Superacids and Their Derivatives. VII.[1] Cationic Polymerization of Tetrahydrofuran Initiated with Ethyl and Methyl Fluorosulfonates. Kinetic and Mechanistic Studies by Means of ^{19}F and ^{1}H Nuclear Magnetic Resonance Spectroscopy

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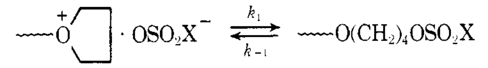
ABSTRACT: This paper deals with the kinetic and mechanistic studies on the cationic ring-opening polymerization of tetrahydrofuran (THF) initiated with ethyl ($EtOSO_2F$) and methyl ($MeOSO_2F$) fluorosulfonates. Kinetic analyses were performed by means of ^{19}F and ^{1}H NMR spectroscopy. The oxonium (3) and macroester (4) species of propagating end were directly monitored by ^{19}F NMR spectroscopy. Solvent effect on the polymerization was examined in six solvents of CCl_4, $CHCl_3$, CH_2Cl_2, C_6H_6, $C_6H_5NO_2$, and CD_3NO_2. An equilibrium between 3 and 4 was observed in $CHCl_3$, CH_2Cl_2, C_6H_6, and $C_6H_5NO_2$. However, polymerization proceeded exclusively via 3 in CD_3NO_2 and via 4 in CCl_4. Rate constants of initiation (k_i) and of propagation due to 3 ($k_{p(i)}$) and 4 ($k_{p(e)}$) and the apparent rate constants of propagation ($k_{p(ap)}$) were obtained. The magnitude of $k_{p(e)}$ was comparable to that of $k_{p(i)}$. It is of interest to note that the reactivity of macroester species of THF was extremely high compared with that of other cyclic ethers.

Quite recently we have reported kinetic studies on the ring-opening polymerization of tetrahydrofuran (THF) initiated by superacid esters such as ethyl trifluoromethanesulfonate ($EtOSO_2CF_3$),[2,3] fluorosulfonate ($EtOSO_2F$),[2] chlorosulfonate ($EtOSO_2Cl$),[2] and 2,4,6-trinitrobenzenesulfonate (EtOTn).[1] Recent papers[4,5] have also dealt with a similar subject. In these systems, the oxonium ion (1)–ester (2) equilibrium ($K = k_1/k_{-1}$) of the propagating species (eq 1) has been proposed.



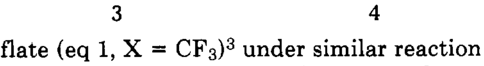
(1)

1 2

$X = CF_3, F, Cl, 2,4,6\text{-}(NO_2)_3C_6H_2$

Although ^{1}H NMR spectroscopic studies have given semiquantitative results showing the presence of the ester species 2,[1-3,5] a ^{19}F NMR spectroscopic investigation has given clear-cut evidence that the equilibrium of eq 1 ($X = CF_3$) is actually present during the THF polymerization initiated with $EtOSO_2CF_3$.[3]

Among superacid ester initiators examined, $ROSO_2F$ and $ROSO_2CF_3$ (R = Et or Me) provide counteranions containing the fluorine atom. This enabled us to perform kinetic analyses by means of ^{19}F NMR spectroscopy to compare the difference in behavior between the two counteranions, OSO_2F^- and $OSO_2CF_3^-$, in the THF polymerization. The present paper deals with kinetics of the THF polymerization obtained by using ^{19}F and ^{1}H NMR spectroscopy. Initiators employed were $EtOSO_2F$ and $MeOSO_2F$.[6] The following equilibrium between the two propagating species (eq 2) was observed in four solvents of $CHCl_3$, CH_2Cl_2, C_6H_6, and $C_6H_5NO_2$. The value of the equilibrium constant ($K = k_1/k_{-1} = [4]/[3]$), however, was different from that with triflate (eq 1, $X = CF_3$)[3] under similar reaction conditions. With triflates, K was usually lower; i.e., the equilibrium concentration of [O$^+$] is usually higher in the same solvent. With fluorosulfonates, two extreme cases were observed; i.e., the propagation proceeded exclusively via 3 in CD_3NO_2 and via 4 in CCl_4 solvent.



