can become more complicated. We illustrate this with homopolymerization of A_3 in which one of the A units reacts more slowly; denote this unit as A′. In this case AA bonds form at a rate proportional to A × A, AA′ bond proportional to A × A′, and A′A′ bonds proportional to A′ × A′. Thus the kinetics can be described by

$$dA_t/dt = -2r_{00}A_t^2 - r_{01}A_tA'_t \qquad (A15)$$

$$dA'_t/dt = -r_{01}A_tA'_t - 2r_{11}A'_t{}^2$$

$$dAA_t/dt = +r_{00}A_t^2$$

$$dAA'/dt = +r_{01}A_tA'_t$$

$$dA'A'_t/dt = r_{11}A'_t{}^2$$

These equations must be solved numerically for the five quantities A_t, A'_t, AA_t, AA'_t, and $A'A'_t$. Note that $A_t + 2AA_t + AA'_t = A_0$ and $A'_t + AA'_t + 2A'A'_t = A'_0$. Let $q_{00}(t)$ equal the proportion of A units which have reacted with other A units and $q_{01}(t)$ equal the proportion of A units which have reacted with A′ units; define $q_{11}(t)$ and $q_{10}(t)$ analogously. Then

$$q_{00}(t) = 2AA_t/A_0$$

$$q_{01}(t) = AA'_t/A_0$$

$$q_{11}(t) = 2A'A'_t/A'_0 \qquad (A16)$$

$$q_{10}(t) = AA'_t/A'_0$$

$$A_t = \frac{2AA_t + 2AA' + 2A'A'}{A_0 + A'_0}$$

It is possible to numerically calculate the extent of reaction vector

$$(q_{00}, q_{01}, q_{11}, q_{10}) \qquad (A17)$$

as a function of p_A. These values can be used in eq 23.

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Polymerization of Tetrahydrofuran by Proton Acids

G. Pruckmayr* [1] **and T. K. Wu**[2]

Chemicals, Dyes and Pigments Department and Plastic Products and Resins Department,
E. I. du Pont de Nemours & Company, Inc., Experimental Station,
Wilmington, Delaware 19898.

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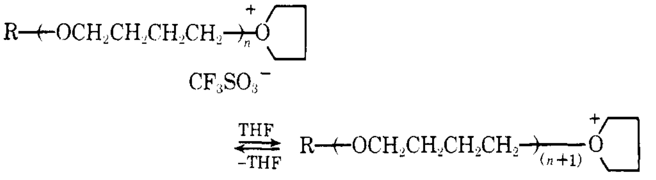
ABSTRACT: The mechanism for the polymerization of tetrahydrofuran with strong proton acid initiators has been investigated. Nonhydrolyzable acids such as trifluoromethanesulfonic acid lead to very high molecular weight polymer by a combination of chain coupling–ring opening steps. Hydrolyzable proton acids, such as the halosulfonic acids, lead to polymeric species of lower molecular weight through mono- and dialkyl sulfate formation. Sulfate formation is normally irreversible and slower than chain propagation, causing molecular weights to go through a maximum. Such polymerizations are not "living", but "slowly dying", the rate of termination depending on the polymerization conditions.

The equilibrium polymerization of tetrahydrofuran (THF) with alkyl esters of trifluoromethanesulfonic acid (triflic acid) or fluorosulfonic acid as initiators has recently been investigated in great detail.[3–6] These systems are generally considered to be "living" polymerizations, although chain transfer and cyclization reactions do occur.[7]



Much less has been reported on polymerization of THF with free proton acid initiators.[8] The mechanism of polymerization with proton acids is less straightforward than with initiation by alkyl esters, and some contradictory papers have been published over the years.[9–11]

Chlorosulfonic acid and fluorosulfonic acid were among the earliest examples of catalysts for the cationic ring opening polymerization of THF.[12] Meerwein reported the formation of alkyl sulfate esters during polymerization with chlorosulfonic acid initiation and discussed the necessity for hydrolysis of such esters in order to obtain hydroxy terminated polymer.[13]

The present paper investigates in more detail the alkyl sulfate ester formation during polymerization of THF and

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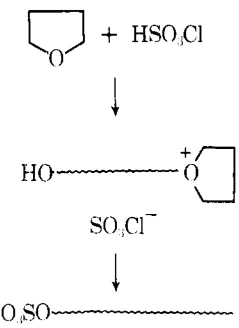


compares polymerizations initiated by hydrolyzable acids, such as halosulfonic acids, with polymerizations initiated by nonhydrolyzable acids, such as triflic acid.

Experimental Section

Dry tetrahydrofuran distilled under N_2 and stored over metallic sodium was used as the monomer. Trifluoromethanesulfonic acid and fluorosulfonic acid were distilled under N_2 at atmospheric pressure prior to use. All other reagents or solvents are commercially available in reagent grade purity and were used without further purification.

Polymerizations were carried out by weighing reactants and solvent into Pyrex polymerization tubes, sealed with rubber serum caps. The reactants were mixed thoroughly for 10 s on a mechanical vortex shaker, and the polymerization tube was immediately placed into a constant temperature bath, which controlled the temperature to ±0.2 °C. ^{1}H NMR spectra were recorded on Varian HA-100 and HR-220 MHz spectrometers and fluorine NMR spectra on a Varian XL-100 spectrometer. Teflon liners were used in all polymerizations containing $HFSO_3$ in order to prevent side reactions of HF with the glass walls.

