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Initiation of Vinyl Ether Polymerization by Trimethylsilyl Triflate, Dimethyl Sulfide, and Adventitious Water[†]

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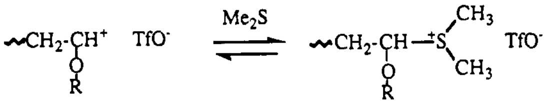
ABSTRACT: In an effort to use trimethylsilyl trifluoromethanesulfonate (TMSOTf) as an initiator for the living polymerization of isobutyl vinyl ether (IBVE) in the presence of dimethyl sulfide the M_n versus conversion plot showed a linear relationship for a given solvent. The slope, however, deviated from the calculated one based on an initiator efficiency of 1; i.e., the molecular weights were higher than expected. The addition of water or alcohol increased the initiator efficiency. This result indicated that triflic acid formed by hydrolysis of the TMSOTf was the true initiator. Indeed, in the presence of 2,6-di-*tert*-butyl-4-methylpyridine (DTBMP), a proton trap, no polymerization was observed up to 0 °C. Living polymerization occurred, however, with DTBMP in the system when an aldehyde or ketone was added. In these examples, a trimethylsiloxy group was shown to be covalently bound to the polymer by proton NMR. The number-average molecular weight, calculated by assuming there is one trimethylsilyl group per chain, agreed well with that obtained by GPC.

Introduction

We[1] and others[2] have recently reported that the polymerization of isobutyl vinyl ether (IBVE) in CH_2Cl_2 at low temperatures initiated by triflic acid (CF_3SO_3H) becomes living in the presence of excess alkyl sulfides, at relatively high $[R_2S]_0/[CF_3SO_3H]_0$ ratios. The propagating carbocationic chain ends are presumably stabilized by the sulfide to yield an equilibrium mixture of carbenium- and onium-type chain ends (eq 1). Nearly monodispersed polymers are obtained, indicating that the propagation rate of the stabilized chain ends is slower than the initiation rate and that chain transfer and termination are minimal. The key controlling factor for the rate of polymerization is the $[R_2S]_0/[CF_3SO_3H]_0$ ratio. We have also found that other low-efficiency initiation systems can be improved by the addition of R_2S. Thus aldehydes, acetals, or orthoesters can be used as initiators for the living polymerization of alkyl vinyl ethers, in the presence of a Lewis acid and R_2S.[3] Similar examples of increased initiation efficiency have been recently reported[4,5] for the living cationic polymerization of isobutylene in the presence of dimethyl sulfoxide or dimethylacetamide and in the polymerization of vinyl ethers with Lewis acids in the presence of esters and ethers.[6] Trialkylsilyl compounds bearing electron-withdrawing groups have been widely used in organic chemistry as reagents for silylation reactions.[7] In this respect, the trimethylsilyl group has been described as a "bulky proton".[8] A few cationic polymerizations of electron-rich vinyl and oxacyclic monomers have been reported.[9-12] Polymers with broad molecular weight distributions were obtained by Gong and Hall[9] using trialkylsilyl triflates to initiate the polymerization. Sawamoto et al.[10] have observed living polymerization of vinyl ethers with Me_3Si/acetone/ZnI_2 in toluene and methylene chloride solvents. They suggested that a ZnI_2-complexed addition product, $Me_3SiOC(CH_3)_2{-}I \rightarrow ZnI_2$, is the initiator. Lin and Matyjaszewski,[11] on the other hand, showed that trimethylsilyl trifluoromethanesulfonate (TMSOTf) did not polymerize styrenes in the presence of the proton trap 2,6-di-*tert*-butyl-4-methylpyridine (DTBMP). Polymers were formed in the absence of DTBMP, which led them to conclude that the initiation occurred via the triflic acid formed by the hydrolysis of the TMSOTf with adventitious water. A similar conclusion has been made by Hall et al.[13] The purpose of the present study was to investigate the living cationic polymerization of IBVE initiated by TMSOTf and by TMSOTf/carbonyl adducts in the presence of Me_2S.



