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Notes

Cationic Polymerization of Isobutyl Vinyl Ether Initiated by Tin Tetrachloride in the Presence of Trimethylsilyl Azide

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Introduction

Recently, we have shown that an organic azide/Lewis acid combination can give a specific functionalizing polymerization of olefins such as 2-methylpropene (MP). According to the nature of azide RN_3, it can act either in the termination step or in both the initiation and termination steps of the polymerization. Thus, polymerization of MP initiated by trimethylsilyl azide (TMSA)/Lewis acid (BCl_3, $TiCl_4$, $SnCl_4$) leads to a polymer bearing different terminal end groups such as unsaturation, tertiary chlorine, and azide which shows that TMSA acts only in the termination step.[1] With the initiating system 2-azido-2-phenylpropane/Lewis acid (BF_3, BCl_3, $TiCl_4$, $AlEtCl_2$), $TiCl_4$ gave a polymer which was partly functionalized by an azide end group and BF_3 gave a complete azide functionalization within experimental accuracy.[2] In the case of a difunctional initiating system such as 1,4-bis(2-azido-2-methylethyl)-benzene/Lewis acid, $TiCl_4$ and BCl_3 gave also a polymer partly functionalized by azide,[3] whereas $AlEt_2Cl$ led to a "living" polymerization of MP without external electron donor and with a complete azide functionalization.[4] From these results obtained with an olefin like MP, we thought that it was interesting to apply these initiating systems to polymerize vinyl ether monomers. This short communication presents the first results of this investigation: polymerization of isobutyl vinyl ether (IBVE) initiated by $SnCl_4$ in the presence of trimethylsilyl azide.

Experimental Section

Reactants were purified and dried according to our laboratory technique: distillation over CaH_2 and vacuum distillation over P_2O_5 before use for CH_2Cl_2 and vacuum distillation over CaH_2 for TMSA and IBVE. $SnCl_4$ in solution in hexane (Aldrich, 1 M) was used as received.

Polymerization Techniques. Polymerization was carried out under vacuum in a reactor fitted with a magnetic stirrer. IBVE, solvent, and TMSA were introduced in this order, and at the desired temperature, $SnCl_4$ was added via syringe through a rubber septum. The polymerization was stopped by quenching with methanol. Polymer recovery was carried out by precipitation in methanol, so that low molecular weight oligomers can be lost in the filtrate.

Molecular Characterization

The azide functionality can be obtained from the equation:

$$F_{N_3} = (\bar{X}\bar{M}_n)/42$$

where $\bar{X}$ is the mole number of azide per gram of polymer according to the IR calibration technique used in the case of MP published elsewhere.[5] The accuracy of this determination depends on the true value of $\bar{M}_n$.

If $\bar{M}_n$ is determined by size exclusion chromatography (SEC) with poly(styrene) standards there could be a problem linked with the fact that poly(IBVE) may have a hydrodynamic volume different from that of poly(styrene), and the use of the average number molecular weight determined in equivalent poly(styrene) could be a source of systematic error. In the literature it is possible to see that most of the laboratories make use of the molar mass determined in equivalent poly(styrene) as far as poly(IBVE) is concerned. For instance, Sigwalt's group mentioned that "osmotic measurements showed that the molecular weight obtained were in good agreement with the values derived from G.P.C.".[6] In a similar context, studying the "livingness" of IBVE polymerization in the presence of electron donors, Kobayashi also makes use of the average number molecular weight given by SEC as the true one.[7] It was mentioned in this paper that this value was in good agreement with the calculated value by assuming that one living polymer chain is formed per unit cationogen. For the same type of determination of the conditions for "livingness", Higashimura's group stated in a paper that "the M_n values ... though based on a polystyrene calibration, ... were in excellent agreement with the calculated values assuming that one polymer chain forms per unit" (initiator).[8] It was decided to check the relationship between the "true" average number molar mass and the one which could be calculated from SEC using poly(styrene) standards. Thus, a monodisperse poly(IBVE) sample, kindly provided by Deffieux (Bordeaux, France) and synthesized using living conditions, was measured by SEC in both laboratories. The two determinations were in excellent agreement, both giving an average number molecular weight of 10 000 within an accuracy of ±2%. A special determination by laser light scattering using a dn/dC experimentally determined in our laboratory was carried out on the same sample, and a relatively good agreement was found: $\bar{M}_n = 12\,000$. Given the difficulties of this last determination and the above reports mentioned in the literature, it was decided to use in the following the SEC values determined with poly(styrene) as the true molar mass.