Conversion and degree of polymerization were calculated from 100 or 220 MHz NMR spectra, using the intensity of the monomer signals at 3.75 and 1.83 ppm, the polymer signals at 3.40 and 1.60 ppm, and the end group signals at the chemical shifts discussed below. Perdeuterated solvents were used for all NMR experiments.

Tetramethylsilane (Me_4Si) was used as internal or external reference, and proton chemical shifts are reported in ppm downfield from Me_4Si. Fluorine chemical shifts are reported in ppm from trichlorofluoromethane as internal standard.

For molecular weight determination of hydroxy terminated polymer by IR spectroscopy, the polymerization mixture was quenched with water, and unreacted monomer was removed by distillation. Heating was continued until hydrolysis was complete. The polymer was extracted with toluene, and the toluene solution was neutralized with 0.5 N NaOH. Solvent and water were removed by distillation under atmospheric pressure and the residual polymer was dried for 2 h at 80 °C (0.2 mm) and filtered. The molecular weight of the polymer was obtained by comparing the absorbance of the -OH polymer end groups at 3500 cm^{-1} with the -OH absorbance of known standard polymer samples.[14]

Trifluoro acetate derivatives were prepared by adding a twofold excess of trifluoroacetic anhydride to a 10% solution of the polymer in $CDCl_3$. The solution was allowed to stand overnight at room temperature which resulted in complete trifluoroacetylation of the -OH groups. Molecular weights were calculated from the ratio of the acetate methylene protons CF_3COOCH_2∼∼ (4.25 ppm) to the total α protons of the polymer.[14]

Results and Discussion

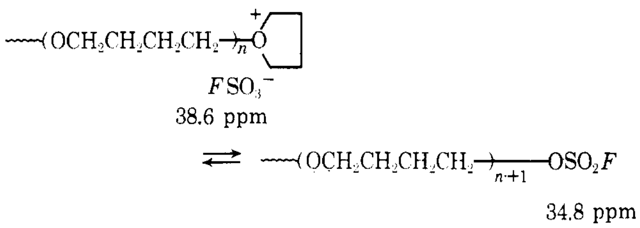
In our previous publication, we proposed a mechanism for the polymerization of THF initiated by triflic acid.[14] The proposed reaction scheme involves a ring-opening/chain-coupling mechanism, resulting in the formation of both macrocyclic oligomers and very high molecular weight linear polymers. The growing polymer molecules carry hydroxy and oxonium sites at opposite ends of the chain, which can participate in inter- and intramolecular coupling reactions. Polymer molecular weight in these cases is not a simple function of catalyst concentration. We believe that this is a general mechanism for the reversible polymerization of THF catalyzed by nonhydrolyzable proton acids.

The mechanism of THF polymerization with hydrolyzable proton acid initiators such as chlorosulfonic acid or fluorosulfonic acid is complicated by the possibility of secondary reactions, as pointed out earlier.[15]

The most suitable analytical technique for studying the mechanism of these systems is NMR spectroscopy, particularly a combination of fluorine and proton NMR techniques. Such a combination was essential for a correct assignment of signals.

^{13}F NMR methods have been used earlier to study the different species in equilibrium in THF/alkyl fluosulfate systems;[3,15] a signal at 38.6 ppm was assigned to the fluorosulfate anion FSO_3^-, and a signal at 34.5 ppm to the covalent macroester species, ∼∼CH_2OSO_2F.[15] Using similar techniques, we studied the reaction of THF with fluorosulfonic acid in a polar solvent, CH_3NO_2, and in a nonpolar solvent, CH_2Cl_2.

In either solvent, a single large signal is detected immediately after mixing the monomer solution and the initiator. This signal was assigned to the FSO_3^- anion of secondary and tertiary oxonium ions, as shown by comparison with the ^{19}F signal of $HFSO_3$ in diethyl ether, where fluorosulfate anion is the only type of fluorine present. Soon, a second weak signal appeared at 34.6 ppm which was assigned to the covalent fluorosulfate ester ∼∼CH_2OSO_2F, as described previously.[15] At this stage of reaction, both ionic and covalent end groups are therefore present in the polymerization.



A third small signal was detected at −191.0 ppm, which rapidly increased in intensity. On scale expansion, this signal was found to be quite broad, indicating participation in some exchange reaction. It was also nonstationary, in contrast to the other signals, and slowly moved downfield to −179.2 ppm during the polymerization (Figure 1). This signal was identi-

