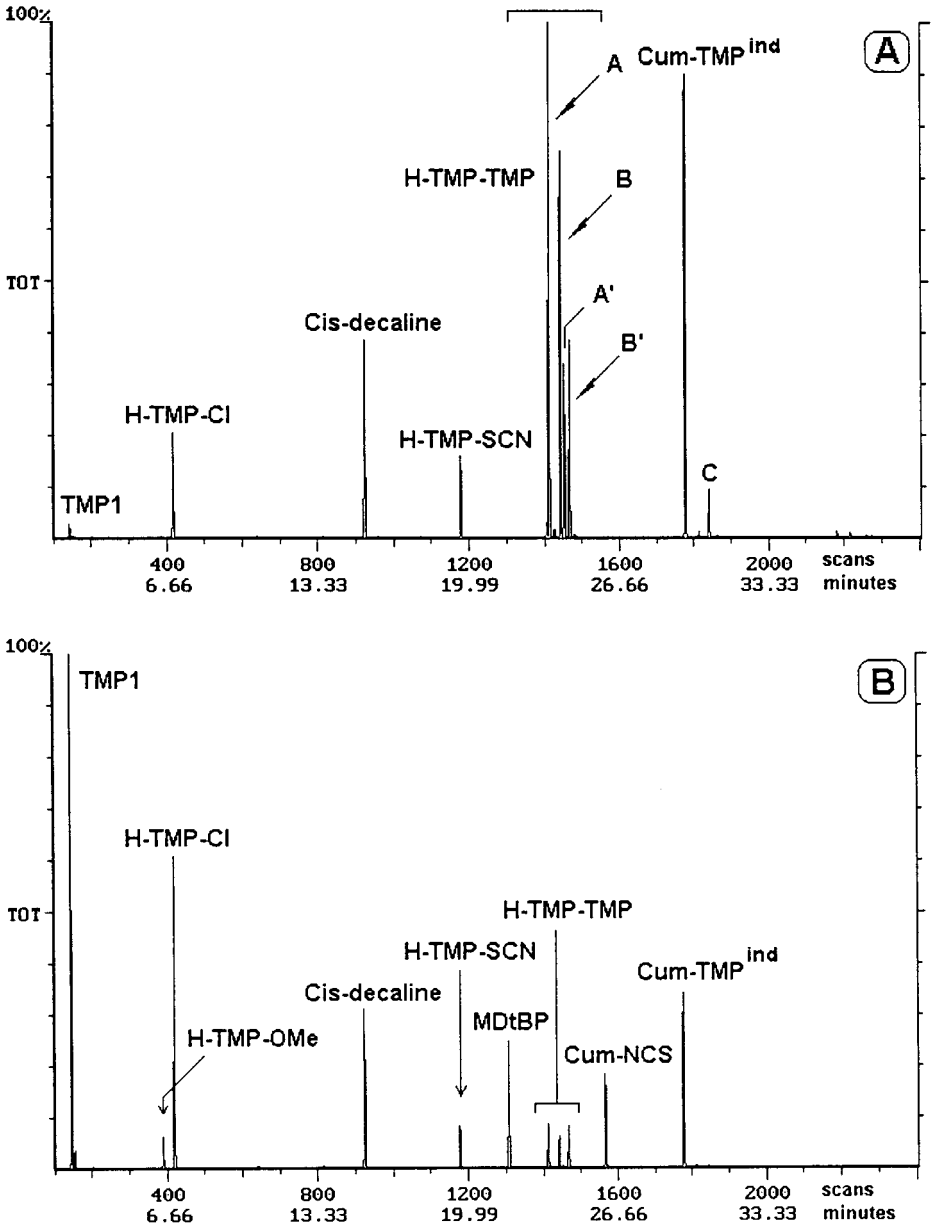
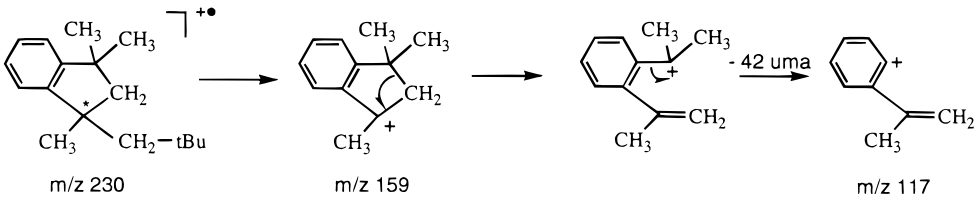


Figure 3. GC/MS chromatogram of the Cum-NCS + TMP1 + $TiCl_4$ reaction products: (A) in the absence of MDtBP; (B) in the presence of MDtBP.

Scheme 5



The steric hindrance of the carbenium ion does not allow a further insertion of α-MeSt monomer so that the propagation is interrupted by transfer. Cum-αMeSt (**I**) is due to an elimination reaction, whereas Cum-αMeSt (**II**) is due to an indanic cyclization. Their respective mass spectra are shown in Figure 1 and Figure 2.

For compound Cum-αMeSt (**I**), the formation of theion *m*/*z* 119 (Cum^+) is favored since it corresponds to a rupture, both in the allylic and benzylic positions. Thus, the mass spectrum does not show any molecular ion. The retention times of the Cum-αMeSt (**I**) and (**II**) compounds are sufficiently close to suggest two isomeric structures.

In the case of Cum-αMeSt (**II**), two structures are compatible with a molecular ion at *m*/*z* 236 (Scheme 2). The absence of the $(M - 77)^+$ ion seems more compatible with an indanic structure. The ion at *m*/*z* 221 $(M - 15)^+$ should be favored by the presence of three methyl groups. A consecutive elimination of C_6H_6 leads to an ion at *m*/*z* 143 (Scheme 3).

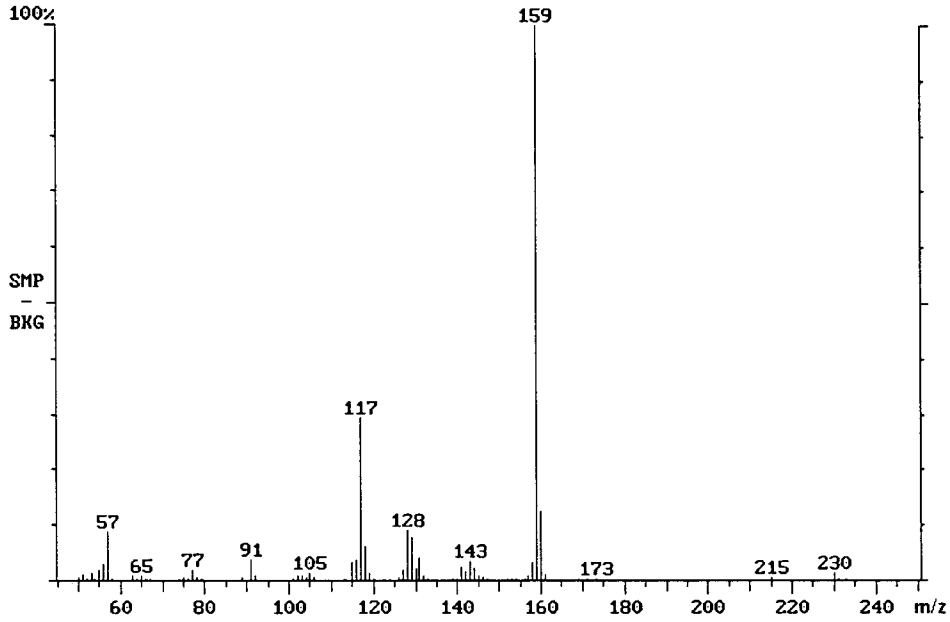
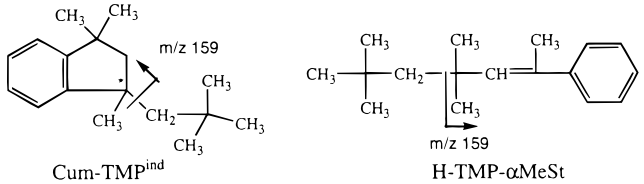


Figure 4. Mass spectrum of Cum-TMP^{ind}.

Scheme 6

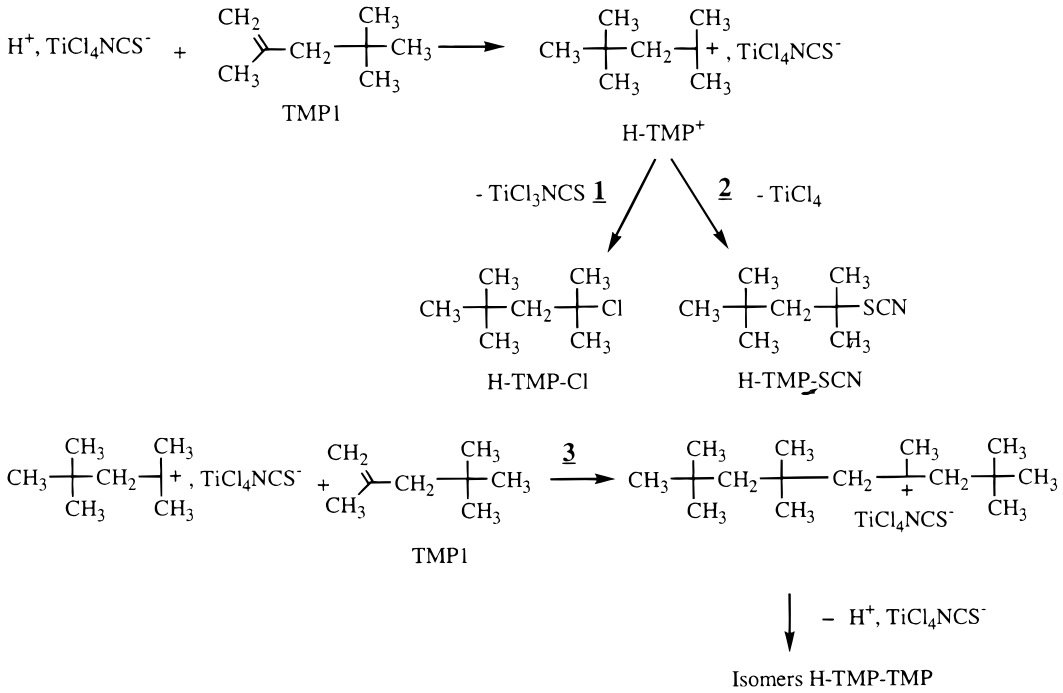


Cum-NCS + TMP1 + $TiCl_4$ Reaction (MeOH Quench). The same experiment was carried out in the presence of TMP1, the molar ratios being [Cum-NCS]:[TMP1]:[$TiCl_4$]:[*cis*-decaline] = 1:10:2:1. The chromatogram (Figure 3A) shows the presence of H-TMP-Cl, H-TMP-SCN, H-TMP-TMP isomers and of Cum-TMP^{ind} (reported in Table 2); Cum-NCS and TMP1 being largely consumed. The Cum-TMP^{ind} concentration appears overestimated both by FID and especially by MS detection because of the lack of an authentic standard in this case. Cum-TMP^{ind} concentration should be equal to the initial Cum-NCS concentration.

