comes very difficult to detect a weak loss in this frequency range.

At low frequencies, the primary glass–rubber relaxation usually leads to a much larger mechanical loss than the secondary main-chain relaxation.[6] At hypersonic frequencies in PPG the secondary process dominates the loss spectrum. In PPG, it appears that hypersonic relaxation is the only technique that resolves the two processes at high frequencies. Both dielectric and magnetic relaxation were unable to detect the secondary relaxation in this frequency range.

Brillouin scattering can be carried out with all amorphous polymers which are reasonably colorless. Even more highly colored materials may be studied as films.[14] Thus it is a very general technique for studying mechanical relaxation at high frequencies. The resolution of both a primary and secondary loss peak in polymers other than PPG is being actively pursued.

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Macrocyclic Tetrahydrofuran Oligomers. 2.[1] Formation of Macrocycles in the Polymerization of Tetrahydrofuran with Triflic Acid

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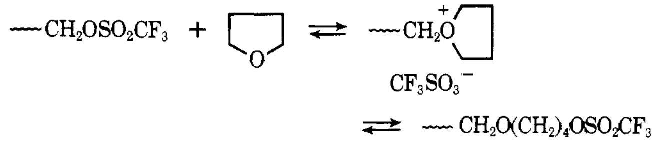
ABSTRACT: The formation of macrocyclic oligomers in tetrahydrofuran polymerization systems initiated with ethyl trifluoromethanesulfonate (ethyl triflate) and with trifluoromethanesulfonic acid (triflic acid) has been investigated. In polymerization systems initiated with ethyl triflate, linear and cyclic oligomers are found by gas chromatography/chemical ionization mass spectrometry. In systems initiated with triflic acid only cyclic oligomers are found under similar polymerization conditions. From these findings, as well as from conversion and solution viscosity data, a chain coupling–ring opening mechanism is discussed for the polymerization of tetrahydrofuran with triflic acid.

The mechanism of the polymerization of tetrahydrofuran (THF) has been investigated recently in great detail,[4,5] particularly the polymerization initiated with esters of trifluoromethanesulfonic acid (triflic acid).[6–9] An equilibrium between an oxonium ion and a covalent ester at the propagating chain head was found to depend on the polarity of the medium: In a medium of high polarity, the propagating species was the expected oxonium ion. In a medium of low polarity, the predominant end group was found to be a covalent ester, formed by attack of the counterion at the α-methylene carbons of the oxonium ion.[10] Chain propagation occurs by nucleophilic attack of monomer at the α-methylene of the oxonium ion or the ester to form a new oxonium ion, which may subsequently again be ring opened by the counterion.



A series of polymerization ⇄ depolymerization equilibria thus exist in such a system, and one would expect the formation of at least some macrocyclic oligomers through "backbiting" reactions. Such macrocycles have indeed been found recently. In a previous publication, we reported the identification of "THF crown ethers", formed during the polymerization of tetrahydrofuran (THF) with trialkyl oxonium salts.[1] We now wish to report the identification of such crown ethers in THF polymerizations initiated by alkyl triflate and triflic acid.

The mechanistic implications of crown ether formation in acid-catalyzed polymerizations are discussed, and a possible mechanism for such polymerizations is proposed.

Experimental Section

Dry tetrahydrofuran stored over metallic sodium was used as the monomer. Trifluoromethanesulfonic 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 and were used without further purification.

Polymerizations were carried out by weighing reactants and solvent into 15-cm Pyrex polymerization tubes sealed with rubber serum caps. For example, 10.0 g of THF and 3.5 g of CD_3NO_2 were mixed in a polymerization tube, and 0.9 g (0.53 mL) of CF_3SO_3H was added through the septum with a 1-mL syringe. The reactants were mixed thoroughly for 10 s on a mechanical vortex shaker, and the polymerization tube was immediately placed into a constant temperature bath. Samples were withdrawn periodically through the serum cap. The constant temperature bath, used for polymerizations and viscosity measurements, controlled the temperature to ±0.2 °C.

Viscosities were determined in Ostwald viscometer tubes, which were equipped with drying tubes, loosely packed with Aquasorb to prevent access of atmospheric moisture. Standard volumes (10 mL) of the polymerization mixtures were injected into the viscometer tubes and flow times measured to the closest 0.1 s.