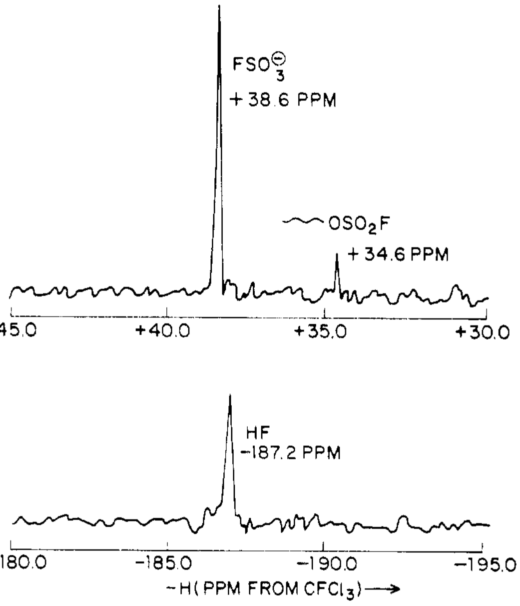


Figure 1. ^{19}F-NMR spectrum (94.1 MHz) of THF/CH_2Cl_2/$HFSO_3$ (mol ratio = 11.58/3.27/1.00) after 2 h at 25 °C. (Spectral areas without F signals have been omitted.)

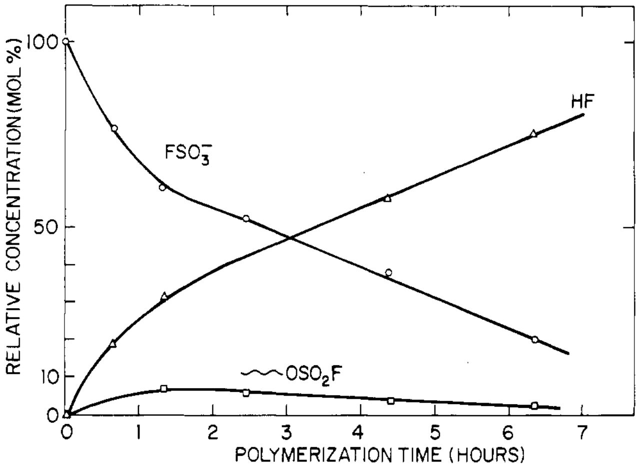


Figure 2. Relative concentration of F species during the polymerization of $THF/CH_2Cl_2/HFSO_3$ (mol ratio = 11.58/3.27/1.00) at 25 °C.

fied as HF, and the assignment was verified by addition of a small amount of free HF to the polymerization mixture.

During the course of the polymerization the concentration of fluorosulfate anion rapidly decreases, the concentration of covalent fluorosulfate ester goes through a shallow maximum and then also decreases toward zero, while the intensity of the signal identified as HF approaches 100% after polymerization times of 10 h or more at room temperature, i.e., in polymerization mixtures which appeared to be "equilibrated" (Table I). The disappearance of FSO_3^- counterion, the formation of HF, and the concentrations of macroester fluorine are graphically shown in Figure 2. It is seen that macroester fluorine represents only a very small fraction of the total fluorine at any time even in solvents of low polarity, such as CH_2Cl_2 (Table II), while most of the fluorine is present either as FSO_3^- or, later on, as HF.

In anhydrous systems, HF can be generated by the following possible reactions, all involving polymer end groups:

$$\sim\!\sim CH_2OH + HFSO_3 \rightleftharpoons \sim\!\sim CH_2OSO_3H + HF \qquad (1)$$

$$\begin{array}{ccc} \sim\!\sim CH_2OH + HFSO_3 \rightleftharpoons \sim\!\sim CH_2OSO_2F & + & H_2O \\ \swarrow & & \downarrow{\scriptstyle HFSO_3} \\ \sim\!\sim CH_2OSO_3H + HF & & H_2SO_4 + HF \end{array} \qquad (2)$$

$$\sim\!\sim CH_2OSO_2F + HOCH_2\sim\!\sim \rightleftharpoons \sim\!\sim CH_2OSO_3CH_2\sim\!\sim + HF \qquad (3)$$

The formation of HF should therefore be accompanied by an increase in the concentration of alkyl sulfuric acid and/or dialkyl sulfate groups, which should be readily observable by ^1H NMR techniques. This has now been verified.

The chemical shift of the α-methylene protons of alkyl sulfates was estimated from the spectra of diethyl sulfate and dibutyl sulfate as 4.33 ppm (Table III). Since the chemical shift of butylsulfuric acid, prepared from *n*-butyl alcohol and $ClSO_3H$, is 4.35 ppm in $CDCl_3$, a mixture of dibutyl sulfate and butylsulfuric acid would be expected to give a distorted triplet at ca. 4.3 ppm because of the two superimposed signals. Such a triplet is indeed observed in the polymerization mixture of THF/FSA in polar or nonpolar solvents (Figure 3).

Figure 3 shows a 60-MHz ^1H NMR spectrum of a mixture of $THF/HFSO_3$ in benzene, after a polymerization time of 2 h. The lowest field signal at 4.85 ppm (A in Figure 3) has earlier been assigned to the α-methylene protons of a tertiary oxonium ion.[5,15] The signal due to the covalent macroester at 4.6 ppm is quite weak in acid catalyzed polymerizations and can only be observed in nonpolar solvents at high field strength. Figure 4 shows the 220 MHz α-proton NMR region of a $THF/HFSO_3$ polymerization mixture after 2.5 h, in a nonpolar solvent ($CDCl_3$). The signal due to the α-methylene protons of the macroester is observable as a small, sharp triplet at 4.62 ppm. The signal intensity ratio of the six oxonium methylene protons to the two α-methylene protons of the fluorosulfate ester groups is about 3/1, i.e., there are equal numbers of tertiary oxonium ions and fluorosulfate ester groups present under these conditions. Since ^{19}F-NMR spectra show a much higher concentration of FSO_3^- than of $\sim\!\sim CH_2OSO_2F$ after a polymerization time of 2.5 h (Tables I and II), we conclude that there is a higher concentration of secondary than of tertiary oxonium ions present in the polymerization mixture, and that therefore only a fraction of the acid initiator was consumed at this point.

