

Cationic Ring-Opening Polymerization of Tetrahydrofuran with Boron, Aluminum, and Gallium Tris(triflate)

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SYNOPSIS

Boron, aluminum, and gallium tris(triflate) are new effective catalysts for the polymerization of tetrahydrofuran (THF). High-molecular-weight polytetrahydrofuran (PTHF) was obtained in excellent yield in the bulk polymerization of THF at ambient temperature with all three catalysts. The PTHF samples were characterized and some of their thermodynamic and mechanical properties were investigated and discussed.

INTRODUCTION

Since the discovery of the polymerization of tetrahydrofuran (THF) in the late 1930s by Meerwein and his coworkers,^{2a,b} interest in polytetrahydrofuran (PTHF) has increased steadily throughout the world. Advances in the understanding of polymerization of THF have been rapid and various aspects of this ring-opening polymerization have been discussed in the literature regularly.³

A negative free energy of polymerization of about 800 cal/mol at 25°C has been obtained for THF.⁴ Therefore, under the proper conditions polymerization can occur. The underlying fundamental requirement for THF polymerization is that an oxonium ion must be formed that is associated with a suitable negatively charged species, such as PF₆⁻, AsF₆⁻, SbF₆⁻, SbCl₆⁻, BF₄⁻, SO₃CF₃⁻, SO₃F⁻, ClO₄⁻, etc.³

The oxonium ion can be generated by using various types of initiators. Protic acids,^{4,5} carbenium ions,⁶ oxonium ions,^{4,5,7} metal salts,^{8,9} and Lewis acids,^{2b,4,10} have been used under different polymerization conditions to obtain PTHF of varying molecular weights and distributions.

Protic acids initiate THF polymerization through

the formation of a secondary oxonium ion. The cyclic secondary oxonium ion is a relatively unreactive species. Thus, initiation by protic acid is a slow reaction.

Carbenium ions, and especially trialkyloxonium ions, can effectively initiate THF polymerizations.¹¹

Most Lewis acids have low activity to initiate THF polymerization. A promoter such as epichlorohydrin usually is necessary¹² that in conjunction with the Lewis acid rapidly generates oxonium salts. For example, AlCl₃, FeCl₃, SbCl₅, and BF₃ can effectively initiate THF polymerization in the presence of epichlorohydrin.⁹ Certain Lewis acids such as ZnCl₂, BeCl₂, BCl₃, AlBr₃, BiCl₃, SiF₄, SbCl₃, and TiCl₄, however, do not initiate polymerization even in the presence of epichlorohydrin because of the formation of alcoholates instead of oxonium salts.⁹

Other Lewis acids such as PF₅, AsF₅, NbCl₅, TaCl₅, WCl₆, SeF₆, P(CN)₃, and Au(SO₃F)₃ are sufficiently reactive to initiate THF polymerization by themselves without any added promoters or epoxides.^{3,13} High-molecular-weight PTHF has been prepared using such systems.^{14,15}

We recently reported a new class of effective general Friedel-Crafts catalysts based on the trifluoromethanesulfonates of group IIIA elements.¹⁶ Aluminum triflate was previously reported by Gandini et al. in polymerization of alkenes, dienes, and vinyl ethers.¹⁷ Boron triflate was found to be a powerful Lewis acid for the generation of carbocations in the rearrangement of strained polycyclic hydrocarbons

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Table I Molecular Weights of PTHF^a

| Initiator | Ini. : THF Molar Ratio | $M_w \times 10^{-5}$ | $M_n \times 10^{-6}$ |
|--|---------------------------|----------------------|----------------------|
| B(OSO ₂ CF ₃) ₃ | 1.0 : 1000 | 3.69 | 1.84 |
| Al(OSO ₂ CF ₃) ₃ | 1.0 : 1000 | 11.27 | 6.09 |
| Ga(OSO ₂ CF ₃) ₃ | 1.0 : 1000 | 19.40 | 8.93 |

^a Reaction time is 48 h.

to cage compounds,¹⁸ as well as in the isomerization of straight chain to branched hydrocarbons.¹⁹ Boron, aluminum, and gallium triflates catalyze electrophilic aromatic substitutions with cyclic,¹⁶ polycyclic alkyl, and acylhalides.²⁰

In continuation of our interest in ionic polymerization, we report the study of the ring-opening polymerization of THF using these new Lewis acid catalysts. The characterization of the resulting PTHF via infrared (IR), nuclear magnetic resonance (NMR), gel permeation chromatography (GPC), differential scanning calorimetry (DSC), and thermogravimetric analysis (TGA), as well as the study of thermodynamic and mechanical properties, will also be included.

