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Synthesis of Polymers Containing Pseudohalide Groups by Cationic Polymerization. 17.† Oligomerizations of Isobutylene with 2-Isothiocyanato-2-phenylpropane/$AlEt_2Cl/AlEtCl_2$ or $SnCl_4$ as Initiating System. Characterization by Means of the Off-Line Combination of GC/MS, SEC, and SFC

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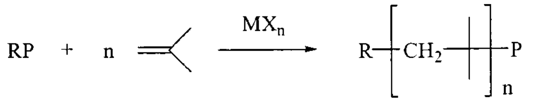
ABSTRACT: Isobutylene (IB) was oligomerized using 2-isothiocyanato-2-phenylpropane as initiator in the presence of $SnCl_4$ or a mixture of Lewis acids $AlEt_2Cl/AlEtCl_2$. The different oligomers were analyzed by a combination of chromatographic techniques (supercritical fluid chromatography, size exclusion chromatography, and gas chromatography) and mass spectrometry. The indanic cyclizations occurring after the formation of $\phi\text{-}C^+(CH_3)_2$ and the addition of one IB molecule were limited in the presence of the softest Lewis acid ($SnCl_4$). Moreover, the combination of $SnCl_4$/dimethyl sulfoxide (DMSO) as an initiating system gave the best results in terms of efficiency of co-initiation, functionalization (80%), and polydispersity (∼1.25).

Introduction

Extensive efforts are under way in our laboratories to develop functionalized polymers of isobutylene (IB) from organic pseudohalide (RP)/Lewis acid (MX_n) combinations.



We showed that an aliphatic azide ($R-N_3$) such as 2-azido-2,4,4-trimethylpentane in combination with a Lewis acid led to polymers bearing azide end groups.[1] We also 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 functionalized only with azide end groups.[2] Living polymerizations were also achieved with a weaker Lewis acid such as $AlEt_2Cl$ without addition of an electron donor.[3]

The functionalizing polymerization of isobutylene was also studied with another pseudohalide group, the isothiocyanate function (−NCS), using 2-isothiocyanate-2,4,4-trimethylpentane[4,5,6] and 2-isothiocyanato-2-phenylpropane[7] (Cum−NCS) as initiators. The experiments showed that 2-isothiocyanato-2,4,4-trimethylpentane does not act as an initiator, while Cum−NCS does. Several side-reactions were observed using $TiCl_4$ as Lewis acid.

This paper reports the synthesis of oligomers of isobutylene, carried out with Cum−NCS as the initiator, in the presence of $SnCl_4$ or a mixture of Lewis acids $AlEt_2Cl/AlEtCl_2$, or $SnCl_4$ in combination with dimethyl sulfoxide as an electron donor. The products were characterized using supercritical fluid chromatography (SFC), and the off-line combination of size exclusion chromatography (SEC) with gas chromatography/mass spectrometry (GC/MS). The different oligomer series and byproducts were identified in order to elucidate side-reactions.

Experimental Section

Reactants. Methylene dichloride (SDS, 99.9%) was dried twice by distillation over phosphorus pentoxide, the second time under vacuum inside the polymerization equipment. IB (SETIC-LABO, 99.9%) was successively dried over molecular sieves, barium oxide and calcium chloride. Then it was condensed in a graduated tube under vacuum at liquid nitrogen temperature. Lewis acids $TiCl_4$, $SnCl_4$, and $AlEt_2Cl/AlEtCl_2$ in CH_2Cl_2 solutions (sure seal bottles 1 M, Aldrich), dimethyl sulfoxide (Aldrich, 99.9%), and MeOH (Carlo Erba, 99.9%) were used as received. The initiator, 2-isothiocyanato-2-phenylpropane (Cum−NCS), was synthesized in two steps:[8] hydrochlorination of α-methyl-styrene and nucleophilic substitution with sodium isothiocyanate. After distillation under reduced pressure, its purity by GC/MS was 97%.

Polymerization. The polymerizations were carried out in a thick-wall glass reactor under vacuum (10^{-4} Torr). The solvent (50 mL of CH_2Cl_2) was introduced first, followed by the solution of 2-isothiocyanato-2-phenylpropane (0.5 mL, 2.9×10^{-3} mol). IB was then introduced by vacuum distillation (12 mL, 1.3×10^{-1} mol). If it was needed, DMSO (0.1 mL, 1.4×10^{-3} mol) was added. When the mixture was at −50 °C, 5 mL (5×10^{-3} mol) of Lewis acid was introduced by a syringe through a rubber cap. After 30 min of reaction, the polymerizing mixture was quenched with 2.5 mL of methanol and the polymer was recovered. The molar ratios of the reactants were [Cum−NCS]:[IB]:[Lewis acid]:[DMSO] ≈ 1:50:2:0.5 with [Cum−NCS] = 4.3×10^{-2} mol·L^{-1} kept constant for all the experiments.

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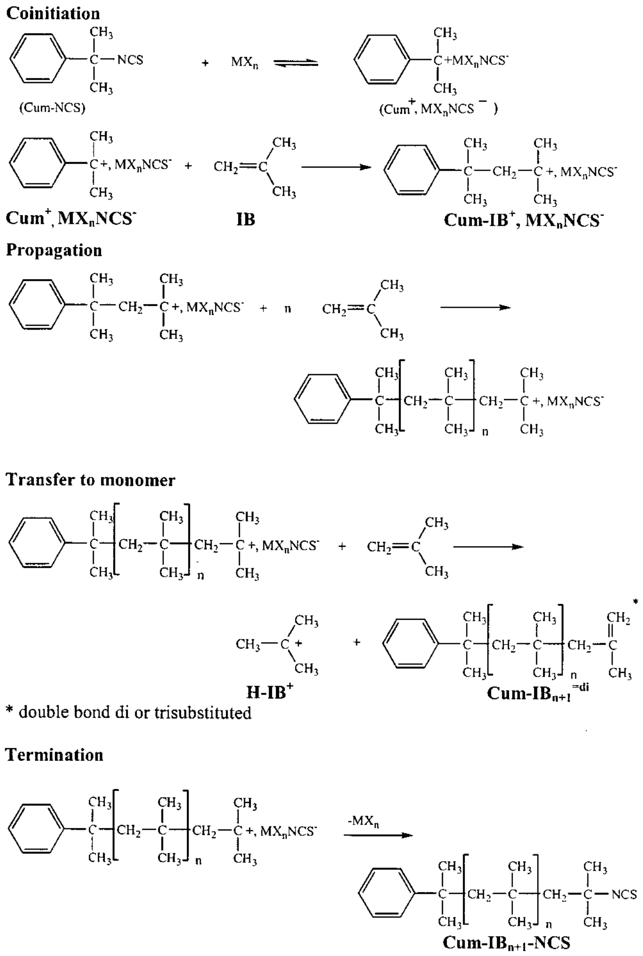
Scheme 1



Characterization. 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. This column was held at 50 °C during 5 min after the sample injection, then ramped to 250 °C at 4 °C/min and held at that temperature for 5 min. 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) at room temperature. Both UV (254 nm) and refractometric detectors were used. The system was calibrated with polystyrene.