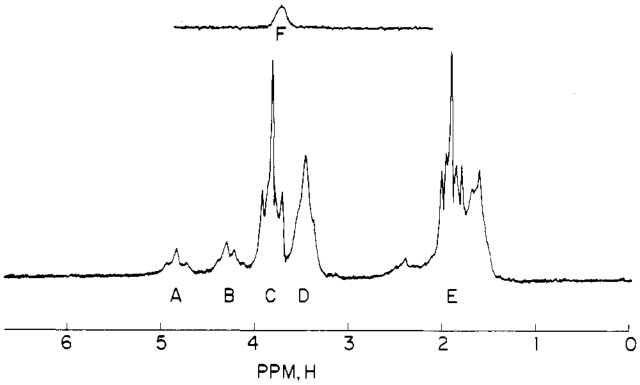
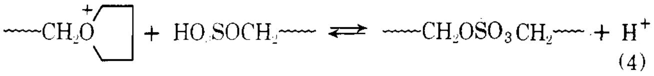


Figure 3. H-NMR spectrum (60 MHz) of $THF/C_6H_6/HFSO_3$ (mol ratio = 6.90/3.17/1.00) after 2 h at 35 °C: A–D = α-proton signals (A = oxonium ion, B = alkyl sulfates, C = THF, D = PTME); E = β-proton signals; F = acid proton (17.1–11.6 ppm).

The multiplet at 4.3 ppm (B in Figure 3), now assigned to alkyl sulfates based on the model compounds described above, is resolved at high field strength into a partially superimposed pair of triplets (Figure 4). During the course of the polymerization, these signals become gradually stronger as more alkyl sulfates are formed and the polymer system deviates more and more from a reversible equilibrium. The rate of sulfate formation strongly depends on temperature: at low temperatures, sulfate formation is slow and the system behaves like a "living" system for a longer period, while at higher temperatures, sulfate formation is fast and the polymerization system loses its living character very fast (Figure 5).

It is of interest to study the formation of alkyl sulfuric acid end groups and of dialkyl sulfate groups separately. In the initial stages of the polymerization there should be mostly alkyl sulfuric acids present, formed according to eq 1. In the later stages more and more dialkyl sulfate groups should be formed according to eq 3 and 4



$$\sim\!\sim CH_2\overset{+}{O}\langle\, + HO_3SOCH_2\sim\!\sim \rightleftharpoons \sim\!\sim CH_2OSO_3CH_2\sim\!\sim + H^+ \qquad (4)$$

This is in agreement with experimental evidence. The signal due to the α-methylene protons of the alkyl sulfuric acid is shifted upfield on addition of a basic solvent, e.g., deuterated DMF, while the dialkyl sulfate signal is not shifted (Figure 6). This technique allows separate determination of these species and demonstrates the slow increase in the concentration of dialkyl sulfate groups (Table IV).

Conversion, molecular weight of the polymer fraction, formation of oxonium ion, and formation of ester groups are tabulated in Tables V and VI and shown graphically in Figure 7. In the initial stages of the polymerization, particularly at low temperatures, slow initiation and interchain coupling of hydroxy chain ends with oxonium ion sites lead to very high

Table I
Concentration of F-Containing Species in the Polymerization Mixture of THF/HFSO$_3$ in CD$_3$NO$_2$[a]

Polymerization time, h	Concn, mol %[b] FSO$_3^-$ (+37.6 ppm)	$\sim$OSO$_2$F (+34.1 ppm)	HF	Chemical shift of HF (ppm from int. CFCl$_3$)
0.00	100.0	0.0	0.0	(−191.0)
0.75	66.9	2.5	30.6	(−190.4)
1.33	58.0	2.0	40.0	(−189.5)
2.40	46.7	1.7	51.6	(−188.8)
4.60	30.8	1.0	68.1	(−186.8)
7.50	15.9	<0.1	84.0	(−185.0)
24.00	0.0	0.0	100.0	(−179.2)

[a] Composition of polymerization system, in molar ratios: THF/CD$_3$NO$_2$/HFSO$_3$ = 11.58/4.34/1.00. Polymerization temperature, 25 °C. [b] Concentrations as percent of all F signals detected.