Results and Discussion

Polymerizations were carried out in CH_2Cl_2 as polar solvent. Since the NMR spectra of poly(IBVE) never

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Table 1. Effect of Temperature on the Polymerization of IBVE in the Presence of TMSA[a]

run	T, °C	yield, %	$\bar{M}_n$[b]	I[c]	F_{N_3}
1	−30	0			
2	0	86	2100	2.2	0.23
3	20	70	1250	2.4	0.30
4	30	66	1500	2.6	0.15

[a] Conditions: [IBVE] = 0.7 M; [SnCl$_4$] = 4.7 × 10^{-2} M; [TMSA] = 1.4 × 10^{-2} M; t = 20 min; V_t = 110 mL. [b] $\bar{M}_n$ = molecular weight determined by SEC (see Experimental Section). [c] $I = \bar{M}_w/\bar{M}_n$.

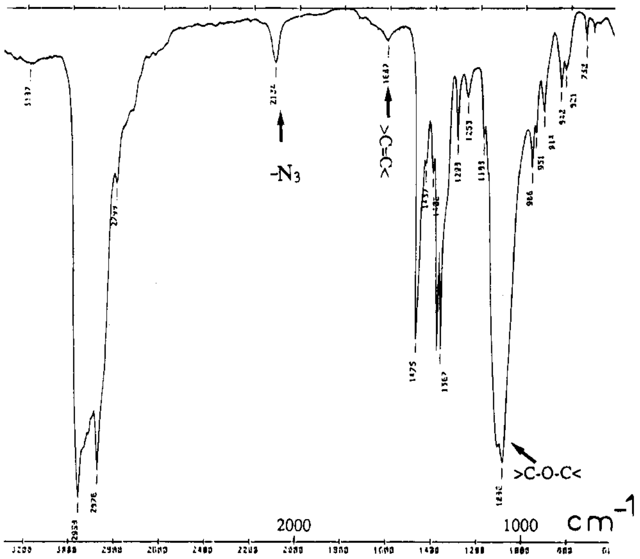
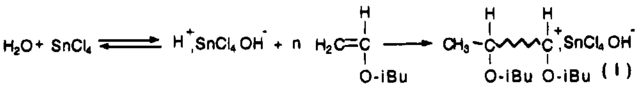


Figure 1. IR spectrum of poly(IBVE) from run 2 (Table 1).

show the presence of a Si(CH$_3$)$_3$ chain end, the polymerization of IBVE cannot occur via a trimethylsilyl cation initiation process so that the protonic initiation process probably comes from moisture, as shown by Matyjaszewski in the case of styrene polymerization initiated by trimethylsilyl triflate.[9] Table 1 presents some results of the effect of polymerization temperature in the range −30 to +30 °C. For constant concentrations [IBVE] = 0.7 M, [SnCl$_4$] = 4.7 × 10^{-2} M, and [TMSA] = 1.4 × 10^{-2} M, conversion is not quantitative and $\bar{M}_n$ is low with a large polydispersity index (2.2–2.6). The azide functionality F_{N_3} is relatively low with the best value for 20 °C. Figure 1 is an IR spectrum of a polymer (PIBVE) where peaks at 2104 cm^{-1} (azide), 1607 cm^{-1} (double bond), 1474, 1382, 1367 cm^{-1} (isobutyl), and 1090 cm^{-1} (ether) are detected.