(2)

3 4

Results and Discussion

^{19}F NMR Spectroscopy. Figure 1a shows an example of the ^{19}F NMR spectrum of the THF polymerization system initiated with $EtOSO_2F$ in CH_2Cl_2, which was taken after 100 min at 0°. The molar ratio of THF to $EtOSO_2F$ was 5:1. The ^{19}F chemical shifts are given in parts per million from an external standard of CF_3CO_2H capillary. Peak A at −113.3 ppm is due to the initiator of $EtOSO_2F$. Peak B at −116.3 ppm is ascribed to the counteranion of 3 (OSO_2F^-), whereas peak C at −112.8 ppm is assigned to the macroester species of 4 ($\sim CH_2OSO_2F$). It is interesting to note that, contrary to the observation in the $EtOSO_2CF_3$ system,[3] the signal of the anion (OSO_2F^-) appears at a field lower than that of the neutral ester species of initiator or 4. A similar result has already been observed by Ahmed et al.[7] in the reactions of $EtOSO_2F$ with various compounds containing oxygen and/or nitrogen. No other peaks were detected in the ^{19}F NMR spectrum of the kinetic run. Therefore, the ^{19}F NMR spectroscopy allows the direct determination of the instantaneous concentrations of initiator, 3 and 4.

In CD_3NO_2 only a signal at −115.0 ppm (peak D) due to the ion 3 appeared. No signal due to the macroester 4 was detected (Figure 1b). In CCl_4, on the other hand, peak E (−112.9 ppm) assigned to 4 was the only new signal that appeared. No peak due to the ion 3 was detected throughout the kinetics (Figure 1c). Similar analyses were carried out in $CHCl_3$, C_6H_6, and $C_6H_5NO_2$ with $EtOSO_2F$ and with $MeOSO_2F$ initiator. The ^{19}F NMR chemical shifts of 3 and 4 changed very little according to the solvent (Table I).

Oxonium–Ester Equilibrium. Figure 2 illustrates the changes of ([O$^+$] + [E]) (curve A) and [O$^+$] (curve B) with respect to time during the THF polymerization by $EtOSO_2F$ in CH_2Cl_2 at 0°, where [O$^+$] and [E] denote the concentrations of 3 and 4, respectively. The equilibrium of eq 2 is actually present. The molar ratio of [3]/[4] was 80:20 at 0° after the equilibrium was reached. At the end (after 100 min) of the kinetic run where more than 30% of THF was consumed, 16% of the charged initiator was converted into the two propagating species (Figure 2).

The 3 $\rightleftarrows$ 4 equilibrium was very dependent upon the polymerization solvent employed. In C_6H_6 and $CHCl_3$ both 3 and 4 were present, [O$^+$] being 21 and 55% at 0°, respectively. In $C_6H_5NO_2$, the fraction of [O$^+$] was about 90% at

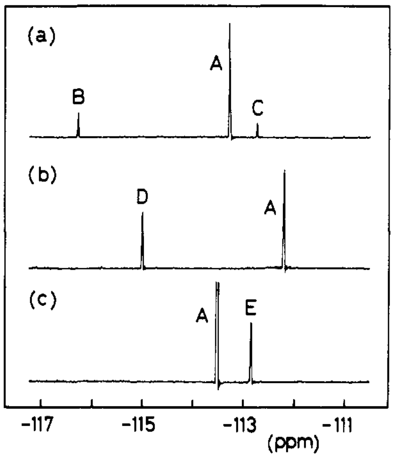


Figure 1. ^{19}F NMR spectra of the THF polymerization mixture by $EtOSO_2F$ initiator at 0° (a) in CH_2Cl_2 after 100 min, (b) in CD_3NO_2 after 50 min, and (c) in CCl_4 after 200 min.