Conversions and degrees of polymerization were calculated from 100 or 220 MHz NMR spectra, using the intensities of the monomer

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signals at 3.75 and 1.83 ppm, the polymer signals at 3.40 and 1.60 ppm, and end group signals ($\sim CH_2O^+(CH_2-)_2$) at 4.85 ppm, ($\sim CH_2OSO_2CF_3$) at 4.65 ppm, ($\sim OCH_3$) at 3.25 ppm, and ($\sim OCH_2CH_3$) at 1.12 ppm. Perdeuterated solvents were used for all NMR experiments.

Proton noise decoupled ^{13}C-NMR spectra were obtained on a Brucker WH-90 Fourier transform spectrometer operating at 22.63 MHz.[11] Tetramethylsilane (TMS) was used as internal reference, and all chemical shifts are reported in parts per million downfield from TMS.

For a molecular weight determination by IR spectroscopy of hydroxy-terminated polymer, the polymerization mixture was neutralized with 0.5 N NaOH, and enough THF was added to keep the polymer in solution. Solvent and water were removed from the neutral solution by vacuum stripping at 80 °C, and the polymer was extracted with toluene from the dry residue. After filtration, toluene was removed by vacuum stripping, and the residual polymer was dried for 2 h at 80 °C and 0.2 mm. The molecular weight of this polymer was obtained by comparing the absorbance of the OH polymer end groups at 3500 cm^{-1} with the OH absorbance of known standard polymer samples under standard conditions. The trifluoroacetate derivative was prepared by adding a twofold excess over the stoichiometrically required amount of $(CF_3CO)_2O$ to a 10% solution of the polymer in $CDCl_3$. The solution was then allowed to stand overnight at room temperature. This procedure was found to result in complete trifluoroacetylation of the OH groups. Methoxy end capped polymer was prepared by quenching the polymerization mixture with a solution of 1% MeONa in absolute MeOH.

Gas chromatograms were obtained on a Varian Aerograph Series 2700 model with flame ionization detectors. Sixty-centimeter columns packed with 10% SE-30 on chromosorb W-HP were used. Injection port and detector temperatures were maintained at 280 °C. Column temperature was programmed at 20 °C/min form 100 to 275 °C and maintained at 275 °C, as described earlier.[8] Samples of the polymerization mixtures were neutralized with a solution of 1% MeONa in absolute MeOH, and the neutralized or weakly basic samples were injected directly into the glass-lined injection port. The internal standard was BHT (2,6-di-*tert*-butyl-4-methylphenol).

Chemical ionization mass spectra were obtained on a Du Pont 21-491 GC/MS system, with isobutane as the reagent gas.[1]

Results and Discussion

The polymerization of THF with trimethyloxonium tetrafluoborate ($Me_3O^+BF_4^-$) was recently shown to produce two homologous series of volatile oligomers, which were separated and identified by gas chromatography/mass spectrometry.[1] A gas chromatogram of these oligomers showed an alternating pattern of linear and macrocyclic components up to octamer. A similar distribution has now been found with other initiators, e.g., esters of CF_3SO_3H. After quenching a THF/CF_3SO_3Me polymerization mixture with MeOH/MeONa, all the macrocyclic oligomers found earlier are present, in proportions depending on polymerization conditions. The individual GC peaks were again identified by chemical ionization mass spectrometry, as described earlier.[1] The oligomers present in higher concentration were found to be the linear dimethoxy ethers (2, 3, 4, etc., in Figure 1), while the series of lower concentration oligomers, corresponding to the smaller GC peaks (③, ④, etc., in Figure 1), were identified as the macrocyclic oligomers.

The absolute concentrations of the individual crown compounds are uncertain at this point because the GC response factors have not yet been determined with accuracy. However, assuming a response factor similar to THF, the estimated concentration of, e.g., 20-crown-4, after 24 h in CH_3NO_2 at 25 °C would typically be about 0.4% of the total polymer fraction.

The polymerizations described above generally afford a mixture of polymeric products and a fraction of volatile linear and macrocyclic oligomers. The situation is quite different when strong proton acids such as CF_3SO_3H are used as the catalyst: only polymer and a single type of volatile oligomer are found (Figure 2). The molecular weights of the oligomers corresponding to the individual GC peaks were found by chemical ionization mass spectroscopy to be 216, 288, 360, 432, 504, and 576. In analogy to the spectroscopic results reported earlier,[1] they were assigned cyclic structures: peak ③ of Figure 2 therefore corresponds to the trimer, 15-crown-3, peak ④ to the tetramer, 20-crown-4, etc. The largest ring detectable under our GC conditions was 45-crown-9. As an example of a chemical ionization spectrum used in the identification of these macrocycles, the spectrum of 35-crown-7 is shown in Figure 3. The strongest peak is the protonated molecular ion signal ($M + 1$) at m/e 505, corresponding to a compound with molecular weight 504, i.e., the cyclic heptamer. In addition to this base peak, a series of small ion peaks with $m/e = (M + 1) - 72n$ are observed, where $n = 1, 2, \ldots, 6$. These probably correspond to ions derived from the parent ion by loss of single

