Macrocyclic Tetrahydrofuran Oligomers. 3.[1] Formation of Macrocycles in Tetrahydrofuran Copolymerizations

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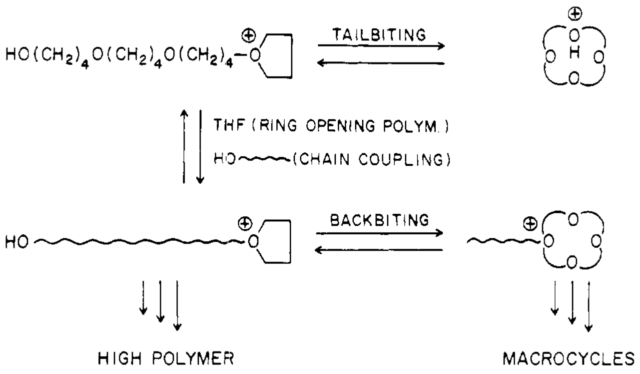
ABSTRACT: Previous work demonstrated formation of cyclic oligomers and high molecular weight linear polymer during polymerization of tetrahydrofuran (THF) with nonhydrolyzable proton acid initiators. A similar mechanism is now shown to be operative in ethylene oxide (EO) homopolymerizations and EO/THF copolymerizations. In EO/THF copolymerizations, the predominant oligomers are cyclic tetramers. The absence of linear oligomers in these systems supports the general nature of the proposed chain-coupling mechanism.

Recently we have reported the exclusive formation of macrocyclic oligomers in the polymerization of tetrahydrofuran (THF) with nonhydrolyzable strong acid initiators, such as trifluoromethanesulfonic acid (CF_3SO_3H).[1] Briefly, the proposed mechanistic pathway involves chain-coupling and back-biting steps which lead to very high molecular weight linear polymer chains with hydroxy groups and oxonium ions at opposite chain ends and to a series of macrocyclic oligomers. The complete absence of linear oligomers is due to the rapid reaction of hydroxy and oxonium ends, resulting in either chain coupling to form high molecular weight polymers or tail biting to form macrocycles.



In the present paper we report on the polymerization of EO and EO/THF systems, initiated by trifluoromethanesulfonic acid. We will discuss the formation and nature of the cyclic oligomers in ethylene oxide homopolymerizations and in ethylene oxide/tetrahydrofuran (EO/THF) copolymerization systems.

Experimental Section

Dry tetrahydrofuran (DuPont) stored over metallic sodium was used as the monomer. Trifluoromethanesulfonic acid (triflic acid) was distilled under N_2 at atmospheric pressure prior to use (bp 160 °C). All other reagents or solvents are commercially available in reagent grade purities and were used without further purification.

Polymerizations were carried out by placing reagents and solvent into a Pyrex multineck microflask, equipped with thermometer, condenser, and N_2 inlet and sealed with drying tubes and rubber serum caps. In a typical experiment, THF (10.0 g, 138.9 mmol), EO (10.0 g, 227.3 mmol), and CH_3NO_2 (5 g, 81.9 mmol) were mixed, added to the polymerization flask, and externally cooled to 0 °C. Trifluoromethanesulfonic acid (0.42 g, 2.8 mmol) in CH_3NO_2 (5 g, 81.9 mmol) was added through the septum with a syringe to the magnetically stirred solution. The desired polymerization temperature was then adjusted by externally controlled heating or cooling. Samples were withdrawn periodically through the serum cap.

Gas chromatograms were obtained on a Varian Aerograph Series 2700 model with flame ionization detectors. One hundred and eighty centimeter columns packed with 10% OV-101 (Supelco, Inc.) on Gas Chrom Q (Applied Science Labs) were used. Injection port and detector temperatures were maintained at 280 °C. Column temperature was normally programmed from 80–280 °C at 20 °C/min and held at 280 °C. Samples of the polymerization mixtures were neutralized with a 1% solution of CH_3ONa in absolute CH_3OH or by treatment with the basic ion exchange resin Amberlite IRA-94. The neutral or weakly basic samples were injected directly into the glass-lined injection port. The internal standard was 2,6-di-*tert*-butyl-4-methylphenol (BHT).