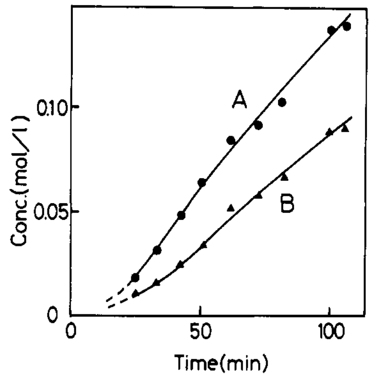
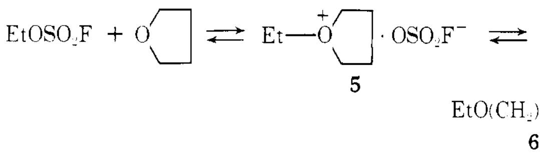


Figure 2. Polymerization of THF by $EtOSO_2F$ in CH_2Cl_2 at 0° monitored by ^{19}F NMR spectroscopy. Relationships of ($[O^+]$ + [E])-time (curve A) and of $[O^+]$-time (curve B): $[M]_0$ = 5.5 mol/l., $[I]_0$ = 1.1 mol/l.

0°, which was equilibrated with the macroester **4** (the fraction was 10%). With $EtOSO_2CF_3$ initiator, however, the ester species **1** (X = CF_3) was almost negligible in $C_6H_5NO_2$.[3]

In relation to the **3** ⇄ **4** equilibrium in the polymerization, a 1:1 molar reaction of THF with $EtOSO_2F$ was examined in CH_2Cl_2 at 35°. The initial concentration of each component was 0.97 mol/l., which was much lower than the equilibrium monomer concentration in polymerization, $[M]_e$ (4.00 mol/l. at 35°)[8], and hence the polymerization of THF did not occur. Both ^{19}F and ^1H NMR spectroscopy showed that the following reaction (eq 3) mainly took place; i.e., the ester species of $EtOSO_2F$ and of 4-ethoxybutyl fluorosulfonate (**6**) were in equilibration with the cyclic oxonium **5**. A [**5**]/[**6**] ratio of 60:40 was held during the reaction. This indicates that the oxonium species are more stabilized at lower temperatures (see Table IV). After 12 hr at 35° when the equilibrium of eq 3 was already attained, the concentrations of $EtOSO_2F$, **5**, and **6** were respectively 0.55, 0.25, and 0.17 mol/l.



(3)

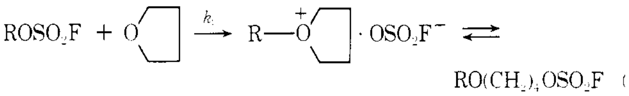
Kinetics. The following scheme explains the elementary processes of the THF polymerization by $ROSO_2F$ initiator.

Table I
^{19}F NMR Chemical Shifts[a] in the THF Polymerization at 0°

Solvent	Initiator (R of $ROSO_2F$)	Oxonium (OSO_2F^-)	Macroester ($\sim CH_2OSO_2F$)
CCl_4	−113.5 (Et)		−112.9
C_6H_6	−113.0 (Et)	−116.5	−112.4
$CHCl_3$	−109.7 (Me)	−116.3	−112.9
CH_2Cl_2	−113.3 (Et)	−116.3	−112.8
CH_2Cl_2	−109.3 (Me)	−116.3	−112.9
$C_6H_5NO_2$	−112.9 (Et)	−116.6	−112.5
CD_3NO_2	−112.2 (Et)	−115.0	

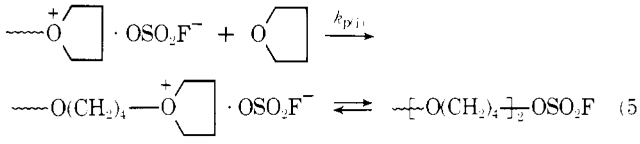
[a] In parts per million relative to CF_3CO_2H external standard.