$$\sim CH_2{-}\underset{\underset{R}{|}}{\underset{O}{|}}{CH^+}\ TfO^- \xrightleftharpoons{Me_2S} \sim CH_2{-}\underset{\underset{R}{|}}{\underset{O}{|}}{CH}{-}\overset{+}{S}(CH_3)_2\ TfO^- \quad (1)$$

Experimental Section

Materials. IBVE (Aldrich) was purified as reported previously.[14] Dimethyl sulfide (Aldrich) was distilled over 9-borabicyclo[3.3.1]nonane. Solutions of triflic acid were prepared as reported.[1] TMSOTf (Fluka) was used as received. Ethanol (absolute) was refluxed with $Mg(OEt)_2$ and distilled from this mixture before use. Triflic anhydride, acetaldehyde, acetone, benzaldehyde, and acetophenone were obtained from Aldrich and used as received. DTBMP (Aldrich) was purified by vacuum distillation. Methylene chloride (EM Science) was treated with concentrated sulfuric acid and then fractionally distilled, twice over calcium hydride or successively over phosphorus pentoxide and calcium hydride, under dry argon. *n*-Hexane (Aldrich) was refluxed over sodium wire in the presence of benzophenone. It was then distilled from this mixture before use.

Polymerization Setup. A round-bottomed flask was used with a modified two-way Teflon stopcock. All glass parts and syringes were thoroughly cleaned, baked overnight in an oven at 150 °C, assembled while hot, and flushed with argon (dry, oxygen-free). The solvents, which were contained in flasks equipped with stopcock and rubber septa, were transferred to the polymerization flask using a two-sided stainless steel needle by applying an argon pressure. The monomer, Lewis base (neat or in solution), other additives, and the initiators (neat or in solution) were introduced into the flask through the septum and stopcock by the aid of syringes. All manipulations involving solvents, additives, reactants, and the polymerization itself were carried out under argon and under strictly anhydrous conditions. The polymerization temperature was controlled within 1 °C by a bath equipped with an immersion cooler.

Procedures. Method A. (This method was used for most of the polymerization runs.) TMSOTf was added to a solution

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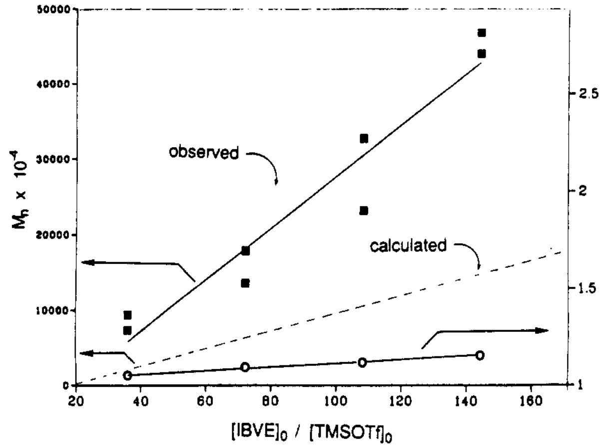


Figure 1. M_n versus $[IBVE]_0/[TMSOTf]_0$ for the polymerization with 100% conversion in CH_2Cl_2. $[TMSOTf]_0 = 0.90$ mmol, $[Me_2S]_0 = 30$ mmol, reaction temp −30 °C, reaction time 5–6 h. Polymerization method A was used.

of dimethyl sulfide in 125 mL of CH_2Cl_2 and the additive (e.g., water, ethanol, DTBMP, aldehyde, ketone, triflic anhydride, etc.). The mixture was then cooled to the required temperature and stirred for 10–20 min, and the polymerization was started by injecting the IBVE. In a number of polymerizations, a solution of IBVE was added dropwise into the reaction mixture during t_1 min. After a given time, t_2, the polymerization was quenched by injecting 10 mL of triethylamine/methanol (1/2 v/v) solution, or a 10% solution of *tert*-butylamine in methanol. Unreacted monomer and solvent were removed under reduced pressure. The residue was dried under vacuum (1 Torr) at ca. 40 °C for 2 days, and the yield was measured gravimetrically. The molecular weights and their distributions (M_w/M_n) were measured by gel permeation chromatography (GPC) with poly(methyl methacrylate) standards.[15] The polymer mixture was dissolved in *n*-hexane, washed with water three times to remove triethylammonium triflate, and then dried again. Proton NMR spectra were recorded on a 300-MHz GE NMR spectrometer. The integral ratio of the trimethylsilyl group to the two methyl groups of the isobutyl side chain was used to calculate the M_n. The ^{29}Si spectra were recorded on a NT 300 wide-bore instrument.