Cum-TMP^{ind} was one of the expected adducts, formed by a co-initiation process as shown by the set of reactions in Scheme 4. Only one compound among the six expected was found. This fact can be explained by the formation of an indanic compound as follows.

An indanic cyclization is not surprising because of the steric hindrance of the carbenium Cum-TMP$^+$ and the stability for this type of adduct.[8] Thus, it prevents further propagation and favors folding and cyclization. Cum-TMP^{ind} was identified from its mass spectrum (Figure 4).

Scheme 7



The mass spectrum of this compound shows a base peak at m/z 159 $(M - 71)^+$ corresponding to $(M - CH_2\text{-}tBu)^+$; the formation of this ion is followed by a loss of 42 amu as shown in Scheme 5.

None of the five linear isomers shown in Scheme 4 could easily form the ion with m/z 159. The **a (E/Z)** isomers should eliminate 15, 57, and 77 mass units by allylic rupture, whereas the **b (E/Z)** and **c** isomers should show the same base peak at m/z 119, corresponding to the Cum^+ ion.

However, another structure (H-TMP-αMeSt, Scheme 6) is compatible with this mass spectrum (Figure 4). Such a compound could result from a completely different mechanism: the protonic initiation of TMP1, followed by the addition on the double bond of αMeSt and the loss of a proton by transfer.

To decide on a structure, ^1H and ^{13}C NMR experiments have been carried out on two mixtures of hydrocarbons separated by size exclusion chromatography: H-TMP-TMP dimers in the absence of Cum-TMP^{ind} (or H-TMP-αMeSt) and H-TMP-TMP dimers in the presence of Cum-TMP^{ind} (or H-TMP-αMeSt). The comparison of NMR spectra of the dimers+Cum-TMP^{ind} mixtures with those of dimers alone made possible to assign the signals attributed to Cum-TMP^{ind}. In particular by ^1H NMR (250 MHz), a doublet ($\delta = 2.15$ ppm, $J \approx 25$ Hz) corresponding to one of the two protons of the indane ring in α position in relation to the asymmetric carbon is clearly characteristic. This doublet appearing at $\delta >$ 2 ppm is incompatible with the H-TMP-αMeSt compound.

The Cum-TMP^{ind} formation is accompanied by that of HNCS + $TiCl_4$. The other reaction products (H-TMP-Cl, H-TMP-SCN, H-TMP-TMP isomers) can result from a consecutive initiation process by H^+, $TiCl_4NCS^-$ as shown by the set of reactions given in Scheme 7:

1 is a termination reaction; Cl^- neutralizing H-TMP^+.

2 is another termination reaction; NCS^- neutralizing H-TMP^+.

3 is the dimerization of TMP1.

Concerning the H-TMP-TMP dimers, a discussion of their structural assignments has been recently detailed in the case of the TMP1+$TiCl_4$ reaction.[6] The following structures (**A**, **A′**, **B**, **B′**) were proposed:

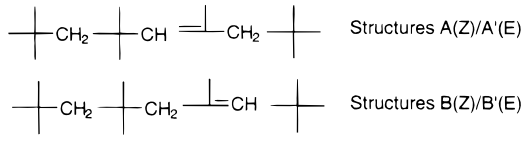


Table 2 shows that the reaction of the cumyl cation with the model monomer is faster than with the anion, since there is no production of Cum-Cl in the presence of TMP1. Despite the discrepancy between MS and FID detection, Table 2 shows a quantitative production of Cum-TMP^{ind}, in the absence of MDtBP. It is worth noticing that this product is not functionalized, which demonstrates not only that a second monomer molecule cannot add to the Cum-TMP^+ cation, due to steric hindrance, but also that recombination with the anion cannot occur, to produce Cum-TMP-Cl or Cum-TMP-SCN, most probably for the same reason. The proton which is transferred from Cum-TMP^+ induces the TMP1 cationation and dimerization. However, the total concentration of molecules, the production of which consumes these protons (H-TMP-Cl and H-TMP-SCN), is approximately twice the maximum quantity available from Cum-TMP^{ind}. This strongly suggests that some of these molecules are formed by direct initiation, as already shown from the 2-isothiocyanato-2,4,4-trimethylpentane/titanium tetrachloride/TMP1 system.[6]

The presence of Cum-TMP^{ind} in the reaction products indicates clearly that Cum-NCS can act as an initiator.

Cum-NCS + TMP1 + $TiCl_4$ + MDtBP Reaction (MeOH Quench). The products obtained in the presence of a proton scavenger, are shown in the TIC (Figure 3b). The molar ratio of the reactants being [Cum-NCS]:[TMP1]:[$TiCl_4$]:[MDtBP]:[*cis*-decaline] = 1:10:2:0.5:1, the results are also presented in Table 2. The reactivity of the system is widely affected by the presence of MDtBP. Around 70% of the initial TMP1 and 35% of the initial Cum-NCS remain unreacted. However, it isclear that this system is active, despite the presence of MDtBP. The products are H-TMP-OMe, H-TMP-Cl, H-TMP-SCN, and various dimers of TMP1 and Cum-TMP^{ind}. Concerning the formation of these products, except Cum-TMP^{ind}, the presence of the proton scavenger prevents protonic initiation. The problem of initiation in the presence of a hindered pyridine has been previously studied in detail.[6] It was concluded that direct initiation was the cause of the reaction. It was not possible to decide the exact mechanism, i.e., whether it is self-ionization or direct metalation. However, in this experiment, while a loss of H-NCS,$TiCl_4$ is associated with the formation of Cum-TMP^{ind}, the quantity of the hindered pyridine was not sufficient to scavenge all the protons. While Cum-TMP^{ind} and H-NCS,$TiCl_4$ only come from Cum-NCS, the quantity of H-NCS, $TiCl_4$ has been estimated from the quantity of reacted Cum-NCS rather than from Cum-TMP^{ind}, which has been quantified without an appropriate standard (quantity of H-NCS, $TiCl_4$: 0.65 vs 0.5 of proton scavenger). Thus, some H-TMP-species can also be formed by protonic initiation.

However, this experiment carried out in the presence of MDtBP confirms that some of the products come from direct initiation: the production of Cum-TMP^{ind} is still important, and the TMP1 monomer consumed is mostly transformed into larger quantities of H-TMP-Cl than initiation by H^+, $TiCl_4NCS^-$ permits (Table 2). Since the presence of MDtBP enhances the production of this last compound, it is possible to conclude that it is due to direct initiation followed by hydrolysis upon quenching with methanol. The presence of MDtBP induces a strong decrease of dimers production because transfer to TMP1 is decreased, either because this transfer is a spontaneous transfer, or because the solvation of the carbenium ions by the pyridine prevents the reaction of Cum-TMP^+ with the monomer (direct transfer).

Another point of importance is that the quantity of organically bound chlorine (H-TMP-Cl) is of the same order of magnitude as the initial quantity of $TiCl_4$. This is another indication that neutralization is favored under our conditions:

$$2TiCl_4 + TMP1 \rightarrow TiCl_3\text{-}TMP^+, TiCl_5^-$$

$$TiCl_3\text{-}TMP^+, TiCl_5^- \rightarrow TiCl_3TMP\text{-}Cl + TiCl_4$$

$$TiCl_3\text{-}TMP\text{-}Cl \rightarrow H\text{-}TMP\text{-}Cl + TiCl_3OMe \text{ (by methanolysis)}$$

We have used the notation $cation^+$, $anion^-$ whithout paying attention to the actual state of the ion-pair (contact, solvated, ...).

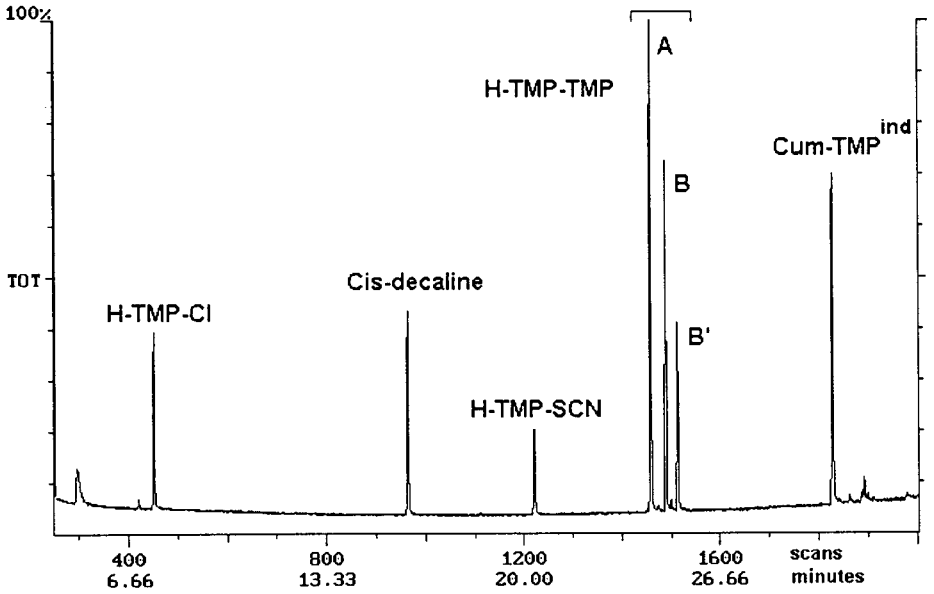


Figure 5. GC/MS chromatogram of Cum-NCS + TMP1 + $TiCl_4$ + DMSO reaction products.