Initiation



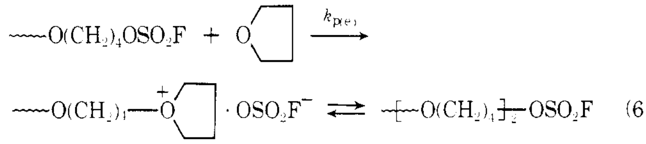
(4)

Propagation



(5)

and



(6)

The integrated rate equations of initiation and propagation are given by eq 7 and 8, respectively[1-3]

$$\ln \frac{[I]_{t_1}}{[I]_{t_2}} = k_i \int_{t_1}^{t_2} [M]\,dt \qquad (7)$$

and

$$\ln \frac{[M]_{t_1} - [M]_e}{[M]_{t_2} - [M]_e} = k_{p(ap)} \int_{t_1}^{t_2} [P^*]\,dt \qquad (8)$$

where $k_{p(ap)}$ and $[P^*]$ denote the apparent rate constant of propagation and the total concentration of propagating species, *i.e.*

$$[P^*] = [O^+] + [E] \qquad (9)$$

Therefore, the following relationship is derived

$$k_{p(ap)} \int_{t_1}^{t_2} [P^*]\,dt = k_{p(i)} \int_{t_1}^{t_2} [O^+]\,dt + k_{p(e)} \int_{t_1}^{t_2} [E]\,dt \qquad (10)$$

where $k_{p(i)}$ and $k_{p(e)}$ are the rate constants of propagation due to the oxonium ion **3** and macroester **4**, respectively.

In our previous studies, the [M]-time relationship was obtained by ^1H NMR spectroscopy[1-3] and the [I]-time variation was determined by both ^{19}F and ^1H NMR spectroscopy.[3] Also in the present study, the combined data of ^{19}F and ^1H NMR spectroscopy were successfully utilized for the kinetic analysis according to eq 7, 8, and 10.

Table II shows the results with $EtOSO_2F$ and $MeOSO_2F$ initiators in six solvents at 0°. It is seen that the k_i value was usually higher in more polar systems of polymerization. $MeOSO_2F$ reacted several times faster than $EtOSO_2F$.

Table II
Kinetic Data of the THF Polymerization Initiated by EtOSO$_2$F and MeOSO$_2$F in Six Solvents at 0° [a]

Solvent	Initiator	ϵ of the mix.[b]	$k_i \times 10^5$, l./(mol sec)	$k_{p(ap)} \times 10^3$, l./(mol sec)	[O$^+$] fraction,[c] %	$k_{p(i)} \times 10^3$, l./(mol sec)	$k_{p(e)} \times 10^3$, l./(mol sec)
CCl_4	EtOSO$_2$F	4.5	0.21	0.90	0		0.90
C_6H_6	EtOSO$_2$F	4.5	0.25	1.7	21		
$CHCl_3$	MeOSO$_2$F	6.0	1.9	1.1	55		
CH_2Cl_2	EtOSO$_2$F	8.3	0.76	1.4	67		
CH_2Cl_2	MeOSO$_2$F	8.3	3.9	1.7	80		
$C_6H_5NO_2$	EtOSO$_2$F	23.4	1.5	3.9	90		
CD_3NO_2	EtOSO$_2$F	24.0	3.8	2.1	100	2.1	
CD_3NO_2[d]	EtOSO$_2$F[d]	24.0	2.9	2.5	100	2.5	

[a] $[M]_0$ = 5.5 mol/l. and $[I]_0$ = 1.1 mol/l. unless otherwise indicated. [b] Dielectric constant (ϵ) of the reaction mixture calculated by assuming the molar additivity in the ϵ value of solvent and THF. Values of THF (7.58) and of six solvents were taken from ref 9. [c] At equilibrium. [d] $[M]_0$ = 5.5 mol/l., $[I]_0$ = 0.49 mol/l.

Table III
Rate Constants, Activation Parameters, and the [O$^+$] Fraction in the THF Polymerization by EtOSO$_2$F Initiator in CCl$_4$[a]

Temp, °C	$k_i \times 10^5$, l./(mol sec)	$k_{p(ap)}(=k_{p(e)}) \times 10^3$, l./(mol sec)	[O$^+$] fraction, %
0	0.21	0.90	0
13	0.81	2.2	0
25	1.8	3.4	0
$\Delta H^\ddagger$, kcal/mol	14	8	
$\Delta S^\ddagger$, eu	−33	−42	

[a] Solution polymerization in CCl$_4$; $[M]_0$ = 5.5 mol/l., $[I]_0$ = 1.1 mol/l.