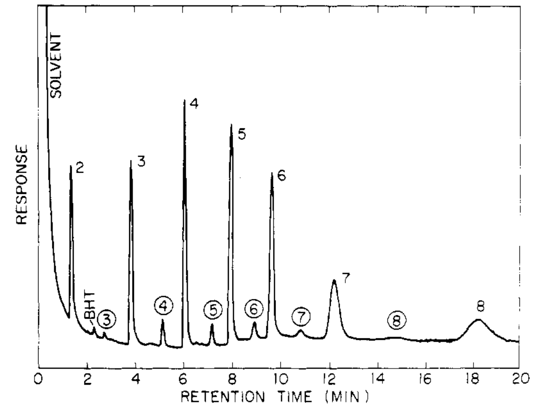


Figure 1. Gas chromatogram of a $THF/CH_3NO_2/CF_3SO_3CH_3$ (molar ratios = 20.8:24.6:1.00) polymerization mixture (GC conditions described in the Experimental Section). 2, 3, 4, etc., linear oligomers; ③, ④, etc., cyclic oligomers.

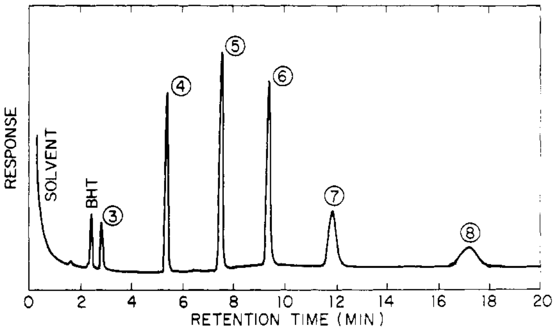


Figure 2. Gas chromatogram of a $THF/CH_3NO_2/CF_3SO_3H$ (molar ratios = 20.8:24.6:1.00) polymerization mixture (GC conditions described in the Experimental Section). ③, ④, etc., cyclic oligomers.

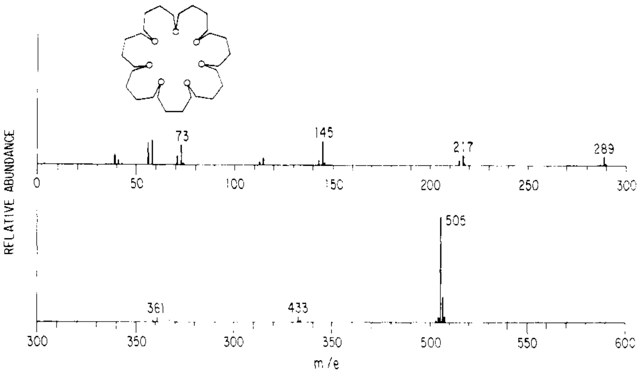


Figure 3. Chemical ionization mass spectrum of 35-crown-7.

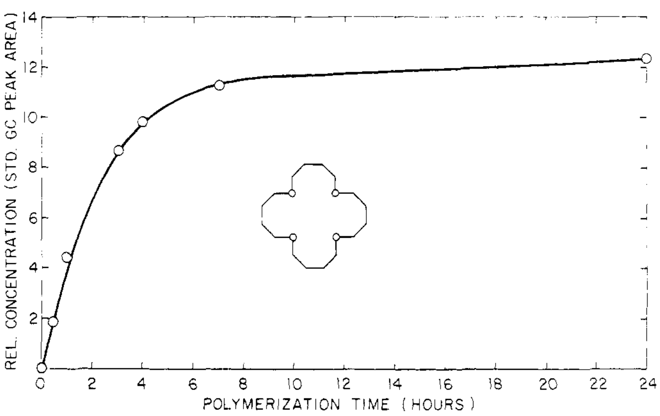


Figure 4. Increase in relative concentration of 20-crown-4 with polymerization time (internal standard = 1.00).

or multiple THF units under the chemical ionization conditions.

Macrocyclic ethers are thus the only type of oligomer found in the polymeric product from anhydrous THF/CF_3SO_3H, regardless of polymerization time. The only changes with polymerization time seem to be an increase in the overall crown ether concentration and a change in their relative distribution. An example of the increase in crown ether concentration is illustrated in Figure 4, where the relative concentration of 20-crown-4 is plotted against polymerization time. The change in distribution of the crown ethers can be seen in Table I, which lists the concentrations of four crown ethers relative to the internal standard at different polymerization times; the initial predominance of the cyclic tetramer is gradually lost with time.

