Nuclear Magnetic Resonance Studies on the Polymerization of Cyclic Ethers

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ABSTRACT: High-resolution proton nmr spectroscopy was used to investigate the solution polymerization of cyclic ethers. The concentrations of secondary and tertiary oxonium ions, the propagating species, have been determined from nmr spectra. In "living" systems, where chain transfer and terminations are negligible, the kinetic molecular weight can also be monitored during the polymerization process. Molecular weight maxima were found in systems where the formation of tertiary oxonium ion is slower than the propagation. This method is generally applicable to study the cationic polymerization of cyclic ethers which do not have proton peaks interfering with the oxonium ion signals.

The cationic polymerization of cyclic ethers has been studied extensively by many investigators, and a mechanism involving propagation by oxonium ions is generally accepted.[1] The polymerization rates of many systems have been determined under different conditions and have been reviewed in a recent publication.[2]

The main problem in the kinetic treatment of propagation rates is the determination of the concentration of growing chains. This can be done by one of two general methods. (1) A direct method, in which certain physical properties of the system under investigation are being measured during the polymerization, such as conductivity or uv spectra. Certain assumptions have to be made here about the nature of the measured quantity and its relation to the concentration of active centers.[2] (2) An indirect method, in which the polymerization is quenched with a reagent which combines with the growing chain ends, and which can conveniently be measured after purification. Although somewhat cumbersome, this is an accurate method, provided there are no side reactions or other complications, which may alter the results. The polymerization rates of four-, five-, and seven-membered cyclic ethers have been studied by this method, using sodium phenoxide as the capping reagent.[3-5]

We wish to report a new direct method of monitoring the solution polymerization of cyclic ethers by high-resolution nmr spectroscopy, whereby the different oxonium ions can actually be observed and measured during the polymerization process. Furthermore, the ratio of active centers to total polymer concentration can be used to calculate a kinetic molecular weight in living polymer systems.

We have studied the polymerization of a number of different cyclic ethers by this method and will discuss the different parameters obtainable from nmr spectra.

Experimental Section

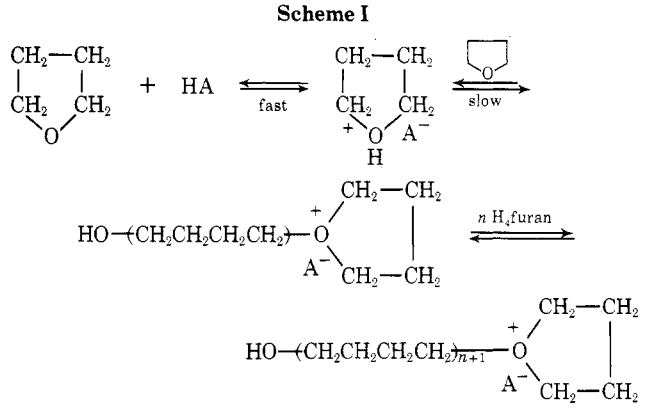
The cyclic ethers used in this investigation were commercial samples, dried and redistilled by conventional methods. Monomer and solvent were introduced into a dry, N_2-purged multineck microflask, equipped with condenser with drying tube, N_2 inlet, thermometer, and serum-capped addition adapter. The solution was stirred with a magnetic stirrer and cooled with a Dry Ice–trichloroethylene bath to −40°. The catalyst was then introduced by syringe at such a rate that the solution temperature never exceeded −30°. After addition of the catalyst, a sample of the homogeneous mixture was transferred to an nmr tube and cooled with Dry Ice until ready for insertion into the spectrometer probe. From previous experiments it was known that the initiation rate at that temperature was negligible for the initial 10 min, and we assumed the time of insertion into the spectrometer to be the start of the polymerization. The sample remained in the spectrometer during the entire polymerization, except for runs over 8 hr. In that case the sample was kept in constant-temperature chambers for the remaining periods. Initial scans were taken every 10 min, later every 30 min, and finally every hour. The instruments used were Varian A-60 and HR-220 nmr spectrometers. The solvent peak position was used as internal reference, and the values are reported in parts per million with respect to tetramethylsilane.