Table II
Concentration of F-Containing Species in the Polymerization Mixture of THF/HFSO$_3$ in CH$_2$Cl$_2$[a]

Polymerization time, h	Concn, mol %[b] FSO$_3^-$ (+38.6 ppm)	$\sim$OSO$_2$F (+34.6 ppm)	HF	Chemical shift of HF (ppm from int. CFCl$_3$)
0.00	100.0	0.0	0.0	(−191.6)
0.66	76.9	4.2	18.8	(−189.6)
1.33	59.9	6.9	33.1	(−188.6)
2.50	52.8	4.8	42.3	(−187.2)
4.40	39.8	3.7	56.5	(−185.6)
6.33	20.5	3.0	76.5	(−184.0)
24.00	0.0	0.0	100.0	(−179.0)

[a] Composition of polymerization system, in molar ratios: THF/CH$_2$Cl$_2$/HFSO$_3$ = 11.58/3.27/1.00. Polymerization temperature, 25 °C. [b] Concentrations as percent of all F signals detected.

Table III
Chemical Shift of the α-Methylene Protons of Alkyl Sulfate Model Compounds (CDCl$_3$, internal Me$_4$Si)

$CH_3CH_2OSO_3CH_2CH_3$	4.36 ppm
$CH_3(CH_2)_3OSO_3(CH_2)_3CH_3$	4.30 ppm
$CH_3(CH_2)_3OSO_3H$	4.31 ppm
$CH_3(CH_2)_3OSO_2Cl$	4.61 ppm

molecular weight polymer, similar to the polymer obtained from triflic acid catalysis.[14] As the hydroxy end groups are converted to the less nucleophilic sulfate ester groups, the molecular weight distribution changes and the number average molecular weight decreases due to formation of new oligomeric chains and possibly also by depolymerization. The molecular weight therefore goes through a maximum, which is determined by the polymerization conditions: the lower the polymerization temperature, the higher will be this maximum,[10] and the closer this system will initially resemble the THF/triflic acid case.

The proposed mechanism also explains the changing chemical shift of the acid proton, from about 16.5 ppm at the start to about 11.0 ppm at the end of the polymerization, depending on the polarity of the medium. The chemical shift of the acid proton depends on acid strength,[16] and as the strong acid HFSO$_3$ is slowly converted into the weaker acids HF and $\sim$CH$_2$OSO$_3$H, the signal shifts upfield and becomes stationary at the end of this transformation. No analogous transformation occurs with nonhydrolyzable acids such as trifluoromethanesulfonic acid, and the chemical shift of the acid proton in such a system remains unchanged at about 16.3 ppm throughout the entire polymerization.

The mechanism of the polymerization of THF with hydrolyzable strong proton acids is therefore more complicated than previously assumed. It involves the different end group reactions discussed earlier, which occur simultaneously and/or consecutively. In the final stages of the polymerization, polymer with one or more sulfate groups per molecule will be present. Since the concentrations of tertiary oxonium ions and fluorosulfate macroester approach zero, the system is no

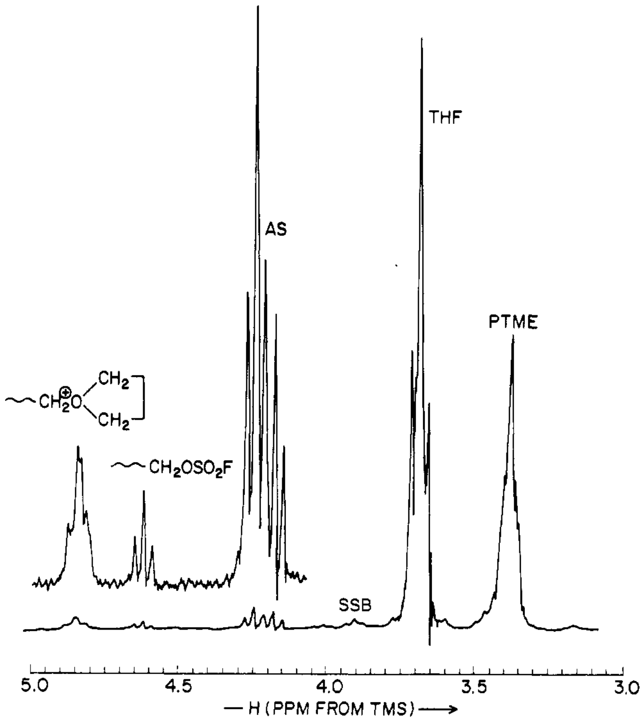


Figure 4. Partial H-NMR spectrum (220 MHz) of THF/CDCl$_3$/HFSO$_3$ (mol ratios = 11.58/2.31/1.00) after 2.5 h of polymerization time at 25 °C (AS = alkyl sulfate; PTME = polytetramethylene ether; SSB = spinning side band).

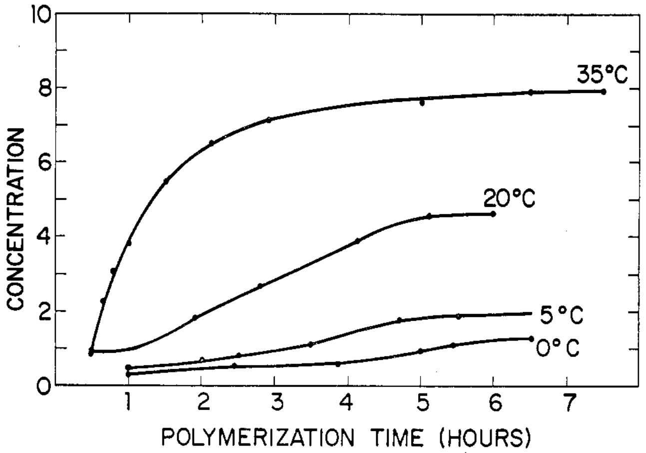


Figure 5. Rate of alkyl sulfate formation in THF/C_6H_6/$HFSO_3$ (mol ratio = 6.90/3.17/1.00). Concentration of alkyl sulfate methylene protons as percent of total α-proton signal.

