Table II
Rate Constants in the Cyclodimerization of Ethylene Oxide Catalyzed by Superacid Esters at 35° [a]

Catalyst	Solvent	$k_i \times 10^5$, l./(mol sec)	$k_p(\mathrm{ap}) \times 10^5$, l./(mol sec)
EtOTf	CCl_4	2.8	2.5
EtOTf	CH_2Cl_2	4.1	3.3
EtOTf		7.4	6.3
EtOTf	$C_6H_5NO_2$	22	15
MeOTf	CH_2Cl_2	5.6	2.9
$EtOSO_2F$		4.8	4.2

[a] $[EO]_0 = 9.2$ mol/l. in solution reaction and $[I]_0$ was 5.0 mol % for EO.

$$\ln [I]_0/[I]_t = k_i \int_0^t [EO]dt \qquad (7)$$

and

$$\ln [EO]_{t_1}/[EO]_{t_2} = k_i \int_{t_1}^{t_2} [I]dt + k_{p(ap)} \int_{t_1}^{t_2} [P^*]dt \qquad (8)$$

Since the k_i value and the relationship of [I] vs. time were obtained, the term of $k_i \int_{t_1}^{t_2} [I]dt$ in eq 8 became a known value. Thus, k_i and $k_{p(ap)}$ values were determined according to eq 7 and 8. In order to show the rate at what the reaction proceeded the preliminary results of several systems are given (Table II). Both the k_i and $k_{p(ap)}$ values increased in more polar media. It is interesting to note that in every case the value of $k_{p(ap)}$ is slightly smaller than that of k_i when $EtOSO_2X$ ($X = CF_3$ and F) is employed as a catalyst.

Further study is necessary to predict a definite mechanism of the present reaction, especially of the cyclodimerization process. As to the mechanism, however, it is important that the propagating end is an ester type species as observed in the superacid ester catalyzed polymerization of other cyclic ethers of oxepane,[1] tetrahydrofuran,[2-4,18] and 3,3-bis(chloromethyl)oxetane.[7] We are presently undertaking the kinetic and mechanistic studies on the cyclodimerization of EO in more detail, the reactions of substituted 1,2-epoxides, as well as the depolymerization of poly(ethylene oxides), all of which are catalyzed by superacids and their derivatives.

References and Notes

(1) Part VIII: S. Kobayashi, N. Tsuchida, K. Morikawa, and T. Saegusa *Macromolecules*, **8**, 942 (1975).
(2) S. Kobayashi, K. Morikawa, and T. Saegusa, *Macromolecules*, **8**, 386 (1975).
(3) S. Kobayashi, H. Danda, and T. Saegusa, *Macromolecules*, **7**, 415 (1974).
(4) S. Kobayashi, T. Nakagawa, H. Danda, and T. Saegusa, *Bull. Chem. Soc. Jpn.*, **47**, 2706 (1974).
(5) S. Kobayashi, H. Danda, and T. Saegusa, *Bull. Chem. Soc. Jpn.*, **46**, 3214 (1973).
(6) S. Kobayashi, T. Saegusa, and Y. Tanaka, *Bull. Chem. Soc. Jpn.*, **46**, 3220 (1973).
(7) S. Kobayashi, H. Danda, and T. Saegusa, *Bull. Chem. Soc. Jpn.*, **47**, 2699 (1974).
(8) S. Kobayashi, T. Ashida, and T. Saegusa, *Bull. Chem. Soc. Jpn.*, **47**, 1233 (1974).
(9) R. J. Gillespie, *Acc. Chem. Res.*, **1**, 202 (1968).
(10) H. Staudinger and H. Lehmann, *Justus Liebigs Ann. Chem.*, **505**, 41 (1933).
(11) D. J. Worsfold and A. M. Eastham, *J. Am. Chem. Soc.*, **79**, 897 (1957).
(12) D. J. Worsfold and A. M. Eastham, *J. Am. Chem. Soc.*, **79**, 900 (1957).
(13) G. A. Latremouille, G. T. Merrall, and A. M. Eastham, *J. Am. Chem. Soc.*, **82**, 120 (1959).
(14) G. T. Merrall, G. A. Latremouille, and A. M. Eastham, *Can. J. Chem.*, **38**, 1967 (1960).
(15) J. Dale et al., *Chem. Technol.*, 3 (1975).
(16) J. B. Lambert and D. H. Johnson, *J. Am. Chem. Soc.*, **90**, 1349 (1968).
(17) G. A. Olah and P. J. Szilagyi, *J. Org. Chem.*, **36**, 1121 (1971).
(18) K. Matyjaszewski and S. Penczek, *J. Polym. Sci., Polym. Chem. Ed.*, **12**, 1905 (1974).