Besides the surprising absence of linear oligomers in acid catalysis, there are other significant differences between THF polymerizations initiated by ester and by free acid. Polymerization with alkyl esters of super acids, e.g., ethyl triflate, generally result in the formation of one chain per initiator molecule, and at a given conversion the molecular weight of the polymer therefore depends on the initiator concentration. As an example, the molecular weight of the polymer fraction in a THF/CH_3NO_2/$CF_3SO_3CH_2CH_3$ (molar ratios 23.1/9.1/1.00) polymerization mixture was calculated; after a polymerization time of 24 h, 47.0% of THF was converted to polymer. Assuming that each ester molecule initiated one chain, the molecular weight of the polymer fraction should be about 780. From end group analysis by NMR spectroscopy, a molecular weight of 740 was found, in good agreement with the calculated number. In contrast, a polymerization system containing an equivalent amount of triflic acid catalyst under similar conditions contained 40% of polymer after 24 h, but the molecular weight was found to be in excess of 10 000, as determined by IR spectroscopy of the isolated polymer. (The end group signals in the NMR spectra of the polymerization mixture were too weak to be useful for molecular weight calculations.) The high molecular weight of the polymer formed under these conditions indicates that only a small fraction of the acid present was utilized as catalyst.

There is therefore no correspondence between ester and free acid catalysis, since high molecular weight polymers are formed even in the presence of high acid concentrations, while little polymerization occurs in the presence of very low acid concentrations in comparable polymerization periods. This is shown in Table II and illustrated in Figure 5, where relative viscosity is plotted vs. polymerization time. At constant temperature, relative viscosity in this system is a function of conversion and molecular weight. Conversion to polymer was determined by ^1H NMR spectroscopy, and the relative viscosity of these systems therefore allows conclusions about molecular weight changes. The relative viscosity of systems with ethyl triflate quickly reaches equilibrium plateaus which correspond to the initiator concentrations: The lower the ester concentration, the higher the viscosity plateau. Systems with triflic acid, on the other hand, behave quite differently: At high acid concentration (Figure 5A), the relative viscosity shows a very steep increase after a short induction period. Initial conversions to polymer are much lower than in the ester case (29.6% after 1 h, see Table II), and the molecular weights are therefore much higher. Low acid concentrations (Figure 5B) produce little polymer under identical conditions, as shown by the relatively small change in viscosity and by the low conversion to polymer found by ^1H NMR analysis (Table II). At still lower acid concentrations no polymer was formed in 1 h, and only 4% oligomers or polymers were found after 24 h (Table II, B-3).

The mechanisms of polymerization of THF with triflate ester and free triflic acid therefore seem to be different, although the polymer formed with triflic acid catalysis also behaves like a living polymer, as demonstrated by the fact that it can be depolymerized and repolymerized by repeated temperature cycling. One polymerization–depolymerization–repolymerization cycle is shown in Figure 6 in terms of relative viscosity vs. reaction time. After an initial polymerization phase at 35 °C, the system was depolymerized by heating it to 75 °C followed by rapid cooling to 35 °C. The second polymerization cycle is reflected in the similarly steep increase in the relative viscosity curve (Figure 6).

The growing chain head in THF polymerizations is usually assumed to be a tertiary oxonium ion or a covalent ester in equilibrium with a tertiary oxonium ion. Both types of end

Table I
Relative Concentrations of THF Crown Ethers in a THF/CF_3SO_3H System[a]

Polymerization time	Standardized GC peak areas[b]			
	15-Crown-3	20-Crown-4	25-Crown-5	30-Crown-6
30 min	0.29	1.88	0.47	0.16
1 h	1.06	4.41	1.65	1.53
2 h	1.76	6.60	2.84	2.75
3 h	2.52	8.88	4.38	4.12
4 h	3.01	9.83	5.45	5.40
7 h	3.23	11.22	7.12	6.97
24 h	4.13	12.43	10.90	9.83

[a] Polymerization conditions: THF/CH_3NO_2/CF_3SO_3H (mol ratio = 20.8/24.6/1.00); 35.0 ± 0.2 °C. [b] GC conditions and sample preparation as described in the Experimental Section (Area of Internal Standard: 1.00).