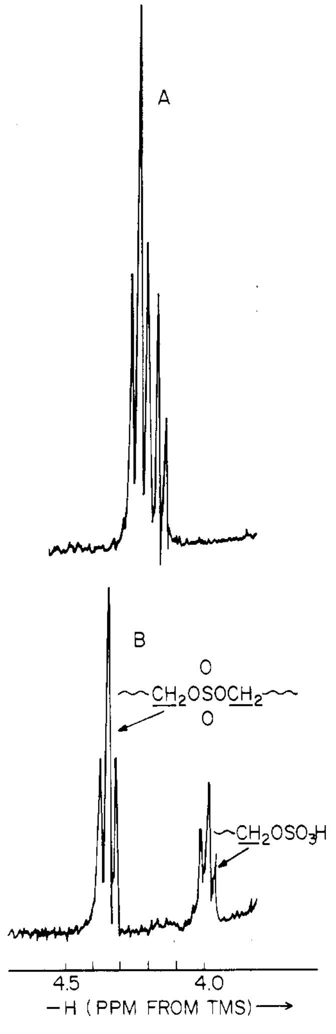


Figure 6. Partial H-NMR spectrum (220 MHz) of the polymerization mixture of THF/$HFSO_3$ (mol ratio = 11.58/1.00) in $CDCl_3$ (A) and in $CDCl_3$/$(CD_3)_2NCDO$ (B).

Table IV
Concentration Ratios[a] of Dialkyl Sulfate to Alkyl Sulfuric Acid Groups in a THF/HFSO$_3$ Polymerization in CDCl$_3$[b] (100 MHz ^{1}H NMR Data, in DMF-d_7)

Polymerization time,[c] h	$\sim CH_2OSO_3CH_2\sim$ (4.3 ppm)	$\sim CH_2OSO_3H$ (4.0 ppm)
1.9	0.22	0.78
3.0	0.43	0.57
5.6	0.49	0.51
7.0	0.52	0.48
24.0	0.99	<0.01

[a] The concentrations have been corrected to account for the different number of α protons. [b] Composition of polymerization system, in molar ratios: THF/$CDCl_3$/$HFSO_3$ = 11.58/2.31/1.00. Polymerization temperature, 25 °C. [c] The polymerization was carried out in Teflon-lined NMR tubes. In glass tubes a higher ratio of alkylsulfuric acid end groups is found caused by hydrolysis due to reaction of HF with the glass walls.

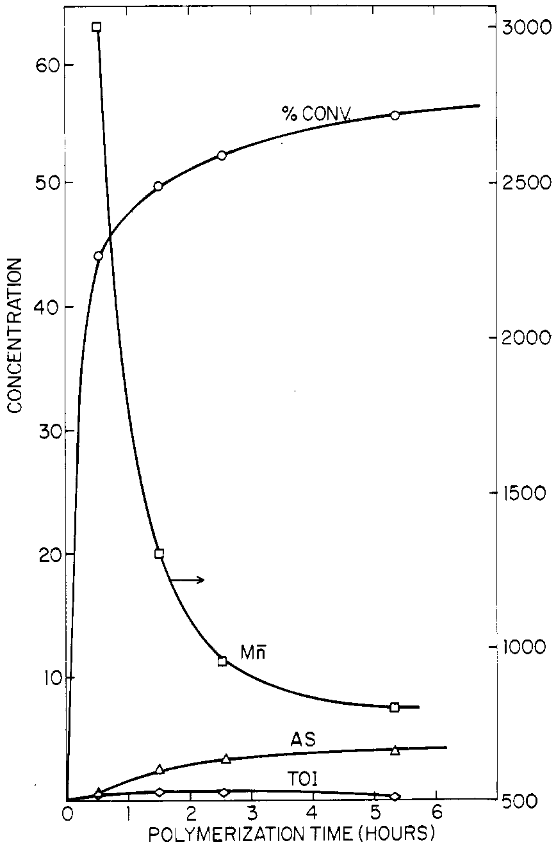


Figure 7. Molecular weight, conversion, and relative concentrations of tertiary oxonium ions (TOI) and alkyl sulfates (AS) in a THF/$CDCl_3$/$HFSO_3$ (mol ratios = 11.58/2.31/1.00) polymerization at 25 °C (concentrations as percent of total α-proton signal).

longer a "living" system, and addition of fresh monomer at this point will no longer lead to rapid formation of more polymer, as would be expected in a reversible equilibrium system.

A schematic outline of polymerization steps is shown below. For clarity, species with covalent macrofluorosulfate end groups are now shown in this outline, and other possible reactions involving this group are therefore also omitted.