For molecular weight determinations by vapor-phase osmometry or hydroxyl number, the polymer solution in the microflask was quenched with water, and the polyether was extracted with toluene. The toluene solution was then neutralized, washed, and dried, and the solvent was removed under high vacuum (2 hr at 100° (0.5 mm)). For molecular weight comparison, an nmr scan was taken of a sample drawn immediately before quenching.

Results and Discussion

The polymerization of five-membered cyclic ethers represents a true equilibrium polymerization, without branching, producing straight polyether chains exclusively. In the simplest case, the steps shown in Scheme I are involved in the polymerization.[6]

Scheme I



HA represents any strong proton acid, which will catalyze the polymerization, such as trifluoromethanesulfonic

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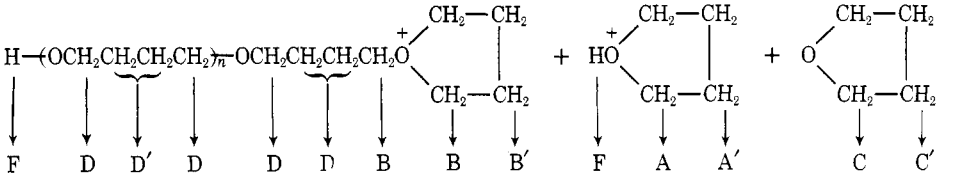
(1) K. C. Frisch and S. L. Reegen, Ed., "Ring-Opening Polymerizations," Marcel Dekker, New York, N. Y., 1969.
(2) P. H. Plesch, *Advan. Polym. Sci.*, 8, 137 (1971).
(3) T. Saegusa, Y. Hashimoto, and S. Matsumoto, *Macromolecules*, 4, 1 (1971).
(4) T. Saegusa and S. Matsumoto, *J. Macromol. Sci., Chem.*, 4, 873 (1970).
(5) T. Saegusa, T. Shiota, S. Matsumoto, and H. Fujii, *Macromolecules*, 5, 34 (1972).
(6) P. Dreyfuss and M. P. Dreyfuss, *Advan. Polym. Sci.*, 4, 528 (1967).

Table I
Spectral Assignments in the Polymerization Mixture of Tetrahydrofuran in Benzene



Signal	Chemical Shift in ppm (from Me_4Si)
A	4.65 (t)
B	4.25 (t)[a]
C	3.75 (m)
D	3.41 (m)
E A′	2.40 (m)
E B′	2.19 (m)
E C′	1.87 (m)
E D′	1.65 (m)
F	16.6–11.0 (bs)

[a] Two superimposed triplets; multiplicity: t = triplet, m = multiplet, and bs = broad singlet.

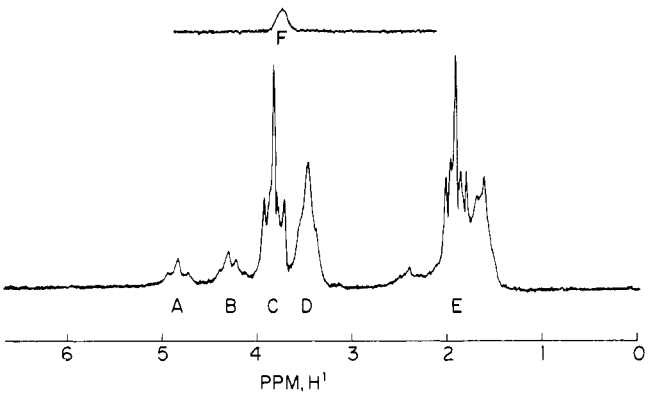


Figure 1. Nmr spectrum (60 MHz) of the polymerization mixture of H_4furan in benzene after 2 hr at 35°. (Peak F is centered at 12.1 ppm.)