EXPERIMENTAL

Tetrahydrofuran (Mallinckrodt) was dried over sodium under refluxing conditions. The distilled THF was dried again over LAH and the dryness was checked through the formation of the naphthalene dianion with Li powder. Glassware and reaction flasks (Schlenk) were thoroughly cleaned and flame

dried prior to use. Boron, aluminum, and gallium triflates were prepared and purified according to our previously reported procedure.¹⁶ Boron triflate was used as a solution ($7.4 \times 10^{-2} M$) in Freon -113. Freon -113 was doubly distilled over P₂O₅.

Polymerization

One hundred ml dried THF was added to a dry Schlenk flask (500 ml capacity) that contained a magnetic stirrer and had been evacuated and flushed with argon several times. Then, 400 mg aluminum or gallium triflate, weighed in the dry box, was transferred to the stirred flask under dry argon. The triflates are reasonably soluble in THF. With 6–8 h, magnetic stirring ceased because a highly viscous solution had been formed. The reaction mixture was left standing for 48 h and a colorless rubber was obtained. The polymer was then dissolved in ether or chloroform to form a viscous solution that was then washed with water and dried over anhydrous Na₂SO₄. The dried solution was concentrated in a vacuum oven or in a rotovap to give a very viscous solution. The concentrated solution was added dropwise to mechanically stirred methanol in a large beaker that precipitated the polymer. The precipitated PTHF was separated as a fibrous mass by decanting the methanol and then was dried in a vacuum oven for 2 days at 40°C. The polymerizations with other initiator ratios were similarly carried out and worked up. Boron triflate was used as a solution in Freon -113; appropriate amounts of this solution were injected into the THF under argon in the dry box. The subsequent polymerization and work-up were then carried out according to the procedure described above.

Table II Self-Initiation Capabilities of Lewis Acids

| Initiator | Ini. : THF Molar Ratio | M_w ($\times 10^{-5}$) | Reaction Time (h) | Yield (%) | Ref. |
|-------------------|---------------------------|-------------------------------|-------------------------|--------------|--------|
| NbCl ₅ | 2.5 : 1000 | 0.39 ^a | 24 | 31 | 21 |
| TaCl ₅ | 2.5 : 1000 | 0.69 ^a | 16 | 52 | 21 |
| WCl ₆ | 5.0 : 1000 | 0.99 ^a | 4 | 64 | 21 |
| PF ₅ | 1.0 : 1000 | 2.80 | 6 | 60 | 14, 15 |

^a Values of M_w were evaluated using the following equation²²:

$$[\eta] = 1.31 \times 10^{-3} M_w^{0.6}$$

and the reduced viscosity at a concentration of 0.2% was used instead of the intrinsic viscosity because there is no intrinsic viscosity data in the reference.

Table III Effect of Initiator Concentration on Molecular Weight^a

| Initiator | Initiator Conc. ^b (mol/L) | $M_w \times 10^5$ | $M_n \times 10^5$ | M_w/M_n |
|--|---|-------------------|-------------------|-----------|
| B(OS ₂ CF ₃) ₃ | 3.71 | 3.69 | 1.84 | 2.00 |
| | 7.24 | 3.30 | 1.38 | 2.39 |
| | 14.84 | 1.60 | 0.61 | 2.62 |
| | 22.26 | 0.72 | 0.26 | 2.77 |
| | 29.68 | 0.64 | 0.22 | 2.91 |

^a Reaction time is 48 h.^b Initiator : monomer = 1.0 : 1000.

Characterization

¹³C and ¹H NMR spectra of the resulting PTHF were measured with a VXR-200 superconducting NMR spectrometer. IR analysis was carried out in a Perkin-Elmer Fourier transform infrared (FTIR) spectrometer Model 1550. GPC analysis was obtained on a Perkin-Elmer series 10-GPC-5 system. The GPC column was calibrated with PTHF standards obtained from Polysciences.