The alkyl sulfate signal at 4.3 ppm (B in Figure 3) has earlier been attributed to the tertiary oxonium ion[10] and to the α-methylene protons of the covalent macrofluorosulfate ester in equilibrium with the oxonium ion.[11,17] Even in the absence of ^{19}F-NMR data, such assignments are difficult to reconcile with the fact that in THF/$HFSO_3$ polymerizations the oxonium ion signal goes through a maximum and then continuously decreases, even in polar media where oxonium ions are favored, while the signal at 4.3 ppm steadily increases in intensity.[10] Unfortunately, these erroneous assignments have

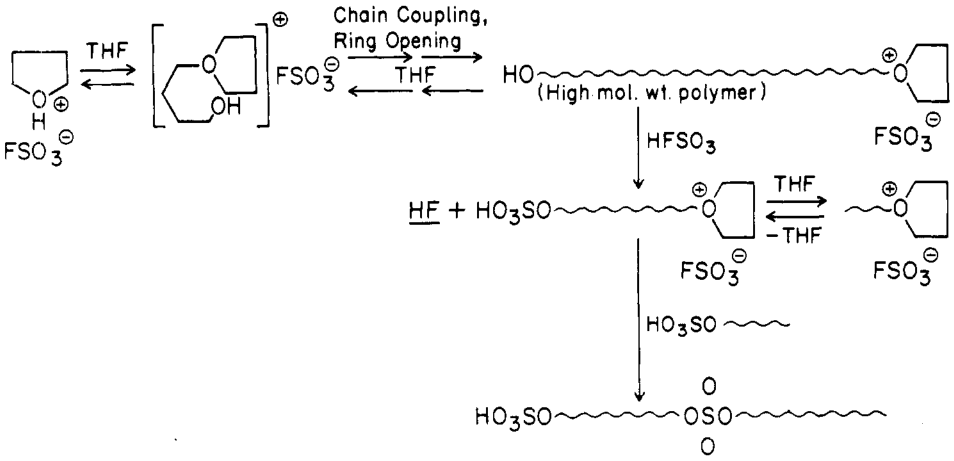


Table V
Polymerization of THF in Nitromethane[a]

Polymerization time, h	Tertiary oxonium ion[b] (4.95 ppm)	Fluosulfate ester[b] (4.65 ppm)	Alkyl sulfates[b] (4.35 ppm)	% conversion to PTME	$\overline{M}_n$	Chem shift H^+ (ppm from Me_4Si)
0.70	1.30	~0.08	0.80	48.0	2100	14.1
1.90	2.00	0.11	1.20	52.0	1440	13.7
3.80	1.90	0.10	2.76	52.8	1250	13.4
4.80	1.50	0.08	3.50	53.4	950	13.2
24.00	0.00	0.00	4.90	55.5	910	11.2

[a] Composition of polymerization system, in molar ratios: $THF/CD_3NO_2/HFSO_3$ = 11.58/4.34/1.00. Polymerization temperature, 25 °C. [b] Concentration, as percent of total α-proton signal at 220 MHz.

Table VI
Polymerization of THF in Chloroform[a]

Polymerization time, h	Tertiary oxonium ion[b] (4.95 ppm)	Fluosulfate ester[b] (4.65 ppm)	Alkyl sulfates[b] (4.35 ppm)	% conversion to PTME	$\overline{M}_n$
0.50	<0.26	<0.1	0.5	44.2	~3000
1.50	0.9	0.2	2.8	49.8	1350
2.55	0.9	0.4	3.3	52.6	950
5.33	0.46	<0.2	4.2	55.7	800
24.00	0.0	0.0	5.1	61.5	800

[a] Composition of polymerization system, in molar ratios: $THF/CDCl_3/HFSO_3$ = 11.58/2.31/1.00. Polymerization temperature, 25 °C. [b] Concentration, as percent total α-proton signal at 100 MHz.

led to a number of misinterpretations in the literature. The absence of a signal at 4.25 ppm appears to have been the reason for the initial failure by Kobayashi et al. to find macroester in the systems $THF/EtOSO_2F$ and $THF/EtOSO_2Cl$.[17] The authors used the reaction product of 4-ethoxy-1-butanol [$EtO(CH_2)_4OH$] and sulfuryl chloride, which has a triplet at 4.25 ppm, as a model compound for the covalent macrohalosulfate.[17] However, we believe this signal is due not to chlorosulfate but to alkyl sulfate, by analogy to the alkyl sulfate esters discussed earlier (Table III). Interpretation of the results from a $EtO(CH_2)_4OH/SO_2Cl_2$ model system is complicated by the occurrence of side reactions. If 2 equiv of $EtO(CH_2)_4OH$ in $CDCl_3$ are slowly added to SO_2Cl_2 in $CDCl_3$ at dry ice temperature, and the mixture is brought to room temperature, ^1H NMR scans show, among other signals, evidence of the presence of $EtO(CH_2)_4OSO_2Cl$ (triplet at 4.65 ppm), $EtOSO_2Cl$ (quartet at 4.6 ppm), and a large signal due to $EtO(CH_2)_4OSO_3(CH_2)_4OEt$ or $EtO(CH_2)_4OSO_3H$ (triplet at 4.28). If, on the other hand, the order of addition is reversed, a corresponding ^1H NMR scan shows a rapidly decreasing triplet at 4.65 ppm due to the monoaddition product $EtO(CH_2)_4OSO_2Cl$, and an increasing triplet at 4.2 ppm due to $EtO(CH_2)_4OSO_3H$. This signal was shifted upfield by about 0.2 ppm on addition of deuterated DMF, in agreement with the upfield shift of alkyl sulfuric acid protons discussed earlier. The triplet at 4.25 ppm found by Kobayashi et al.[17] is therefore reassigned to the α-methylene protons of alkyl sulfate esters, and the chemical shift of the α-methylene protons of ethoxybutyl chlorosulfate to 4.65 ppm (Table VII). The correct chemical shift of the α-methylene protons of the macrofluorosulfate in THF polymerizations was subsequently confirmed as 4.65 ppm with the aid of ^{19}F-NMR spectroscopy.[15] This is close to the chemical shift of the corresponding trifluoromethyl sulfonate macroester protons at 4.6 ppm.[5,20]