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. A flame ionization detector (FID) was used.

Results and Discussion

Cum−NCS + IB + $AlEt_2Cl/AlEtCl_2$. The polymerization of isobutylene (yield 98%) was carried out in the presence of Cum−NCS and a mixture of Lewis acids: $AlEt_2Cl/AlEtCl_2$ (50/50). According to Scheme 1, the mechanism occurs by co-initiation followed by propagation. Transfer and termination, which can also occur, are unwanted. After transfer to monomer, $H-IB^+$ can also initiate polymerization, giving a species bearing a *tert*-butyl end. Termination by −NCS can be due to the usual dormant−active species equilibrium as previously discussed.[13]

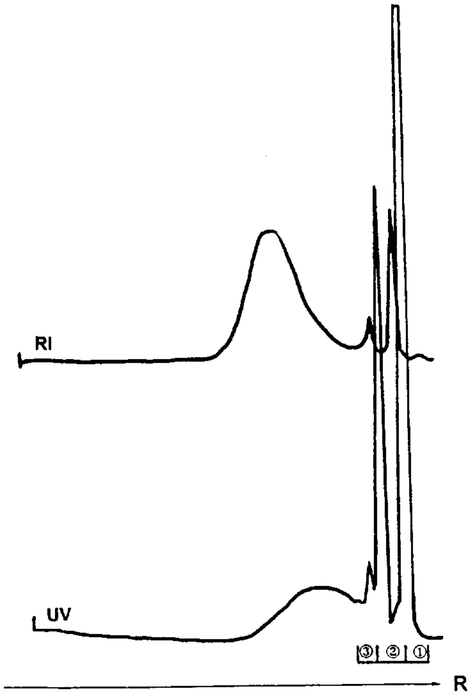


Figure 1. SEC chromatogram of the reaction products of Cum−NCS + IB + $AlEt_2Cl/AlEtCl_2$.

Analysis of the polymer by SEC (Figure 1) shows the presence of low molecular weight compounds in the polymer. The average molar masses of the polymer were $\bar{M}_n = 2000$, $\bar{M}_w = 3900$, and $I_p = 1.97$ according to UV measurements and $\bar{M}_n = 4100$, $\bar{M}_w = 6400$, and $I_p = 1.62$ according to refractometric measurements (RI). The differences between the average molar masses suggest an uneven distribution of chromophores in the macromolecular chains.

The SFC analysis (Figure 2) shows a wide distribution of chains. This separation, more resolved in the low molecular weight range, shows several products. Scheme 1 cannot explain the formation of all of these products. Analysis by GC/MS of fraction 1, obtained by semipreparative SEC (Figure 1), indicates the presence of two unexpected products: $Cum-IB^{ind}$ (85%) and Cum−H (15%). Fraction 2 contains mainly $Cum-IB^{ind}-Cum$. These molecules (Scheme 2) are side products. Scheme 2 shows the major sites of cleavage determined by mass spectrometry under electronic impact.[7]

$Cum-IB^{ind}$ results from an indanic cyclization after the co-initiation process (Scheme 3). Cum−H results from an unexpected termination reaction by hydride transfer, probably accompanied by loss of ethylene. This reaction is apparently induced by the use of the mixture $AlEt_2Cl/AlEtCl_2$. This type of termination has been evidenced by Kennedy et al. in model systems.[9,10] $Cum-IB^{ind}-Cum$ results from addition of Cum^+ on the double bond of $Cum-IB^{=di}$ (Scheme 4) followed by indanic cyclization and loss of H^+.

$Cum-IB^{ind}-Cum$ is not abundant in the mixture, but the two aromatic rings present in the molecule increase the UV response. Moreover, this species is eluted with various oligomers bearing cumyl ends. On the basis of our combination of chromatographic techniques, approximately 62% of Cum−NCS were converted into $Cum-IB^{ind}$, 12% into Cum−H, and only 26% into isobutylene

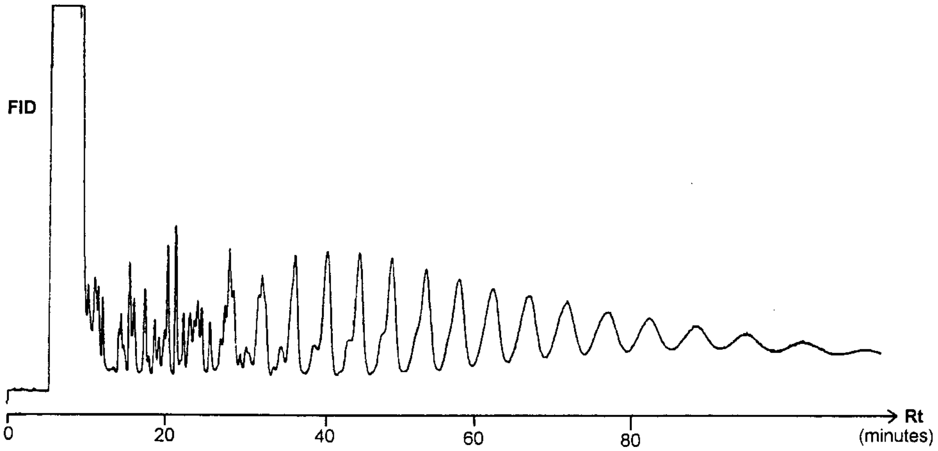
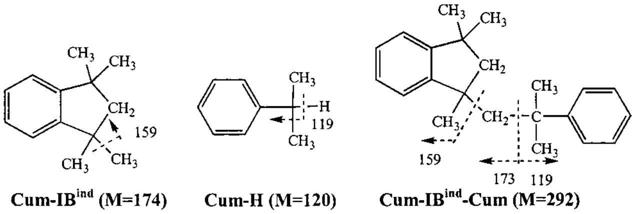
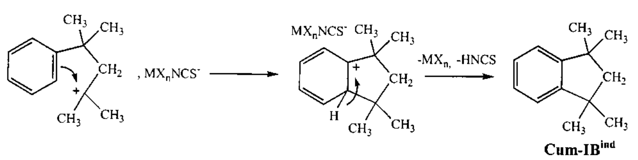


Figure 2. SFC chromatogram of the reaction products of Cum−NCS + IB + $AlEt_2Cl/AlEtCl_2$.