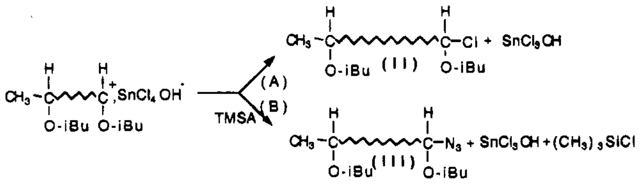
According to previous results obtained in the case of MP, the polymerization of IBVE is assumed to follow:

−a protonic initiation process



$$H_2O + SnCl_4 \rightleftharpoons H^+,SnCl_4OH^- + n\ H_2C{=}\underset{O\text{-}iBu}{\overset{H}{C}} \longrightarrow CH_3\text{-}\underset{O\text{-}iBu}{\overset{H}{C}}\sim\sim\underset{O\text{-}iBu}{\overset{H}{\overset{|}{C}}}{}^{+},SnCl_4OH^- \quad (I)$$

−competitive termination reactions by recombination of the electrophilic propagating species with N$_3^-$ or Cl$^-$, the former coming from the counterion after exchange reaction:[3,4]



$$CH_3\text{-}\underset{O\text{-}iBu}{\overset{H}{C}}\sim\sim\underset{O\text{-}iBu}{\overset{H}{C}}{}^{+},SnCl_4OH^- \xrightarrow{(A)} CH_3\text{-}\underset{O\text{-}iBu}{\overset{H}{C}}\sim\sim\underset{O\text{-}iBu}{\overset{H}{C}}\text{-}Cl + SnCl_3OH \quad (II)$$

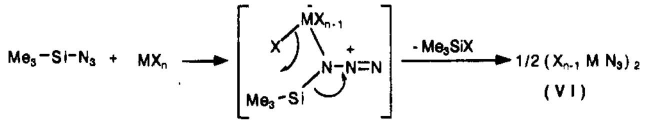
$$\xrightarrow[TMSA]{(B)} CH_3\text{-}\underset{O\text{-}iBu}{\overset{H}{C}}\sim\sim\underset{O\text{-}iBu}{\overset{H}{C}}\text{-}N_3 + SnCl_3OH + (CH_3)_3SiCl \quad (III)$$

Table 2. Effect of TMSA Concentration on the Functionalization of Poly(IBVE)[a]

run	10^2[TMSA], M	yield, %	$\bar{M}_n$[b]	I[c]	F_{N_3}
5	1.4	70	1200	2.4	0.30
6	4.1	70	1300	2.3	0.75
7	6.2	67	1400	2.5	1.0
8	10.3	83	1400	2.2	1.1
9	13.7	95	1300	2.1	1.1

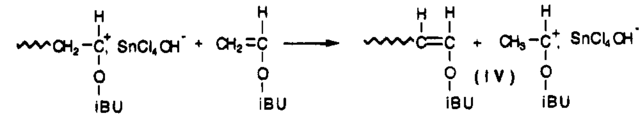
[a] Conditions: [IBVE] = 0.7 M; [SnCl$_4$] = 4.7 × 10^{-2} M; t = 20 min; T = 20 °C; V_t = 110 mL. [b] $\bar{M}_n$ = molecular weight determined by SEC (see Experimental Section). [c] $I = \bar{M}_w/\bar{M}_n$.

It is worth recalling that in the case of MP, the percentages of these two chain ends depend on the Lewis acid strength (BCl$_3$, TiCl$_4$, AlEt$_2$Cl, ...). Step B is similar in its mechanism to the reaction of SnCl$_4$ with TMSA leading to the formation of an adduct:

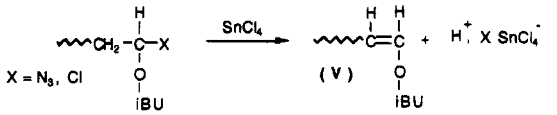


The existence of this was demonstrated by Wiberg et al. in the case of SbCl$_5$ and SnCl$_4$.[10,11]