GC retention times and area integrations were calculated by computer analysis. Real time data acquisition (DART) and analysis was carried out on the DuPont PDP-10 GC Data Analysis System.

Chemical ionization mass spectra were obtained on a DuPont 21-491 gas chromatograph/mass spectroscopy system, with isobutane as the reagent gas.[2]

Conversion and degrees of polymerization were calculated from 100 or 220 MHz NMR spectra recorded on Varian HA-100 and HR-220 MHz spectrometers, with tetramethylsilane as internal reference. Perdeuterated solvents were used for all NMR experiments.

Results and Discussion

The polymerization of THF with nonhydrolyzable strong proton acids leads to high molecular weight linear polymer and macrocyclic oligomers by a mechanism involving ring-opening and chain-coupling steps.[1] We believe that this mechanism is quite general for ring-opening polymerization of cyclic ethers initiated by nonhydrolyzable strong proton acids. Recent experiments with EO and EO/THF polymerization systems, reported in the present paper, support the proposed mechanism.

The formation of macrocyclic oligomers in the cationic polymerization of certain cyclic ethers has been known for some time.[3] More recently, Dale reported the formation of cyclic oligomers of EO, unaccompanied by open-chain oligomers, using acidic fluorine compounds such as BF_3, PF_5, or SbF_5 as initiators and HF as cocatalyst.[4] In the presence of a substance capable of furnishing permanent end groups to the polymer, such as diethyl ether, a mixture of, e.g., ethoxy-terminated chains was formed instead. Oxygen-containing acids, such as *p*-toluenesulfonic acid, led to rapid formation of the half-esters of ethylene glycol.[5] Saegusa and co-workers studied the reaction of EO with CF_3SO_3H and described a "cyclodimerization" of EO to 80% 1,4-dioxane, the rest being converted to poly(ethylene oxide).[6] The following discussion will show that these reports are consistent with the mechanism proposed for THF/CF_3SO_3H systems.

In a series of test polymerizations of EO with CF_3SO_3H initiation we verified that the major volatile reaction products are indeed the expected EO crown ethers. A gas chromatographic scan of the reaction products of EO/CF_3SO_3H in CH_3NO_2 at 20 °C after they were quenched

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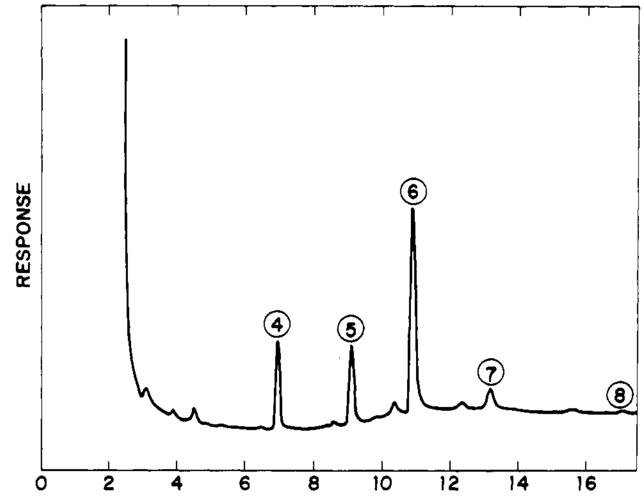


Figure 1. Gas chromatogram of a $EO/CH_3NO_2/CF_3SO_3H$ (molar ratios = 2.21/15.00/0.01) polymerization mixture after 2 h at 20 °C. (GC conditions described in the Experimental Section): circled numbers indicate EO crown ethers (i.e., a circled 4 means 12-crown-4, etc.).