Table II
Conversion to Polymer in THF/$CF_3SO_3C_2H_5$ and THF/CF_3SO_3H Polymerizations at 35 °C

Catalyst[a]	Conversion, %		
	1 h	2 h	24 h
(A) $CF_3SO_3C_2H_5$			
(1) 1.00	48.6	49.5	47.0
(2) 0.33	43.1	44.5	42.2
(3) 0.10	38.5	42.5	49.6
(B) CF_3SO_3H			
(1) 1.00	29.6	37.5	40.0
(2) 0.33	4.7	5.8	24.4
(3) 0.10	0.0	<0.5	4.0

[a] Composition of Polymerization System (molar ratios): THF, 23.1; CD_3NO_2, 9.1.

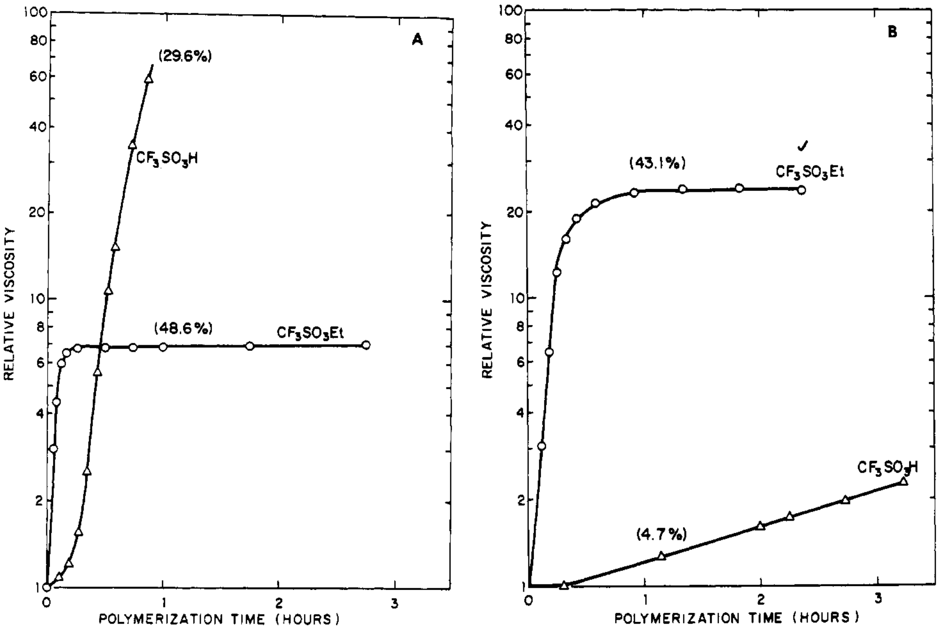


Figure 5. (A) Relative viscosity (35 °C) of THF polymerization mixtures in nitromethane (molar ratios = THF:CH_3NO_2:catalyst = 23.1:9.1:1.00); catalyst: (▲) CF_3SO_3H and (○) $CF_3SO_3C_2H_5$. (Percentages in parentheses indicate conversions after 1 h). (B) Relative viscosity (35 °C) of THF polymerization mixtures in nitromethane (molar ratios = THF:CH_3NO_2:catalyst = 23.1:9.1:0.33); catalyst: (▲) CF_3SO_3H and (○) $CF_3SO_3C_2H_5$. (Percentages in parentheses indicate conversions after 1 h.)

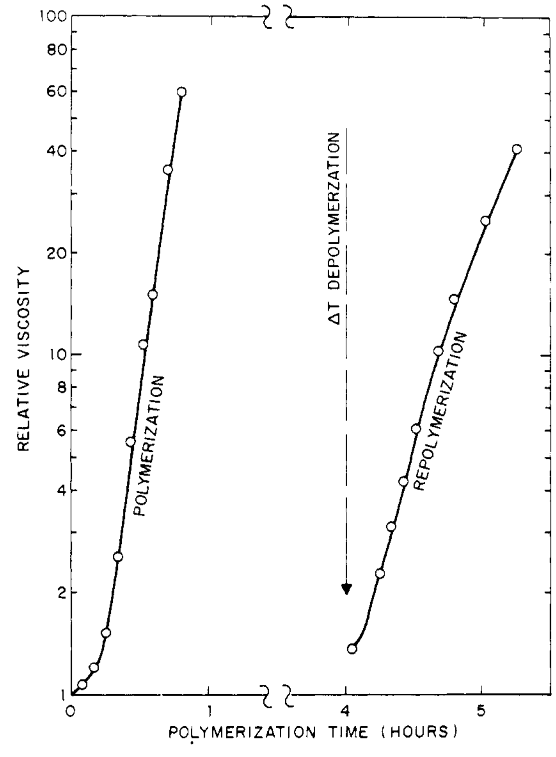


Figure 6. Viscosity change (35 °C) during polymerization and one repolymerization cycle of THF/CH_3NO_2/CF_3SO_3H (molar ratios = 23.1:9.1:1.00).