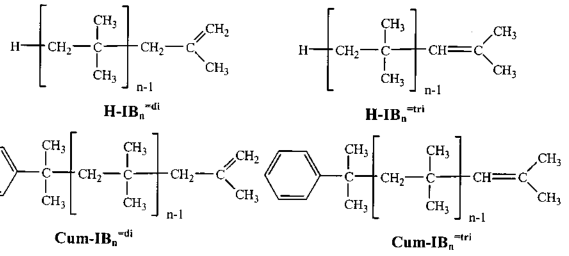
Scheme 2



Scheme 3



Scheme 4

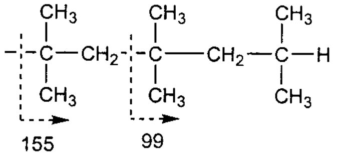


oligomers. The SFC chromatogram obtained with FID shows that Cum−IB^{ind} + Cum−H represent only 10%$_w$ of the mixture. Taking into account the yield and the length of chains ($9 < DP < 12$), this result demonstrates that many chains do not absorb in the UV. This is confirmed by the GC/MS analysis of the lower mass oligomers (fractions 1 + 2 + 3: Figure 3). As expected, this figure shows the relative importance of the molecules of the various fractions discussed above. Cum−IB^{ind} is the major compound in the mixture, but the main series are H−IB$_n^{=di/tri}$ and Cum−IB$_n^{=}$ (Scheme 4).

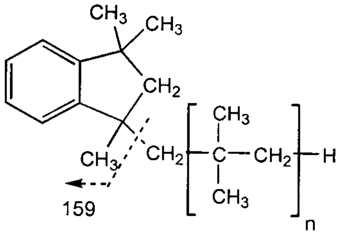
The structural assignment by mass spectrometry of these various oligomers was discussed in a previous paper.[7] The molecules bearing a cumyl end result from co-initiation. These oligomers do not contain either an isothiocyanate group or a thiocyanate group at their ends. Therefore, co-initiation and propagation are followed by monomer transfer. The unsaturated and *tert*-butyl ends and the spreading of the distribution indicate that several transfer reactions take place during the polymerization.

Besides Cum−IB^{ind}, this mixture contains other indanic compounds previously described when using $TiCl_4$ as a Lewis acid:[7] H−IB−Cum−IB^{ind} and isomers **I** (Scheme 5). However, in the case of $AlEt_2Cl/AlEtCl_2$, there is much less alkylation of the indanic ring of Cum−IB^{ind} with only a small amount of isomers **I** and no isomers **II**.

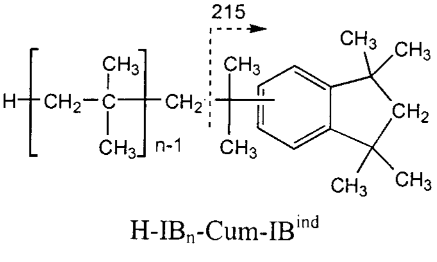
The GC/MS analysis also indicates the presence of a minor series bearing a saturated −IB$_n$−H end. The mass spectra of these oligomers show ions at *m*/*z* 99 and *m*/*z* 155. The other chain end is not well-defined. Like the Cum−H compound, this series apparently originates from a termination reaction by hydride transfer.


$$-C(CH_3)_2-CH_2-C(CH_3)_2-CH_2-C(CH_3)_2-H$$

The mass spectra of another minor series, Cum−IB^{ind}−IB$_n$−H, show ions at *m*/*z* 159 and *m*/*z* 117 (loss of propene from *m*/*z* 159). According to the retention times, the series is associated with the first members Cum−IB^{ind} and Cum−IB^{ind}−IB−H. These mass spectra are inconsistent with the isomers H−IB$_n$−Cum−IB^{ind} resulting from alkylation of Cum−IB^{ind} by polyisobutylene chains, since there are no ions at *m*/*z* 215.