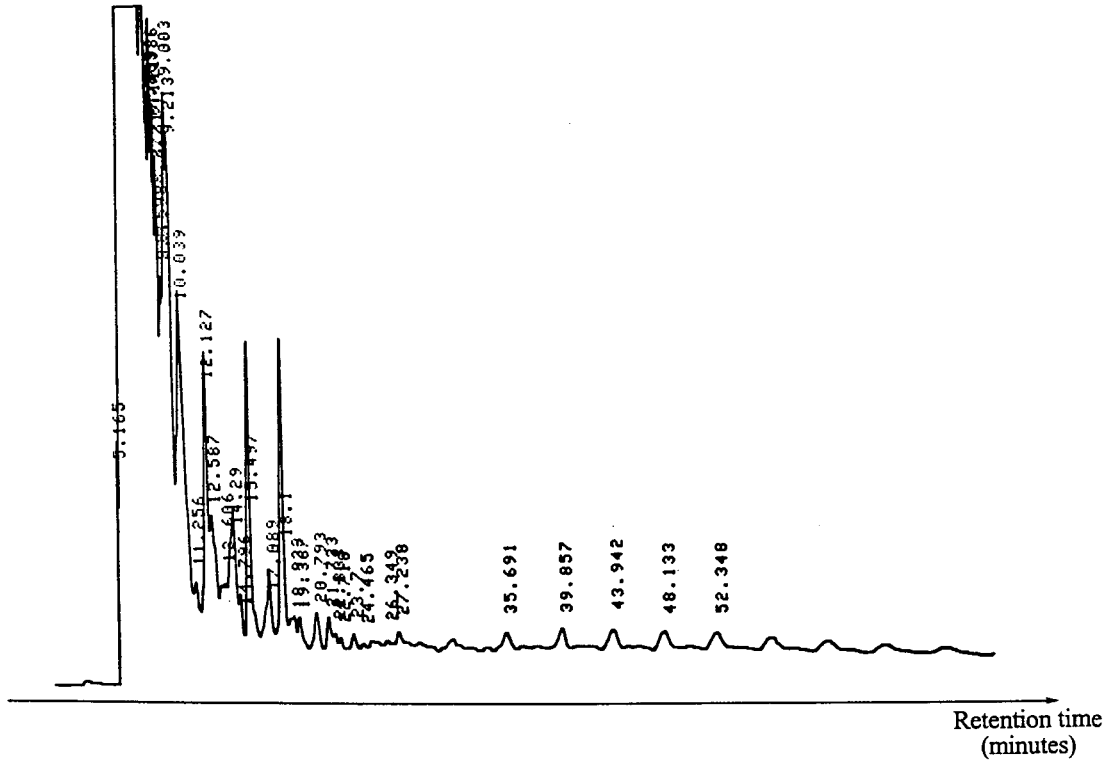


Figure 6. SFC chromatogram of Cum-NCS + IB + $TiCl_4$ reaction products.

The production of H-TMP-NCS in the presence of the hindered pyridine deserves a comment. The SCN moiety must come from Cum-NCS through its ionization. If an exchange reaction would be involved at this stage

$$TiCl_3\text{-}TMP^+, TiCl_5^- + Cum^+, TiCl_4NCS^- \rightarrow$$
$$TiCl_3\text{-}TMP^+, TiCl_4NCS^- + Cum^+, TiCl_5^-$$

some quantity of Cum-Cl should be found as shown by Table 1. Since this is not the case, it must be concluded that the exchange must come from the $Cum\text{-}TMP^+$, $TiCl_4NCS^-$ rather than from Cum^+, $TiCl_4NCS^-$. This conclusion means that the addition of TMP1 to the firstproduct of cationation Cum^+ is fast. This reaction is followed by the exchange reaction:

$$TiCl_3\text{-}TMP^+, TiCl_5^- + Cum\text{-}TMP^+, TiCl_4NCS^- \rightarrow$$
$$TiCl_3\text{-}TMP^+, TiCl_4NCS^- + Cum\text{-}TMP^+, TiCl_5^-$$

It is clear that H-TMP-OMe comes from the quenching of $TiCl_3\text{-}TMP^+$, $TiCl_5^-$ by methanol. It is possible to calculate roughly the number n of TMP1 molecules which have been activated by direct initiation:

$$n = [\text{H-TMP-OMe}] + [\text{H-TMP-Cl}] + [\text{H-TMP-SCN}] - [\text{Cum-TMP}^{ind}]$$

Table 3. Relative Molar Content of Cum-NCS(1) + TMP1(10) + $TiCl_4$(2) + DMSO(0.4) Reaction Products Determined by FID and MS Referenced to *cis*-Decaline (*cis*-Decaline = 1 as Internal Reference (3.1×10^{-2} mol L^{-1}))

detection	TMP1	H-TMP-Cl	H-TMP-SCN	H-TMP-TMP	Cum-TMP^{ind}
MS	0.5	0.95	0.7	2.7	1.7

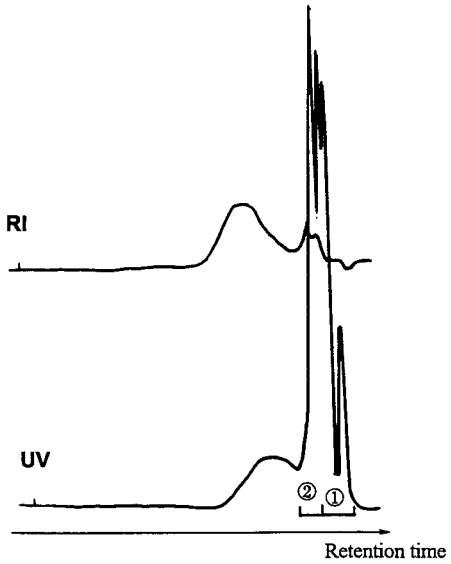


Figure 7. SEC of Cum-NCS + TMP1 + $TiCl_4$ reaction products.

Using FID or MS detection (Table 2) the number is close to 2, which means that the direct initiation used the whole quantity of $TiCl_4$ in the presence of the hindered pyridine. This fact does not demonstrate that a direct metalation leading to a zwitterionic species is observed:

$$TiCl_4 + TMP1 \rightarrow {}^{-}TiCl_4\text{-}TMP^{+} \rightarrow TiCl_3\text{-}TMP\text{-}Cl$$

Since a sequence of reactions can give the same result

$$2\ TiCl_4 + TMP1 \rightarrow TiCl_3\text{-}TMP^{+},\ TiCl_5^{-}$$

then

$$TiCl_3\text{-}TMP^{+},\ TiCl_5^{-} \rightarrow TiCl_3TMP\text{-}Cl + TiCl_4$$

The titanium tetrachloride molecule generated by the second reaction can in turn participate in the cationation of a new TMP1 molecule. It must be noted that if direct initiation proceeds more rapidly than co-initiation limited by the step

$$TiCl_4 + Cum\text{-}NCS \rightarrow Cum^{+},\ TiCl_4NCS^{-}$$

then it means that this last reaction is due to the acidity of the $TiCl_3$-TMP-Cl molecule and not to $TiCl_4$ itself, since it should have been consumed. On the other hand, if co-initiation proceeds more rapidly than direct initiation producing $TiCl_3NCS$ according to:

$$Cum\text{-}NCS + TiCl_4 \rightarrow Cum^{+},\ TiCl_4NCS^{-}$$

$$Cum^{+},\ TiCl_4NCS^{-} + TMP1 \rightarrow Cum\text{-}TMP^{+},\ TiCl_4NCS^{-}$$

$$Cum\text{-}TMP^{+},\ TiCl_4NCS^{-} + TMP1 \rightarrow Cum\text{-}TMP^{ind} + H\text{-}TMP^{+},TiCl_4NCS^{-}$$

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

or

$$\downarrow H\text{-}TMP\text{-}Cl + TiCl_3NCS$$

It must be deduced that $TiCl_3NCS$ is also able to participate in the self-initiation mechanism. This last scheme has the advantage that it can explain at the same time the production of H-TMP-SCN and H-TMP-Cl without involving an exchange reaction as discussed above. However, since the consumption of Cum-NCS is not complete, it is most probable that direct initiation is faster than co-initiation. This is in agreement with the presence of an equivalent of H-TMP-Cl.

On the other hand, since there are at least traces of H-TMP-OMe, it shows that the titanium derivatives produced by the system can co-initiate, not only with

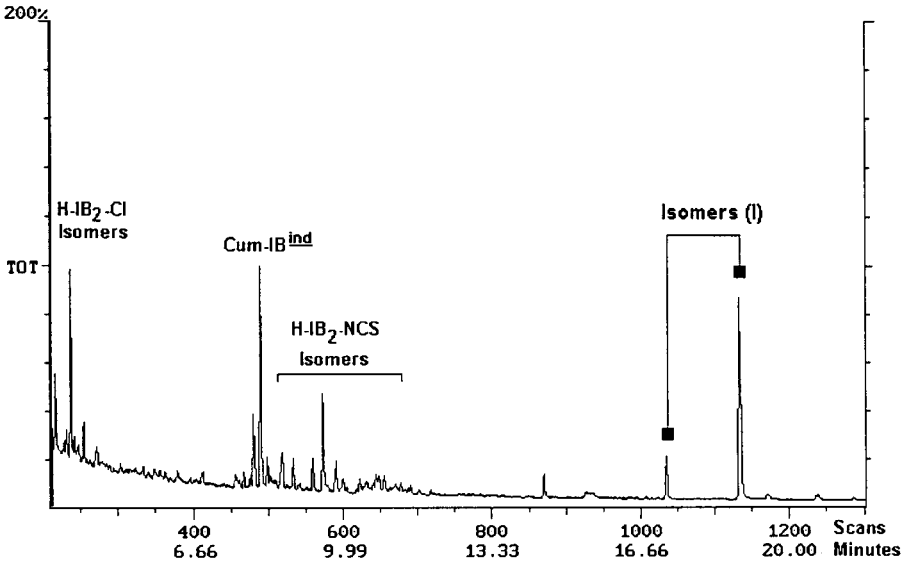


Figure 8. GC/MS chromatogram of the products of fraction 1 extracted by SEC (Cum-NCS + IB + $TiCl_4$).