Table I
EO Crown Ethers Identified by Chemical Ionization/Mass Spectroscopy in EO/CF_3SO_3H Systems

retention time,[a] min	*m/e*	compd
6.9	177	12-crown-4
9.2	221	15-crown-5
11.1	265	18-crown-6
13.6	309	21-crown-7
17.6	353	24-crown-8

[a] GC conditions: column OV-101, (10% on GCQ), 180 cm × 0.25 cm; temperature program, 80–280 °C (20 °C/min) + 280 °C isotherm; injection port (glass insert), 280 °C.

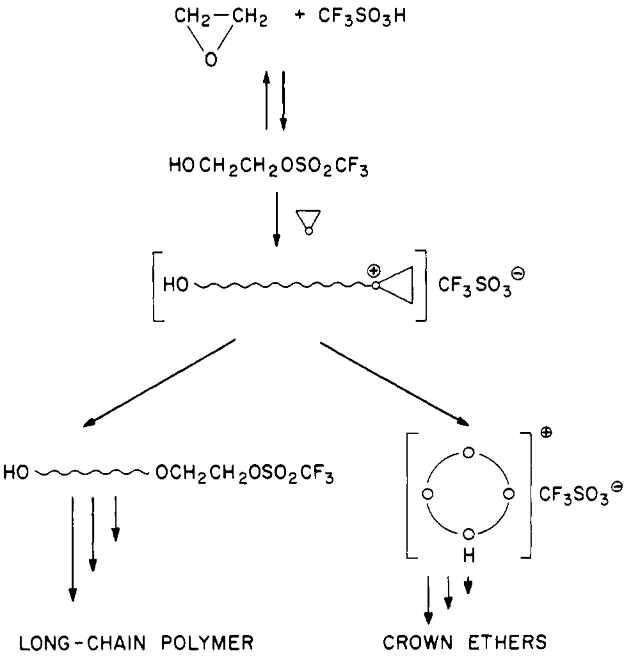
and neutralized with a basic ion exchange resin (Amberlite IRA-94) is shown in Figure 1. This ion exchange resin has pendant tertiary amine groups and was preferred over neutralization with CH_3ONa in order to prevent any possible shift in crown ether distribution due to ion template effects.[7] The preferred crown ethers formed under these conditions were found to be 12-crown-4, 15-crown-5, and 18-crown-6, but cyclic ethers up to 24-crown-8 have been identified by chemical ionization/mass spectroscopy (Table I) and up to 30-crown-10 by GC retention time. In Table II, the composition of the cyclic oligomer fraction is given as area percent of the total of the oligomeric species detectable by gas chromatography under our test conditions. Initially the concentration of 1,4-dioxane is of the same order of magnitude as the concentration of the crown ethers, but after 20 h it is the predominant cyclic ether present, in agreement with the finding of Saegusa.[6] This delayed formation of dioxane is consistent with a proposed indirect formation by polymer degradation.[8]

Table II
Composition of the Major Volatile Reaction Products of EO/CF_3SO_3H as the Percent of Total Volatile Reaction Products of EO/CF_3SO_3H (GC Area)

	polymerization time[a]			
product	30 min	1 h	2 h	20 h[b]
1,4-dioxane	12.2	20.8	34.3	93.9
12-crown-4	13.7	15.8	15.8	1.1
15-crown-5	38.4	32.8	23.0	0.7
18-crown-6	>2.0	2.4	6.0	0.7
21-crown-7	4.7	5.5	8.6	0.5
24-crown-8		2.6	2.1	0.06

[a] Polymerization conditions: $EO/CH_3NO_2/CF_3SO_3H$ (mol ratios = 2.21/15.00/0.01); temperature, 5 °C. GC conditions, see Table I. [b] 6 h at 5 °C + 18 h at 20 °C.