Cum-IB^{ind}-IB$_n$-H



H-IB$_n$-Cum-IB^{ind}

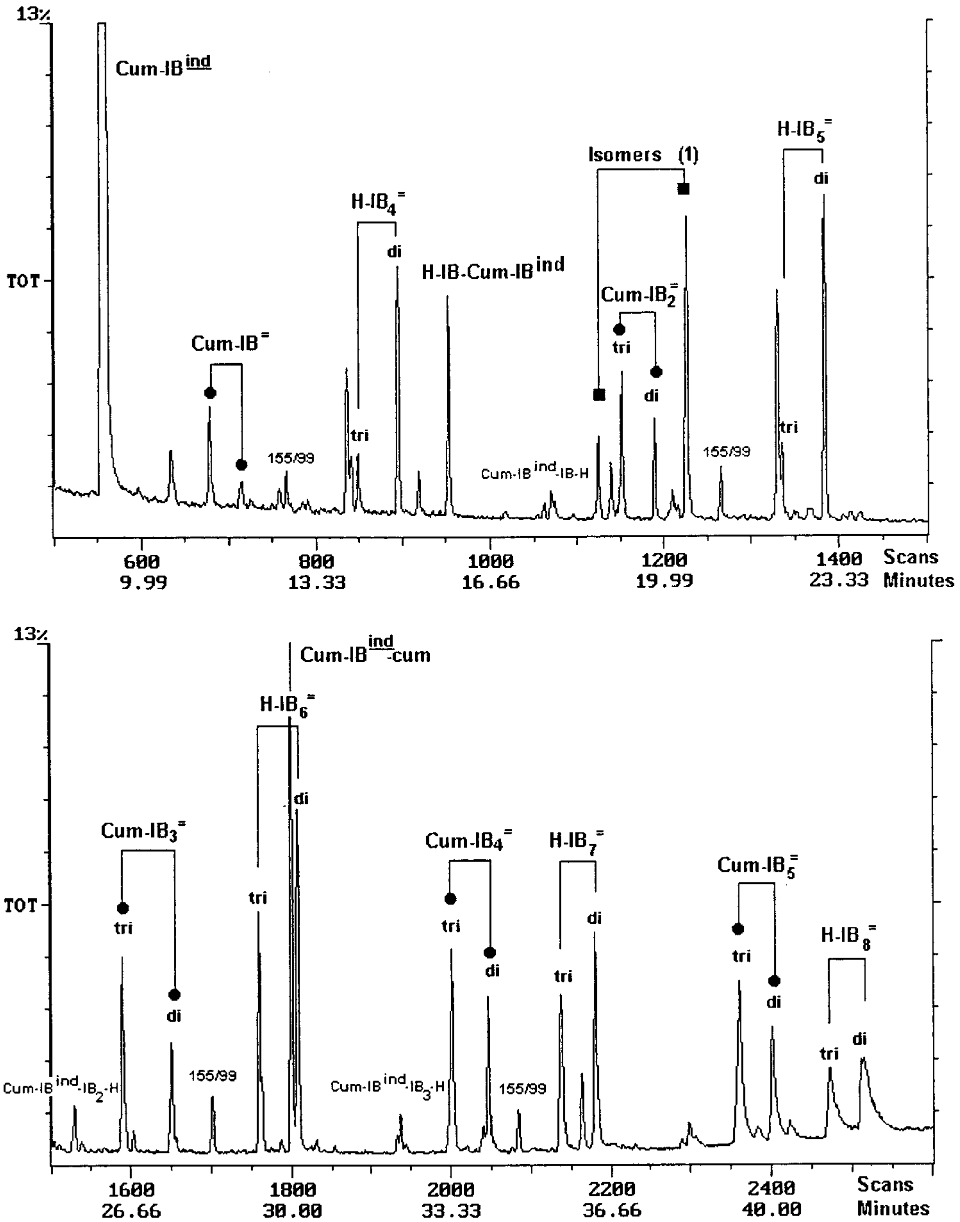
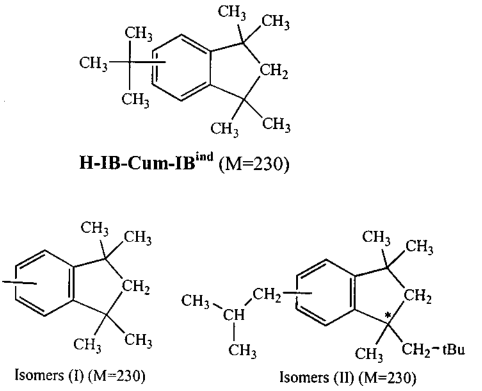
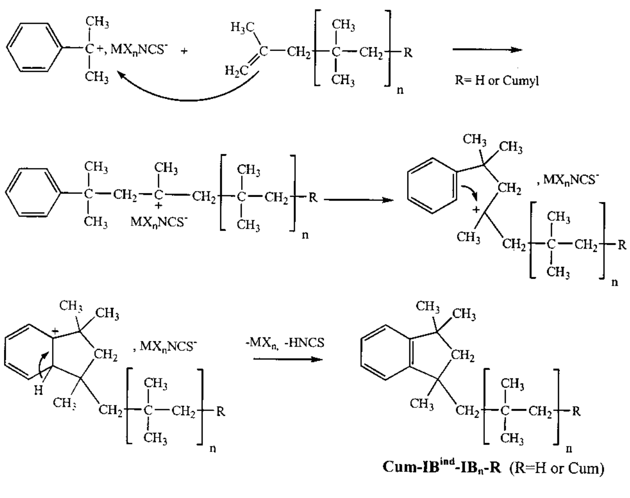


Figure 3. GC/MS chromatogram of the oligomers of the reaction of Cum−NCS + IB + $AlEt_2Cl/AlEtCl_2$.

Scheme 5



Scheme 6



In the same way, other oligomers Cum−IB^{ind}−IB$_n$−Cum ($n \geq 1$), associated with the Cum−IB^{ind}−Cum structure are present in the mixture. It appears that all of the chains bearing a terminal disubstituted double bond (i.e., H−IB$_n$$^{=di}$ or Cum−IB$_n$$^{=di}$) can react with Cum$^+$ to produce, after cyclization, a chain bearing an indanic ring (Scheme 6).

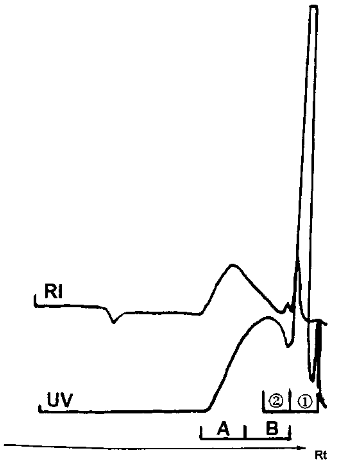


Figure 4. SEC chromatogram of the reaction products of Cum−NCS + IB + $SnCl_4$.

Because of the complexity of the SFC chromatogram in the lower mass region and the loss of resolution at higher weights, we cannot extrapolate the GC/MS assignments to the entire sample in order to estimate the importance and $\overline{DP}_n$ of each series. Although several undesirable reactions take place (indanic cyclizations, transfer to monomer, termination by hydride transfer) they are less important than in polymerizations using $TiCl_4$.[7] The polymer resulting from coinitiation is clearly identified owing to the cumyl end, but none of the oligomers carry isothiocyanate or thiocyanate groups.

Cum−NCS + IB + $SnCl_4$. Isobutylene was also polymerized using Cum−NCS as the initiator in the presence of another Lewis acid: tin tetrachloride. The yield was not quantitative and the analysis by SEC (Figure 4) gave $\bar{M}_n = 1400$; $\bar{M}_w = 2700$, $I_p = 1.88$ (UV); $\bar{M}_n = 1900$, $\bar{M}_w = 2700$, $I_p = 1.43$ (RI). The chains were

