Synthesis of Narrow Distribution Poly(tetrahydrofuran) Initiated by Alkylboron Triflates

Brendan J. McCarthy and Thieo E. Hogen-Esch*

Donald P. and Katherine B. Loker Hydrocarbon
Research Institute and Department of Chemistry,
University of Southern California, University Park,
Los Angeles, California 90089-1661

Received September 6, 1995
Revised Manuscript Received January 29, 1996

One of the most widely studied and generally best understood cationic ring-opening polymerization processes involves that of tetrahydrofuran (THF). Since the original report of oxonium salt initiated polymerization of THF by Meerwein in the late 1930s,[1] a plethora of compounds have been reported as suitable initiators including strong protic acids,[2] Lewis acids,[3] carbenium ions,[4] oxonium ions,[5] metal salts,[6] and esters of strong acids. A search of the scientific literature, however, reveals few systems capable of producing narrow molecular weight distribution (MWD) polyTHF with good molecular weight control. Notable exceptions involve systems having the non-nucleophilic PF_6^- or SbF_6^- as counterions.[8] In only one instance has a “living” system suitable for the synthesis of narrow MWD, low MW polyTHF involved the triflate counterion.[9] However, the authors acknowledged their results to be inconsistent with previously reported polymerization data using the same initiator (MeOTf). We now wish to report that dibutylboron triflate (DBBT) and butylboron bis(triflate) (BBBT), under suitable conditions, are excellent initiators for the cationic polymerization of THF, producing narrow molecular weight distribution polyTHF with good molecular weight control.

A series of DBBT-initiated polymerizations of THF were carried out both in CH_2Cl_2 and in bulk at temperatures of −20 and 28 °C (first nine entries of Table 1). In general, the polyTHF formed possesses a relatively narrow distribution ($M_w/M_n < 1.20$) over a wide range of molecular weights, depending on the extent of reaction, polymerization temperature, and reaction conditions (bulk or solution). At higher conversion there is observed a slight broadening of the molecular weight distribution. This may be due to a significant increase in the viscosity of the polymerization mixture, especially under bulk conditions, and to the occurrence of a propagation equilibrium at longer reaction times[5a] or perhaps due to back-biting. Control experiments (entries 6 and 7) performed under similar conditions in the presence and absence of the proton trap 2,6-di-*tert*-butyl-4-methylpyridine (DBMP) lead to the formation of polyTHF of essentially the same molecular weight, indicating the absence of polymerization processes initiated by triflic acid.[10,11]

The first five entries of Table 1 represent a set of experiments that were performed in order to follow the course of the DBBT-initiated THF polymerization. Thus an amount of neat DBBT was dissolved in THF at 0 °C and divided into ampules that were stored at −20 °C. After various times, 4 mL of a 15% NaOH solution was added to the ampules to terminate the reaction. Figure 1 and Table 1 reveal that the polyTHF formed possesses an extremely narrow molecular weight distribution over a wide polymerization time span. Initially, above 1.10, the molecular weight distribution narrows to 1.06 as the chains propagate. As the reaction time increases, the solutions begin to show an obvious rise in viscosity, until finally, the polymerization solutions (runs 4 and 5 of Figure 1) are barely flowing and a significant broadening results in their distribution.[12]

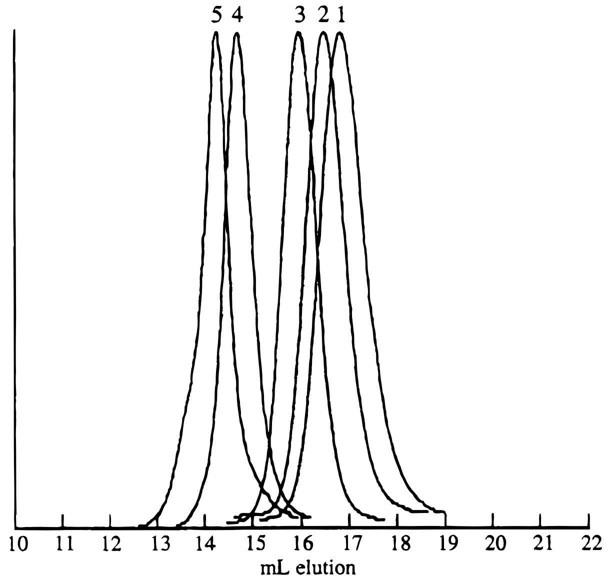


Figure 1. SEC chromatograms following the course of bulk THF polymerization initiated by DBBT at −20 °C. The runs correspond to the first five entries of Table 1, where increasing MW corresponds to decreased elution volume. Calibration based on polystyrene standards.