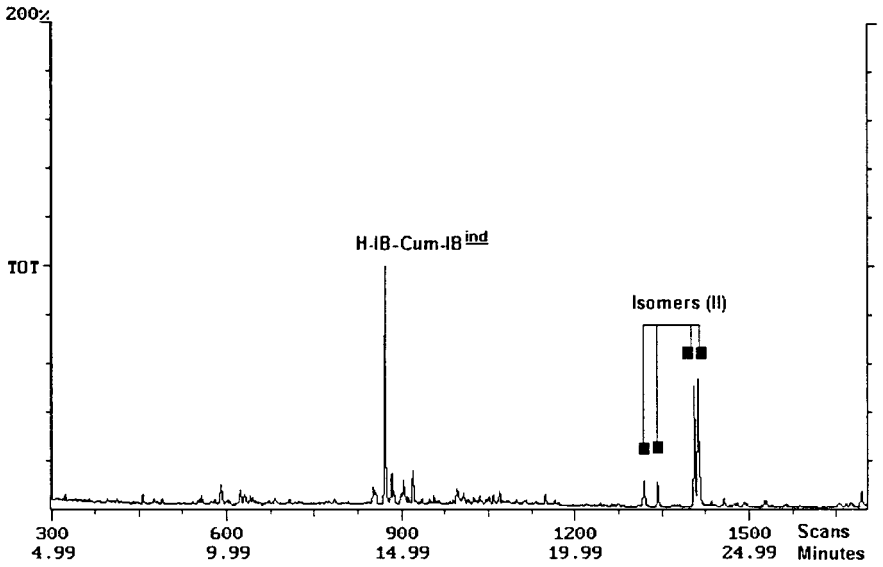


Figure 9. GC/MS chromatogram of the products of fraction 2 extracted by SEC (Cum-NCS + IB + $TiCl_4$).

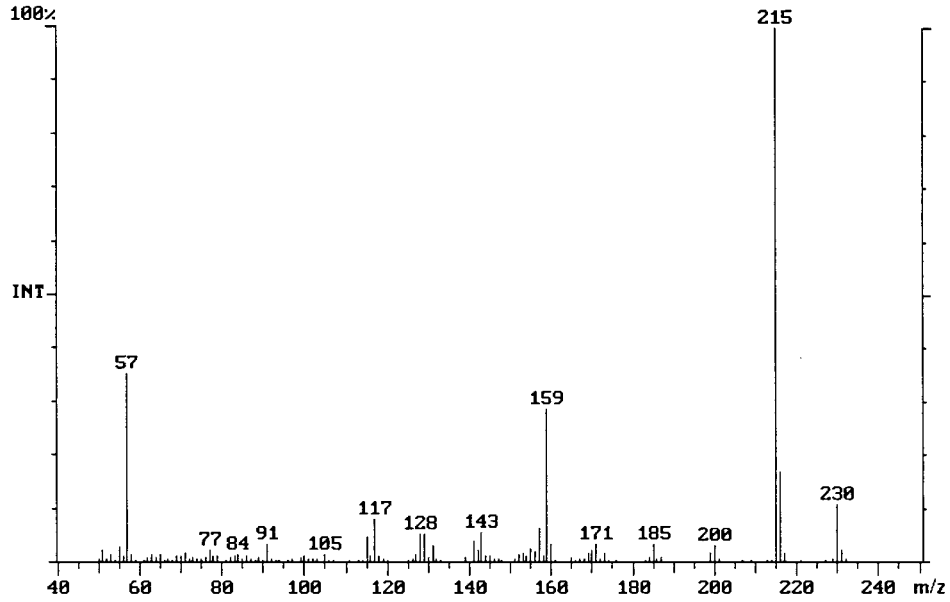


Figure 10. Mass spectrum of Cum-IB[ind].

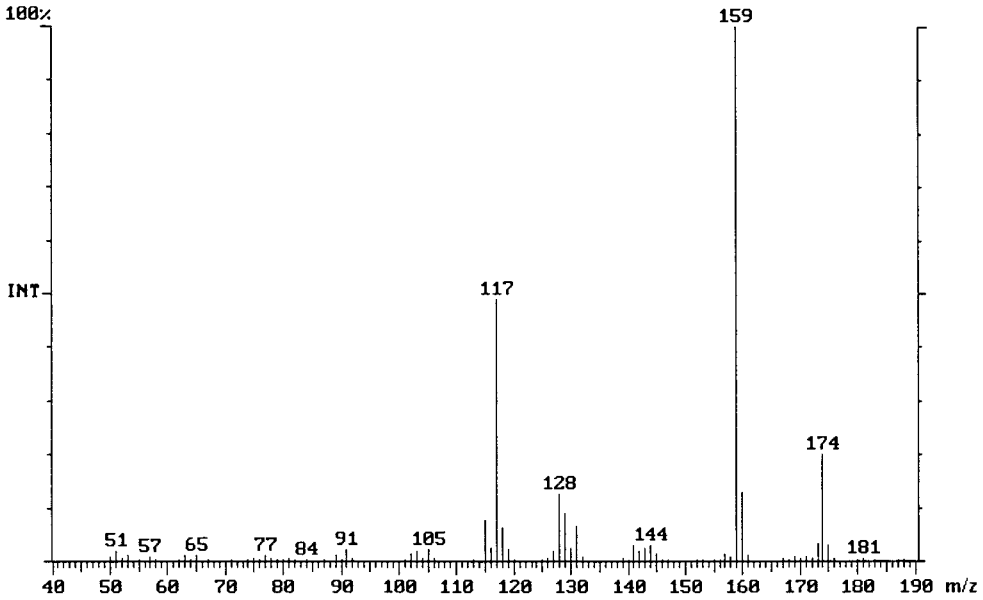


Figure 11. Mass spectrum of H-IB-Cum-IB[ind].

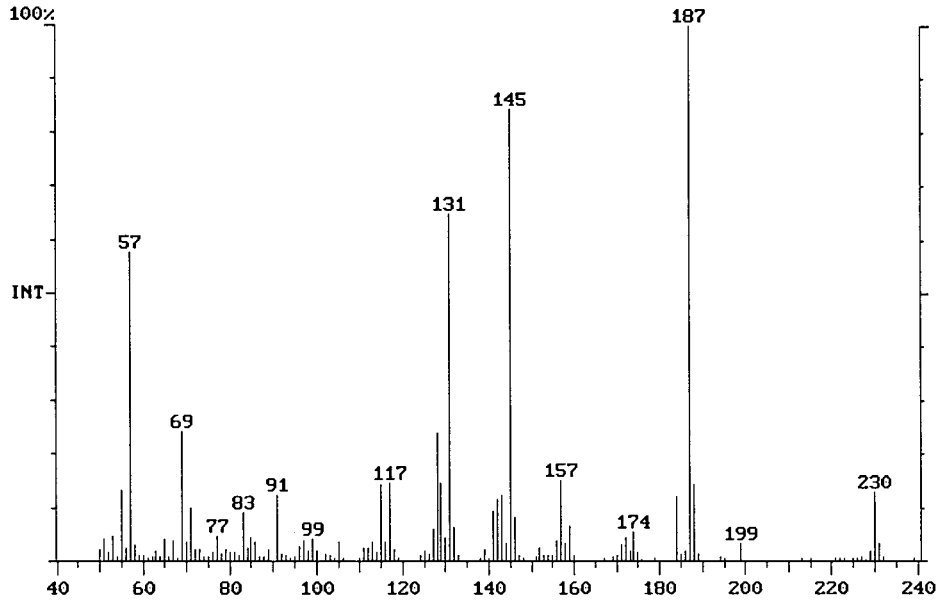


Figure 12. Representative mass spectrum of isomers **I**.

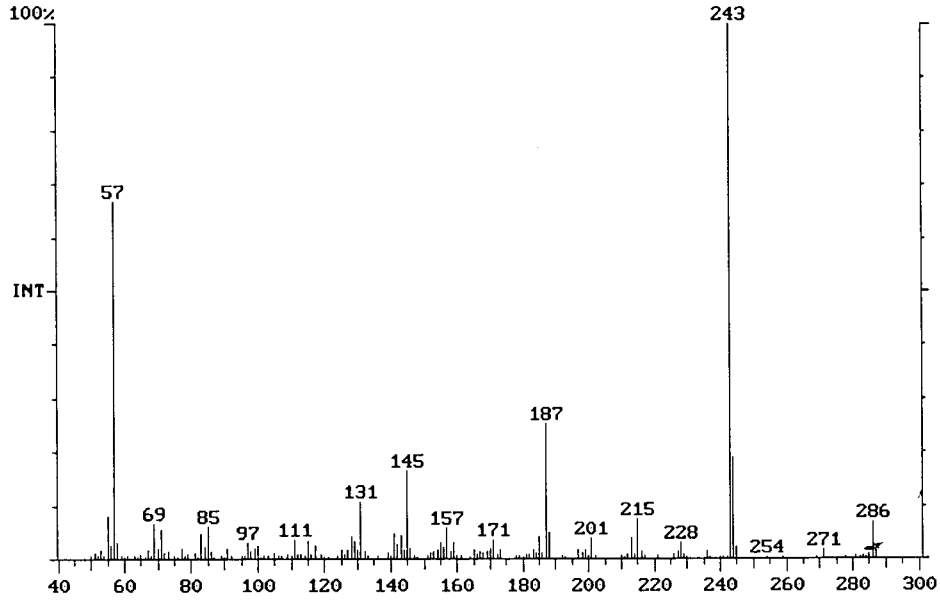


Figure 13. Representative mass spectrum of isomers **II**.