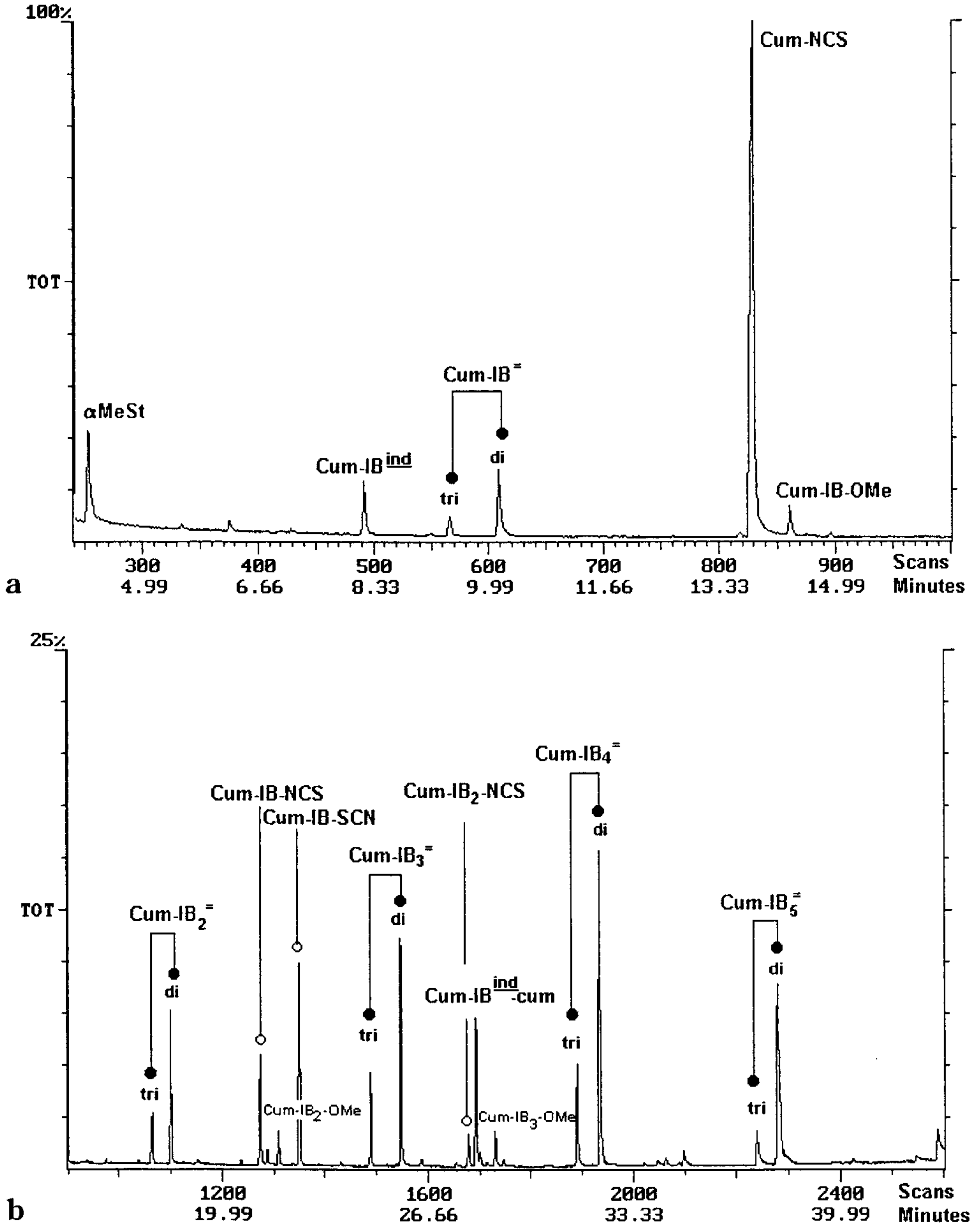


Figure 5. (a) Chromatogram GC/MS of fraction 1 from the SEC (Figure 4) of the products of the polymerization Cum−NCS + IB + $SnCl_4$. (b) GC/MS chromatogram of fraction 2 from the SEC (Figure 4) of the products of the polymerization Cum−NCS + IB + $SnCl_4$.

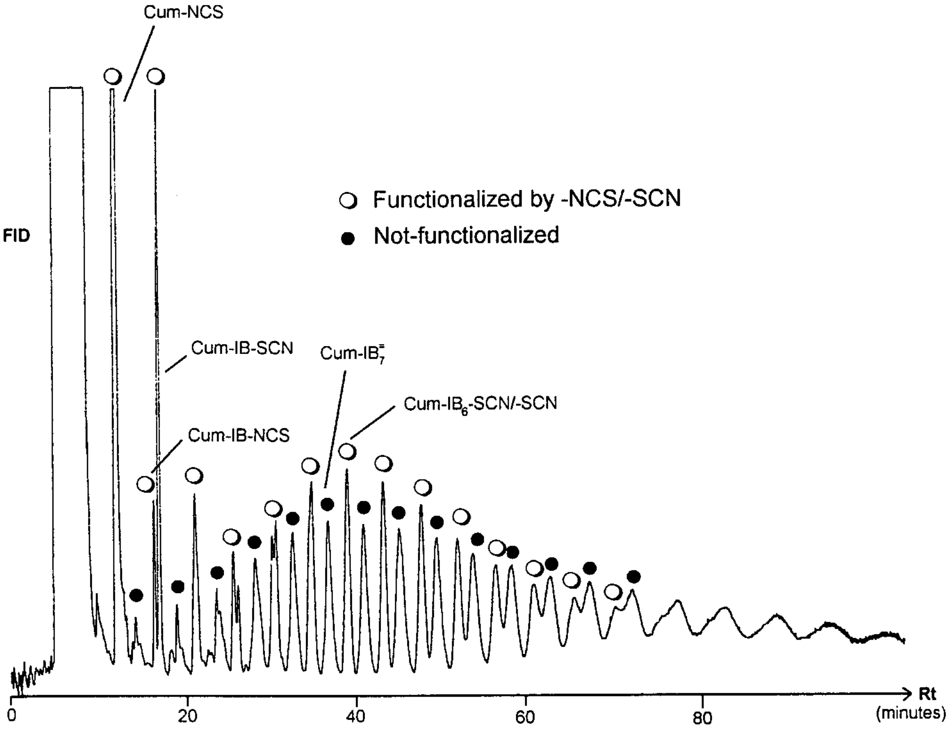


Figure 6. SFC chromatogram of the reaction products of Cum−NCS + IB + $SnCl_4$.