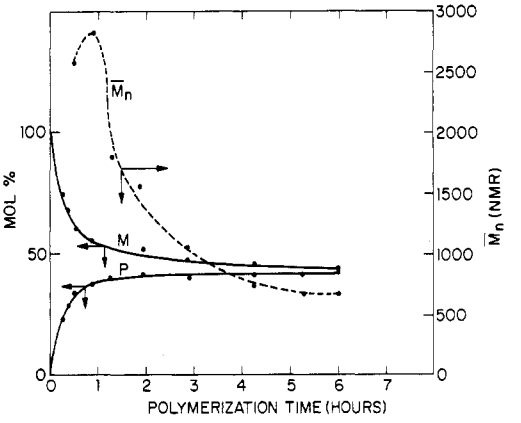


Figure 2. Monomer (M) and polymer (P) concentrations and molecular weights (M_n) during a polymerization of H_4furan in benzene at 20°.

acid, fluosulfonic acid, fuming sulfuric acid, etc. Strong Lewis acids, such as $SbCl_5$, PF_5, etc., work similarly but give slightly different results. They will be discussed later.

According to the above equation, one would expect to find a finite concentration of each species in the polymerization mixture at any time. This is seen in Figure 1, which shows an nmr spectrum of a room-temperature polymerization after 2 hr. Table I summarizes the chemical shift assignments.

The first group of signals (A, B, C, and D) are caused by the different α-methylene protons, while the overlapping multiplets at E are due to all β protons. (However, as shown later (Figure 3), the monomer and polymer signals of group E are well separated in the 220-MHz spectrum.)

Peak C at 3.75 ppm is due to the α protons of the monomer. After ring opening, the α-proton signal of the polymer is shifted upfield to 3.41 ppm (signal D). Peak A at 4.65 ppm is due to the α protons of the protonated H_4furan (secondary oxonium ion), while the corresponding β-proton signal (A′) can be found on the downfield side of peak E, around 2.4 ppm. These chemical shifts agree fairly well with published chemical shifts of protonated H_4furan in a "super acid" medium.[7]

(7) G. Olah, P. J. Szilagyi, *J. Organ. Chem.*, **36**, 1121 (1971).

The broad triplet at 4.25 ppm (peak B) is assigned to the six protons which are in α position to the tertiary oxonium ion of the growing chain end. The signals of the ring methylene protons coincide here with the open-chain methylene protons, although in higher dilution the open-chain methylene protons shift slightly upfield, similar to the usual upfield shift of open-chain protons *vs.* ring protons in five-membered cyclic ethers.

Peak F, finally, is attributed to the exchangeable protons of "free" acid, secondary oxonium ions, and hydroxyl end groups. As the acidic protons are being used up during the polymerization, this peak will continue to shift upfield from about 16.0 ppm to about 11.0 ppm, maintaining the same intensity. This shift can be used to monitor the progress of the polymerization: when the peak becomes stationary, equilibrium has been reached.

The changes in concentration of the different species can now easily be followed by comparing the intensities of the different signals. Figure 2 graphically shows these changes during a polymerization at 20°.

The concentration of monomer sharply decreases during the first hour, then levels off at 45% after about 6 hr. Conversely, the polymer concentration increases rapidly at first, leveling off after the same reaction time. The concentration of secondary oxonium ion is very small in the

Table II
Polymerization of H_4furan in Benzene[a]