Similarly, Mahmud et al.[18] appear to have assigned the alkyl sulfate signal to the macrofluorosulfate and thus reported the transformation of tertiary oxonium ion (TOI) to macrosuperacid ester (SAE) during the course of polymerization. The

Table VII
Proton Chemical Shift of 4-Ethoxybutanol and Derivatives (in ppm from internal Me_4Si)

	$CDCl_3$	DMF-d_7
$C_2H_5O(CH_2)_3\mathit{CH}_2OH$	3.50	3.50
$C_2H_5O(CH_2)_3\mathit{CH}_2OSO_2Cl$	4.65	
$C_2H_5O(CH_2)_3\mathit{CH}_2OSO_3H$	4.25	4.05

authors therefore ascribe the very slow rate of polymer formation after addition of fresh monomer to an "equilibrated" system to the slow rate of propagation of the macrosuperacid ester, apparently the only propagating species present. Since our present data demonstrate that there are no measurable quantities of fluorosulfate ester left in such an "equilibrated" system, this conclusion has to be revised. The authors further report a deviation from the macroion $\rightleftarrows$ macrofluorosulfate equilibrium at low temperature and low initiator concentrations in the early stages of the polymerization, since they could not observe the NMR signal which they had assigned to the macrosuperacid ester (SAE). In view of the present discussion it becomes clear that the presumed macrosuperacid ester signal is indeed due to alkyl sulfate, which is formed very slowly at low temperature (see Figure 5). The THF/$HFSO_3$ system therefore approaches a "living" system at low temperature in the early stages of the polymerization, particularly at low initiator concentrations, and deviation from a reversible equilibrium only becomes apparent at higher temperatures and/or longer polymerization times.

Conclusion

We have tried to reconcile some experimental anomalies in the polymerization of THF initiated by strong acid with high resolution NMR results. Based on these and other published results,[13,19] the THF/halosulfonic acid systems cannot be classified as true "living" or even "immortal" systems such as the THF/alkyltriflate systems under ideal conditions. Rather, they should be considered "slowly dying" systems, the "death rate" depending on the type of initiator and on the polymerization conditions.

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Star-Branched Polymers. 1. The Synthesis of Star Polyisoprenes using Octa- and Dodecachlorosilanes as Linking Agents

N. Hadjichristidis,[1a] A. Guyot,[1b] and L. J. Fetters*

Institute of Polymer Science, The University of Akron, Akron, Ohio 44325.

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ABSTRACT: Star-branched polyisoprenes with near-monodisperse molecular weight distributions containing 8 or 12 arms have been synthesized by anionic polymerization. The linking agents were octa- and dodecafunctional chlorosilanes that were synthesized from tetravinylsilane and the appropriate di- or trichlorosilane. Both the 8- and 12-armed stars were obtained in high yield. Characterization was carried out by light scattering, osmometry, and gel permeation chromatography. The applicability of the GPC universal calibration was also examined.

The use of tri- and tetrachlorosilanes as linking agents for the formation of star-branched polymers was first demonstrated to be a feasible concept by Morton and co-workers[2] in 1962; in this case for polystyryllithium. The polymerization system involved *n*-butyllithium with benzene as the solvent. As a consequence of the termination-free aspects of this polymerization system,[3] these star-branched polystyrenes contained relatively narrow molecular weight distributions. Thus, this synthesis procedure permits the predetermined manipulation of molecular weight and the molecular weight distributions.

This general reaction involving methyltrichloro- and tetrachlorosilane with monocarbanionic chains was subsequently extended to polybutadiene[4–6] with the finding that tri- and tetrachain polymers could be formed in high yield. Roovers and co-workers[7–10] have synthesized and studied a series of 4- and 6-armed polystyrene and polyisoprene stars using 1,2-bis(dichloromethylsilyl)- and 1,2-bis(trichlorosilyl)ethane, respectively. Their work represents the most thorough synthesis and characterization of a series of model star-branched polymers to appear in the literature to date. Thus far, the results of Roovers and co-workers[7–10] involving the hexachlorodisilyl compound represent the highest degree of uniform branching achieved involving the use of an electrophilic linking agent.

The results reported in this paper show that star-branched

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