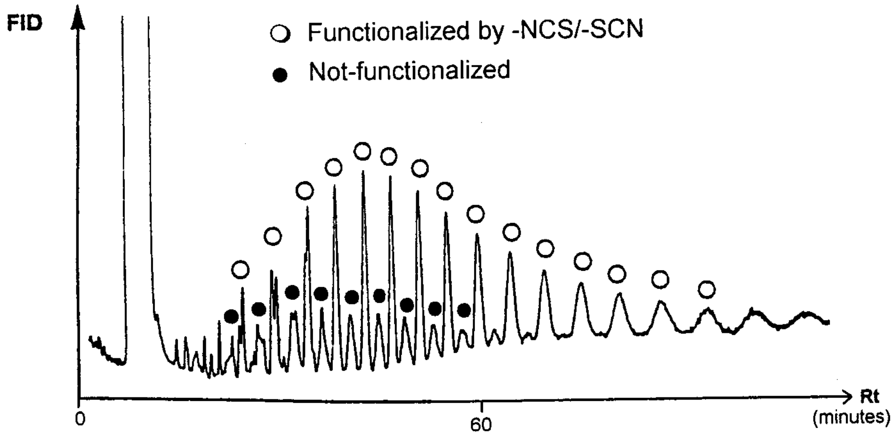


Figure 7. SFC chromatogram of fraction A from Figure 4 extracted by SEC from the products of Cum−NCS + IB + $SnCl_4$.

shorter at similar reaction times than with $TiCl_4$ or the mixture $AlClEt_2/AlCl_2Et$.

The GC/MS (Figure 5a) of fraction 1 from Figure 4, isolated by semipreparative SEC proves that Cum−NCS was not totally consumed. The amounts of Cum−IB^{ind}, αMeSt and Cum−IB−OMe are smaller than those of the initiator. αMeSt can come from the degradation of Cum−Cl in the injector of the GC, Cum−OMe is formed during the addition of MeOH. The UV spectrum shows that only 22% of Cum−NCS actually generated isobutylene oligomers.

The GC/MS of the oligomers of fraction 2 (Figure 5b) demonstrates that 22% of Cum−NCS generate oligomers by co-initiation. The first members of the different series were identified by mass spectrometry: mainly Cum−IB$_n^{=di/tri}$, Cum−IB$_n$−NCS/−SCN. The series Cum−IB$_n$−OMe seems to be of minor importance. Only the Cum−IB^{ind}−Cum species appears; higher members of the Cum−IB^{ind}−IB$_n$−Cum series are not observed.

The SFC chromatogram (Figure 6) shows that incorporation of one isobutylene monomer into a chain increases the retention time, by about 5 min regardless the nature of the end groups. The molecules Cum−IB$_n$−NCS/−SCN were identified owing to Cum−NCS (T_R = 12.5 min) which brings a starting point in the assignment. According to the orders of elution by GC/MS, the other peaks mainly correspond to the Cum−IB$_n^{=di/tri}$ series. The degree of polymerization and relative importance of the main series estimated from the SFC analysis are Cum−IB$_n$−NCS/−SCN, $\overline{DP}_n$ = 9 ± 1, 45%, and Cum−IB$_n^{=di/tri}$, $\overline{DP}_n$ = 7 ± 1, 55% (w/w).

The infrared spectrum of the UV-absorbing polymer, separated from the initiator by SEC (fraction A + B) confirmed the presence of isothiocyanate and thiocyanate groups. A broad peak at 2081 cm^{-1} was assigned to the asymmetric stretching of $-N=C=S$ groups, while a sharp peak at 2153 cm^{-1} was attributed to the stretching of $C\equiv N$ in the $-S-C\equiv N$ group.[11]

Cum−IB−NCS species and particularly Cum−IB−SCN seem to be more abundant than their oligomers (Cum−IB$_n$−NCS/−SCN) in the SFC chromatogram. Mayr et al.[12] have shown that during the polymerization of isobutylene initiated by Cum−Cl in the presence of BCl_3, the addition step of a second molecule of isobu-