Scheme I



Due to the high ring strain of a three-membered cyclic oxonium ion, the propagating species in EO/CF_3SO_3H polymerizations is rapidly converted to the strainless triflate ester, or to a macrocyclic crown ether of lower ring strain, by tail biting or back biting (reaction Scheme I). Only a tail-biting cyclization, resulting in the formation of a secondary macrocyclic oxonium ion, is shown in this reaction scheme, but back-biting cyclizations to form tertiary macrocyclic oxonium ions may also occur, particularly in the later stages of the polymerization. The higher stability of the covalent ester species in these systems explains the formation of some oligomeric glycols on hydrolysis (small peaks in Figure 1). The initial intermediate half-ester $CF_3SO_3CH_2CH_2OH$ can be detected by gas chromatography and NMR spectroscopy in the polymerization mixture at short reaction times and/or low temperatures (chemical shift of the α-methylene protons of the half-ester $CF_3SO_3\mathit{CH}_2CH_2OH$, 4.73 ppm). In THF/CF_3SO_3H systems, on the other hand, the predominant propagating species in polar solvents is the more reactive oxonium ion, and no oligomeric glycols are found under these conditions.[1]

If a weaker sulfonic acid, such as CH_3SO_3H, is used, the oligomeric half-esters are quite stable and constitute the main reaction products (chemical shift of the α-methylene protons of the half-ester $CH_3SO_3\mathit{CH}_2CH_2OH$, 4.35 ppm). Due to the lower reactivity of methane sulfonate esters, the linear oligomeric esters are not removed by coupling reactions even at high polymerization temperatures. A gas chromatogram of an EO/CH_3SO_3H mixture in CH_3NO_2 is shown in Figure 2. The individual compounds corresponding to the different gas chromatographic peaks were identified by chemical ionization/mass spectroscopy. Only traces of crown ethers were found in these systems (small peaks between the half-ester peaks in Figure 2), an indication that ring opening of the intermediate oxonium ion to the corresponding covalent ester was faster than any back-biting reactions. It is interesting to note that little

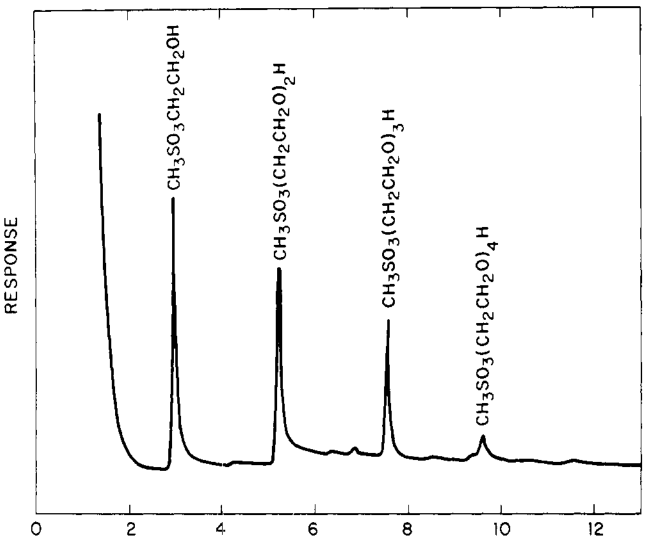


Figure 2. Gas chromatogram of a $EO/CH_3NO_2/CH_3SO_3H$ (molar ratios = 11:16:1) polymerization mixture after 2 h at 20 °C (GC conditions described in the Experimental Section).