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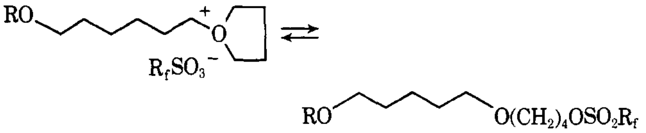
^{13}C Nuclear Magnetic Resonance Studies on the Polymerization of Cyclic Ethers

The polymerization of cyclic ethers has received considerable attention lately.[1-3] The polymerization kinetics have been established for many systems, based on the concentration of the propagating species, which were determined by phenoxy end capping,[4,5] and more recently by proton[2,6,8,9] and fluorine[3,7] NMR spectroscopy. In the polymerization of tetrahydrofuran (THF) a macroion ⇄ macroester equilibrium has been proposed,[9] and both end groups could be observed directly in high-resolution proton NMR spectra.[2]



The proton NMR signals are generally rather weak, unless large initiator concentrations are used, and due to strong solvent effects the assignments are not always unambiguous.[3,6,7] In polymerization systems where the initiator contains fluorine atoms, a clear distinction between covalent macroesters and ionic species can be made based on their different ^{19}F NMR signals.[3] However, the use of this technique is obviously restricted to polymerization systems with fluorine-containing initiators. Furthermore, it only allows a determination of the concentration of the counterion and does not permit monitoring of the actual propagating oxonium chain head during polymerization.

We have now utilized ^{13}C NMR spectroscopy to study these propagating chain heads and to monitor structural changes in the active species during the cationic polymerization of cyclic ethers. Not only can the presence of macroions or macroesters be clearly demonstrated in a noise-decoupled ^{13}C NMR spectrum, but a distinction can also be made between different types of ionic species formed in the course of the polymerization. This is generally not feasible by proton NMR spectroscopy. We wish to report preliminary results of these investigations.

The proton-noise decoupled spectra were obtained on a Bruker WH-90 Fourier transform NMR spectrometer, operating at 22.63 MHz. Typically, the spectra were recorded at 6024 Hz sweep width, and accumulation of 1000 pulses with phase alternating pulse sequence was found to give spectra with adequate signal-to-noise ratios. Field-frequency stabilization was maintained by deuterium lock on external perdeuterated benzene. The samples were prepared in 10 mm o.d. NMR sample tubes, with tetramethylsilane (TMS) as internal reference, and all chemical shifts are reported in ppm downfield from TMS. Spectral assignments were facilitated by spectra of model compounds and model polymers, which will be described in more detail at a later date.

Figure 1A shows the ^{13}C NMR spectrum of the polymerization mixture of tetrahydrofuran–methyl fluorosulfate (6:1) in nitromethane (64% by weight), after a reaction time of 20 min. Figure 1B shows a corresponding polymerization in carbon tetrachloride. The signal at lowest field in Figure