Polym Time (hr)	Mol % H_4furan	Mol % Polymer	Mol % Secondary Oxonium Ion	Mol % Tertiary Oxonium Ion	$M_{n(nmr)}$	Chem Shift of H^+ (ppm)
		A. Concentration: 66.6% in Benzene; Temperature: 20°				
0.00	100.0	0.0	0.0	0.0		
0.25	74.3	23.2	0.51	0.34		
0.30	66.2	28.9	0.98	0.64		
0.50	60.0	34.1	1.44	0.96	2560	
0.83	55.0	37.5	1.92	0.96	2810	
1.25	53.1	39.8	2.90	1.61	1780	
1.92	51.2	41.1	3.38	1.87	1580	
2.83	48.6	39.9	3.70	2.77	1030	
4.25	45.8	40.8	3.21	3.97	740	
5.25	46.2	42.1	2.78	4.60	655	
30.00	37.0	50.0	0.93	7.76	490	
40.00	38.0	50.0	0.46	7.43	485	
		B. Concentration: 66.6%; Temperature: 35°				
0.00	100.0	0.0	0.0	0.0		16.00
0.50	69.0		2.4	0.8	2600	15.25
0.67	67.3	24.4	4.6	2.3	1050	14.03
0.83	65.0	25.7	4.6	3.1	580	13.70
1.00	62.5	26.8	4.6	3.8	520	13.36
1.50	58.0	30.0	4.4	5.5	400	12.71
2.83	53.8	35.8	1.7	7.1	370	11.88
5.00	49.5	41.5	0.0	7.6	415	11.25
7.50	48.0	42.6	0.0	7.9	410	11.03
30.00	45.0	44.0	0.0	8.0	420	11.20
		C. Concentration: 66.6%; Temperature: 0°				
0.00	100.0	0.0	0.0	0.0		
0.33	97.0	2.5	0.35	0.25	750	16.91
0.50	96.0	3.5	0.25	0.20	1280	16.91
0.83	90.5	9.4	0.25	0.33	2060	16.58
1.00	86.5	13.9	0.25	0.33	3040	16.50
1.42	73.3	22.0	0.49	0.32	4950	16.45
2.00	64.0	34.6	0.99	0.33	7550	16.30
2.33	57.5	40.2	1.45	0.49	5900	16.25
3.83	47.0	48.0	1.92	0.77	4440	16.08
5.00	44.5	50.5	2.40	0.96	3800	15.88
5.12	43.8	52.0	2.00	1.20	3100	15.75
6.67	42.5	52.0	3.03	1.35	2770	15.05
30.00	40.6	52.5	6.40	2.33	1560	14.17
240.00	35.7	55.7	1.77	6.50	620	12.67
720.00	35.2	54.5	0.00	8.10	480	12.92
900.00	36.8	53.1	0.00	7.80	490	13.00
		D. Concentration: 50%; Temperature: 0°				
0.00	100.0	0.0	*b*			
0.25	96.7	2.9	*b*	0.28		16.73
0.67	95.0	4.9	*b*	0.64	550	16.67
1.00	93.1	5.8	*b*	0.64	650	16.63
1.50	89.1	10.0	*b*	0.64	1130	16.53
2.25	81.0	17.6	*b*	0.90	1410	16.42
4.25	63.9	33.5	*b*	1.23	1960	16.17
4.67	60.8	36.9	*b*	1.49	1790	16.17
5.75	55.9	37.4	*b*	2.50	1080	16.05
7.50	55.5	41.0	*b*	2.88	1020	15.93
30.00	50.2	41.2	*b*	6.89	430	12.42

[a] Catalyst: 12.5 mol % FSO_3H. [b] Signal due to secondary oxonium ion not detectable.

beginning, reaches a maximum after 3 hr, and then decreases slowly (Table IIA). In a medium of low polarity, *e.g.*, at higher dilution in benzene, this peak is not observed at all (Table IID). This explains the initial slow increase in the protonated-monomer signal, which is a reflection of the changing polarity of the medium.

The concentration of growing chain ends (signal B) steadily increases during the polymerization until an equilibrium value is reached. The time necessary to reach this equilibrium depends on the type and concentration of catalyst, polymerization temperature, monomer concentration, and solvent polarity. After reaching equilibrium the concentration of growing chain ends practically remains unchanged (Table IIA,B), demonstrating the lack of termination and the "living" character of this system.