Method B. In this method, an initiator compound (TfOH, TMSOTf, TfOTf, etc.) was added last to start the polymerization.

Results and Discussion

Apparent Polymerization of IBVE by TMSOTf. IBVE was polymerized by addition to a solution of TMSOTf in CH_2Cl_2 and in a few examples *n*-hexane in the presence of Me_2S at −30 °C. Typical features of a living polymerization system were observed on using optimal $[Me_2S]_0/[TMSOTf]_0$ ratios of about 30. Thus the polymers had narrow molecular weight distributions ($M_w/M_n < 1.2$), and plots of M_n of the polymers obtained (at 100% conversion) versus $[IBVE]_0/[TMSOTf]_0$ showed a linear relationship within the error limits of duplicate runs (Figure 1). A linear relationship was also observed, for various $[IBVE]_0/[TMSOTf]_0$ ratios, in cases where conversions were incomplete (Table I). However, the M_n values of the polymers obtained in this living system were higher than the calculated ones (Figure 1). This observation suggested that only part of the [TMSOTf] was involved in initiation. Polymerizations with differently pretreated reagents (especially the solvent) gave different results with respect to initiator efficiency. This implies that the initiation system is quite sensitive to impurity levels. Polymers of broader MWD ($M_w/M_n > 1.2$) were formed in many cases in spite of using optimal $[Me_2S]_0/[TMSOTf]_0$ ratios. The presence of traces of water or other impurities capable of reacting with the TMSOTf to give TFOH, a known initiator for IBVE, was therefore suspected.

Table I
Polymerization of IBVE by Trimethylsilyl Triflate[a]

$[IBVE]_0/[TMSOTf]_0$	conv, %	M_n GPC	M_n calcd	M_w/M_n
72.2^b	16.0	1300	1160	1.10
72.2^b	18.4	1100	1300	1.10
216^b	35.8	8800	7800	1.26
216^b	31.7	9000	7000	1.26
289^b	29.6	9300	8600	1.04
36.1^c	100	7400	3600	1.03
36.1^c	100	9400	3600	1.06
72.2^c	100	13600	7200	1.02
72.2^c	100	17900	7200	1.11
108.3^c	100	23100	10800	1.14
108.3^c	100	32600	10800	1.09
144.4^c	100	46600	14500	1.15
144.4^c	100	43800	14500	1.11

[a] $[TMSOTf]_0 = 0.90$ mmol, $[Me_2S]_0 = 30$ mmol, reaction temp −30 °C, reaction time 5–6 h. Polymerization method A was used. [b] Polymerization was carried out in *n*-hexane (125 mL). [c] Polymerization was carried out in methylene chloride (125 mL).

Table II
Polymerization of IBVE by $(CF_3SO_2)_2O$ in CH_2Cl_2[a]

run	$(CF_3SO_2)_2O$, mmol	H_2O, mmol	M_n GPC	M_n calcd	M_w/M_n
1	1.0		1400	3000	1.27
2	1.0		11400	3000	1.31
3	1.0		10900	3000	1.00
4^b	1.0	1.0	3620	3000	1.92
5^b	1.0	1.0	3620	3000	2.14

[a] Polymerization method A was used. Reaction temp −30 °C, reaction time 5 h, [IBVE] = 60 mmol, $[Me_2S]$ = 30 mmol, 125 mL of solvent; conversions were quantitative. [b] Water was added and allowed to react 10 min after addition of the TfOTf.

Polymers of IBVE were formed in a triflic anhydride (TfOTf)/Me_2S/CH_2Cl_2 polymerization system, in the absence of any added H_2O or other proton sources (Table II). Assuming that TfOTf by itself is incapable of initiating polymerization, formation of polymer may be regarded as supporting evidence for the presence of water that would generate TfOH in the reaction mixture. In view of the high $[Me_2S]/[TfOTf]$ ratio used, polymers with narrow MWDs were expected. The somewhat broader MWD obtained might suggest that the rate of the in situ conversion of TfOTf to TfOH under the conditions applied was not sufficiently high compared to that of propagation.