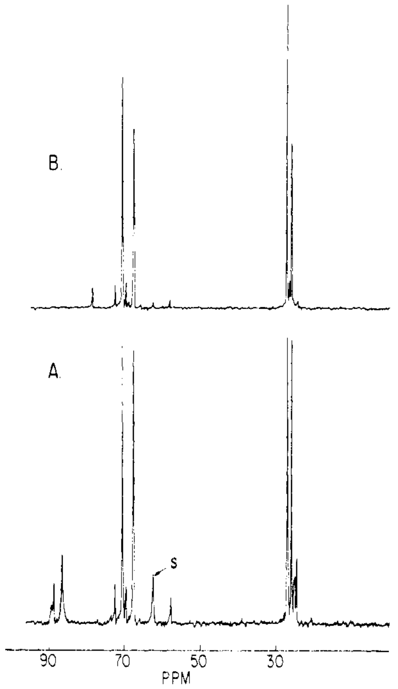
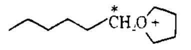
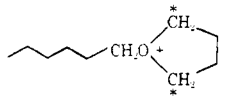
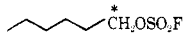
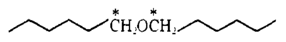
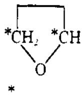
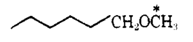
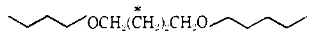
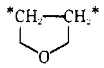


Figure 1. ^{13}C NMR spectra (22.63 MHz) of the polymerization mixture of THF–CH_3OSO_2F (6:1): (A) 64% in CH_3NO_2, after a polymerization time of 20 min (S indicates the solvent peak); (B) 64% in CCl_4, after a polymerization time of 20 min (the scan has not been extended to include the solvent peak at 96.7 ppm).

1A (at 89.6 ppm) is due to the open-chain methylene carbon of the polymeric species next to the oxonium ion at the growing chain end, while the signal at 87.5 ppm arises from the α-methylene carbons of the tetrahydrofurylium ring at the same chain end. The α-methylene carbon of the macroester (Figure 1B, at 79.1 ppm) is about 8 ppm further upfield, and the methyl carbon of the initiator (CH_3OSO_2F) is found at 62.5 ppm in Figure 1B. No residual initiator signal was detected in the nitromethane scan. The methylene carbons adjacent to the oxygen in the polymer chain are seen at 71.1 ppm. The two smaller satellites on either side of this peak are due to penultimate α carbons. The tetrahydrofuran monomer signal is at 68.2 ppm. The small peak at 58.4 ppm was found to be due to the $-OCH_3$ end groups of the polymer chain. This was demonstrated by off-resonance decoupling, which split this signal into a quartet. Solvent peaks are at 96.7 and 63.2 ppm, for CCl_4 and CH_3NO_2, respectively.

The corresponding β-methylene carbon signals are found in the high-field region, between 25 and 30 ppm. The individual peaks are sharp and can easily be separated by scale expansion, but all chemical shift effects are much less pronounced in the β carbons, and they are less useful to monitor chemical reactions. The chemical shift assignments of Figure 1 are summarized in Table I.

Table I
^{13}C NMR Shift Assignments in the Polymerization of Tetrahydrofuran by $MeOSO_2F$

Assignments[a]	^{13}C chemical shifts[b]
	89.6
	87.5
	79.1
	71.1
	68.2
$\overset{*}{C}H_3OSO_2F$	62.5
	58.4
	27.4
	26.2

[a] The carbon atoms of interest are marked by an asterisk. [b] Chemical shifts are given in ppm with respect to internal TMS.