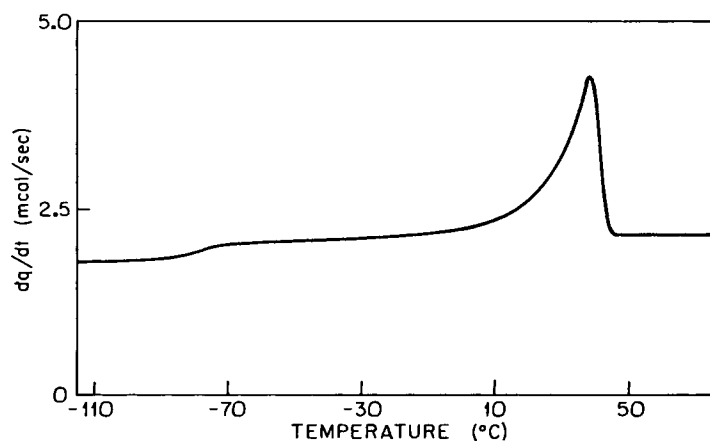
DSC and TGA were carried out on Perkin-Elmer DSC-4 and TGA-2 systems. The DSC-4 was calibrated with an indium standard ($T_m = 156.6^\circ\text{C}$, $\Delta H_m = 6.80 \text{ cal/g}$) obtained from Perkin-Elmer. DSC analysis was carried out using a weighed 5- to 10-mg purified sample sealed in an aluminum DSC pan; an empty aluminum pan was used as a reference and samples were heated from -130 to 80°C in an atmosphere of pure nitrogen (20 mL/min) at different heating rates. TGA experiments were done with 10-mg purified samples in a platinum TGA pan. Here, samples were heated from 50 – 550°C at various heating rates in a pure nitrogen atmosphere (45 mL/

min). The balance and thermocouple of the TGS-2 were autocalibrated.

Mechanical properties were investigated with a DDV-II-C Rheovibron. The dynamic moduli were measured with respect to temperature at a constant frequency of 110 cycles/s.

RESULTS AND DISCUSSION

Without any added promoters, boron, aluminum, and gallium triflates effectively initiated THF polymerization at room temperature and yielded 70–80% high-molecular-weight PTHF after 48 h of reaction. The number average molecular weight of the resulting PTHF ranged from 5.0×10^4 to $1.5 \times 10^6 \text{ g/mol}$. The molecular weight distributions as characterized by polydispersity indexes (M_w/M_n) were between 1.5 and 3.5. Table I shows the results obtained at an initiator to monomer molar ratio of 1.0 to 1000. It can be seen that both aluminum- and gallium-triflates-initiated THF polymerization pro-

**Figure 1** DSC analysis of PTHF in nitrogen at a heating rate of $20^\circ\text{C}/\text{min}$.

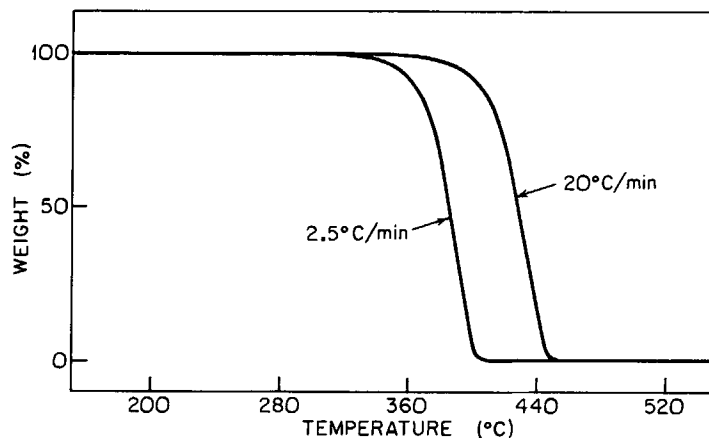
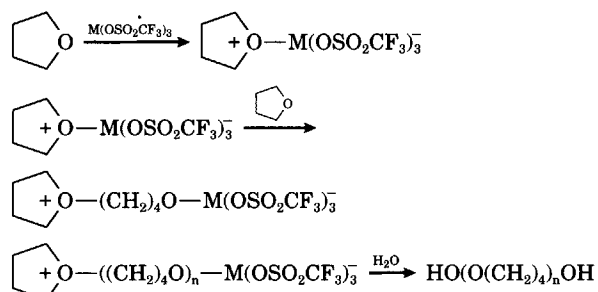