Polymerization in the Presence of 2,6-Di-*tert*-butyl-4-methylpyridine, a Proton Trap. That the presence of traces of H_2O was responsible for the polymerization has been confirmed by attempting to carry out the polymerization in the presence of the proton trap DTBMP. DTBMP reacts readily with a proton, but not with Lewis acids such as boron trifluoride or trimethylsilyl cation. Thus any initiation by proton sources present in the system would be quenched. The application of DTBMP in the study of cationic polymerizations is well documented.[16-18] The results of representative experiments (summarized in Table III) show that, in the presence of DTBMP, initiation of the polymerization of IBVE by TMSOTf/Me_2S does not occur or is very slow up to 0 °C.

Injection of triflic acid into a mixture of monomer and the proton trap (Table III, run 1) gave polymer. It therefore appears that both the initiation by TfOH and its reaction with the proton trap are of comparable rates. Likewise, when TMSOTf is added to the monomer solution (run 2), the triflic acid generated by reaction with impurity

Table III
Polymerization of IBVE by Trimethylsilyl Triflate in the Presence of a Proton Trap[a]

run	temp, °C	solvent	conv, %	M_w/M_n	M_n GPC	M_n calcd[b]	method[c]
1[d]	-40	CH_2Cl_2	54	1.36	4510	4900	B
2	-30	CH_2Cl_2	19	1.16	39600	1700	B
3	-40	CH_2Cl_2	~0				A
4	-30	CH_2Cl_2	4	1.32	33800	360	A
5	-15	CH_2Cl_2/Me_2S (1/1 vol)	~0				A
6	0	Me_2S	~0				A
7[e]	0	CH_2Cl_2	100	6.07	5640	8900	A

[a] $[IBVE]_0$ = 0.76 M (10 vol %), $[TMSOTf]_0$ = 8.6 mM, $[Me_2S]_0$ = 0.26 M, [DTBMP] = 13 mM, reaction time 2 h, 125 mL of solvent. [b] Calculated from the weight of the polymer divided by $[TMSOTf]_0$. [c] A, monomer was added last; B, TMSOTf was added last. [d] Triflic acid was used as an initiator under the same condition. [e] The polymerization was carried out in the absence of Me_2S.

levels of water reacts with either the monomer, the proton trap, or both. However, if the TMSOTf is added *first* to the DTBMP solution followed by the monomer, the generated triflic acid is consumed by the proton trap and initiation of polymerization is thus minimized (runs 3–6). TMSOTf does initiate IBVE at 0 °C if no Me_2S is present. The polydispersity however is broad (run 7).

Effect of Added ROH (R = H, Et) on the IBVE/TMSOTf/Me_2S System. To further examine the effect of active hydrogen impurities on the course of the polymerization, water and also ethanol were added in molar and excess molar amounts compared to the TMSOTf. The M_n values of the polymers obtained were inversely proportional to the molar concentration of the active hydrogen compound. The slope of the plot for water is twice that of the plot for ethanol, showing that both hydrogens from the water are involved (see Figure 2 for a plot of $1/M_n$ versus [ROH]). On extrapolation to zero additive, the intercept is M_n = 9000 while the M_n value calculated according to eqs 2 and 3, where [ROH] = 0, is 7200.

for H_2O

$$M_n(\text{calc}) = \frac{M_1[\text{M}]_0}{[\text{TMSOTf}]_0 + 2[\text{H}_2\text{O}]_0} \qquad (2)$$

for EtOH

$$M_n(\text{calc}) = \frac{M_1[\text{M}]_0}{[\text{TMSOTf}]_0 + [\text{EtOH}]_0} \qquad (3)$$

where M_1 is the formula weight of monomer.

$$2\text{Me}_3\text{SiOTf} + \text{H}_2\text{O} \rightarrow \text{Me}_3\text{SiOSiMe}_3 + 2\text{TfOH} \qquad (4)$$