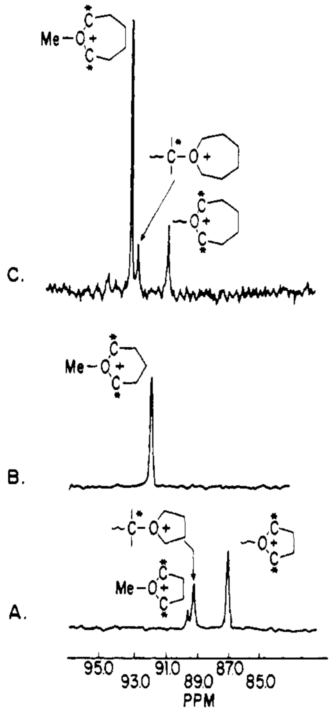
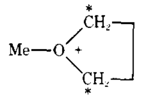
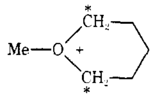
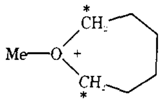
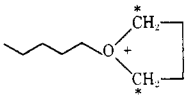
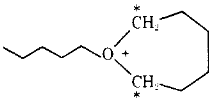
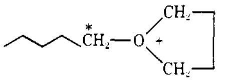
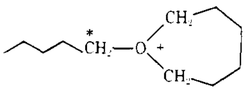


Figure 2. ^{13}C NMR spectra (22.63 MHz) of the oxonium ion region: (A) THF–$CH_3OSO_2CF_3$ (6:1) in CH_3NO_2 (64%), after 15 min; (B) THP–$CH_3OSO_2CF_3$ (6:2) in CH_3NO_2 (67%), after 60 min; (C) OXP–$CH_3OSO_2CF_3$ (2:6) in CH_3NO_2 (67%), after 30 min.

Figure 2 shows the oxonium region in more detail. The curve at the bottom (Figure 2A) is a scan between 83 and 95 ppm of the system THF–CH_3NO_2 (67% by weight) in the presence of a different methyl ester initiator, methyl triflate (THF–CF_3SO_3Me = 6:1). The ring- and open-chain methylene carbons next to the oxonium ion are again found at 89.6 and 87.5 ppm, i.e., the counterion did not have any effect on the chemical shifts. No macroester was detected in this system. The small peak at the low-field side (at 90.1 ppm) was assigned to the α-methylene carbons of the methyl tetrahydrofurylium ring, i.e., the initial tertiary oxonium ion formed in the reaction with THF. In systems with very high concentrations of methyl ester initiator (CH_3OSO_2F, $CH_3OSO_2CF_3$, etc.) this is the predominant peak observed.

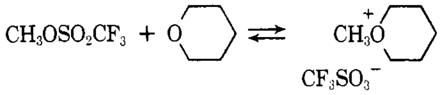
Scan B in Figure 2 shows the oxonium region of an analogous system, using tetrahydropyran (THP) instead of THF. No evidence for ring opening was found in this system. The only major peak in the oxonium region is at 92.1

Table II
^{13}C NMR Chemical Shifts of the "Oxonium" α-Methylene Carbons

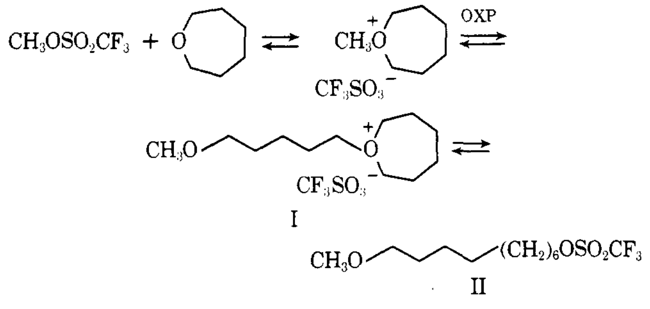
Assignments[a]	^{13}C chemical shift[b]
	90.1
	92.1
	93.5
	87.5
	90.5
	89.6
	92.8

[a] The carbon atoms of interest are marked by an asterisk. [b] Chemical shifts are given in ppm with respect to internal TMS.

ppm, which is due to the α-methylene carbons of the methyl tetrahydropyranylium ring.


