be small. In the previously reported study[3] a solution of emulsifier absorbed oxygen at about one-tenth the rate of the styrene emulsions. The styrene concentrations were comparable to those in the present study and no polymer latex particles were present.

The degree of rate enhancement due to increased viscosity for oxidation of both MMA and styrene is less than observed in bulk polymerization under similar conditions. At 35% conversion, approximately a 14-fold increase is observed in the polymerization rate of MMA.[12] However, the *rate of oxidation of the same mixture of polymer/monomer* is less than twice as fast as that of pure MMA. Similarly, for polymerization of styrene at 35% conversion, the rate is enhanced 2.4 times, while the oxidation rate of the same polymer/monomer mixture is 1.5 times faster than neat styrene. This difference between polymerization and oxidation is related to two factors. First, the rates of reaction of the much larger radicals in the polymerization reactions are more sensitive to viscosity than are the rates of the smaller oxidation radicals. In polymerization, the molecular weight of the chain-carrying radical ranges up to 10^5–10^6, while for oxidation the molecular weight of the chain-carrying peroxy radical is limited to 10^2–10^3 by a rapid chain-transfer reaction.[10,11]

Second, in the oxidation of pure MMA or styrene, less change in viscosity occurs with conversion than observed in polymerization because of the much lower molecular weight of oxidation products. Even at relatively high conversions in the oxidation of MMA or styrene there is little viscosity increase in the medium and a concomitantly small rate enhancement. Thus to the extent that the emulsion rate enhancement phenomenon is dependent on a rapidly increasing viscosity of the growing particle, rate enhancement in emulsion oxidation would not be expected.

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Superacids and Their Derivatives. VIII.[1] Cationic Ring-Opening Polymerization of Oxepane by Superacids and Their Derivatives

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We have hitherto reported kinetic and mechanistic studies on the ring-opening polymerizations of five-[1–5] and four-membered[6] cyclic ethers by superacid esters[1–4,6] and anhydrides[5] and related reactions of six-membered ones.[7] In the present study, this series of reactions has been extended to the polymerization of a seven-membered cyclic ether of oxepane. Superacids used were trifluoromethanesulfonic (CF_3SO_3H), fluorosulfonic (FSO_3H), and chlorosulfonic ($ClSO_3H$) acids.[4]

The polymerization of oxepane was first reported by Saegusa et al.[8,9] and by Gehm[10] with typical Lewis acid catalysts such as BF_3,[8–10] $SbCl_5$,[8] $SnCl_4$,[8] $AlCl_3$,[10] and PF_5.[10] The present study has shown that superacids (No. 1–4), their esters (No. 5–9), and an anhydride (No. 10) are effective catalysts for the ring-opening polymerization of oxepane (Table I).

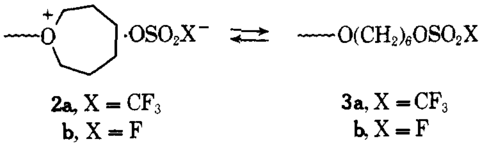
A typical run (No. 5) was as follows. To a mixture of oxepane (1.00 g, 10 mmol) and nitrobenzene (1.14 ml) in a glass tube, ethyl trifluoromethanesulfonate ($EtOSO_2CF_3$) (0.48 mmol) was added at room temperature under nitrogen. *The tube was sealed and kept at 25°. After 93 hr* the reaction mixture was poured into 20 ml of methanol containing 0.05 g of NaOH. White powder precipitated and the mixture was stirred for 20 hr at room temperature. After neutralization of the methanol solution with an aqueous HCl the powdery material was separated by filtration, dissolved in 3 ml of CH_2Cl_2, and reprecipitated again in 30 ml of methanol. The polymer was separated by filtration and dried in vacuo (0.86 g, 86% yield). Anal. Calcd for $(C_6H_{12}O)_n$: C, 71.45; H, 12.10. Found: C, 71.16; H, 11.93. The melting point of the polymer was 57°. The molecular weight was 1940 (vapor pressure osmometry in CH_2Cl_2 at 30°). This value is very close to the calculated value of 1840 ($100 \times 86/4.8 + 46$) on the assumption that 1 mol of initiator produced 1 mol of polymer having structure **1** (n = 17.9). These findings indicate the absence of chain transfer.

$$C_2H_5\left[O(CH_2)_6\right]_nOH$$

1

The highest molecular weight obtained was 6200 (No. 10 in Table I) measured by vapor pressure osmometry (vpo) in CH_2Cl_2. The sample polymer was subjected to gel permeation chromatography (GPC) using tetrahydrofuran solvent. A ratio of M_w/M_n = 1.36 was obtained, indicating that a molecular weight distribution is relatively narrow. The M_n value by GPC was 6370 which is close to that obtained by vpo. The melting point of polymer became higher with an increase of the molecular weight. The rate of polymerization was faster in polar solvents such as nitrobenzene and nitromethane than in less polar ones, e.g., CH_2Cl_2 or bulk (vide infra).