The kinetic chain length, $\bar{L}$, can now be calculated by dividing the corrected polymer concentration ($D + B/3$: α-methylene protons of polymer chain) by the concentra-

Table III
Molecular Weight Changes after Addition of Monomer to an Equilibrated "Living" H_4furan Polymerization System at 20°

Time after Monomer Addition (hr)	$M_{n(nmr)}$
0.16	320
0.33	320
0.58	320
2.16	330
3.16	350
17.50	375
70.00	730

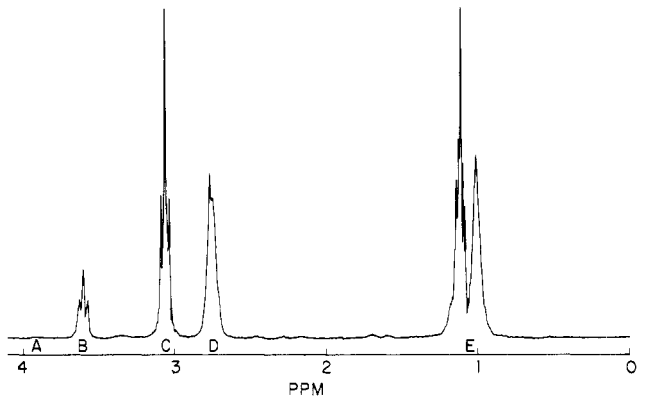


Figure 3. Nmr spectrum (220 MHz) of the polymerization mixture of H_4furan in benzene after 30 hr at 20° (sweep offset: 0.67 ppm).

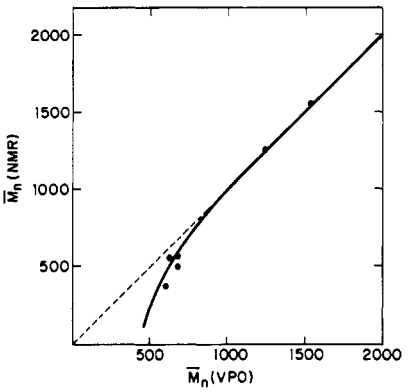


Figure 4. Correlation of molecular weights obtained by nmr and vpo.

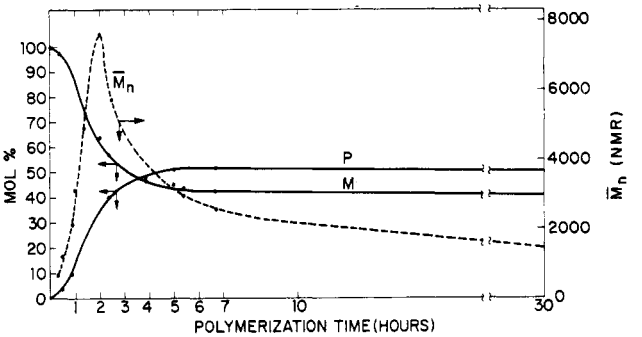


Figure 5. Monomer (M) and polymer (P) concentrations and molecular weights ($\bar{M}_n$) during a polymerization of H_4furan in benzene at 0°.

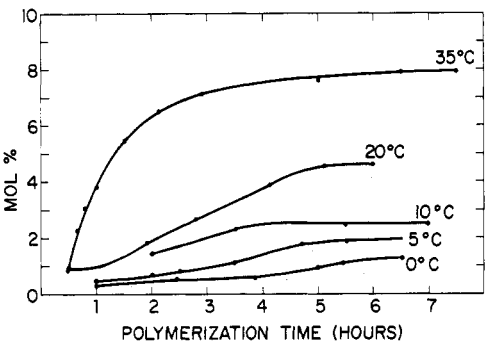


Figure 6. Formation of tertiary oxonium ion during the polymerization of H_4furan in benzene at different temperatures.