Table IV
Rate Constants, Activation Parameters, and the [O$^+$] Fraction in the THF Polymerization by EtOSO$_2$F Initiator in C$_6$H$_5$NO$_2$[a]

Temp, °C	$k_i \times 10^5$, l./(mol sec)	k_p(ap) $\times 10^3$, l./(mol sec)	[O$^+$] fraction,[b] %
0	1.5	3.9	90
9	6.1	7.8	87
24	13	18	86
$\Delta H^\ddagger$, kcal/mol	14	10	
$\Delta S^\ddagger$, eu	−30	−34	

[a] Solution polymerization in C$_6$H$_5$NO$_2$: $[M]_0$ = 5.5 mol/l., $[I]_0$ = 1.1 mol/l. [b] At equilibrium.

These findings are compatible with the previous kinetic results of the oxonium formation reactions between superacid esters and tetrahydropyran.[10]

The value of $k_{p(ap)}$ was in a narrow range between 0.90 and 3.9 × 10^{-3} l./(mol sec) at 0°; i.e., the solvent effect on the magnitude of $k_{p(ap)}$ was not large. The [O$^+$] values, however, were very dependent upon the solvent. The fraction of [O$^+$] in [P*] was increased in highly polar solvents. Since the ester species 4 was not detected during the kinetic run in CD$_3$NO$_2$, i.e., [P*] = [O$^+$], eq 10 leads to $k_{p(ap)} = k_{p(i)}$.

In CCl$_4$, on the other hand, the [O$^+$] was not detected during the kinetics, i.e., [P*] = [E], and hence eq 10 yields $k_{p(ap)} = k_{p(e)}$. It is interpreted in this case that the 3 → 4 conversion in eq 2 (the rate constant = k_1) is faster than the formation of 3 due to reduced stabilization of 3 in CCl$_4$ under the present polymerization conditions.

Kinetic analyses were carried out at other temperatures in CCl$_4$ and in C$_6$H$_5$NO$_2$. No oxonium species was detected at three temperatures examined in CCl$_4$ (Table III). This finding is interestingly compared with the EtOSO$_2$CF$_3$-initiated system in which the [O$^+$] fraction was 45% at 0°. The activation parameter values of propagation well demonstrate the character of a dipole–dipole SN2 reaction to form an ionic intermediate (eq 6): $\Delta H^\ddagger$ being low (favorable for $k_{p(e)}$) whereas $\Delta S^\ddagger$ being more negative (unfavorable for $k_{p(e)}$). This tendency has often been observed in dipole–dipole SN2 reactions such as the Menschutkin reaction[11] and the oxonium formation reaction.[10]

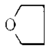
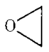
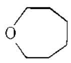
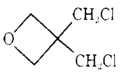
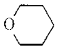
In C$_6$H$_5$NO$_2$ both the oxonium 3 and macroester 4 were present throughout the kinetic run. It seems that the [O$^+$] fraction has a tendency to increase at lower temperatures (Table IV). This is a sharp contrast to the system of EtOSO$_2$CF$_3$ initiator, in which 4 was in a negligible quantity, e.g., <2%.[3]

As to the difference in behavior between the two counteranions (OSO$_2$F$^-$ and OSO$_2$CF$_3^-$), the above findings (Tables II–IV) as well as the equilibrium constant values of the oxonium formation reactions[10] indicate that the counteranion of OSO$_2$F$^-$ is more readily susceptible to form the ester species than that of OSO$_2$CF$_3^-$.[3]