A preliminary study has been carried out to examine the polymerization mechanism by means of ^1H and ^{19}F NMR spectroscopy. The oxonium (**2**)-ester (**3**) equilibrium (eq 1) of the propagating chain end was observed as in the tetrahydrofuran polymerization initiated by superacid esters.[1,2,11,12]



(1)

2a, X = CF_3
b, X = F

3a, X = CF_3
b, X = F

Figure 1 shows a ^1H NMR spectrum of the oxepane polymerization initiated by $EtOSO_2CF_3$ in nitrobenzene at 35° after 97 min, in which the initiator has already been consumed. A multiplet peak A at δ 5.3–5.0 is due to α-methylene protons (6 H) of the oxonium center **2a** and a triplet peak B at δ 4.65 is assigned to α-methylene protons (2 H) of

Table I
Polymerization of Oxepane Initiated with Superacids and Their Derivatives under Various Conditions

No.	Catalyst (mol % for oxepane)	Solvent	$[M]_0$,[a] mol/l.	Temp, °C	Time, hr	Yield, %	Mol wt[b]	Mp, °C
1	CF_3SO_3H (4.0)	$C_6H_5NO_2$	2.7	35	623	87		
2	CF_3SO_3H (2.5)	Bulk	11.1	60	30	12		
3	FSO_3H (3.0)	$C_6H_5NO_2$	2.8	60	30	44		
4	$ClSO_3H$ (5.2)	CH_2Cl_2	2.8	35	126	18		
5	$EtOSO_2CF_3$ (4.8)	$C_6H_5NO_2$	4.3	25	93	86	1940	57[c]
6	$EtOSO_2CF_3$ (0.83)	$C_6H_5NO_2$	2.2	25	290	26	2060	58[c]
7	$MeOSO_2CF_3$ (2.0)	CH_3NO_2	2.8	80	17	65	2240	58[c]
8	$EtOSO_2F$ (17.2)	$C_6H_5NO_2$	2.8	35	9	70		
9	$MeOSO_2Cl$ (11.8)	CH_3NO_2	2.5	25	24	80		
10	$(CF_3SO_2)_2O$ (0.90)	$C_6H_5NO_2$	4.5	35	550	66	6200	62[d]

[a] The charged monomer concentration. [b] Determined by vapor pressure osmometry in CH_2Cl_2 at 35°. [c] White powder. [d] White asbestos-like solid.

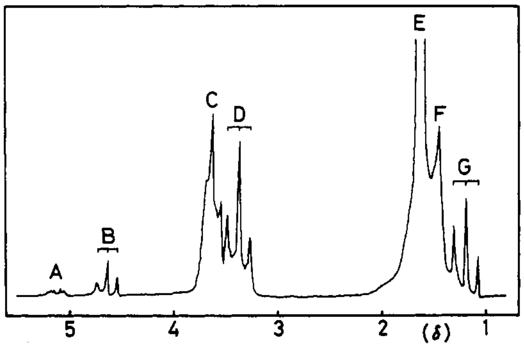
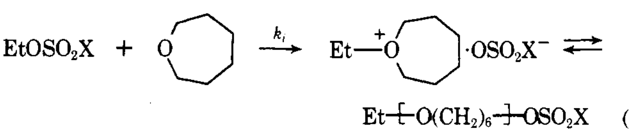


Figure 1. ^1H NMR spectrum of the oxepane polymerization system in nitrobenzene at 35° after 97 min; $[M]_0$ = 2.8 mol/l., $[I]_0$ = 0.55 mol/l.

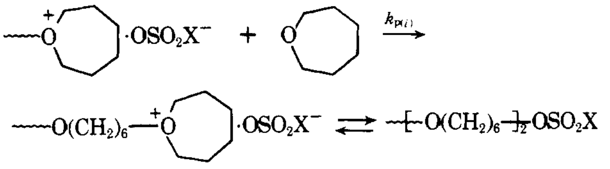
$\sim CH_2OSO_2CF_3$ in **3a**. From the integration ratio of peaks A and B, the ratio of **2a**/**3a** = 21/79 was obtained after the equilibrium of eq 1 was reached during kinetic run. A signal C (δ 3.60) and a triplet D (δ 3.35) were ascribed respectively to the methylene protons α to the oxygen atom of oxepane monomer (4 H) and of polymer (4 H). From these findings the course of the oxepane polymerization with $EtOSO_2CF_3$ ($X = CF_3$) initiator can be formulated as the following elementary reactions of SN2 mechanism (eq 2–4).