groups can normally be detected by proton NMR,[7] carbon-13 NMR,[11] or, indirectly, fluorine-19 NMR[8,9] methods. In triflic acid catalysis, however, the end group concentration is so low that no end groups can be detected by either of these methods at catalyst concentrations of 0.1 mol or less per mol of monomer. Since only a small fraction of the acid catalyst is connected with polymer end groups, a large excess of acid has to be used in order to obtain a measurable end group signal. Under such conditions, tertiary oxonium ions can indeed be detected by proton NMR (4.86 ppm) or carbon-13 NMR (endo-C, 81.5 ppm; exo-C, 89.6 ppm)[11] as the chain head (Figure 7).

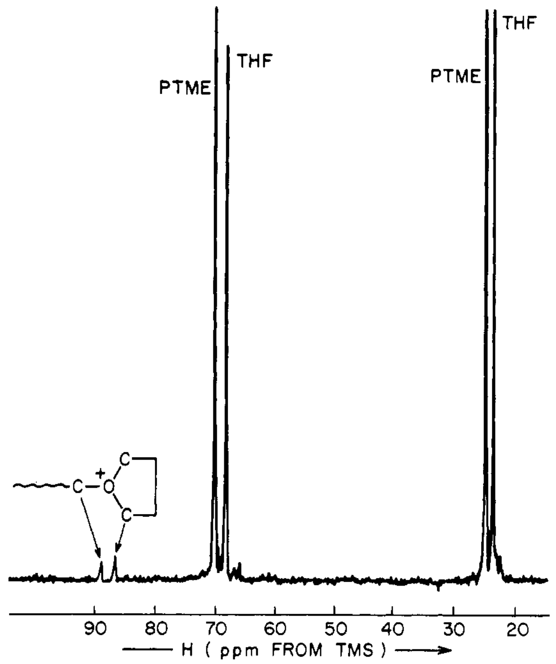
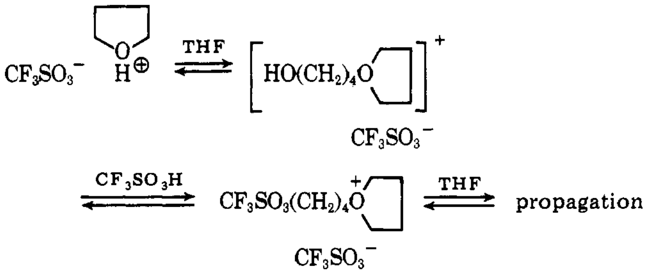
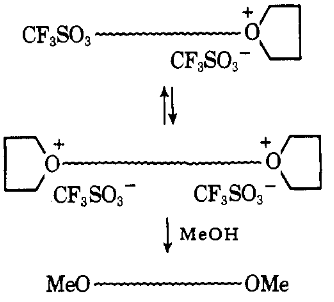


Figure 7. ^{13}C-NMR spectrum (22.63 MHz) of polymerization mixture of THF/CD_3NO_2/CF_3SO_3H (molar ratios = 6.25:2.45:1.00), after 120 min at 30 °C (PTME = poly(tetramethylene ether)).

The tail end of the chain could be a hydroxy group or it could be an ester ⇄ oxonium group, which would result in difunctional propagating polymer chains similar to the species observed by Smith and Hubin in systems containing triflic anhydride.[12,13] The longer induction times at low acid concentrations suggest a rate-determining initial step, either a slow formation of tertiary from secondary oxonium ions, or possibly a slow esterification to form an ester ⇄ oxonium end group prior to chain propagation:

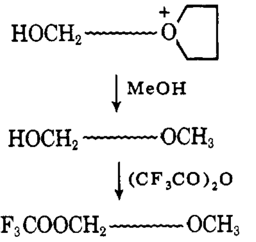


In order to determine the nature of the tail end, a THF/CF_3SO_3H polymerization mixture in CH_3NO_2 was quenched with an excess of MeOH after 2 h at 55 °C. A chain growing from both ends should be converted into a dimethoxy derivative:[12]



Chains with a single propagating site should give a methoxy–hydroxy polymer.