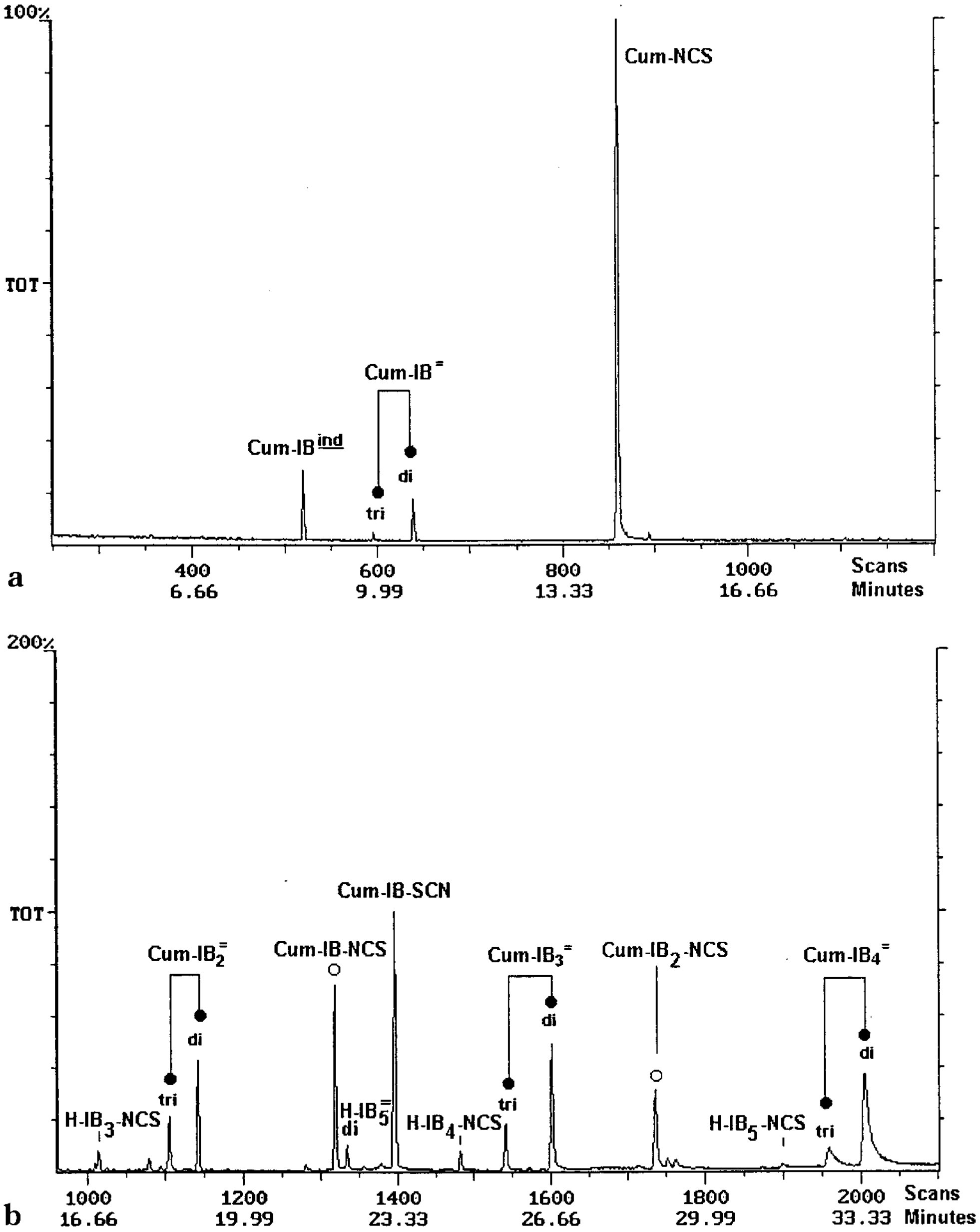


Figure 8. (a) GC/MS chromatogram of fraction 1 isolated by SEC from the products of the polymerization Cum−NCS + IB + $SnCl_4$ + DMSO. (b) GC/MS chromatogram of fraction 2 isolated by SEC from the products of the polymerization Cum−NCS + IB + $SnCl_4$ + DMSO.

tylene is slow because of the stability of the ionic complex $Cum-IB^+BCl_4^-$. This shows that the electrophilic center interacts with the electronic cloud of the benzyl ring, stabilizing it and bringing the end of the chain to a favorable position for indanic cyclization. This explains why the synthesis of $Cum-IB_n-Cl$ oligomers produces a significant fraction of Cum−IB−Cl and $Cum-IB^{ind}$ byproducts. In our situation, the large amount of Cum−IB−NCS and Cum−IB−SCN species can also be explained by the stability of $Cum-IB^+SnCl_4$-NCS^-. The stability of such a complex seems to favor the formation of thiocyanate ends rather than isothiocyanates. However, Descours-Michallet et al.[5] have reported that the functionalization by −SCN is thermodynamically favored in the presence of 2,6-di-*tert*-butylpyridine. If a hindered pyridine playing the role of proton scavenger cannot interact easily with a Lewis acid because of steric hindrance, the stabilization brought about by the proton scavenger seems to cause the same preferred functionalization.

GC/MS analysis only shows the first two members of the series $Cum-IB_n-NCS/SCN$, while we observe oligomers with terminal double bonds of higher molecular weights. The relative proportions of $Cum-IB_n^=$ ($n = 1,2$) species and those of Cum−IB−NCS/SCN seem to differ from by GC/MS and SFC analysis.

SFC analysis of the UV absorbing polymer, fraction A extracted by SEC (Figure 4), shows clearly that it is enriched in functionalized oligomers (Figure 7), while the SFC analysis of fraction B is enriched in nonfunctionalized oligomers. This demonstrates that a secondary effect by SEC leads to a quicker elution of functionalized oligomers, explaining why fraction 2 from Figure 4 contains only part of $Cum-IB_n-NCS/SCN$ and why longer oligomers from the same series are not observed, while the SFC analysis presents the actual distribution. These observations demonstrate the limits of our analytical strategy. The first members of some series cannot be observed by GC/MS.

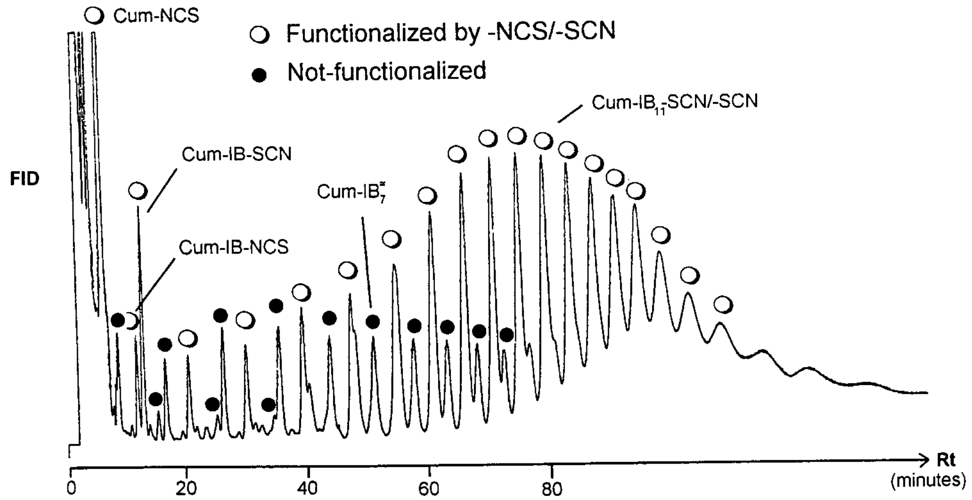


Figure 9. SFC chromatogram of the reaction products of Cum−NCS + IB + $SnCl_4$ + DMSO.

The values of $\bar{M}_n \approx 1600$ and $\bar{M}_w = 2700$ calculated from the SEC analysis differ from the $\overline{DP}_n \approx 8$ ($\bar{M}_n \approx 600$) estimated by SFC. This discrepancy was also observed in the $TiCl_4$[7] polymerization. In the present situation, the SFC and GC/MS analyses of various fractions of the mixture (1, 2, A, and B) allowed us to identify the nature of the polymer distribution observed by SEC (Figure 4). It seems that SFC displays the whole distribution of polymer, without losing the high molecular weight portion. $\overline{DP}_n$ of commercially available PIBs ($\bar{M}_n$ = 500 and 1000) estimated by SFC always agreed with the supplier's values. Thus, the distribution observed by SFC is reliable, while SEC calibrated with polystyrene standards overestimates $\bar{M}_n$ and $\bar{M}_w$ due to secondary effects.

The terminal double bonds do not result from transfer reactions. Protonic initiation by H−NCS in the presence of $TiCl_4$ would lead to propagation with similar kinetics (same counterions as in the case of co-initiation), and to the formation of chains bearing a *tert*-butyl group. However, GC/MS analysis of oligomers does not detect chains with *tert*-butyl groups. These double bonds could form during the quench, with the nature of the termination agent influencing the degree of functionalization. The active species would then be living at the end of the reaction time. The presence of Cum−IB_n−OMe confirms this hypothesis.