Initiation



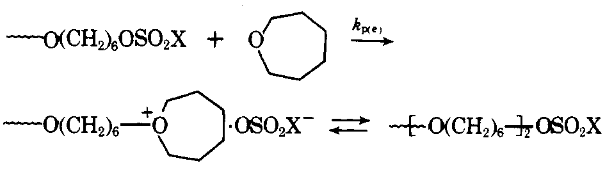
(2)

Propagations due to the oxonium ion **2**



(3)

and due to the macroester **3**



(4)

The integrated rate equations of initiation and propagation are given by eq 5 and 6, respectively[1,2]

$$\ln \frac{[I]_{t_1}}{[I]_{t_2}} = k_i \int_{t_1}^{t_2} [M]dt \qquad (5)$$

and

$$\ln \frac{[M]_{t_1} - [M]_e}{[M]_{t_2} - [M]_e} = k_{p(ap)} \int_{t_1}^{t_2} [P^*]dt \qquad (6)$$

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

$$[P^*] = [O^+] + [E] \qquad (7)$$

and $[M]_e$ is the equilibrium monomer concentration of polymerization. The oxepane polymerization has been shown to be a reversible process between monomer and polymer.[8] Since the present polymerization is of a system of relatively fast initiation and of slow propagation, eq 6 was adopted after the initiation process has been over, e.g., t_1 in eq 6 was longer than the time required for the complete consumption of initiator. Then, the relationship of $[P^*] = [I]_0$ was found by NMR spectroscopy and the right term of eq 6 actually becomes equal to $k_{p(ap)}[I]_0(t_2 - t_1)$ in which $[I]_0$ is the initial concentration of initiator. The following relationship is derived

$$k_{p(ap)} \int_{t_1}^{t_2} [P^*]dt = k_{p(i)} \int_{t_1}^{t_2} [O^+]dt + k_{p(e)} \int_{t_1}^{t_2} [E]dt \qquad (8)$$

where $k_{p(i)}$ and $k_{p(e)}$ denote the rate constants due respectively to the oxonium ion **2** and to the macroester **3**, and $[O^+]$ and $[E]$ are the concentrations of **2** and **3**, respectively.

By monitoring the polymerization by ^1H NMR (Figure 1), kinetic analyses could be made according to eq 5 and 6 to give values of $k_i = 17.3 \times 10^{-5}$ l./(mol sec) and $k_{p(ap)} = 11.1 \times 10^{-5}$ l./(mol sec) at 35° in nitrobenzene. The $[O^+]$ fraction in $[P^*]$ (21%) was much smaller than that (more than 98% at 0°) of the tetrahydrofuran polymerization.[2]

The ^{19}F NMR spectroscopy gave a further support for the equilibrium **2a** ⇄ **3a**. Figure 2 shows a ^{19}F NMR spectrum of the same polymerization system as that of Figure 1. Chemical shifts are given in parts per million relative to an external standard of CF_3CO_2H capillary. Peaks A (−2.23 ppm), B (+0.14 ppm), and C (−2.50 ppm) are assigned to OSO_2CF_3 signals of the initiator, the oxonium counteranion **2a**, and the macroester **3a**, respectively. Therefore, the consumption of initiator as well as the ratio of **2a**/**3a** were determined by ^{19}F NMR spectroscopy. Both ^{19}F and ^1H NMR spectroscopy gave very close results.

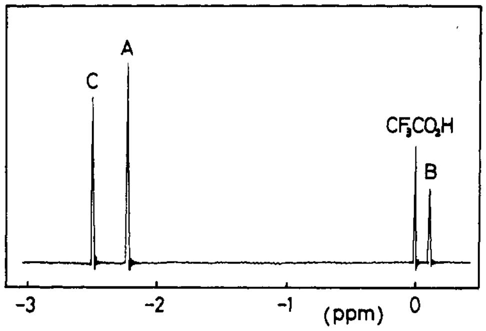


Figure 2. ^{19}F NMR spectrum of the oxepane polymerization system in nitrobenzene at 35° after 23 min; $[M]_0 = 2.80$ mol/l., $[I]_0 = 0.55$ mol/l. Chemical shifts are given in ppm relative to an external standard of CF_3CO_2H capillary.

In CCl_4 with $EtOSO_2CF_3$ initiator, a proton signal due to **2a** was not distinctly observed probably owing to the limitation of resolution and sensitivity of ^1H NMR. However, ^{19}F NMR clearly showed the presence of **2a** in about 10% for **3a.** Rate constants obtained were $k_i = 0.68 \times 10^{-5}$ l./(mol sec) and $k_{p(ap)} = 0.33 \times 10^{-5}$ l./(mol sec) in CCl_4 at 35°, respectively.