The low initiating efficiency of DBBT in the polymerization of THF is of special interest (Table 1). The efficiency for DBBT is reduced in solution compared to bulk polymerization and increases with increasing temperature but generally is between 5 and 10%. Matyjaszewski et al. observed similar low initiator efficiencies for trimethylsilyl triflate (<10%) which could be increased through the addition of strained cyclic ethers such as propylene oxide (PO).[13] The middle entries of Table 1 outline experiments aimed at increasing the initiating efficiency of DBBT through the addition of ethylene or propylene oxide as promoters. Close to 5 equiv of promoter (with respect to initiator) was mixed with THF, and *DBBT was then added to* this solution and reacted for the indicated polymerization times. This procedure was effective in facilitating increased initiator efficiencies (∼50%) combined with narrow distributions. Apparently, in the presence of THF, the promoters enhance the DBBT initiation efficiency with little or no compromise of the narrow MWD (i.e. M_w/M_n typically less than 1.20).

Nonetheless, the initiation efficiency of these cyclic ether promoted DBBT polymerizations of THF never exceeds 50%, and multinuclear NMR experiments were undertaken to explore this. Boron-11 NMR revealed the presence of butylboron bis(triflate) (BBBT, a statistical side product in the synthesis of the monotriflate) in fractionally distilled DBBT (spectrum A, Figure 2). Authentic samples of BBBT were synthesized by the reaction of DBBT with 1.0 or 0.8 equiv of triflic acid (spectra B and D of Figure 2, respectively).[14] The strong Lewis acid BBBT is observed to initiate the polymerization of THF with significantly faster rates than its monotriflate analog, generating lower molecular weight but broader MWD ($D \sim 1.70$) polyTHF at high conversions and with nearly quantitative initiator efficiencies (Table 1).

0024-9297/96/2229-3035$12.00/0

Table 1. Cationic Ring-Opening Polymerization of THF Initiated by Alkylboron Triflates in CH_2Cl_2 and in Bulk

initiator	[THF], mol·L^{-1}	[I], mol·L^{-1}	temp, °C	time, min	yield, %	M_n[b] (adjusted)	M_w/M_n[a]	% initiator efficiency[c]
DBBT	11.9	0.12	−20	30		3430	1.12	
DBBT	11.9	0.12	−20	120		4680	1.06	
DBBT	11.9	0.12	−20	240		7220	1.06	
DBBT	11.9	0.12	−20	780		23090	1.09	
DBBT	11.9	0.12	−20	1140		33500	1.29	
DBBT	6.18	0.13	−20	1500	32	16700	1.09	6.8
DBBT[d]	6.73	0.14	−20	1500	28	16800	1.05	5.7
DBBT	10.5	0.61	28	45	24	3280	1.03	9.2
DBBT	11.8	0.15	28	100	12	19900	1.15	10.1
DBBT/PO[e]	8.99	0.45	28	30	50	1430	1.24	49
DBBT/EO[e]	9.62	0.43	28	30	57	1770	1.19	50
DBBT/EO[e]	9.15	0.50	28	45	55	1600	1.17	44
DBBT/EO[e]	9.47	0.47	28	45	57	1750	1.12	46
BBBT	11.4	0.44	28	9	56	2600	1.70	100
BBBT	7.70	0.12	28	46	37	1980	1.74	96
BBBT	8.78	0.10	28	22	45	3660	1.78	87
DBBT/BBBT[f]	11.9	0.56	28	20	36	4480	1.17	96
DBBT/BBBT[f]	11.8	0.39	28	20	42	4410	1.16	97
DBBT/BBBT[f]	11.7	0.46	28	19	43	4100	1.19	96