$k_{p(e)}$ Values. The above data show that the magnitude of $k_{p(e)}$ (in CCl$_4$) is comparable to that of $k_{p(i)}$ (in CD$_3$NO$_2$). In the previous study on the THF polymerization by EtOSO$_2$CF$_3$ initiator, there was no system in which the propagation proceeded in 100% via the macroester 2 (X = CF$_3$),[3] and it was assumed that "the magnitude of $k_{p(e)}$ must be at least smaller than that of k_i which was about 140–280 times smaller than that of $k_{p(i)}$, i.e., $k_{p(i)} \gg k_{p(e)}$."[3] In view of the present results, however, the above assumption may not be adequate. The contribution of the term $k_{p(e)}\int_{t_1}^{t_1}[E]dt$ in eq 10 is probably significant or cannot be negligible in C$_6$H$_6$, CHCl$_3$, CH$_2$Cl$_2$, and C$_6$H$_5$NO$_2$ solvents. Therefore, the separate evaluation of $k_{p(i)}$ and $k_{p(e)}$ values of the systems involving both 3 and 4 must wait until a reliable value of $k_{p(i)}$ or $k_{p(e)}$ is determined independently in a respective solvent. As stated in the previous view, "the precise determination of $k_{p(e)}$ value is required for the further study."[3]

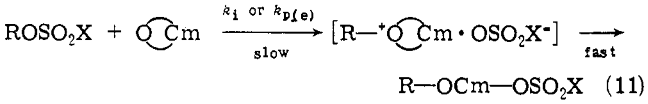
In the course of our studies on the polymerizations[1-3,12-14] and reactions[10] of cyclic ethers using superacid esters we have so far found several systems propagating only via the ester type species. They are the polymerizations of ethylene oxide (EO),[12] oxepane (OXP),[13] and 3,3-bis(chloromethyl)oxetane (BCMO)[14] initiated with superacid esters. Their rate constants are given in Table V, which also includes those of the oxonim formation reac-

Table V
Comparison of the Reactivities of Five Cyclic Ethers at 35°

No.	Reaction[a]	Solvent	$k_i \times 10^5$,[a] l./(mol sec)	$k_{p(e)}$,[a] l./(mol sec)	$k_{p(e)}/k_i$	Ref
1.	$ROSO_2F$ + 	CCl_4	4.6[b]	5.9×10^{-3} [b]	130	This work
2.	$ROSO_2CF_3$ + 	CCl_4	2.8	2.5×10^{-5}	0.9	12
3.	$ROSO_2F$ + 	CCl_4	0.34	1.5×10^{-6}	0.4	13
4.	$ROSO_2CF_3$ + 	$C_6H_5NO_2$	15[c]	3.0×10^{-8} [c]	0.0002	14
5.	$EtOSO_2F$ + 	CH_2Cl_2	2.43			10
6.	$EtOSO_2CF_3$ + 	$C_6H_5NO_2$	27.3			10

[a] Values of k_i and $k_{p(e)}$ represent those for R = Et and R = polymer alkyl of a respective cyclic ether (no. 1–4), respectively. [b] Extrapolated value from the data in Table III. [c] Extrapolated value.

tions (no. 5 and 6 in Table V) for the sake of comparison. Both initiation and propagation (through ester species) of these monomers can generally be formulated by eq 11 in



(11)

which k_i and $k_{p(e)}$ represent the values in the cases of R = Et and R = ~OCm, respectively (no. 1–4 in Table V). The propagating species (~OCmOSO$_2$X) of THF, EO, OXP, and BCMO are given by **4** and **7–9**.

$$\sim\!O(CH_2)_4OSO_2F$$

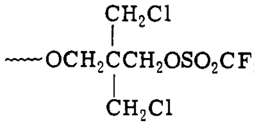
4

$$\sim\!O(CH_2)_2OSO_2X$$

7, X = CF_3, F, etc.

$$\sim\!O(CH_2)_6OSO_2X$$

8, X = CF_3, F, etc.