After isolation and drying, the methanol-quenched THF/CF_3SO_3H polymer did indeed show a hydroxyl band at 3500 cm^{-1} in the IR spectrum, indicating hydroxy end groups in the growing polymer chains. In order to determine the ratio of methoxy to hydroxy groups, a sample of this polymer was converted to the trifluoroacetate with $(CF_3CO)_2O$.



From the proton ratio of $CF_3COOC\mathit{H}_2$ (at 4.25 ppm) to $C\mathit{H}_3O$ (at 3.25 ppm) in a 220-MHz ^1H NMR spectrum (Figure 8), the ratio of hydroxy to methoxy end groups was found to be 1:1.2.

We therefore conclude that growing polytetrahydrofuran chains formed by triflic acid catalysis contain an oxonium ion at the propagating site and a hydroxy group at the other chain end.

The fact that the growing chains are hydroxyterminated explains the absence of linear oligomers: they are removed by chain-coupling reactions between hydroxy tails and oxonium heads of different chains, forming very high molecular weight polymer. At high acid concentrations, long polymer chains are formed rapidly by a combination of chain-coupling and ring-opening polymerization, accompanied by the formation of macrocycles by backbiting. At very low acid concentrations the intermolecular chain coupling becomes less probable. Little polymer is found under these conditions in comparable time periods, only very low concentrations of macrocycles, possibly formed by tailbiting, i.e., intramolecular head–tail cyclization. Under the low-acid conditions of Table II (B-3: 0.0043 mol of CF_3SO_3H/1 mol of THF) the only condensation product detectable after 2 h at 35 °C was cyclic tetramer, 20-crown-4. After 24 h, 15-crown-3, 20-crown-4, and 25-crown-5 were found, but the total concentration of cyclic oligomer and polymer was only about 4 mol % (Table II). After 50 h, the conversion had increased to a total of 17.6 mol %.

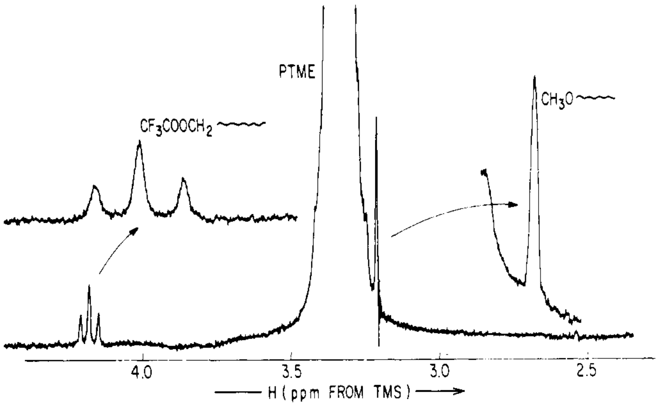
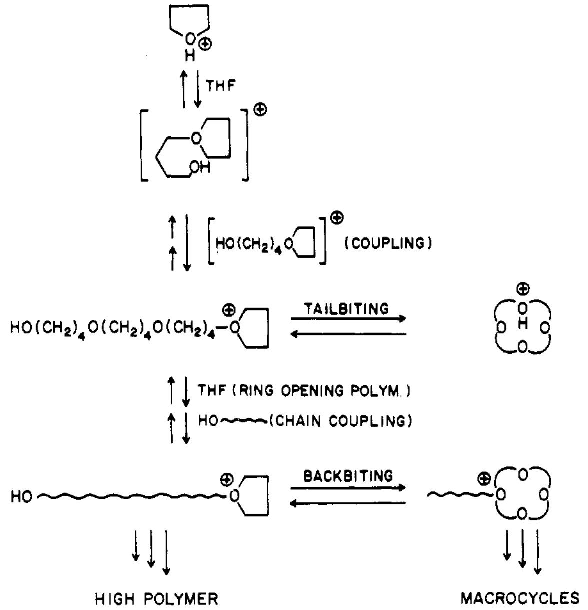


Figure 8. Partial 220-MHz ^1H NMR spectrum of the polymer from THF/CF_3SO_3H (molar ratios = 20.8:1.00; 2 h at 55 °C) after methanol quench and trifluoroacetylation (in $CDCl_3$) (PTME = poly(tetramethylene ether)).

Chain coupling thus appears to be an important step in polymer formation with proton acid catalysis: once intramolecular interaction between the hydroxy group and the oxonium site is prevented through separation of the chain ends by chain coupling, chain extension by ring-opening polymerization (and further chain couplings) can occur. The long induction periods observed with very low acid concentrations may be a reflection of the low probability of chain coupling in the initial stages of such systems.