[a] M_n and M_w are determined by SEC based on polystyrene standards. [b] Adjusted for polyTHF from (0.592)(M_{nSEC}).[15] [c] The percent initiator efficiency is derived from [(g of polymer)/($M_{n\ adjusted}$)(mol initiator)] × 100. [d] 1.26 molar equiv (with respect to initiator) of a 0.43 M solution of 2,6-di-*tert*-butyl-4-methylpyridine (DBMP) in CH_2Cl_2. [e] Addition of 5 equiv (with respect to DBBT) of propylene oxide (PO) or ethylene oxide (EO). [f] Initiator contains 49% BBBT and 51% DBBT, calculated stoichiometry by ^{11}B NMR.

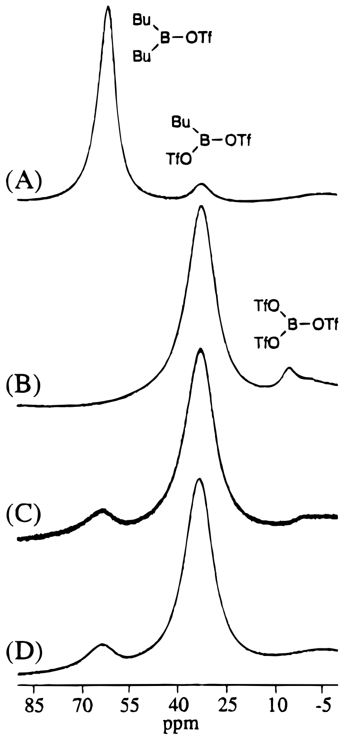
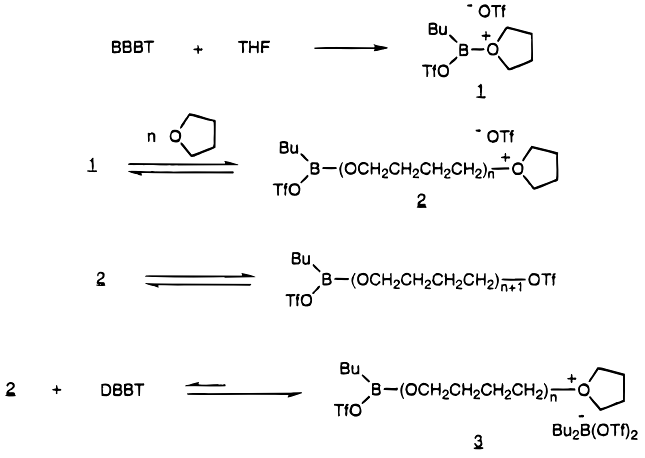


Figure 2. ^{11}B NMR spectra of various neat boryl triflates, $BF_3{\cdot}Et_2O$ external standard; (A) fractionally distilled DBBT; (B) the product of the reaction of DBBT and 1.0 equiv of triflic acid (HOTf); (C) the product of the reaction of DBBT and 0.8 equiv of HOTf; (D) the fractionally distilled product (C) at a vacuum pressure of 1100 mTorr.

Scheme 1. Tentative Mechanism for the Polymerization of THF Initiated by a BBBT−DBBT (1:1) Mixture



These results suggest that the low efficiencies of the DBBT polymerizations in the absence of promoters may be attributed to the presence of small amounts (5−10%) of BBBT *in* DBBT. This BBBT is not due to disproportionation of DBBT into BBBT and tributylboron, as shown by the fact that no changes in the ^{1}H, ^{13}C, or ^{11}B NMR were observed upon standing for periods up to several months. The higher initiator efficiencies observed in the ethylene oxide promoted DBBT-initiated polymerizations also suggest that DBBT is a weaker Lewis acid than BBBT, requiring the presence of EO or PO as coinitiators. The nearly quantitative initiator efficiencies observed for BBBT reveal this Lewis acid to be strong enough for "unpromoted" polymerizations, yet not without side reactions, as evidenced by the broad MWD's. Interestingly, narrow MWD polyTHF is obtained only in the presence of DBBT.