tion of the growing chain ends ($2B/3$: α-ring protons of growing chain end): $\bar{L} = (D + B/3)/2B/3$. The molecular weight derived from this equation is also plotted in Figure 2. It is seen that the molecular weight goes through a maximum early in the polymerization and then falls off to an equilibrium value. The steep decrease after the initial maximum molecular weight is due to an increase in the number of growing chains and does not represent an actual depolymerization. On adding monomer to an equilibrated system, *i.e.*, a system with a determined concentration of active chain ends, no such maximum should occur. This is shown in Table III: the molecular weight slowly increased without going through a maximum. The propagation rate in the initial stages of polymerizations catalyzed by proton acids is therefore much faster than the initiation, *i.e.*, the formation of tertiary oxonium ion. These rate differences become even more pronounced at low temperatures, where the initial molecular weight maxima can be much higher. The rate of formation of tertiary oxonium ions is also concentration dependent. It is faster at higher dilution, leading to lower initial molecular weight maxima and faster equilibration, as seen by comparing Table IIC,D.

The molecular weight after 30 hr at 20°, determined from spectrum (Figure 3), was 490. The corresponding molecular weight determined by vapor phase osmometry was 685. This difference is not surprising, considering the different nature of the two determinations: The molecular weight by nmr counts all open chains, even monomeric units which would be removed in the purification process preceding vapor-phase osmometry. The discrepancy between these two values would therefore be expected to be smaller at higher molecular weights which contain a smaller amount of low oligomers. This is indeed verified. For molecular weights above 1000, both methods give values within the limits of experimental error (Figure 4).

Similar information can be obtained from polymerizations at different temperatures and with different catalyst systems (Tables IIC,D and IV). Figure 5 shows the changes in monomer and polymer concentrations and the molecular weight during a solution polymerization at 0°. The monomer-to-polymer conversion reaches a plateau after 5–6 hr, while the molecular weight, after an initial maximum, keeps decreasing until it finally becomes identical with that of the higher temperature runs. This molecular weight seems to be the true equilibrium value, characteristic of catalyst and polymerization conditions. Initiation at 0° is very slow, and the molecular weight maximum is correspondingly high here, exceeding the equilibrium value by more than tenfold (Table IIC). The rate of formation of growing chain ends at different polymerization temperatures is shown in Figure 6.

Table IV
Polymerization of H_4furan in Benzene[a]

Polym Time (hr)	Mol % H_4furan	Mol % Polymer	Mol % Tertiary Oxonium Ion	$M_{n(nmr)}$	Chem Shift of H^+ (ppm)
0.00	100.0	0.0			
0.25	99.0	1.05			17.17
0.58	98.5	1.48			17.12
1.00	98.0	1.50			17.12
1.50	97.5	1.50			17.07
2.00	97.0	3.00			17.07
3.25	92.5	6.85	0.70	700	17.03
4.00	85.0	15.35	0.70	1580	17.00
5.00	74.4	20.80	0.64	2340	16.98
6.00	72.6	23.8	1.18	1450	16.97

[a]Catalyst: 5 mol % CF_3SO_3H; concentration: 66.6%; temperature: 0°. Signal due to secondary oxonium ion not detectable.

Table V
Polymerization of H_4furan in Benzene[a]

Polym Time (hr)	Mol % H_4furan	Mol % Polymer	Mol % H_4furan·$SbCl_5$ Adduct[b]	Mol % Tertiary Oxonium Ion
0.33	100			
0.50	57	32.4	6.75	1.8
0.75	57	32.8	6.65	1.6
2.00	57	32.2	6.65	2.2
15.00	54	36.3	6.10	2.5
48.00	53	39.7	5.75	3.7

[a]Catalyst: 12.5 mol % $SbCl_5$; concentration: 66.6%; temperature: 35°. [b]Chemical shift of the α protons of this adduct is similar to that of the secondary oxonium ion.

Table VI
Polymerization of Bis(chloromethyl)oxetane in CH_2Cl_2

Polym Time (hr)	Mol % BCMO	Mol % Polymer	Mol % Tertiary Oxonium Ion	Chem Shift of H^+ (ppm)
0.00	100.0			
0.08	60.8	28.5	10.8	10.75
0.50	53.6	32.7	12.4	9.83
1.00	53.0	34.4	12.4	9.28
2.00	49.2	38.7	12.2	8.53
2.50	46.8	40.7	12.2	7.92
3.50	42.2	45.5	12.8	7.25
5.50	40.0	47.0	12.0	6.33
100.00	8.2	75.4	16.4	3.00

[a] Catalyst: 13.5 mol % FSO_3H based on BCMO; concentration: 50%; temperature: 0°.