The sequence of steps in the polymerization of THF by proton acids is not entirely clear, particularly at what stage chain coupling becomes important. Assuming that the first coupling step occurs at the dimer stage, the process might occur as shown in the schematic outline. Counterions are not indicated in this simplified schematic outline, nor are covalent esters shown as possible propagating chain heads, although such end groups could be present in the equilibrium, particularly in media of low polarity.



The macrocyclic oligomers are probably formed by both backbiting and tailbiting. The predominance of 20-crown-4 at short polymerization times (Table I) may be due to a tailbiting cyclization. However, since long polymer chains are formed very rapidly in this system, while the concentration of crown compounds increases much more slowly (Table I), end-to-end cyclization will contribute very little to the formation of macrocycles.

It is interesting to compare acid-catalyzed polymerizations of THF and dioxolane. The apparent differences between both systems have been pointed out repeatedly.[14,15] In view of the present discussion, some similarities become evident: in both cases, the concentration of end groups is very low, in both cases macrocyclic oligomers are formed,[16] and in both cases the number of end groups is consequently much smaller than would be expected for the number of polymer molecules.[14]

The polymerization of dioxolane with proton acids might therefore involve a similar sequence of chain coupling–ring opening steps. Such a mechanism would explain the presence of macrocycles, the absence of linear oligomers, and the very low concentration of end groups normally found in acid-catalyzed dioxolane polymerizations.[15,17]

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Asymmetric Induction by Copolymerization of Indene with Maleic Anhydride in the Presence of Lecithin

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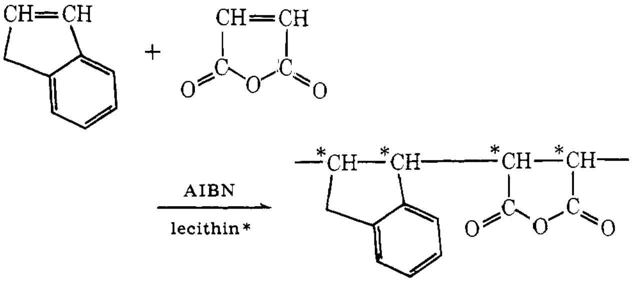
ABSTRACT: The copolymerization of indene (IN) with maleic anhydride (MAn) was studied in the presence and absence of lecithin as a chiral surface active substance, using 2,2′-azobis(isobutylonitrile) (AIBN) in benzene. The rate of copolymerization and intrinsic viscosity of the resulting copolymer were observed to be lowered by lecithin. Moreover, it was found that IN copolymerizes with MAn to give an alternating copolymer and that an optically active copolymer is formed by addition of lecithin to the copolymerization system. The optical activity observed is presumed to be due to asymmetry induced in the backbone of the copolymer by the chirality of lecithin. The influence of lecithin on the copolymerization is considered to be caused by an electrostatic interaction between MAn and the polar head group of lecithin.

In previous papers, the authors revealed that lecithin acts as an asymmetric inducing agent in oil/water interfacial emulsion systems, in which some water-insoluble and unsymmetric ketones are reduced asymmetrically with an aqueous $NaBH_4$ solution[1] and styrene copolymerizes stereospecifically with maleic acid dissolved in an aqueous phase to give an optically active copolymer.[2] It was concluded that these asymmetric inductions are based almost entirely on stereochemical controls at the micelle–water interface, in the vicinity of which the asymmetric carbon atom of lecithin is present.

Moreover, an asymmetric induction was achieved under water-free conditions. Thus, an optically active copolymer was obtained by copolymerization of a nonpolar vinyl monomer, styrene (St), with a polar α,β-disubstituted olefin, maleic anhydride (MAn), in the presence of a chiral surface active substance, lecithin.[3] The authors concluded that in the copolymerization of St with MAn in the presence of lecithin the polar monomer (MAn) is captured within the reversed lecithin micelle, in which an electrostatic interaction between MAn and the polar head group of lecithin is present, and that the asymmetric induction proceeds via CT complex of St and MAn affected by the chiral surface active (amphiphilic) substance, lecithin. It is attractive to examine possibilities of asymmetric induction copolymerization of other nonpolar monomers with other polar monomers in the presence of lecithin.

This paper deals with the asymmetric induction copolymerization of a nonpolar α,β-disubstituted olefin, indene (IN), with a polar α,β-disubstituted olefin, maleic anhydride (MAn), in the presence of lecithin.



Experimental Section

Materials. Lecithin (from soy beans) was supplied by the Katayama Chemical Co. Ltd. and was used without further purification. $\bar{M}_w$