To probe this effect of DBBT, the bulk polymerization of THF inititated by a DBBT−BBBT mixture (49 mol % BBBT) was carried out. For each of the three runs the polymerization was terminated (15% aqueous NaOH) when the medium became difficult to stir due to the increased viscosity and an aliquot of the terminated polymerization mixtures was characterized by SEC. In each case the MWD was relatively narrow ($D < 1.20$), compared with the MW distribution obtained using BBBT alone (Table 1). Both initiator systems give comparable yields and nearly quantitative inititiator efficiencies with respect to the amount of BBBT present.

These results suggest that DBBT should be present at least in equimolar quantities with respect to BBBT in order to generate narrow MWD polyTHF. Since the triflate anion is known to react with oxonium ions to produce less reactive triflate esters,[8b] the results appear to be consistent with DBBT acting as a triflate scavenger and giving rise to a less nucleophilic bis(butyl) bis-

(triflyl) borate anion (Scheme 1). In support of our tentative mechanism, preliminary experiments indicate that the triflate anion is indeed capable of displacing THF from the 1:1 DBBT−THF complex and furnishing the borate anion.[16] These investigations are continuing.

Acknowledgment. Support for this work was provided by the Department of Education through a GAANN fellowship to one of us (B.J.M.) and by BASF Corp. We also appreciate helpful discussion with G. Olah and S. Prakash as well as with R. Williams whose suggestions on ^{11}B NMR proved especially helpful.

References and Notes

(1) (a) Meerwein, H.; Hinz, G.; Hoffman, P.; Kroning, E.; Pfeil, E. *J. Prakt. Chem.* **1937**, *147*, 257. (b) Meerwein, G. German Pat. 747,476, 1939.

(2) (a) Matsuda, K.; Tanaka,Y.; Sakai, T. *J. Appl. Polym. Sci.* **1976**, *20*, 2821. (b) Pruckmayr, G.; Wu, T. K. *Macromolecules* **1978**, *11*, 265. (c) Pruckmayr, G.; Wu, T. K. *Macromolecules* **1978**, *11*, 662. (d) Andrews, G. D.; Vatvars, A.; Pruckmayr, G. *Macromolecules* **1982**, *15*, 1580. (e) Dreyfuss, P.; Dreyfuss, M. P.; Pruckmayr, G. In *Encyclopedia of Polymer Science and Technology*, Bikales, N. M., ed. Wiley-Interscience, New York, 1989; Vol. 16, pp 649−681.

(3) (a) Saegusa, T.; Matsumoto, S. *Macromolecules* **1968**, *1*, 442. (b) Saegusa, T.; Hashimoto, Y.; Matsumoto, S. *Macromolecules* **1971**, *4*, 1. (c) Grinevich, T. V.; Shupik, A. N.; Korovina, G. V.; Entelis, S. G. *Eur. Polym. J.* **1981**, *17*, 1107. (d) Olah, G. A.; Farooq, O.; Li, C. X.; Farina, M.; Aklonis, J. J. *J. Appl. Polym. Sci.* **1992**, *45*, 1355.

(4) Dreyfuss, M. P.; Westfahl, J. C.; Dreyfuss, P. *Macromolecules* **1968**, *1*, 437.

(5) (a) Dreyfuss, P.; Dreyfuss, M. P. *Adv. Polym. Sci.* **1967**, *4*, 528. (b) Meerwein, H.; Delfs, D.; Morshel, H. *Angew. Chem.* **1960**, *72*, 927. (c) Yamashita, Y.; Kozawa, S.; Hirota, M.; Chiba, K.; Matsui, H.; Hirao, A.; Kadama, M.; Ito, K. *Makromol. Chem.* **1971**, *142*, 171.

(6) (a) Franta, E.; Reibel, J.; Lehmann, J.; Penczek, S. *J. Polym. Sci., Polym. Symp.* **1976**, *56*, 139. (b) Taroni, F. A.; Scheer, M.; Rempp, P.; Franta, E. *Makromol. Chem.* **1978**, *179*, 849.