Cum-NCS (leading to Cum-TMP^{ind}) but also self-ionize (leading to H-TMP-OMe) according to:

$$2TiCl_3\text{-TMP-Cl} \rightleftharpoons TiCl_3\text{-TMP}^+, {}^-TiCl_4\text{-TMP-Cl}$$

followed by methanolysis:

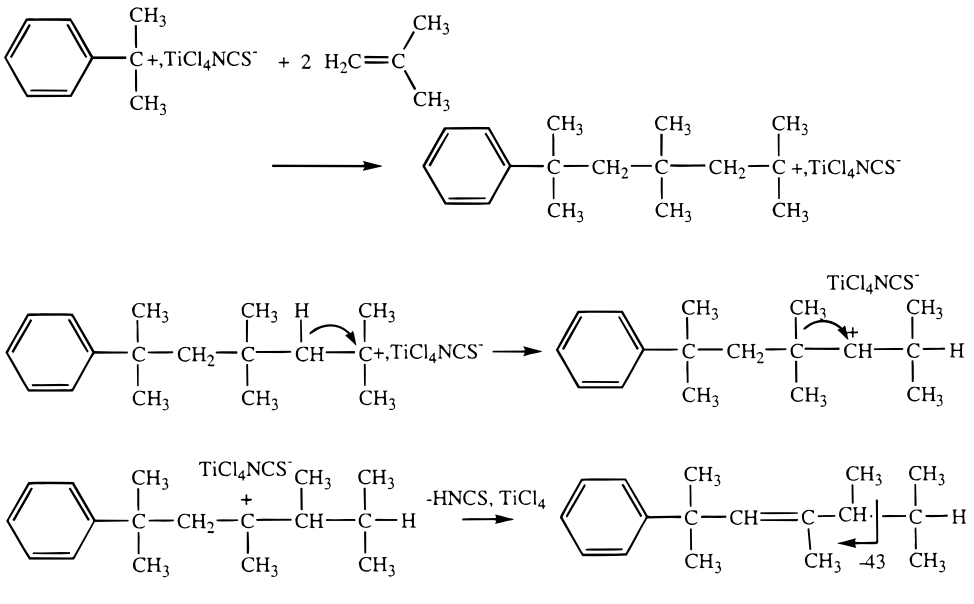
$$TiCl_3\text{-TMP}^+, {}^-TiCl_4\text{-TMP-Cl} + MeOH \rightarrow$$
$$H\text{-TMP-OMe} + H\text{-TMP-Cl} + TiCl_4 + TiCl_3OMe$$

It is also clear from the compararison of the two lines of Table 2 that MDtBP stablilizes the carbenium species, thus playing the role of an electron donor. The formation of Cum-TMP^{ind} is affected by the presence of MDtBP. MDtBP clearly inhibits the co-initiation process by Cum-NCS. This experiment shows that the hindered pyridine interacts with the Lewis acid or with the active centers.

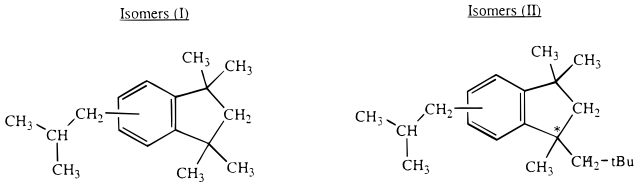
It is worth noting the exclusive formation of H-TMP-SCN, rather than H-TMP-NCS, in the presence of MDtBP. This observation was already reported for IB polymerization.[7] From an analytical point of view, it must be emphasized that mass spectra of H-TMP-NCS and H-TMP-SCN species are almost identical. They present the same ions which differ slightly from their relative abundance. Fortunately, these compounds may be differentiated from their retention times.

Cum-NCS + TMP1 + $TiCl_4$ + DMSO (MeOH Quench). This reaction has been carried out in the presence of DMSO, which is an electron donor. The products obtained at the end of the reaction (TIC, Figure 5) and their relative proportions (quantification, Table 3) are almost the same as those observed in the absence of DMSO. Only the dimer of TMP1, H-TMP-TMP (**A′**), is absent at the end of the reaction. The molar ratio of the reactants being [Cum-NCS]:[TMP1]:[$TiCl_4$]:[DMSO]:[*cis*-decaline] = 1:10:2:0.4:1, the results show that the presence of DMSO just slightly modifies the percentages of the various dimers. In this system, the pseudohalide group is still present exclusively in its thiocyanate form. It is to be noticed that DMSO and MDtBP play the same

Scheme 8



Scheme 9



role at this stage. The presence of DMSO does not change very much the results as shown by the comparison between Table 3 and the first line of Table 2.

It is interesting that the total of products due to a protonic reaction (H-TMP-Cl + H-TMP-SCN) corresponds to the amount of Cum-TMP^{ind}, showing that the functionalization by a SCN group is only obtained by a protonic initiation (thanks to the reaction of H^+, $TiCl_4NCS^-$ with TMP1) and not by an exchange reaction.

The model experiments indicated not only the formation of oligomers due to direct initiation but also the expected formation by co-initiation of oligomers bearing a cumyl end. At the other end, the presence of −Cl or −SCN is expected by functionalizing termination; 70−80% of the Cum-NCS leads to thiocyanate functionalization (the double bond of H-TMP-TMP dimers appears not to be representative because of facile elimination).

II. Oligomerization of Isobutylene initiated by Cum-NCS/ $TiCl_4$. Cum-NCS (1) + IB (50) + $TiCl_4$ (2) Polymerization (MeOH Quench). The polymerization of IB (global yield: 85%) was achieved with the reactants ratio equal to [Cum-NCS]:[IB]:[$TiCl_4$] = 1:50:2 in order to obtain oligomers of low molecular weight (M < 650, 650 amu being our upper mass limit in GC/MS analyses). However, the conditions used for the polymerizations allowed masses of up to 2000−2500 Da to be formed. The SFC chromatography was used because it can separate a larger range of masses than GC. The SFC chromatogram of the reaction products (Figure 6) can be divided into two parts. The first part ($5 < t_r <$ 30 min) corresponds to the lower mass oligomers which seem predominant (relative amount ~90%$_w$). The second part ($30 < t_r < 60$ min) corresponds to a polymer.

The SEC chromatogram (RI and UV detection 254 nm, Figure 7) can also be divided into two parts. Since

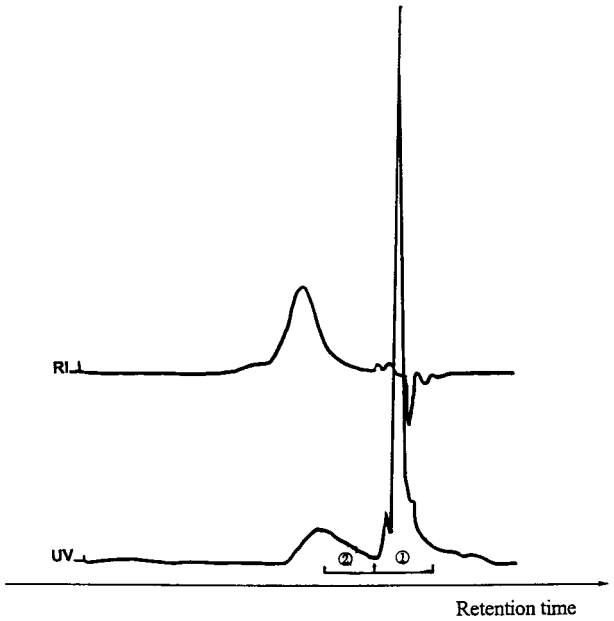


Figure 14. SEC of Cum-NCS + IB + $TiCl_4$+ MDtBP.

Cum-NCS was totally consumed, as shown by the GC/MS analysis, around 80% of Cum-NCS was converted to low mass compounds (fractions 1 + 2), while 20% of Cum-NCS was converted to isobutylene oligomers (polymer fraction). The average molecular weights of the polymer were $\bar{M}_n$ = 2000, $\bar{M}_w$ = 3800, and I_p = 1.89 according to UV measurements and $\bar{M}_n$ = 2000, $\bar{M}_w$ = 3100, and I_p = 1.60 according to refractometric measurements. These average molecular weights seem overestimated when we compare these values to the results of the SFC analysis ($\overline{DP}_n \approx 10$ corresponding to M = 600). This difference may be due to the fact that the calibration of the CES system by polystyrene standards is not well-suited for this experiment. Taking into account the complexity of the mixture, this experiment is not open to a molar balance or to an estimation of the theoretical value of the $\bar{M}_n$.

The GC/MS analysis of fractions 1 and 2 separated by semipreparative SEC (Figures 8 and 9 respectively), shows the presence in fraction 1, of skeletal isomers of

Scheme 10

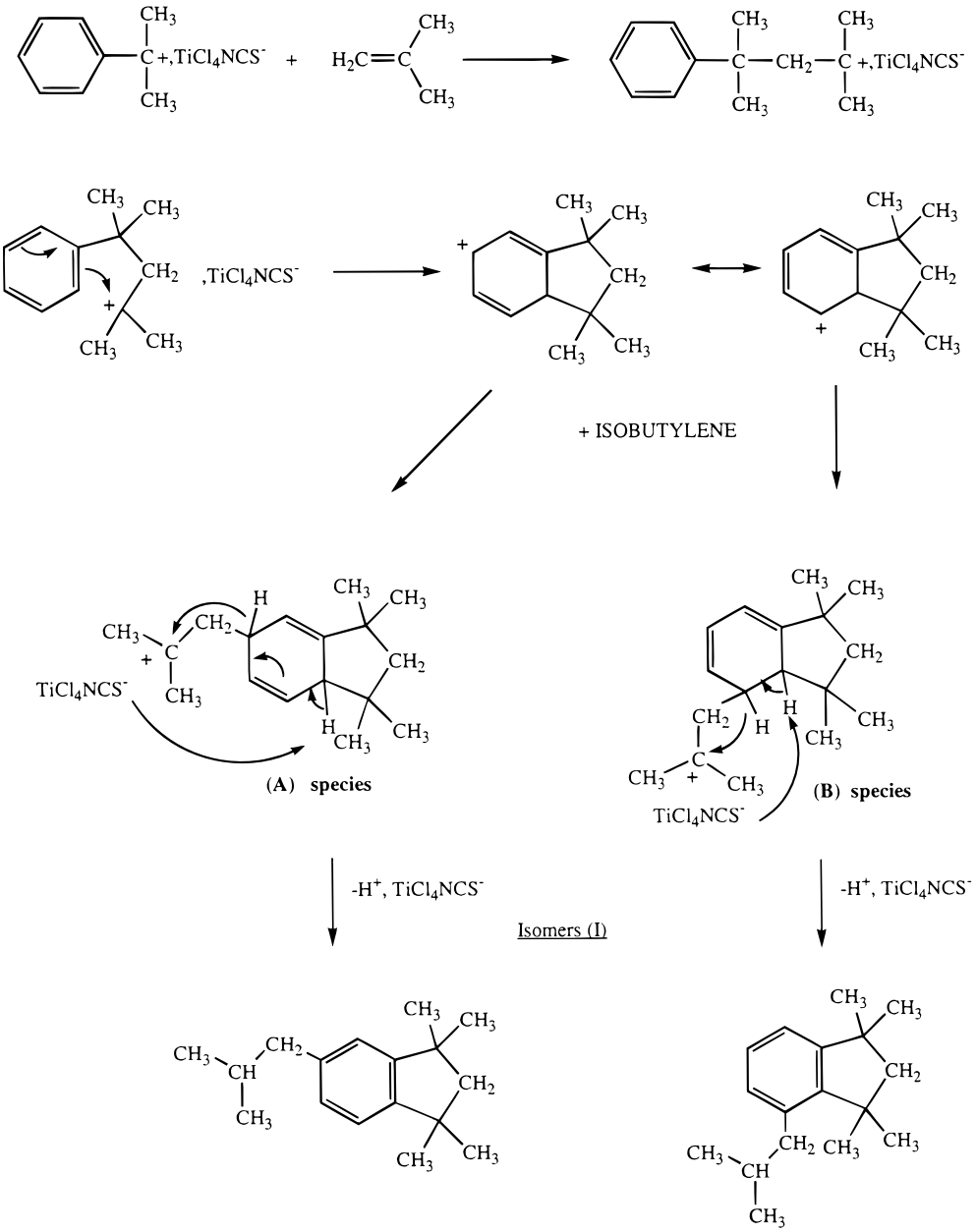
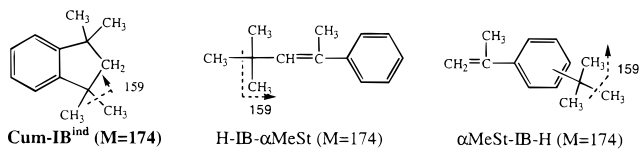