Figure 2 TGA weight loss curves of PTHF in nitrogen at heating rates of 2.5 and 20°C/min.

duced significantly higher-molecular-weight PTHF than did boron triflate, which is consistent with boron triflate being a stronger monomeric Lewis acid. Trace impurities can cause the polymerization to terminate. For comparison, Table II summarizes the self-initiation capabilities of other Lewis acids.

A study of the effect of initiator concentration on the molecular weight of PTHF produced was conducted with boron triflate. The results are shown in Table III. It can be seen that the molecular weight of PTHF increases as the initiator concentration decreases. When the initiator to monomer molar ratio is raised from 1.0 : 1000 to 1.0 : 125, the polydispersity index increases from 2.00 to 2.91, a strong indication of the occurrence of substantial side reactions. The fundamental polymerization mechanism for these triflate-initiated THF reactions is proposed to be:



The prepared PTHF samples were characterized by IR, ^1H , and ^{13}C NMR spectroscopy. The IR spectrum was obtained from a film made by casting a benzene solution on KBr. The spectrum is consistent with the published result,²¹ as are the ^1H and ^{13}C NMR spectra. The spectra show only two kinds of protons at 1.59 and 3.39 ppm, consistent with the PTHF structure.

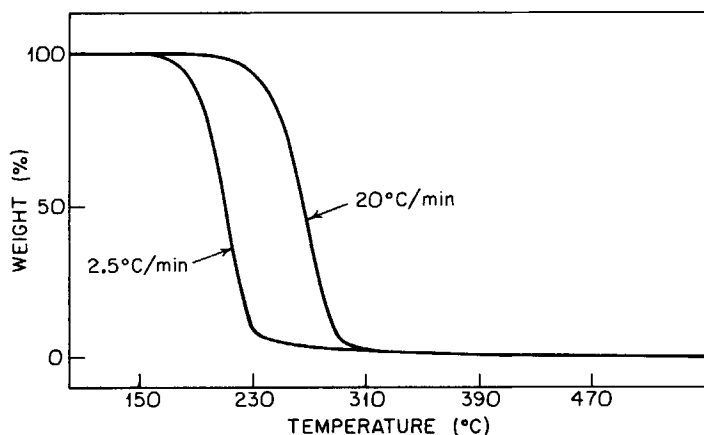


Figure 3 TGA weight loss curves of PTHF in air at heating rates of 2.5 and 20°C/min.

Table IV Thermodynamic Properties of PTHF

| ΔH_m (kcal/mol) | ΔS_m (cal/K · mol) | Ref. |
|----------------------------|-------------------------------|-----------|
| 1.25 | 4.03 | This work |
| 1.62 | 5.11 | 24 |
| 2.63 | 8.32 | 25 |
| 2.96 | 9.42 | 26 |

The prepared PTHF was further characterized by DSC and TGA. DSC analysis in pure nitrogen showed that PTHF has a melting temperature of 37°C and an enthalpy (ΔH_m) of 1.25 kcal/mol. The glass transition temperature of PTHF was found to be -80°C. These results, measured at a heating rate of 20°C/min, are shown in Figure 1. In a TGA study, it was found that in pure nitrogen PTHF started to degrade at temperatures ranging from 300–340°C, the lower the heating rate, the lower the degradation temperature. In pure air, the temperature at which PTHF started to degrade were between 170–210°C, again varying with the heating rate. When the sample was heated to 500°C, the PTHF was degraded completely, leaving no residue. Figures 2 and 3 show the TGA weight loss curves of the PTHF samples run at two different heating rates in nitrogen and air, respectively.