With the use of $MeOSO_2F$ initiator in nitrobenzene, ^{19}F signals of $MeOSO_2F$, the oxonium counteranion **2b**, and the macroester **3b** appeared respectively at −109.3, −116.8, and −112.7 ppm as sharp singlets. The $[O^+]$ fraction was very small, e.g., about 4% after equilibration.

In CCl_4 with fluorosulfonate initiator, on the other hand, only macroester **3b** could be seen by ^{19}F NMR spectroscopy, and the ion **2b** was not detected at all by ^{19}F NMR spectroscopy. With $EtOSO_2F$ initiator in the oxepane polymerization $k_i = 0.34 \times 10^{-5}$ l./(mol sec) and $k_{p(ap)} = 0.15 \times 10^{-5}$ l./(mol sec) were obtained. Furthermore, the propagating species of fluorosulfonate system was exclusively **3b** even in CH_2Cl_2, a more polar solvent than CCl_4. In cases where the concentration of **2b** could be taken as null, $k_{p(ap)}$ may be taken to be equal to $k_{p(e)}$ as observed in the tetrahydrofuran polymerization initiated by $EtOSO_2F$ in CCl_4.[1] However, the possibility of the contribution of ionic propagating species which might be present in a very small amount cannot be ruled out at the present stage of kinetic analysis.

Thus, it has been shown that rate constants (both k_i and $k_{p(ap)}$) and the $[O^+]$ fraction of the propagating end were very dependent upon the solvent employed. The equilibrium concentration of $[O^+]$ of the oxepane polymerization was always much lower than that of the tetrahydrofuran polymerization in the same solvent.[1,2]

This type of ion $\rightleftarrows$ ester equilibria including the polymerization system of tetrahydrofuran may be related to other types of reactions. In the solvolysis of ω-methoxy-*n*-alkyl *p*-bromobenzenesulfonates Winstein et al. observed a considerable rate enhancement for the butyl and pentyl derivatives,[13] which is interpreted in terms of neighboring-group participation involving cyclic trialkyloxonium intermediates.[13-15]

More detailed studies on the kinetics and mechanism will be published later.

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Partial Molar Volume of a Polymer in Supercritical Solution

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In supercritical solution deviations of the partial molar volume from the molar volume can give rise to thermodynamic anomalies and, according to transition state theory, to kinetic ones as well. Negative partial molar volumes of the less volatile component can occur, for example, in supercritical ethane–*n*-heptane mixtures and are attributable to the size difference between the two components of a homologous series.[1] The question as to whether such effects are sufficiently large in supercritical polymer solutions to be of thermodynamic or kinetic significance is of interest and important, for example, in connection with the free-radical polymerization of ethylene[2] which is carried out in supercritical solution.[3] An experimental determination of the partial molar volume of the polymer is difficult under such conditions.

The equation of state of Flory, Orwoll, and Vrij[4] (FOV) allows one to make reasonable estimates of molar and, within certain limits, of partial molar volumes for supercritical ethane–*n*-heptane mixtures.[1] We wish to show how a reduced equation of state, such as that of FOV, can be used to calculate the partial molar volume of a polymer in supercritical solution to obtain results which are good enough to settle questions such as that raised.

We consider a homologous binary mixture of solvent and polymer (ethane–polymethylene is a sufficiently good model for ethylene–polyethylene) and characterize it by the reduced variables $\tilde{V} = V/V^*$, $\tilde{T} = T/T^*$, $\tilde{P} = P/P^*$, where the quantities with asterisks and without superscripts refer to the reference parameters and molar properties of the mixture, respectively. The mixture parameters (unsubscripted) are related to those of the components (subscripted) by $V^* = x_1V_1^* + x_2V_2^* = v^*(r_1x_1 + r_2x_2)$, $\tilde{T} = \varphi_1\tilde{T}_1 + (1 - \varphi_1)\tilde{T}_2$, $P^* = \varphi_1P_1^* + (1 - \varphi_1)P_2^*$, where φ designates the volume fraction, r_1 and r_2 the number of chain segments per molecule, and v^* the core volume per segment, and the subscripts 1 and 2 refer to solvent and polymer, respectively.[11]

We start with the general relation

$$(\partial V/\partial x_2) = \bar{v}_2 - \bar{v}_1 = \tilde{V}(\partial V^*/\partial x_2) + V^*(\partial \tilde{V}/\partial x_2) \quad (1)$$

where $\bar{v}_2$ and $\bar{v}_1$ are the partial molar volumes of polymer and solvent, respectively, and x_2 is the mole fraction of polymer.