$CH_3OSO_2CF_3$ + O(ring) ⇄ CH_3O^+(ring) $CF_3SO_3^-$

Finally, the top scan (Figure 2C) shows the oxonium region in the spectrum of a polymerization mixture containing the seven-membered ring oxepane (OXP).[11] The largest signal (at 93.5 ppm) is due to the α-methylene carbons of the initially formed methyl oxonium ring, which was present in higher concentration in this case because of a high initiator concentration. No macroester signal is found under these conditions. In the presence of higher monomer–initiator ratios (oxepane–$CH_3OSO_2CF_3$ = 4:1, in nitromethane, 70 wt. %) the methyl oxonium signal at 93.5 ppm was absent after 60 min, and the molar ratio of macroion I to macroester II (at 79.5 ppm) was found to be 3:7.



The chemical shifts of the oxonium methylene carbons of Figure 2 are listed in Table II.

The pronounced ring-size effect in these systems is evident, resulting in a downfield shift of about 1.7 ppm per ring expansion by one methylene group, from the five-membered to the seven-membered ring. A corresponding downfield shift of the open-chain and ring methylene carbons in the α position to the propagating chain end of the larger ring is also observed. Carbon-13 NMR spectroscopy may therefore allow quantitative measurement of the different propagating chain ends in ionic copolymerization of cyclic ethers.

Similar chemical shifts have been found in polymerizations initiated by ethyl esters ($EtOSO_2F$ or $EtOSO_2CF_3$), or by free acid (CF_3SO_3H). The clear separation of the different oxonium ions, which in some cases cover a range of almost 10 ppm, and the sensitivity of ^{13}C measurements may permit an estimation of the so-called "dormant" oxonium ions. Such open-chain oxonium ions have been postulated to be present in these polymerization systems.[12] Carbon-13 NMR spectroscopy therefore appears to be a very powerful tool for studying the detailed mechanisms in the cationic polymerization of cyclic ethers.

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References and Notes

(1) T. Saegusa and S. Kobayashi, *ACS Symp. Ser.*, **6**, 150 (1975).
(2) K. Matyjaszewski and St. Penczek, *J. Polym. Sci.*, **12**, 1905 (1974).
(3) T. K. Wu and G. Pruckmayr, *Macromolecules*, **8**, 77 (1975).
(4) T. Saegusa and S. Matsumoto, *J. Macromol. Sci., Chem.*, **4**, 873 (1970).
(5) T. Saegusa, *J. Macromol. Sci., Chem.*, **6**, 997 (1972).
(6) S. Kobayshi, H. Danda, and T. Saegusa, *Bull. Chem. Soc. Jpn.*, **46**, 3214 (1973).
(7) S. Kobayashi, H. Danda, and T. Saegusa, *Macromolecules*, **7**, 415 (1974).
(8) G. Pruckmayr and T. K. Wu, *Macromolecules*, **6**, 33 (1973).
(9) K. Matyjaszewski, P. Kubisa, and St. Penczek, *J. Polym. Sci.*, **12**, 1333 (1974).
(10) S. Kobayashi, T. Ashida, and T. Saegusa, *Bull. Chem. Soc. Jpn.*, **47**, 1233 (1974).
(11) T. Saegusa, T. Shiota, S. Matsumoto, and H. Fujii, *Macromolecules*, **5**, 34 (1972).
(12) T. Saegusa and S. Kobayashi, *Prog. Polym. Sci., Jpn.*, **6**, 107 (1973).
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^{13}C-{^1H} Nuclear Magnetic Resonance Study of Poly(isopropylthiiranes) Prepared from Racemic and Optically Active Monomers

Polymerization of monosubstituted thiirane has been extensively studied during recent years and special attention has been devoted to obtaining stereoregular polymers.[1] Use of optically active pure enantiomers allowed the preparation of corresponding optically active polymers and gave information on the ring-opening mechanism and the structure of the polymers. Thus, *S*(−)-methylthiirane[2] and *S*(−)-*tert*-butylthiirane[3] were prepared and polymerized with various initiators. Stereoregularity was studied by ^{13}C-{^1H} NMR on undeuterated polymers[4–7] and by ^1H NMR on deuterated polymers.[5,8,9]

In the case of methylthiirane it was shown that the tertiary carbon of the chain (A) was sensitive only to dyad ef-