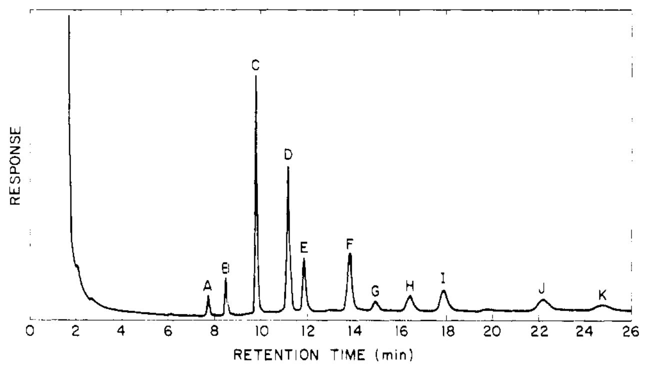


Figure 3. Gas chromatogram of a $EO/THF/CH_3NO_2/CF_3SO_3H$ (molar ratios = 11:14:20:0.3) polymerization mixture after 5 h at 20 °C. (The letters refer to the macrocyclic compounds shown in Table III.)

Table III
Crown Ethers Identified by Chemical Ionization Mass Spectroscopy in EO/THF Polymerization Mixutres

identification code (see Figure 3)	R_T[a]	mol wt ($m/e - 1$)	crown ether composition (EO:THF)
A	7.6	188	1:2
B	8.4	204	3:1
C	9.7	232	2:2
D	11.2	260	1:3
E	11.8	276	3:2
F	13.8	304	2:3
G	14.9	320	4:2
H	16.4	332	1:4
I	17.8	348	3:3
J	21.9	376	2:4
K	24.2	392	4:3

[a] GC retention times under the conditions specified in the Experimental Section.

Table IV
Composition of Reaction Products[a] in $EO/THF/CF_3SO_3H$ Systems[b] after 5 h at 25 °C

	feed composition (wt ratios)		
cyclic product	10 THF 2 EO	10 THF 5 EO	10 THF 10 EO
1,4-dioxane		4.9	6.7
1:2	2.7	1.7	0.4
3:1	1.2	4.5	10.4
2:2	17.9	31.5	31.5
1:3	32.0	19.5	9.1
3:2	2.8	6.6	8.1
2:3	14.2	10.8	9.3
4:2	0.6	1.7	2.1
1:4	11.4	3.4	1.5
3:3	3.7	5.3	4.8
2:4	1.3	4.2	3.4
1:5	5.1	1.5	0.6

[a] Standardized GC areas as percent of total volatile reaction products. [b] Mol ratios $THF:CH_3NO_2:CF_3SO_3H$ = 13.89:20.49:0.30.

dioxane formation was observed in this system, even at very long reaction times, in contrast to the EO/CF_3SO_3H system. This finding is also consistent with an indirect formation of dioxane by polymer degradation.

With still weaker oxygen-containing acids as initiators, such as *p*-toluenesulfonic acid, no chain propagation, coupling, or back biting was reported to occur, and the system stops at the ethylene glycol half-ester stage.[5]

Since we have confirmed the formation of EO crowns and THF crowns in polymerization systems initiated with nonhydrolyzable, strong, protonic acids, it seemed of interest to investigate a EO/THF comonomer system, where in addition to both series of homologous macrocycles, there should also be formed a large number of possible mixed macrocyclic ether oligomers. We have investigated the $EO/THF-CF_3SO_3H$ system in some detail and have identified all oligomeric species which are separately observable by GC.

Figure 3 shows a gas chromatogram of an $EO/THF-CF_3SO_3H$ polymerization system in CH_3NO_2 after neutralization with Amberlite IRA-94. More than a dozen different peaks are observed, without any immediately apparent pattern. First the absence of linear oligomers was established by treatment with *N*,*N*-bis(trimethylsilyl)trifluoroacetamide (BSA), in order to silanate any hydroxy end groups. Silanation decreases retention times of glycols, as verified with an authentic sample of low molecular weight glycols. However, no change occurred in our EO/THF chromatogram, and after silanation the chromatogram looked essentially like Figure 3. This confirmed the absence of linear oligomers and suggested a cyclic structure for all oligomeric components. Next, the individual macrocycles were identified by chemical ionization mass spectroscopy. Molecular weights and the corresponding ring sizes are correlated in Table III.