Table 4. Characterization of the PIB Obtained in the Presence of Cum-NCS/$TiCl_4$ and of Various Additives (Cum-NCS(1)/IB(50)/$TiCl_4$(2), [Cum-NCS] = 4.2 × 10^{-2} mol L^{-1})

additives	global Y^{ld} %	$\bar{M}_n$ (UV)	M_p (UV)	I_p (UV)	M_n (RI)	M_p (RI)	I_p (RI)
none	85	2000	3800	1.89	2000	3100	1.60
DMSO(0.6)	48	1300	2400	1.83	600	900	1.39
MDtBP(0.5)	88	2900	3900	1.35	3500	4500	1.30

H-IB_2-Cl (H-TMP-Cl) and of H-IB_2-NCS (H-TMP-NCS). Similarly, the other compounds do not show the expected carbon skeleton, i.e., Cum-IB_n- or H-IB_n-.

The mass spectrum of Cum-IB^{ind} (Figure 10) could be attributed to the following structures:



Cum-IB^{ind} (M=174) H-IB-αMeSt (M=174) αMeSt-IB-H (M=174)

It must be emphasized that the synthesis of PIBs such as Cum-IB_n-Cl according to Kennedy's procedure[15] leads to the indanic byproduct. Nevertheless, the H-IB-αMeSt and αMeSt-IB-H structures shown above cannot be excluded. H-IB-αMeSt should result from the addition of H-IB^+ to the double-bond of αMeSt, followed by the expulsion of one H^+, while αMeSt-IB-H should correspond to the alkylation by H-IB^+ of the aromatic group of αMeSt. However, the study of model systems above has shown that Cum-NCS alone in the presence of $TiCl_4$ only leads to a small quantity of αMeSt (4%). So, the H-IB-αMeSt and αMeSt-IB-H structures are unlikely.

In fraction 2 (Figure 9), the compound H-IB-Cum-IB^{ind} is clearly an isomer of the indanic structure Cum-TMP^{ind} (Scheme 6). The mass spectrum of H-IB-Cum-IB^{ind} (Figure 11) mainly differs from that of Cum-TMP^{ind} (Figure 4) by the increase of the relative abundance of the *m*/*z* 215 ion at the expense of the *m*/*z* 159 and *m*/*z* 117 ions. This compound could be the linear isomer H-TMP-αMeSt (Scheme 6), but its formation is unlikely

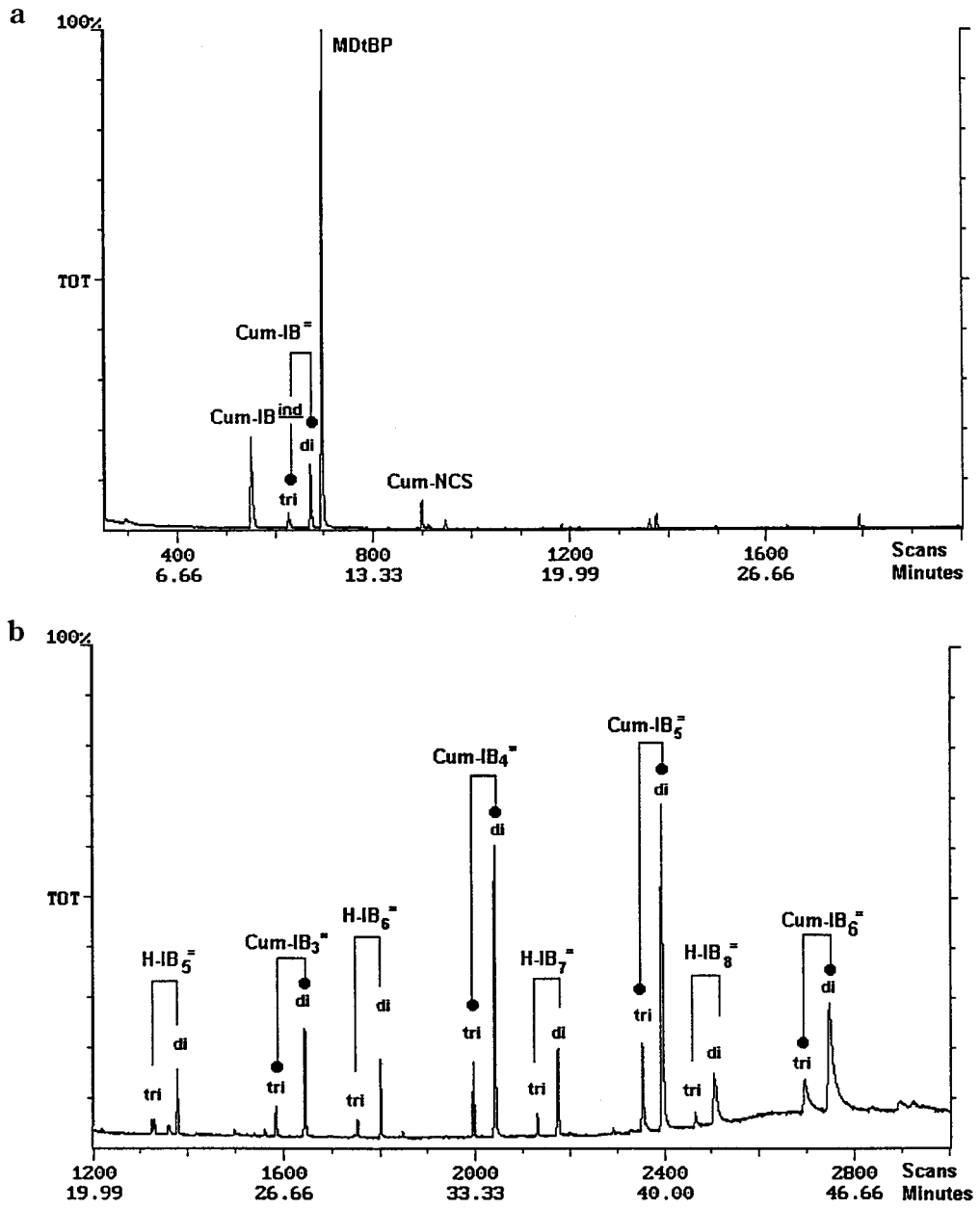
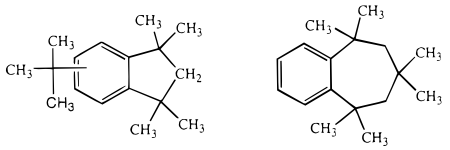


Figure 15. (a) GC/MS chromatogram of fraction 1 extracted by SEC from the products of the polymerization Cum-NCS + IB + $TiCl_4$ + MDtBP. (b) GC/MS chromatogram of fraction 2 extracted by SEC from the products of the polymerization Cum-NCS + IB + $TiCl_4$ + MDtBP.

since it needs the previous formation of αMeSt. The mass spectrum corresponds more likely to a structure resulting from the alkylation of the aromatic group of Cum-IB^{ind}:



H-IB-Cum-IB^{ind} (M=230) Cum-IB_2^{cyc} (M=230)

Steric hindrance could permit the formation of only one isomer resulting from the alkylation in the meta position. In addition, the compound Cum-IB_2^{cyc} resulting from the internal cyclization of Cum-IB_2^+ is unlikely since its mass spectrum would not show an ion at *m/z* 57 corresponding to $C(CH_3)_3^+$.

The two isomers **I** (Figure 8; M = 230, Cum + 2IB, 5 unsaturations) and the four isomers **II** (Figure 9; M = 286, Cum + 3IB, 5 unsaturations) belong to the same family. The isomers **I** differ from the isomers **II** by an additional IB. Owing to their similarity, only two mass spectra representative of the two isomers series are presented in Figures 12 and 13. Under electronic impact, these six compounds present a common loss of 43 amu ((**I**) *m/z* 230 → *m/z* 187; (**II**) *m/z* 286 → *m/z* 243) which is classically attributed to a loss of an isopropyl radical $C_3H_7^{\bullet}$. Others common ions are observed at *m/z* 57, 131, and 145. The structures resulting from a protonic initiation of IB followed by an addition reaction on αMeSt are not likely. The co-initiation reaction by Cum-NCS should constitute the first step of the formation of this type of compounds. On the other hand, the loss of 43 amu suggests the presence of a $C_3H_7-CH_2-$ radical, the formation of which requires an isomerization.