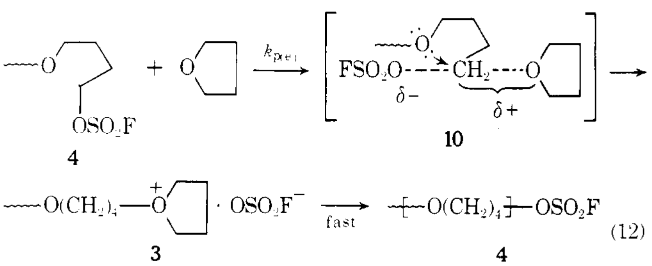


$$\sim\!OCH_2C(CH_2Cl)_2CH_2OSO_2CF_3$$

9

In the cases of no. 1–3, k_i values do not much differ, whereas $k_{p(e)}$ values differ greatly. The $k_{p(e)}$ value of the THF polymerization is remarkably large as reflected by the ratio of $k_{p(e)}/k_i$. The values of the $k_{p(e)}/k_i$ ratio represent the relative electrophilic reactivities of **4** and **7–9** vs. EtOSO$_2$X toward a common monomer in the reaction of eq 11. The $k_{p(e)}$ values of EO and OXP are rather smaller than the corresponding k_i values regardless of X = F and CF_3 in ROSO$_2$X.

The enhanced reactivity of **4** may be ascribed to the stabilization of the developing charge at the transition state through an intramolecular coordination of the adjacent ether group **10** (eq 12). This type of stabilization may be related to the so-called anchimeric assistance by neighboring group; e.g., the rate was most highly increased in solvolysis reactions involving five-membered cyclic intermediates.[15]



4 **10** **3** **4**

(12)

In CCl_4, the only propagating species was a "sleeping species", which is a proposed notation for the macroester **4**.[3] Important is that the polymerization reactivity of the macroeater is comparable to that of the oxonium species **3**. Further studies on the reactivities of macroester species are presently under progress in our laboratory.

Experimental Section

Materials. THF and solvents were purified as previously reported.[3,10] EtOSO$_2$F and MeOSO$_2$F were prepared by the reaction of diethyl and dimethyl sulfates with FSO$_3$H, bp 70–71° (200 mm) (lit.[16] 113° (752 mm)) and 92–94° (lit.[16] 92°), respectively.

Kinetic Procedures. Whole kinetic procedures were performed under nitrogen in a similar manner of the previous study.[3] A typical run was as follows. To an NMR sample tube containing 2.5 mmol of THF, 0.20 ml of CCl_4 and 0.51 mmol of EtOSO$_2$F were added at −78° by using a microsyringe (the initial concentration of $[M]_0$ = 5.5 mol/l. and $[I]_0$ = 1.1 mol/l., respectively). Then, the tube was sealed and shaken at the same temperature. The extent of the reaction was very small at −78°. The tube was placed in the NMR probe insert which was kept at 0°. The reaction was then followed by ^{19}F or ^1H NMR spectroscopy. The instrument used was a Hitachi R-20B NMR spectrometer equipped with radiofrequency units for proton (60 MHz) and fluorine-19 (56.456 MHz) nuclei. The reaction temperature was kept constant within ±1° and the experimental error of the NMR analysis was within about ±2%.

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Graft Copolymerization of 2-Methyl-2-oxazoline onto Chloromethylated Polystyrene and Hydrolysis of Graft Copolymer to a Chelating Resin of Poly(styrene-*g*-ethylenimine)

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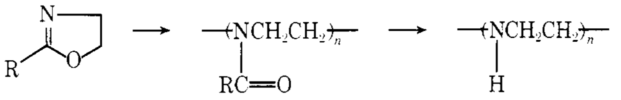
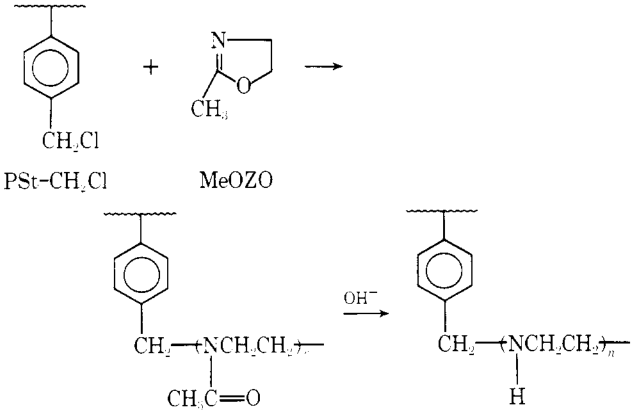
ABSTRACT: Poly(styrene-*g*-MeOZO) (**4**) consisting of polystyrene backbone and poly(*N*-acetylethylenimine) branches was prepared by the polymerization of 2-methyl-2-oxazoline (MeOZO) initiated by chloromethylated polystyrene (PSt–CH$_2$Cl). PSt–CH$_2$Cl used were noncross-linked and cross-linked, macroporous bead polymers. The polymerization rate of MeOZO by PSt–CH$_2$Cl was enhanced by the addition of KI due to the change of the nature of propagating species through the halogen exchange reaction. The graft copolymer **4** was hydrolyzed with alkali to prepare poly(styrene-*g*-ethylenimine) (**5**). The extent of hydrolysis of **4** to **5** reached 87.7%. Thus, it became possible to prepare **5** having long, linear polyethylenimine branches (n in **5** ≤ 16.62). Preparation of such graft copolymer could not be accomplished by the graft polymerization of ethylenimine (EI) by PSt–CH$_2$Cl due to the chain transfer. The reaction of cross-linked PSt–CH$_2$Cl with polyEI produced graft copolymer having a very low content of polyEI. Poly(styrene-*g*-ethylenimine) prepared in the present study was found to be quite effective for the absorption of heavy metal ions such as Cu^{2+}, Hg^{2+}, and Cd^{2+}.