The thermodynamic parameters ΔH_m and ΔS_m were determined by DSC using the polymer sample made with aluminum triflate at an initiator to monomer molar ratio of 1.0 : 1000 according to the procedure detailed above. The results are compared with the literature values in Table IV. Both ΔH_m and ΔS_m vary widely. Because PTHF is a semicrys-

Table V Degree of Crystallinity of PTHF

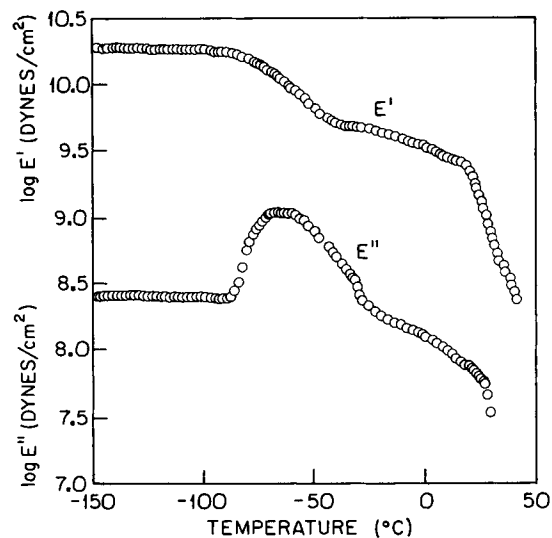
| Cooling Rate (°C/min) | ΔH_m^a (kcal/mol) | ΔH_c^b (kcal/mol) | T_m (°C) |
|--------------------------|------------------------------|------------------------------|---------------|
| 20.0 | 1.25 | -1.11 | 36.9 |
| 10.0 | 1.27 | -1.16 | 36.9 |
| 5.0 | 1.29 | -1.23 | 36.9 |
| 2.5 | 1.32 | -1.38 | 37.0 |
| 0.5 | 1.41 | -1.81 | 39.8 |
| 0.5 ^c | 1.58 | | 47.6 |
| 0.5 ^d | 1.80 | | 64.4 |

^a Measured at a heating rate of 20°C/min.

^b Measured at the different cooling rates indicated.

^c Followed by 1 night annealing at room temperature.

^d Followed by 1 week annealing at room temperature.

**Figure 4** Dynamic storage modulus E' (dynes/cm²) and dynamic loss modulus E'' (dynes/cm²) vs. temperature (°C).

talline polymer, the observed variation is likely due to different degrees of crystallinity in the various samples. To investigate this possibility, the following experiments were conducted. First, the PTHF samples were heated to 80°C in nitrogen at a heating rate of 20°C/min and kept at 80°C for 10 min to ensure samples were completely melted. Then, samples were cooled to -40°C at different cooling rates ranging from 20°C/min to 0.5°C/min and held at -40°C for 10 min to reach thermal equilibrium. Next, samples were reheated to 80°C at a standard heating rate of 20°C/min to measure the enthalpy of fusion (ΔH_m). Furthermore, two samples, after being cooled to -40°C at a cooling rate of 0.5°C/min, were heated to room temperature and left at room temperature (25–30°C) overnight and for 1 week; after this annealing, the enthalpy was measured at a heating rate of 20°C/min. The heat of crystallization (ΔH_c) was also measured at the various cooling rates and all results are shown in Table V. For this system, it is clear that the degree of crystallinity increases as the cooling rate decreases as indicated by the measured values of ΔH_m and ΔH_c . These results show that changing sample preparation conditions considerably influences the degree of crystallinity of PTHF. Also, it is well known that the degree of crystallinity of a semicrystalline polymer can vary with molecular weight.²² The fact that the molecular weight of the PTHF sample studied here was so high probably explains the low ΔH_m and ΔS_m values obtained.

The dynamic moduli were measured with respect to temperature at a frequency of 110 cycles/s. The plots of the storage (E') and loss (E'') moduli vs. temperature are shown in Figure 4. Two major dispersion regions are obvious, one near -68°C and the other in the vicinity of the melting temperature, T_m . It is difficult to accurately characterize the melting temperature in these experiments since above T_m the sample is reasonably liquid like and flows easily. Moreover, a difference between T_g measured in dynamic experiments and in DSC work is to be expected. A very pronounced high-modulus tough "rubbery" region extends from almost -50°C to room temperature at this frequency. The results indicate that even in the vicinity of the glass transition semicrystalline PTHF is not very effective in dissipating mechanical energy. It has been reported that there is a small secondary transition at about -120°C .²² We did not observe this transition.

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