These results indicate that 80% of the TMSOTf has been hydrolyzed by adventitious water (eq 4). The M_n's calculated according to eqs 2 and 3 were in all cases lower than the M_n's (GPC) and the M_w/M_n's increased as the amount of active hydrogen compound was increased (see Table IV). These factors indicate that some chain transfer is occurring by formation of aldehyde and acetal end groups as well as triflic acid according to eqs 5 and 6. Equilibration between acetal and sulfonium end groups (eq 7) would permit further chain growth. The above results point to a surprising insensitivity of the TfOH/Me_2S polymerization system to protonic impurities. Intuitively one might have expected that molar concentrations of water higher than TfOH concentrations would have quenched the polymerization. The reaction of active hydrogen impurities with monomer as shown in eqs 8 and 9 is a possible way to, in effect, remove them.

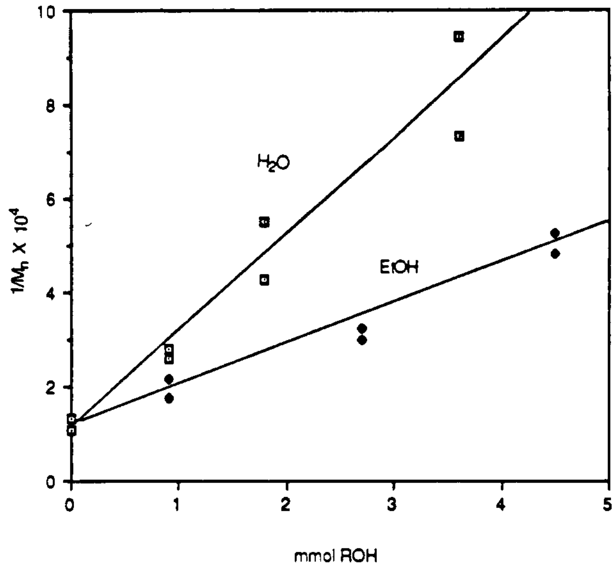
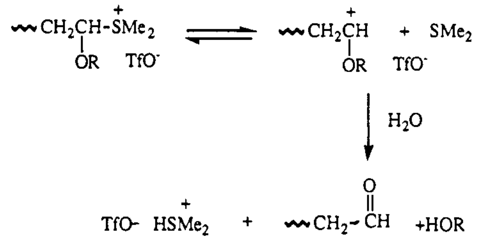


Figure 2. Effect of added ROH (R = H, Et) on the IBVE/TMSOTf/Me_2S polymerization system.

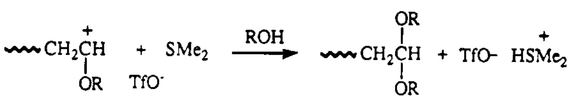
Table IV
Effect of Added ROH (R = H, Et) on the IBVE/TMSOTf/Me_2S Polymerization System[a]

R	[ROH], mmol	[TMSOTf + ROH], mmol	M_n GPC	M_n calcd	M_w/M_n
		0.9	8400	7200	1.04
H	0.9	1.8	3700	2400	1.27
H	1.8	2.7	2100	1200	1.66
H	3.6	4.5	1200	800	2.86
Et	0.9	1.8	5200	3600	1.07
Et	2.7	3.6	3200	1800	1.51
Et	4.5	5.4	2000	1200	1.83

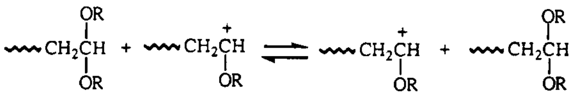
[a] Average of two experiments. [IBVE] = 65 mmol, $[Me_2S]$ = 30 mmol, reaction temp -30 °C, solvent CH_2Cl_2 (125 mL), reaction time 5 h. Polymerization method A was used. Yields of the polymers were quantitative.