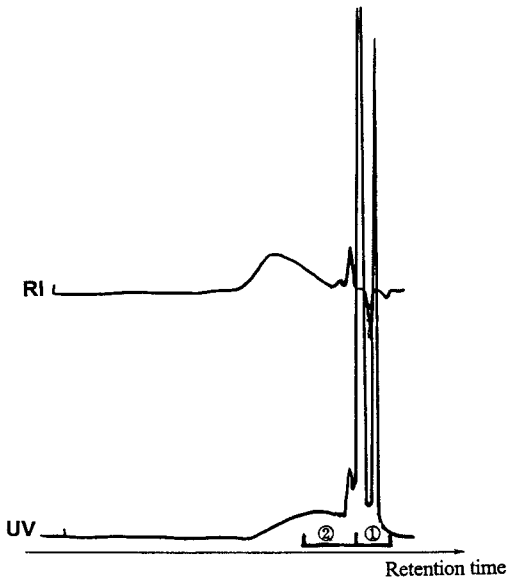


Figure 16. SEC chromatogram of Cum-NCS + IB + $TiCl_4$+ DMSO reaction products.

These compounds can be linear or cyclic. In the case of a family of linear compounds, the mechanism given in Scheme 8 leads to the formation of a structure compatible with an important loss of $C_3H_7^{\bullet}$, but does not allow the formation of an ion at *m*/*z* 57. This type of structure does not allow to obtain the right number of isomers in the right proportions.

In the case of cyclic compounds, the formation of an indanic cycle[2] followed by a Friedel−Crafts alkylation leads to the structures shown in Scheme 9, which are compatible with the loss of 43 amu ($-C_3H_7^{\bullet}$) and the formation of ions at *m*/*z* 57.

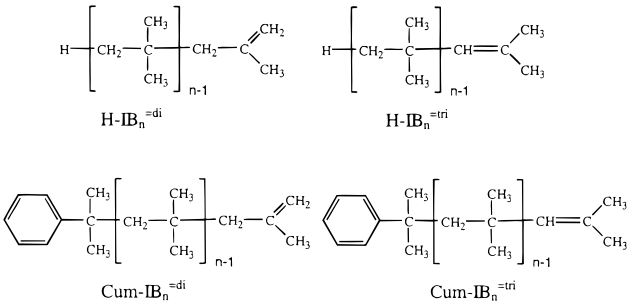
The GC/MS analysis of the sum of fractions 1 + 2 (not shown) allowed us to appreciate the relative importance of each of these compounds. In the case of isomers **I**, the number of isomers depends on the alkylation position leading to two isomers (alkylation ortho or meta), whereas in the case of the isomers **II**, alkylation leads to four isomers whose relative proportions depend on the alkylation position. Because of steric hindrance, the alkylation at the ortho position should be unfavored compared to the alkylation at the meta one.

Scheme 10 proposes a mechanism of formation for the isomers **I**. In the case of the isomers **II**, the mechanism would be similar, the indanic cycle resulting from the condensation of Cum^+ on the dimer of isobutylene (TMP1). Even if the intermediate species (**A** and **B**) can propagate, the increase of stability associated with the return to aromaticity favors the proposed mechanism.

The polymeric distribution could not be analyzed by GC/MS, because the chains were too long. Nevertheless, the combination of these different techniques shows that in the presence of $TiCl_4$, the co-initiation reaction is followed by a substantial number of undesirable reactions (indanic cyclizations), whereas the cocatalysis by H^+, $TiCl_4NCS^-$ predominates because the expulsion of a proton is associated with these undesirable reactions. Some macromolecular chains are probably functionalized by the isothiocyanate or the thiocyanate group, but the system is not controlled. $TiCl_4$ alone is a strong Lewis acid so that it induces side-reactions.

Cum-NCS (1) + IB (50) + $TiCl_4$ (2) + MDtBP (0.5) Polymerization. The polymerization of isobutylene initiated by the system Cum-NCS/$TiCl_4$ was achieved in the presence of the proton scavenger MDtBP (global yield: 88%). Whereas the average masses estimated by SEC (Figure 14) are more important than in the absence of MDtBP, the polydispersity appears weaker (Table 4).

The GC/MS analysis of the fraction 1 extracted by SEC (Figure 15a) shows that the initiator has been almost completely consumed, whereas the Cum-IB^{ind} quantity is relatively low. The GC/MS analysis of fraction 2 (Figure 15b) presents only the first oligomers of the series: Cum-$IB_n^{=di/tri}$ and H-$IB_n^{=di/tri}$. It must be stressed that the pseudohalide functions are totally absent.



The structural assignments are based on their respective mass spectra. The structural assignment is deduced from the presence of diagnostic ions characteristic of the oligomers ends. Thus, an ion of *m*/*z* 57 indicates a *tert*-butyl end (H-IB^+), while an ion of *m*/*z* 119 (Cum^+) corresponds to a cumyl end. In the case of long chains of PIB bearing a terminal disubstitued double bond, the molecular ion is sometimes absent, and most cleavages and Mc Lafferty rearrangements (loss of 56 mass units) are observed. The assignments have been confirmed by analyses of standards allowing for example to differentiate double bond ends from −Cl ends.

Our observations suggest that MDtBP does not only play the role of a proton scavenger. If it was the case, MDtBP would not limit indanic cyclization. MDtBP seems to act as a very weak electron donor. Since MDtBP scavenges all the proton of the residual humidity, the H-$IB^{=di/tri}$ chains must come from either direct transfer reactions, or direct initiation. In the case of direct initiation, the Ti−C bonds are transformed into H−C bonds at the end of the reaction upon quenching with MeOH.

This experiment clearly demonstrated the potential of Cum-NCS/$TiCl_4$ as an initiating system:

$$\text{Cum-NCS} + \text{IB} + TiCl_4 \rightarrow \text{Cum-IB}^+, TiCl_4NCS^-$$

These results show the processes occurring at the very beginning of the IB polymerization initiated by the system Cum-NCS/$TiCl_4$.

Cum-NCS (1) + IB (50) + $TiCl_4$ (2) + DMSO (0.5) Polymerization. The polymerization of IB initiated by the system Cum-NCS/$TiCl_4$ is widely affected by the presence of DMSO. SEC (Figure 16) gives some lower values of average molecular weight, the global yield decreasing (Table 4).

The fractions 1 and 2 were separated by SEC, then analyzed by GC/MS. The analysis of the first fraction (Figure 17a) shows that Cum-NCS had not been totally consumed. This analysis reveals the presence of α-methylstyrene (αMeSt) and Cum-IB^{ind}. However, the peak profile corresponding to αMeSt suggests the presence of Cum-Cl being degraded on the injector. This

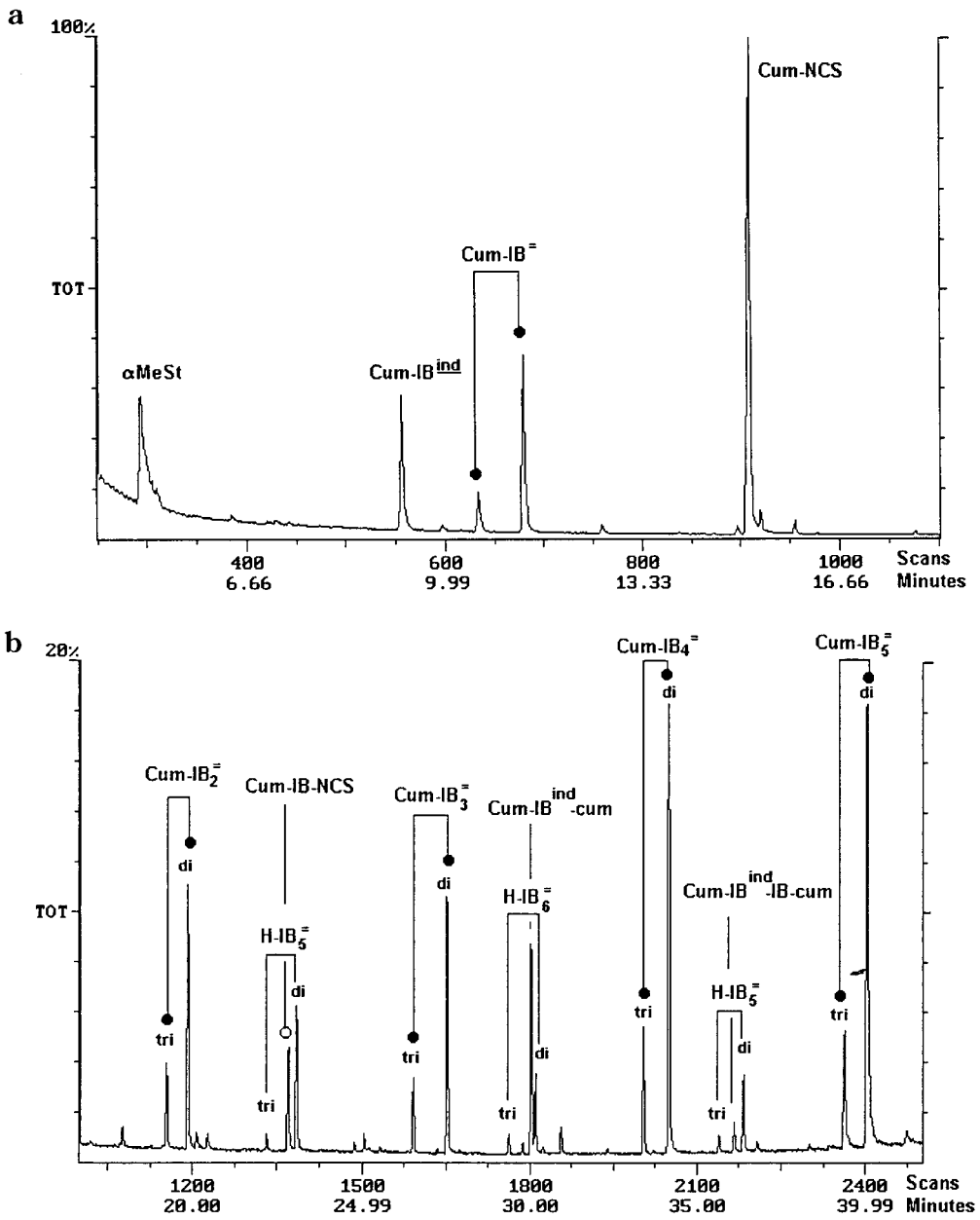


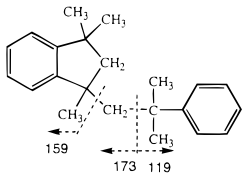
Figure 17. (a) GC/MS chromatogram of fraction 1 extracted by SEC from the products of the polymerization Cum-NCS + IB + $TiCl_4$ + DMSO. (b) GC/MS chromatogram of fraction 2 extracted by SEC from the products of the polymerization Cum-NCS + IB + $TiCl_4$ + DMSO.

event was verified independently. Thus, from SEC (UV detection), only 20% of Cum-NCS had taken part in the oligomerization process.