Catalysis by strong Lewis acids, such as $SbCl_5$, gives similar results, except that a high concentration of H_4furan-Lewis acid complex is formed very early and remains high throughout the polymerization (Table V). The concentration of active chain ends remains low, indicating higher molecular weight, but the possibility of chain transfer and termination steps in this system makes molecular weight calculations less reliable.[8] With weaker Lewis acids, such as BF_3, no polymer or tertiary oxonium ion formation was detected by nmr at room temperature without cocatalysts.

The nmr method can be used to study other cyclic ethers, provided no signals interfere with the oxonium and polymer signals. We have studied several substituted tetrahydrofurans, which are not generally known to homopolymerize.[9] We found that 2-methyltetrahydrofuran contained 11% ring-opened oligomer after a polymerization time of 20 hr at room temperature. From the concentration of tertiary oxonium ions, an average chain length of $n \simeq 3$ was calculated. As expected, the six-membered cyclic ether tetrahydropyran gave no indication of polymer formation under identical conditions.

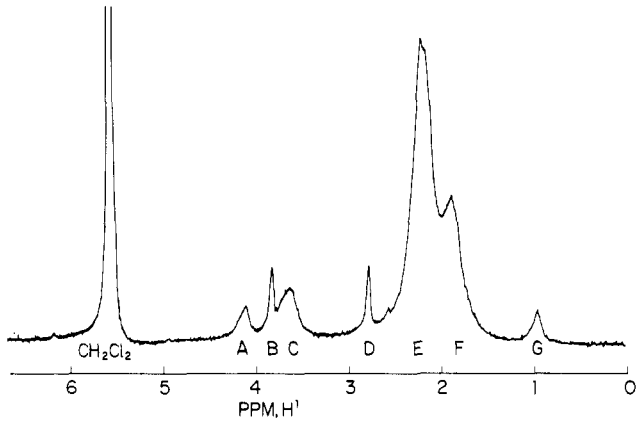


Figure 7. Nmr spectrum (60 MHz) of the polymerization mixture of bis(chloromethyl)oxetane in CH_2Cl_2 after 100 hr.

Four-membered cyclic ethers are highly strained rings, and no polymerization equilibrium can be expected under these conditions.[10] In the polymerization of BCMO (bis-(chloromethyl)oxetane) monomer was slowly depleted, until after 100 hr the polymerization mixture consisted of 8.2% monomer, 75.4% polymer, and 16.4% tertiary oxonium ion (Table VI). A high catalyst ratio was purposely used here to keep the degree of polymerization low, since longer chains of poly[bis(chloromethyl)oxetane] tend to become quite insoluble. The average degree of polymerization of the tabulated example was $n = 4.6$, corresponding to a molecular weight of 710. However, the possible formation of cyclic oligomers prevents the calculation of meaningful molecular weight data in the polymerization of four-membered cyclic ethers.[10]

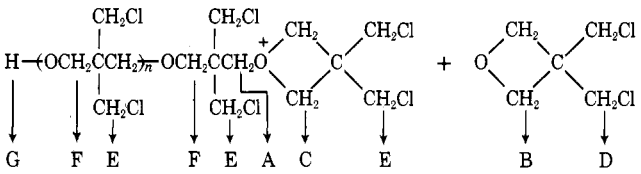
The nmr spectrum of BCMO after 20 hr of polymerization time is shown in Figure 7. Comparison of monomer and polymer spectra facilitated the following assignments (Table VII). Signals B (4.41 ppm) and D (3.91 ppm) are due to residual monomer, B corresponding to the oxetane ring

(8) P. Dreyfuss, *Polym. Prepr., Amer. Chem. Soc., Div. Polym. Chem.*, 13, No. 1, 46 (1972).