$$\sim\!CH_2\underset{OR}{C}H\text{-}\overset{+}{S}Me_2\ TfO^- \rightleftharpoons \sim\!CH_2\underset{OR}{\overset{+}{C}H}\ TfO^- + SMe_2 \xrightarrow{H_2O} TfO^-\ H\overset{+}{S}Me_2 + \sim\!CH_2\text{-}\overset{O}{\overset{\|}{C}H} + HOR \qquad (5)$$



$$\sim\!CH_2\underset{OR}{\overset{+}{C}H}\ TfO^- + SMe_2 \xrightarrow{ROH} \sim\!CH_2\underset{OR}{\overset{OR}{C}H} + TfO^-\ H\overset{+}{S}Me_2 \qquad (6)$$



$$\sim\!CH_2\underset{OR}{\overset{OR}{C}H} + \sim\!CH_2\underset{OR}{\overset{+}{C}H} \rightleftharpoons \sim\!CH_2\underset{OR}{\overset{+}{C}H} + \sim\!CH_2\underset{OR}{\overset{OR}{C}H} \qquad (7)$$

$$\text{CH}_2\text{=CHOR} + \text{ROH} \rightarrow + \text{CH}_3\text{CH(OR)}_2 \qquad (8)$$

$$2\text{CH}_2\text{=CHOR} + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{CHO} + \text{CH}_3\text{CH(OR)}_2 \qquad (9)$$

Possible Initiation of IBVE Polymerization with TMSOTf. The proton trap experiments show that the main route to polymer involves initiation with triflic acid

Table V
Polymerization of IBVE by Trimethylsilyl Triflate/Carbonyl Compounds in the Presence of a Proton Trap[a]

1^b R, R′	temp, °C	conv, %	M_w/M_n	M_n			method[e]
				GPC	calcd[c]	NMR[d]	
H, CH_3 (8)	-40	18	1.47	4500	1600	4800	A
H, Ph (8)	-40	46	1.31	6300	4100	6500 (4400)	A
H, Ph (1)	-30	100	1.26	9580	9000	12600 (8970)	B
H, Ph (8)	-30	100	1.41	8650	9000	12300	B
CH_3, Ph (8)	-30	53	1.23	28700	4800		B
CH_3, CH_3 (8)	-30	75	1.29	22800	6800	50700	B

[a] $[IBVE]_0$ = 0.76 M (10 vol %), $[TMSOTf]_0$ = 8.6 mM, $[Me_2S]$ = 0.26 M, [DTBMP] = 13 mM, reaction time 2 h, solvent CH_2Cl_2 (125 mL). [b] Initial molar ratio of the carbonyl compound to the triflate is in parentheses. [c] Calculated from the weight of the polymer divided by $[TMSOTf]_0$. [d] M_n based on the phenyl group integration is in parentheses. [e] A, Monomer was added last; B, TMSOTf was added last.

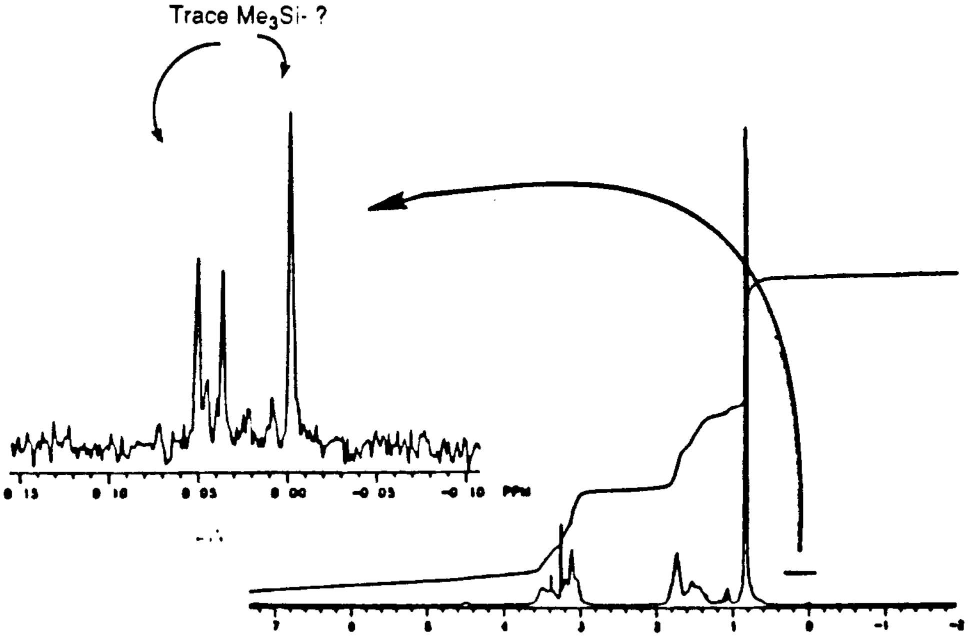
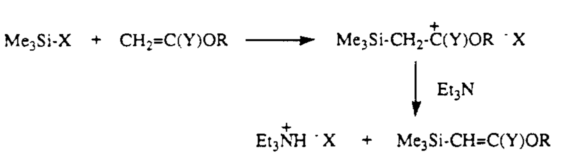