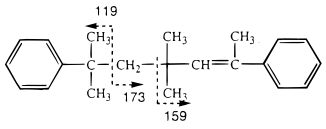
The analysis of the second fraction (Figure 17b) demonstrated the presence of many distinct series in the mixture: Cum-$IB_n^{=di/tri}$, H-$IB_n^{=di/tri}$ and Cum-IB^{ind}-IB_n-cum. The first term of the series Cum-IB_n-NCS is also present.

The structure Cum-IB^{ind}-Cum is the first member of a series coming from a new side reaction. Other oligomers Cum-IB^{ind}-IB_n-Cum ($n \geq 1$) are also present in the mixture. This series would be the result of the reaction of a chain bearing a terminal double bond (i.e., Cum-$IB_n^{=di}$) with Cum^+ to lead after cyclization to a chain bearing an indanic cycle end.

The mass spectrum of Cum-IB^{ind}-Cum, shown in Figure 18, is also compatible with another structure (Cum-IB-αMeSt). However, for already explained reasons, we think that this mass spectrum corresponds



Cum-IB^{ind}-Cum (M=292)



Cum-IB-αMeSt (M=292)

precisely to an indanic structure such as Cum-IB^{ind}-Cum, rather than Cum-IB-αMeSt. In addition, the mass spectra of this series are incompatible with the products of an alkylation of Cum-IB^{ind} by Cum-IB_n^+ since ions at m/z 215 would be systematically observed in this case. The presence of this series shows that some Cumyl cations can be produced while IB polymerization occurred. This finding not only shows that the polymer terminal double bonds can be alkylated but also shows that polymerization is a faster process than initiation.

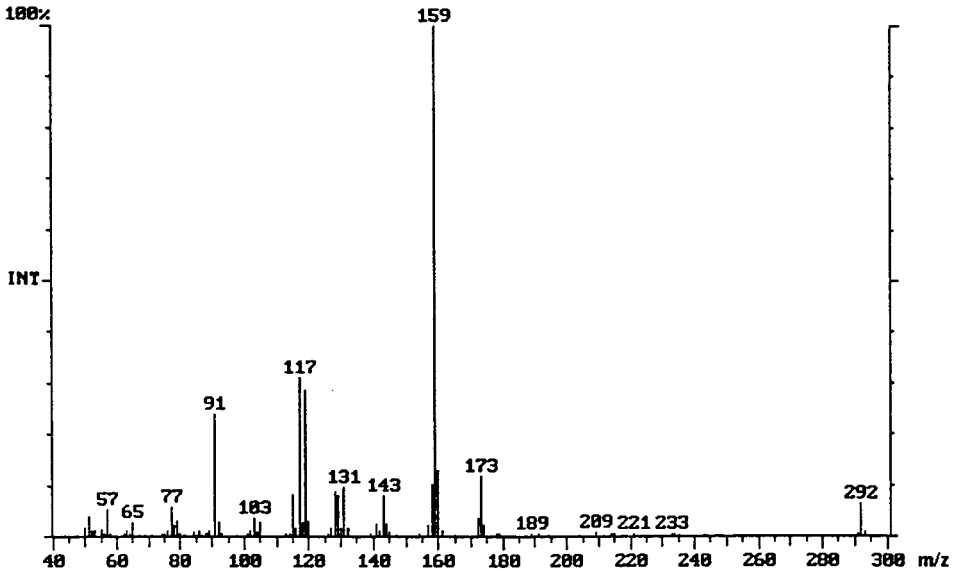


Figure 18. Mass spectrum of Cum-IB^{ind}-Cum.

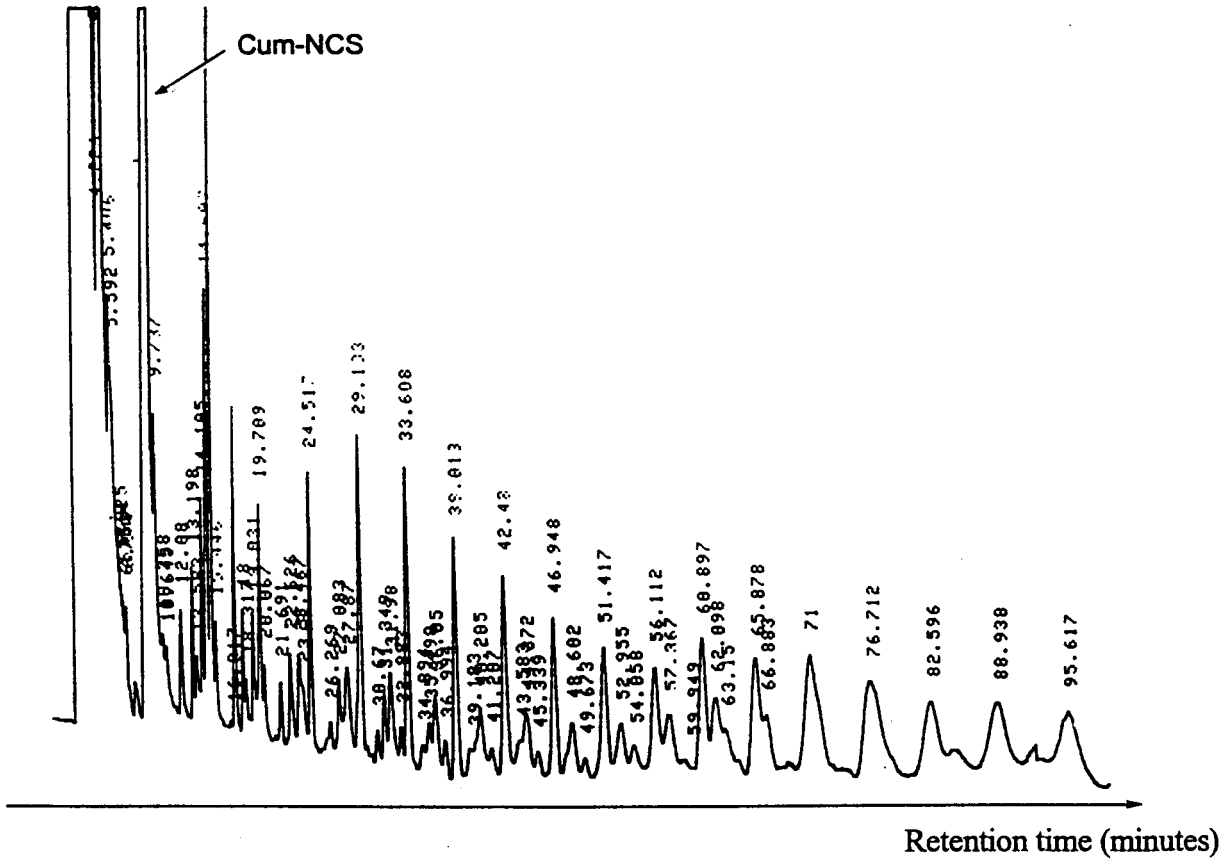


Figure 19. SFC chromatogram of Cum-NCS + IB + $TiCl_4$+ DMSO reaction products.

The analysis of the polymer by SFC (Figure 19) presents the regular distribution of at least five distinct series. From the retention times, the most abondant series seems to correspond to Cum-IB$_n$-NCS. The profiles obtained by GC/MS and by SFC are not easily comparable; thus, it is difficult to extrapolate and to give the nature and the relative proportions of each series. However, it is clear that the presence of DMSO decreases the global reactivity of the system. This leads to an elimination of an important part of the unwanted side-reactions observed in its absence.

Conclusion

Model experiments have been carried out with the 2-isothiocyanato-2-phenyl-propane/$TiCl_4$ combination as an initiating system using 2,4,4-trimethyl-1-pentene as the nonpolymerizable monomer. The thorough analysis of the IB oligomers prepared in the same conditions as the model reactions was performed to complete these studies. The use of capillary SFC allowed the separation of most of the series of PIBs bearing different terminal groups (cumyl, *tert*-butyl, double bond, ...), while GC/MS analysis of the low mass fractions of oligomers of

Table 5. Efficiciency of Coinitiation in the Polymerization of Isobutylene in the Presence of Cum-NCS/$TiCl_4$ and of Various Additives

additives	efficiency of co-initiation[a] % Cum-NCS → Cum-IB_n-	% Cum-NCS → Cum-IB^{ind} [b]
none	21	79
DMSO(0.6)	20	7
MDtBP(0.5)	87	10

[a] Percentage of Cum-NCS consumed for the formation of Cum-IB_n−, estimated from SEC (UV detection). [b] Percentage of Cum-NCS consumed for the formation of Cum-IB^{ind} and derivatives, estimated from SEC (UV detection) in combination with GC/MS.

the same polymer (separated by semipreparative SEC) allowed the identification of the first terms of the different series.

Model experiments were in agreement with the oligomerization of isobutylene (IB). It appeared that 2-isothiocyanato-2-phenylpropane in the presence of $TiCl_4$ initiates the polymerization of IB, despite indanic cyclizations occurring after the co-initiation process and the addition of one IB, as shown in the Tables 4 and 5.

This study showed with the model experiment that titanium tetrachloride is able to initiate cationation of an olefinic monomer by direct initiation. It is obvious that in the case of IB the direct initiation is also operating as shown by the experiments carried out in the presence of MDtBP. In this respect, the choice of titanium tetrachloride is not very suitable to obtain a selective co-initiation by cumyl isothiocyanate. Our work demonstrates the occurrence of an unexpected transfer reaction on the cum-IB^{ind} species by alkylation. To this respect, the presence of the hindered pyridine is favorable since it strongly decreased the quantity of Cum-IB^{ind}. However, the polymerization carried out in the presence of MDtBP does not bring the desired functionalization by an SCN or NCS group, which is explained by the fact that the pyridine seems to favor elimination reactions. The presence of DMSO during IB polymerization improves the functionalization, while the yield is largely incomplete in our conditions. Taking into account these results with $TiCl_4$, which allowed us to get a deeper insight of the side reactions, we will describe in our next paper, a more favorable situation from the point of view of selectivity of functionalization, using other Lewis acids.

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