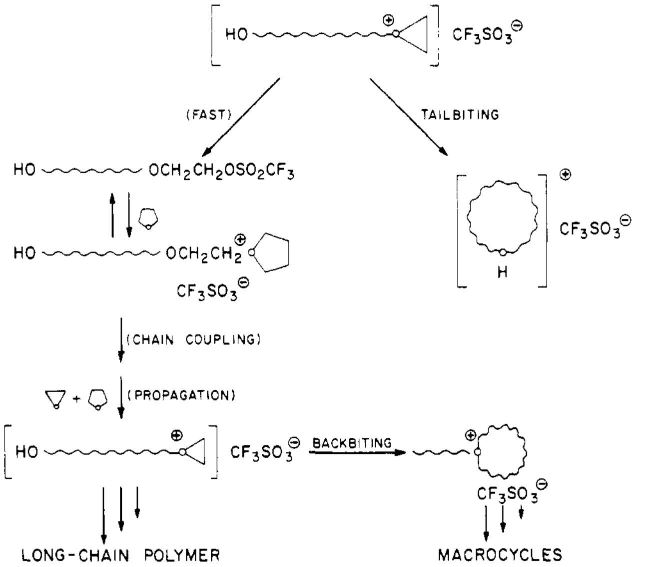
At the comonomer ratios studied, no homologous EO or THF rings were detected, only mixed EO/THF macrocycles. As is frequently observed in other cyclization systems,[3b] a tetrameric ring is formed in highest concentration (Table IV). However, the relative concentrations depend on polymerization conditions, monomer composition, and polymerization time (Tables IV and V). Table IV lists the relative composition of the reaction products of three $EO/THF-CF_3SO_3H$ polymerization systems, containing increasing concentrations of EO. At low starting EO concentration, the preferred macrocycle is the EO:THF = 1:3 ring, while at high starting EO concentrations the 2:2 ring predominates (Table IV). The relative concentrations of the individual macrocycles change also with polymerization time. As an example, in a polymerization system containing equal weights of EO and THF (1:0.6 molar ratio), the macrocycles 3:1, 3:2, and 3:3 increase in relative concentration, while the macrocycles 2:2, 1:3, 2:3, and 1:4 decrease with time (Table V). Total conversion to polymer in this system was 6.5% after 1 h, and 55% after 5 h. The concentration of macrocycles was 6–10%

Table V
Change in Composition of EO/THF-CF_3SO_3H Reaction Products with Reaction Time[a]

cyclic product	standard GC area (% of total reaction products) 1 h[b]	5 h[b]	80 h
1,4-dioxane	2.2	6.7	
1:2	1.6	0.4	1.0
3:1	8.0	10.4	18.1
2:2	32.1	31.5	21.9
1:3	13.4	9.1	6.8
3:2	6.8	8.2	12.0
2:3	11.4	9.3	7.1
3:3	1.5	2.1	5.5
1:4	2.7	1.5	1.3
4:2	5.0	4.8	5.7
2:4	4.9	3.4	2.4
1:5	1.5	0.6	<0.4

[a] Polymerization conditions, see Table IV. [b] Total conversion to oligomer and polymer: 6.5% (1 h), 55% (5 h).

Scheme II



of the total polymer concentration, depending on the polymerization conditions. The molecular weight of copolymer isolated from this sample was relatively high, as expected with CF_3SO_3H initiation:[1] A number average molecular weight of about 9000 was found by spectroscopic end group analysis. Formation of 1,4-dioxane proceeds very slowly in these systems. From Table V it can be seen that dioxane concentration is much lower than the concentration of the larger macrocycles.