Recently we succeeded in the preparation of crystalline polyethylenimine (**3**) by the polymerization of 2-oxazoline (**1a**) and the subsequent hydrolysis of the product polymer poly(*N*-formylethylenimine) (**2a**).[1,2] Poly(*N*-acetylethylenimine) (**2b**), the polymer of 2-methyl-2-oxazoline (**1b**) (MeOZO), has been known to be hydrolyzed by alkaline with difficulty.[3] But we found recently that **2b** was hydrolyzed up to about 90% under strong alkaline conditions.[4] Furthermore, we have observed that MeOZO (**1b**) was polymerized by methyl iodide[5,6] and benzyl chloride.[7]


1a, R = H 2a, R = H 3
b, R = CH$_3$ b, R = CH$_3$

These findings prompted us to prepare poly(styrene-*g*-ethylenimine) (**5**) by the polymerization of MeOZO with chloromethylated polystyrene (PSt–CH$_2$Cl) and the subsequent alkaline hydrolysis of the product copolymer **4**. Polyethylenimine is known to be a good chelating agent for various metal ions; however, its complexes with metal ions are usually soluble in water. For the purpose of the removal of heavy metal ions, it is desirable to prepare chelating agents whose metal complexes are readily separated from the aqueous phase. The present paper describes the preparation of **4** and **5** and the chelating properties of **5** with Cu^{2+}, Hg^{2+}, and Cd^{2+}.


PSt-CH$_2$Cl MeOZO
4 5

Results and Discussion

Preparation of Poly(styrene-*g*-MeOZO). Samples of the backbone polymers of PSt–CH$_2$Cl were cross-linked as well as noncross-linked ones.

Noncross-linked Graft Copolymers. The MeOZO polymerization by PSt–CH$_2$Cl ($\bar{M}_n = 1.7 \times 10^4$) was carried out in various solvents. As the reaction proceeded, the system solidified because of the reduced solubility of graft copolymer in the polymerization solvent. The solvent effect is illustrated in Table I. It was reported that aprotic polar solvents with high dielectric constants such as DMF were suitable for the polymerization of 2-oxazoline.[1] The same tendency was observed in the graft polymerization. All the polymer products prepared in C$_6$H$_5$CN, C$_6$H$_5$NO$_2$, and C$_6$H$_5$OCH$_3$ were soluble in methanol. Polystyrene is insoluble in methanol whereas polyMeOZO is very soluble in it. So, the solubility of the product indicates the formation of graft copolymer. The graft copolymer prepared in DMF was not soluble anymore. This is probably due to the occurrence of cross-linking during polymerization. Actually, gelation was observed by heating independently a DMF solution of PSt–CH$_2$Cl at 110° for 17 hr. Therefore, DMF is not suitable for the preparation of the soluble graft copolymer. Good results were obtained with C$_6$H$_5$CN as the polymerization solvent (Table II).

Cross-Linked Graft Copolymers. In the case of bead