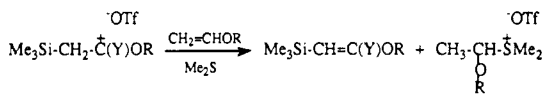
Figure 3. Proton NMR of poly(IBVE) (M_n = 1480, M_w/M_n = 1.10) obtained from the IBVE/TMSOTf/Me_2S/CH_2Cl_2 polymerization system.

formed by hydrolysis of the TMSOTf. However, TMSOTf initiation, although much slower, may be producing some polymer (see run 4, Table III). In addition, a small amount of Me_3SiC structural units show up in the proton NMR of low molecular weight polymers formed by initiation with TMSOTf (Figure 3). Silylation of $CH_2{=}C(R')OR$ (R = Me, Bu; R′ = Me, Et) and $CH_2{=}CHOR$ (R = Et, Bu) by Me_3SiI,[19] and of $CH_2{=}C(OR)_2$ by TMSOTf[20] (both cases in the presence of Et_3N), to give the corresponding β-trimethylsilyl derivatives in high yields, has been recently reported. These results clearly show that a positively charged intermediate $Me_3SiCH_2\text{-}C^+(Y)OR$ (Y = H, R, OR) can be formed by an electrophilic attack of Me_3Si^+ on an electron-rich double bond (eq 10).



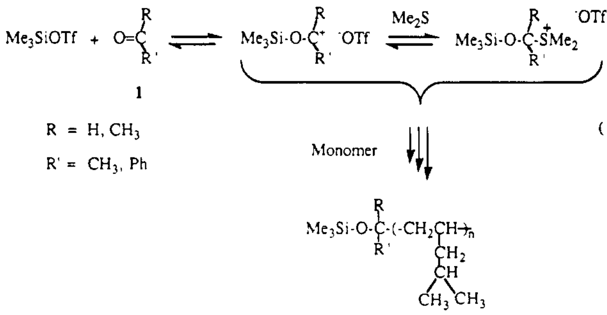
$$\begin{tikzcd} \mathrm{Me_3Si\text{-}X + CH_2{=}C(Y)OR} \arrow[r] & \mathrm{Me_3Si\text{-}CH_2\text{-}\overset{+}{C}(Y)OR\ {}^{-}X} \arrow[d, "\mathrm{Et_3N}"] \\ & \mathrm{Et_3\overset{+}{N}H\ {}^{-}X + Me_3Si\text{-}CH{=}C(Y)OR} \end{tikzcd} \quad (10)$$

A β-proton elimination from the acidic cationic intermediate (C–H bond α to Si)[21] formed in the electrophilic attack of TMSOTf on the vinyl ether, and its transfer to the monomer, might provide one explanation for the absence of Me_3Si groups in the polymers obtained (eq 11). If so, the amount is small since $Me_3SiCH{=}CHOR$ (the other product in eq 11) was not isolated, nor could it be detected by ^{29}Si NMR.



$$\mathrm{Me_3Si\text{-}CH_2\text{-}\overset{+}{C}(Y)OR\ {}^{-}OTf \xrightarrow[Me_2S]{CH_2=CHOR} Me_3Si\text{-}CH{=}C(Y)OR + CH_3\text{-}\underset{OR}{CH}\text{-}\overset{+}{S}Me_2\ {}^{-}OTf} \quad (11)$$

Polymerization by Trimethylsilyl Triflate/Carbonyl Compounds. This polymerization system was studied in CH_2Cl_2 at low temperatures in the presence of a proton trap, DTBMP (Table V). The proton NMR of the polymer obtained by initiation with TMSOTf/acetaldehyde shows the existence of a Me_3SiO group at δ ~0.10 ppm (Figure 4). This suggests that TMSOTf reacts first with the carbonyl compound to generate a carbocation, which in turn initiates the polymerization (eq 12).