(7) (a) Smith, S.; Hubin, A. *J. Macromol. Sci.—Chem.* **1973**, *7*, 1399. (b) Pruckmayr, G.; Wu, T. *Macromolecules* **1973**, *6*, 33. (c) Kobayashi, S.; Danda, H.; Saegusa, T. *Macromolecules* **1974**, *7*, 415. (d) Wu, T. K.; Pruckmayr, G. *Macromolecules* **1975**, *8*, 77.

(8) (a) Groucher, T. G.; Wetton, R. E. *Polymer* **1976**, *17*, 205. (b) Penczek, S.; Kubisa, P.; Matyjaszewski, K. *Adv. Polym. Sci.* **1980**, *37*, 1.

(9) (a) Nomura, R.; Narita, M.; Endo, T. *Macromolecules* **1994**, *27*, 4853. (b) Nomura, R.; Narita, M.; Endo, T. *Macromolecules* **1994**, *27*, 7011.

(10) Under less carefully controlled conditions DBBT was initially observed to polymerize isobutylene and styrene. However, in the presence of the hindered base the two electron rich olefins failed to polymerize. Similar to the case of trimethylsilyl triflate,[11] the dibutylboron triflate may be susceptible to hydrolysis by residual moisture, thus generating triflic acid which is capable of initiating polymerization of these monomers.

(11) (a) Moulis, J. M.; Collomb, J.; Gandini, A.; Cheradame, H. *Polym. Bull.* **1980**, *3*, 197. (b) Hrkach, J. S.; Ruehl, K.; Matyjaszewski, K. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1988**, *29* (2), 112. (c) Lin, C. H.; Matyjaszewski, K. *J. Polym. Sci., Part A: Polym Chem.* **1990**, *28*, 1771. (d) Hall, H. K.; Padias, A. B.; Atsumi, M.; Way, T. F. *Macromolecules* **1990**, *23*, 678.

(12) A series of THF polymerizations were performed using 9-borabicyclo[3.3.1]nonyl triflate (9-BBNT) as initiator. Generally, the 9-BBNT initiates the polymerization with low (2−3%) efficiencies, generating polymers with lower yields and broader molecular weight distributions than its noncyclic analog, DBBT. When 9-BBNT was mixed with the cyclic ether, there was detectably less heat generated than for the case of DBBT. The lower exotherm may reflect a weaker coordination of 9-BBNT with THF, resulting in slower initiation and thus in broader MWD's.

(13) (a) Hrkach, J.; White, M.; Matyjaszewski, K. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1990**, *33* (1), 229. (b) Hrkach, J.; Matyjaszewski, K. *Polym. Prepr. (Am..Chem. Soc., Div. Polym. Chem.)* **1991**, 272. (c) Hrkach, J.; Matyjaszewski, K. *J. Polym. Sci., Part A; Polym. Chem.* **1995**, *33*, 285.

(14) Synthesis of BBBT was achieved by the dropwise addition of triflic acid to a solution of DBBT in CH_2Cl_2 at 28 °C, followed by fractional vacuum distillation. The use of 0.8 equiv of triflic acid minimized the formation of boron tris(triflate), absorbing at 5 ppm (spectra B and C, Figure 2) with respect to a $BF_3{\cdot}Et_2O$ external standard.

(15) Based on previous work,[8a] the value provided by SEC overestimates the polymer MW since the hydrodynamic radius of polyTHF is greater than that for polystyrene of the same molecular weight. A correction factor of 0.592 was therefore used to obtain more accurate molecular weights for our samples.

(16) A quantity of the fractionally distilled 1:1 DBBT−THF complex was dissolved in $CDCl_3$ to furnish a 0.43 M solution. To this solution was added 1.1 equivalents of $Bu_4N^{+}\,{}^{-}OTf$, and NMR samples were isolated before and after addition of the trifate salt. By ^{1}H NMR, the THF protons are shifted upfield (from 4.34 to 4.19 and 2.15 to 2.04 ppm, for the α and β protons, respectively) in the presence of the triflate anion. Since the observed chemical shift of the THF protons is the weighted average of free and complexed THF, this change in chemical shift indicates that nearly 24% of the Lewis acid exists in the borate form.

MA951314N