Formation of macrocycles probably occurs via tail biting and back biting, as described for the THF/CF_3SO_3H system.[1] Since no THF homocyclic oligomers were found in these mixed systems, back biting is most likely to occur when a highly strained EO oxonium ion at the chain end is attacked by a chain oxygen to relieve ring strain (Scheme II). The schematic outline illustrates some possible reaction steps in this system. For example, macrocycles which form rapidly in the initial stages of the polymerization, e.g., EO:THF crown 1:3, are probably formed by tail biting, while others, which slowly increase in concentration (Table V), may be formed by a back-biting reaction of longer chains (the wavy line ∿ represents a copolyether chain).

This rapid initial formation of macrocycles by tail biting, followed by chain formation via ring opening and coupling reactions, could be considered as a two-stage process and might be similar to the two-stage processes observed in the polymerization of cyclic acetals.[9]

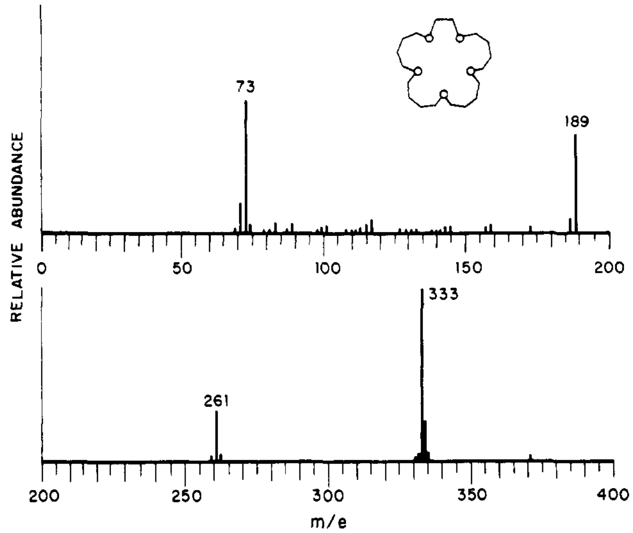
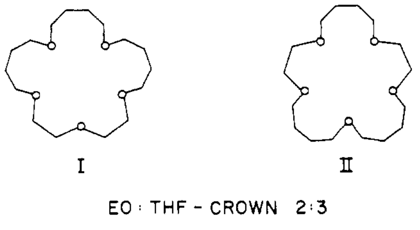


Figure 4. Chemical ionization mass spectrum of EO:THF crown 1:4 (peak H in Figure 3).

Table VI
Chemical Ionization Fragmentation Pattern of EO/THF Crown Ethers[a]

MAJOR FRAGMENTS OBSERVED (EO:THF)	1:2	2:2	1:3	3:2	2:3	1:4	2:4	1:5
(1:5)								404
(2:4)							376	
(1:4)						332		332
(2:3)					304		304	
(3:2)				276				
(1:3)			260			260		260
(2:2)		232			232		232	
(1:2)	188		188	(188)		188		188
(2:0)	88							
(0:1)	(72)	72	72	72	72	(72)	72	72

[a] Molecular weights and composition of parent compounds are underlined; major fragments observed (m/e − 1) are shown in vertical columns.



EO : THF - CROWN 2:3

The crown ether nomeclature[10] cannot be easily adapted to mixed macrocycles without leading to ambiguities. We have found it convenient to use trivial names such as "EO:THF crown 2:3", with the smaller monomer always preceding. Such a name does not distinguish between possible isomers, e.g., 1,4,7,12,17-pentaoxacycloheneicosane (I) and the 1,4,9,12,17-pentaoxaisomer II. However, no isomers have been found so far with the analytical techniques employed. The following EO:THF crown ethers have been identified by chemical ionization/mass spectroscopy: 1:2, 1:3, 1:4, 1:5; 2:2, 2:3, 2:4; 3:1, 3:2, 3:3, 3:4; 4:1, 4:2, 4:3; 5:1. The largest rings identified are the 28-membered ring EO:THF crown 1:5 and the 29-membered EO:THF crown 3:4. Larger rings are also present, as evidenced by GC peaks at longer retention times, but these have not yet been unambiguously assigned.