(12)

Electrophilic additions of $Me_3Si\text{-}X$ (X = I, Br, N_3, CN, etc.) to aldehydes and ketones are well-known.[22] The products are the corresponding α-[(trimethylsilyl)oxy]-

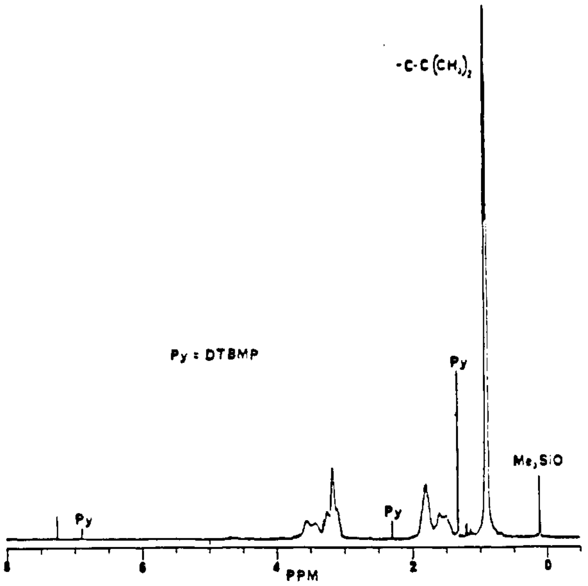


Figure 4. Proton NMR of poly(IBVE) (M_n = 4,500, M_w/M_n = 1.47) obtained from the IBVE/TMSOTf/CH_3CHO/Me_2S/CH_2Cl_2 polymerization system.

alkyl derivatives, most of which are relatively stable compounds either in bulk or in solution. Due to the very low nucleophilicity of TfO^-, the carbocationic intermediate formed by addition of TMSOTf to RR′C=O is very reactive and is capable of initiating the polymerization of vinyl ether even in the presence of Me_2S. TMSOTf/R_2C=O has also been reported to promote polymerization of tetrahydrofuran.[23]

The polymerization was faster when benzaldehyde was used compared to the other carbonyl compounds: acetaldehyde, acetone, and acetophenone. With acetone or acetophenone, the initiation efficiency was quite low, and the proton NMR showed only a trace of Me_3Si resonance (at $\delta \sim 0.07$ ppm). The reproducibility was poor. For the polymers obtained with aldehydes at −40 °C, the M_n (by GPC) agreed quite well with the M_n obtained from the corresponding proton NMR (runs 1 and 2). That the observed M_n is greater than M_n(calc) (runs 1–3) may indicate that the initiation reaction is slower than propagation. This may have also contributed to the observed broadening of the MWD (M_w/M_n = 1.23 - 1.47). It should be noted that two different values of M_n based on proton NMR spectra were obtained for polymers formed in polymerizations conducted in the presence of benzaldehyde (runs 2 and 3). The M_n values based on the phenyl group were slightly lower than those based on the Me_3Si group. This indicates a possible incorporation of benzaldehyde into the polymer backbone. The FTIR spectra of the polymers did not show any absorption peak corresponding to a hydroxyl group, which could have been generated by a partial hydrolysis of the Me_3SiO group.

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Registry No. IBVE, 109-53-5; poly(IBVE) (homopolymer), 9003-44-5; TMSOTf, 27607-77-8; DTBMP, 38222-83-2; H_2O, 7732-18-5; EtOH, 64-17-5; CH_3CHO, 75-07-0; PhCHO, 100-52-7; PhC(O)CH_3, 98-86-2; Me_2S, 75-18-3; $(CF_3SO_2)_2O$, 358-23-6; $H_3CC(O)CH_3$, 67-64-1.