Transfer reactions are important, denoted by the presence of unsaturation which can also rise from elimination reactions



$$\sim\sim CH_2\text{-}\underset{O\text{-}iBU}{\overset{H}{C}}{}^{+}\ SnCl_4OH^- + CH_2{=}\underset{O\text{-}iBU}{\overset{H}{C}} \longrightarrow \sim\sim\overset{H}{C}{=}\underset{O\text{-}iBU}{\overset{H}{C}}\ (IV) + CH_3\text{-}\underset{O\text{-}iBU}{\overset{H}{C}}{}^{+}\ SnCl_4OH^-$$



$$\sim\sim CH_2\text{-}\underset{O\text{-}iBU}{\overset{H}{C}}\text{-}X \xrightarrow{SnCl_4} \sim\sim\overset{H}{C}{=}\underset{O\text{-}iBU}{\overset{H}{C}}\ (V) + H^+,\ X\ SnCl_4^-$$

$$X = N_3,\ Cl$$

The azide functionalization is worth being discussed. For a constant [SnCl$_4$], F_{N_3} increases with the increasing initial [TMSA] and, within experimental accuracy, a quantitative azide chain end functionalization (Table 2) can be reached for a ratio of [TMSA]/[SnCl$_4$] at least higher than 1, as shown in Figure 2. According to previous work, it could be thought that the first action of TMSA is to play the role of an electron donor and to decrease the extent of transfer reaction.[3] On the other hand, the extent of functionalization can be compared to the initial TMSA concentration which shows that only a part of TMSA is used for polymer functionalization. In order to shed more light on the role of TMSA some experiments were carried out by varying the TMSA concentration (Table 2). The results of polymer molecular weight (Table 2) show that apparently TMSA does not influence the extent of transfer reaction. Since polymerization yield increases with [TMSA], its role is not restricted to a simple functionalization of macromolecules after polymerization, and it seems to be more complicated than expected.

The results reported (Table 2) show that the initiating system RN$_3$/MX$_n$ can be applied to vinyl ether monomers and an azide terminal end can be quantitatively obtained under specific conditions. Indeed, the two values of azide functionality slightly higher than 1 (experiments 8 and 9) must be assigned to the experimental difficulties.

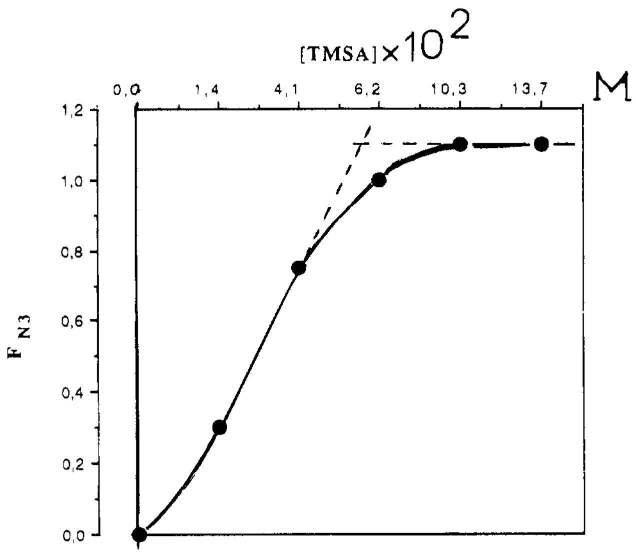


Figure 2. Azide functionality F_{N_3} variation of poly(IBVE) initiated by tin tetrachloride ([SnCl$_4$] = 4.7 × 10^{-2} M) in CH$_2$Cl$_2$ at room temperature, versus [TMSA].

Conclusions

Thus, in the system IBVE−SnCl$_4$−TMSA in CH$_2$Cl$_2$, functionalization by polymerization depends on the ratio [TMSA]/[SnCl$_4$]. This behavior was already observed in the case of MP. This is an another example of a specific functionalization of poly(vinyl ether) by a carbon to nitrogen bond by direct polymerization of the monomer and not by chemical modification of the polymer.

This present system seems to be simpler to use than others which were recently published.[12] The potential of our synthetic method, involving a pseudohalide group containing molecules for the production of specific functionalization by the termination reaction, is demonstrated on a new monomer (IBVE). It would be interesting to know whether a "living" functionalizing polymerization could be obtained under suitable experimental conditions, in the presence of a benzylic-type organic azide similarly to the case of MP polymerization,[4] living behavior which was not observed in the presence of TMSA.[1] This point will be the object of further studies.

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References and Notes

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