Fragmentation patterns show an interesting regularity (Figure 4). Under the mild conditions of chemical ionization, the macrocycles lose single or multiple THF units, and m/e signals appear at $(M + 1) - 72n$, where $n = 1, 2, 3, \ldots$, etc. (Table VI). This is similar to the fragmentation pattern observed earlier with tetrahydrofuran crown ethers.[1,2]

Conclusion

Macrocyclic oligomer formation is common to EO, THF, and EO/THF polymerization systems, initiated by nonhydrolyzable, strong, protonic acids. Formation of high molecular weight linear polymers by oxonium ion ring opening and chain coupling steps is accompained by formation of macrocycles via a tail biting–back biting mechanism. In systems in which the less reactive covalent ester end group is stabilized, some linear oligomers are also found. There is a preference for certain ring sizes and compositions in THF/EO polymerizations, depending on polymerization conditions and monomer concentrations.

Acknowledgment. We would like to thank Drs. G. E. Heinsohn and T. K. Wu for a critical review of the manuscript.

References and Notes

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Block Copolymerization of 3,3-Dimethyl-2-oxetanone. 1. About the Mechanism of α,α-Disubstituted β-Propiolactones Block Copolymerization

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ABSTRACT: Block copolymerization of 3,3-dimethyl-2-oxetanone (or pivalolactone, PVL) has been reported by different authors by applying an anionic process initiated by carboxylate salt end groups. A living (co)polymerization of PVL is observed, and the mechanism could be assume as being of wide application. However, in every successful block PVL copolymerization described, a polarizable group is present in the vicinity of the initiating carboxylate salt. From our observations, it is concluded that the absence of such a structural feature is responsible for PVL homopolymerization. Accordingly, the initiating carboxylate end group cannot be free but must be interacting with a neighboring polarizable group to avoid this unexpectedly drastic limitation. The extension of this requirement to the PVL grafting processes has not been ascertained.

The interest of the thermoplastic elastomers has been dramatically demonstrated by the discovery and applications of the (styrene-*b*-diene-*b*-styrene) copolymers. The range of service of these materials is however limited by the relatively low softening point of the rigid polystyrene sequences (70–80 °C). Accordingly, many attempts have been made to find out new combinations of very soft and extremely cohesive sequences in order to extend considerably this service temperature range.

In our laboratory, we have considered the combination of either polydienes or polysiloxanes on the one hand with Nylon 6 (T_m 220 °C)[1] or poly(pivalolactone) (T_m 240 °C) on the other hand.[2] At the same time, similar researches were developed in other laboratories. As far as polypivalolactone is concerned, the contributions of Yamashita[3,4] and of the Du Pont Co.[5–8] must be mentioned, the block copolymerization always being based on the anionic polymerization of pivalolactone by a polymeric carboxylate salt.

We intend to report in this paper some limitations of this apparently general procedure and to clarify the mechanism of pivalolactone block polymerization by polymeric carboxylate salts. Our work has not been extended to PVL grafting onto polymeric backbone-carrying carboxylate pendant groups whose distribution along the trunk is more often hardly controlled except for some alternating copolymers.[7]

Experimental Section

Preparation of Carboxyl-Terminated Prepolymers. Carboxyl-terminated prepolymers were prepared by three different methods in accordance with the needed structure of the carboxylate end group.

The first aim of this work was to prepare a pivalate-terminated polystyrene as a model initiator for the PVL block copolymerization. This prepolymer was prepared by reacting the lithio salt of 2-isopropyl-4,4-dimethyl-2-oxazoline with 1-bromobutane-terminated polystyrene, followed by the hydrolysis of the oxazoline. The details of the whole synthesis have been published elsewhere.[9]

The hydroxyl-terminated polymers poly(ethylene oxide) (PEO) and poly(caprolactone) (PCL) were converted to carboxyl-terminated polymers by reaction with a twofold molar excess of