Compared to $TiCl_4$ and the mixture $AlEt_2Cl/AlEtCl_2$ during the same reaction time, $SnCl_4$ limits indanic cyclization following the formation of Cum^+ cation (although this reaction is slow), suppresses transfer reactions to monomer and favors functionalization by the pseudohalide group.

Cum−NCS + IB + $SnCl_4$ + DMSO. The yield of polymerization initiated by Cum−NCS/$SnCl_4$ in the presence of DMSO using the same conditions as above is about 20%. The average molecular weights estimated from SEC are higher than those obtained in the absence of DMSO. The polydispersity is narrower. With DMSO: $\bar{M}_n = 2700$, $\bar{M}_{nw} = 3300$, $I_p = 1.22$ (UV); $\bar{M}_n = 2900$, $\bar{M}_w = 3800$, $I_p = 1.28$ (RI). Without DMSO: $\bar{M}_n = 1400$; $\bar{M}_w = 2700$, $I_p = 1.88$ (UV); $\bar{M}_n = 1900$, $\bar{M}_w = 2700$, $I_p = 1.43$ (RI).

Two fractions were collected from the polymers. The GC/MS analysis of fraction 1 (Figure 8a) extracted by SEC shows that the initiator is not totally consumed; 50% of Cum−NCS were involved in co-initiation. The first oligomers of the series identified by GC/MS analysis of fraction 2 (Figure 8b) are Cum−$IB_n^{=di/tri}$, Cum−IB_n−NCS/SCN, H−IB_n−NCS, and H−$IB_n^{=di/tri}$. In contrast to the polymerization obtained without DMSO, there is no Cum−IB^{ind}−IB_n−Cum, while there is the series bearing −OMe ends.

The SFC chromatogram of this polymer is shown in Figure 9. The resolution obtained for low molecular weights oligomers is sufficient to identify the main series and estimate of their relative abondances by comparison with the GC/MS analysis of fraction 2 (Figure 8b): Cum−IB_n−NCS/SCN, $\overline{DP}_n = 11$, 80%. Cum−$IB_n^{=di/tri}$, $\overline{DP}_n = 7$, 20% (w/w). Addition of DMSO favored functionalization by pseudohalide groups, 80% vs 45% without DMSO. However, the presence of H−IB_n−NCS and Cum−$IB^{=di/tri}$ with a lower polymerization degree than those of the functionalized oligomers indicates that transfer reactions took place.

Conclusion

This work showed that SFC analysis combined with off-line coupling of SEC and GC/MS is useful for analyzing PIBs of molecular weight < 1500−2000. If the complexity of the distribution of macromolecular chains is not too important, the nature, degree of polymerization and relative proportions of different series and byproducts of a polymer resulting from a complex synthesis can be characterized. Nevertheless, this strategy presents some limitations due to the degradation of chlorinated chains ends and the difficulty in differentiating an indanic chain end from an α-methylstyryl one. However, our results provided useful information about polyisobutylene, such as characterization of chains ends with di-/trisubstituted double bonds, cumyl ends or of functional groups.

This approach identifies the first steps of the polymerization of isobutylene initiated by Cum−NCS/Lewis acid. The use of a strong Lewis acid, such as $TiCl_4$, favors indanic cyclization after the co-initiation process and the addition of one IB, while the use of a softer Lewis acid, such as $SnCl_4$, reduces this side-reaction. (Tables 1 and 2).

This work showed that the Cum−NCS/$SnCl_4$/DMSO initiating system produces some IB oligomers functionalized with thiocyanate or isothiocyanate groups (Table 2). Obviously initiation is not fast, since 50% of the initiator remained unreacted using our conditions (CH_2-

Table 1. Characterization of the PIBs Obtained in the Presence of Cum−NCS and Various Lewis Acids and Additives ([Cum−NCS]:[IB]:[Lewis acid] ≈ 1:50:2; ([Cum−NCS] = 4.3 × 10^{-2} mol·L^{-1})

Lewis acids and additives	yield (%)	$\bar{M}_n$ (UV)	$\bar{M}_w$ (UV)	I_p (UV)	$\bar{M}_n$ (RI)	$\bar{M}_w$ (RI)	I_p (RI)
$TiCl_4$[7]	85	2000	3800	1.89	2000	3100	1.60
$TiCl_4$ + DMSO[7]	48	1300	2400	1.83	600	900	1.39
$TiCl_4$ +MDtBP[7]	88	2900	3900	1.35	3500	4500	1.30
$AlEt_2Cl/AlEtCl_2$	98	2000	3900	1.97	2600	4200	1.62
$SnCl_4$		1400	2700	1.88	1900	2700	1.43
$SnCl_4$ + DMSO	20	2700	3300	1.22	2900	3800	1.28

Table 2. Efficiency of Coinitiation and Functionalization in the Polymerization of Isobutylene Initiated by Cum−NCS/Lewis Acid in the Presence of Various Additives ([Cum−NCS]:[IB]:[Lewis acid] ≈ 1:50:2; ([Cum−NCS] = 4.3 × 10^{-2} mol·L^{-1})

	efficiency of co-initiation,[a] %		
lewis acids and additives	Cum−NCS → Cum−IB_{n}−	Cum−NCS → Cum−IB^{ind} [b]	% Cum−IBn−NCS + Cum−IBn−SCN[c]
$TiCl_4$[7]	21	79	
$TiCl_4$ + DMSO[7]	20	7	
$TiCl_4$ + MDtBP[7]	87	10	0 (GC/MS)
$AlEt_2Cl/AlEtCl_2$	26	62	0
$SnCl_4$	22	8	45
$SnCl_4$ + DMSO	50	5	80

[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}, estimated from SEC (UV detection), in combination with GC/MS. [c] Percentage of Cum−IB_n−NCS/SCN, estimated by SFC.

Cl_2, 50 °C, 30 min). The polymer is fairly functionalized since 80% of the macromolecules bear a −NCS or −SCN terminus. However, the experimental conditions were not optimized for specificity and selectivity. The work presented aimed at identifying the various mechanisms and trends which could lead to well-functionalized oligomers in high yield. These results support the mechanism that was concluded from our recent paper:[13] Covalent pseudohalide + Lewis acid ⇌ cation, which also explains the structure of the byproducts and the relatively low polydispersity index. It is clear that the electron donor stabilizes the ionized active species, as witnessed by the decrease of the relative importance of the series having an unsatured chain end. The use of relatively weak Lewis acids and of DMSO decreases the importance of side-reactions.

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