(9) R. Chiang and J. H. Rhodes, *J. Polym. Sci., Part B*, 7, 643 (1969).

(10) J. B. Rose *in* "The Chemistry of Cationic Polymerization," P. H. Plesch, Ed., MacMillan, New York, N. Y., 1963.

Table VII
Spectral Assignments in the Polymerization Mixture of Bis(chloromethyl)oxetane in CH_2Cl_2



Signal	Chem Shift in ppm (from Me_4Si)
A	4.56
B	4.41
C	4.31
D	3.91
E	3.60
F	3.47
G	10.8–2.9

protons and D to the chloromethyl protons. On polymerization both signals are shifted upfield, but due to the relief of ring strain the oxetane proton signals are shifted further (F) than the chloromethyl protons (E). A solution of poly[bis-(chloromethyl)oxetane] shows, therefore, two sharp singlets of equal intensity, one at 3.60 ppm, the other one at 3.47 ppm.[11] The low degree of polymerization of the illustrated example causes the polymer peaks to become unequal in intensity, since the chain methylene groups which are α to an oxonium ion are shifted downfield, and the chloromethyl signal appears correspondingly stronger. Peak C (4.31 ppm), which has twice the intensity of peak A (4.56 ppm), was assigned to the ring methylene groups of the growing chain end, while peak A was assigned to the straight-chain methylene group adjacent to the oxonium ion. Signal G, finally, is due to the exchangeable hydroxyl proton (Table VII).

From Table VI it is seen that 40% of the monomer is consumed within the first 5 min. The initial ring opening and formation of tertiary oxonium ions is so fast at 0° that in contrast to five-membered cyclic ethers, no molecular weight maximum could be detected. After the free acid is consumed, the subsequent ring opening is much slower, and almost 6 hr are necessary for 60% of monomer to be consumed.

(11) Jeol Spectrum, No. 184, Sadler Corp., Philadelphia, Pa.

Sequence Analysis of Ethylene Oxide–Propylene Oxide Copolymers by Carbon-13 Nuclear Magnetic Resonance

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ABSTRACT: The chain carbon-13 spectra of ethylene oxide–propylene oxide copolymers are assigned in terms of dyad and triad sequences. Ambiguities in the derivation of sequence distribution from nmr intensities are discussed. In the base-catalyzed copolymers examined, the distribution and tacticity of propylene oxide units are approximately random, but the monomer units are directionally oriented. A rather high probability of chain termination by propylene oxide groups is also noted.

Despite the fact that practical limitations have forced a very heavy emphasis on protons, nuclear magnetic resonance techniques have proved an extremely valuable method for the characterization of polymer structures.[1] The advent of fast Fourier transform methods[2] now makes it practical to extend these methods to carbon-13, where the expanded chemical shift range, longer relaxation times, isotopic dilution, and more direct involvement of the nuclei in the critical bonding features of organic molecules promise an extension considerably beyond the resolution available in proton magnetic resonance studies. Poly(propylene oxide) provides a case in point.[3-5] The present study considers the carbon-13 spectrum of a slightly more complicated copolymer system containing both ethylene oxide and propylene oxide units. Only the main-chain carbons are considered, since the methyl group spectrum shows no resolvable structure and consequently yields little information not available from other sources. With the application of proton decoupling, the carbon-13 spectrum is reduced to one sharp line for each unique chain carbon environment in the molecule, the criterion of uniqueness being defined by the chain length over which structural features affect the chemical shifts. A typical spectrum, shown in Figure 1, shows a multiplicity of lines indicative of the fact that the amount of structural information available is rich. The gross features of this spectrum can be reduced, moreover, to four main bands that are indicated in the figure. Our main concern in this study is to assign these bands to structural features, to relate these features to chemical parameters such as monomer sequencing and tacticity, and to indicate some of the ways in which this information conveys diagnostic information about the polymerization. We have not

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