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Ring-opening Polymerization of Tetrahydrofuran Initiated by the 2-Norbornyl Cation Generated from *exo*-2-Norbornyl Tosylate in the Presence of Lithium Perchlorate

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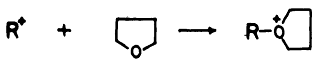
Synopsis. *exo*-2-Norbornyl tosylate initiates ring-opening polymerization of THF in the presence of lithium perchlorate. The deuterium scrambling of *exo*-2-norbornyl-*exo*-3-*d* tosylate indicates the S_N1 nature of the initiation mechanism.

The S_N2 type initiation of the ring-opening polymerization of THF has been extensively studied by Saegusa and his coworkers by use of superacid esters as initiator.[1)] On the other hand, the mechanism of initiation by carbocation is not straightforward. Some stable carbocations such as triphenylmethyl[2)] and tropylium[3)] ions initiate the polymerization, but the actual initiator is believed to be a proton which is expelled from the 2-oxacyclopentyl cation, generated by the hydride-abstraction of THF by the stable carbocations.[2)] In contrast, acyl[4)] and polystyryl[5)] cations react with THF to form oxonium ions at the initiation step (Eq. 1).



(1)

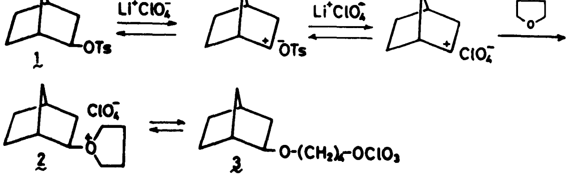
Recently we reported that the ionization of *exo*-2-norbornyl tosylate (**1**) in THF is dramatically promoted by added lithium perchlorate ($LiClO_4$).[6)] Although it has been well known that $LiClO_4$ promotes ionization of organic substrates in ethereal solvents,[7–9)] the fate of the carbocations produced in such reactions has not necessarily been clarified. Here we report that the 2-norbornyl cation thus generated initiates the polymerization of THF following Eq. 1, providing a clear example of S_N1 type initiation.

Results and Discussion

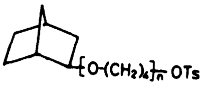
*Time-course and Products in the Reactions of **1** in THF in the Presence of Lithium Perchlorate.* In the absence of $LiClO_4$ the tosylate **1** is stable in THF even heated to 50 °C for 24 h. However, the addition of $LiClO_4$ causes the formation of the species which is easily saponified on titration with aqueous sodium hydroxide.

When the reaction of **1** (0.0981 M, 1 M=1 mol dm^{-3}) in the presence of $LiClO_4$ (0.2984 M) in THF at 50.0 °C is followed titrimetrically, it obeys first-order kinetics ($k_1=2.24\times10^{-5}\,s^{-1}$) until 20% reaction and then slows down, eventually leveling off at 10 h reaction with liberation of acid in 43% on titration. From the reaction mixture was isolated viscous liquid (46% on THF) which solidified on standing. The ^1H and ^{13}C NMR spectra of the polymers indicated that they were produced from THF *via* ring-opening polymerization and that they contained the *exo*-2-norbornyl and tosyl moieties (see Experimental). Integration of ^{13}C NMR signals for the norbornyl and tetramethylene groups indicated that the average degree of polymerization was *ca.* 60, which approximately agreed with the value calculated from the weight of polymers and the amount of the initiator **1**. A GLPC analysis of the reaction mixture prior to isolation of polymers revealed that none of nortricyclene, norbornene, or norbornane were formed, suggesting that the acid titrated was not a free acid arising from possible elimination reactions. Furthermore, saponification of the polymers in 90% ethanol with added sodium hydroxide indicated that 56% of the initial TsO- group was incorporated in the polymers.

These findings strongly indicate that the initiation occurs following an S_N1 mechanism, *i.e.*, ionization of **1** followed by the attack of THF to the produced 2-norbornyl cation. The *exo*-configuration of the terminal 2-norbornyl group indicates that the attack of THF to the norbornyl cation occurs from *exo* side, which is generally the case in S_N1 solvolyses of **1**.[10,11)] Presumably, the



first formed oxonium ion **2** and the propagating oxonium ion are in equilibrium with their corresponding ester forms (*e.g.* **3**),[1b)] and these four species are easily hydrolyzed during titration. The results of the NMR analysis and the saponification experiment indicate the formation of terminated species **4**.



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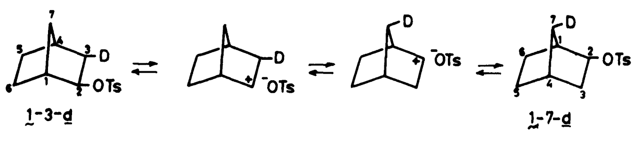
*Deuterium Scrambling in the Reclaimed Tosylate **1**.* Further evidence for ionization of **1** in THF containing $LiClO_4$ was obtained by examining *d*-scrambling of *exo*-2-norbornyl-*exo*-3-*d* tosylate (**1**-3-*d*). When **1**-3-*d* (0.100 M) was heated in THF with added $LiClO_4$ (0.307 M) for 38 min at 50.0 °C, the reclaimed tosylate was found to be a mixture of **1**-3-*d* (87%) and **1**-7-*d* (13%) by examining the *d*-contents at the 3- and 7-positions with ^{13}C NMR. This indicates that the Wagner-Meerwein rearrangement occurs through ionization under the reaction conditions, which is also generally observed in S_N1 solvolyses of **1**.[10)]



Experimental

Materials. THF was distilled from $LiAlH_4$ just before use. Lithium perchlorate ($LiClO_4 \cdot 3H_2O$) was dehydrated at 160 °C and 4 Torr.† The tosylates **1** and **1**-3-*d* were prepared as described previously.12)

Polymerization of THF and Analysis of Polymers. A solution of **1** (0.0981 M) and $LiClO_4$ (0.2984 M) in THF (1.000 cm^3) was heated in a sealed tube under nitrogen at 50 °C for 87 h. The viscous solution was worked up in the usual manner to give a pale brown viscous liquid (0.409 g) which solidified on standing: ^1H NMR ($CDCl_3$, 60 MHz) $\delta=1.57$ (br. t, $J=4$ Hz) and 3.40 (br, t, $J=4$ Hz); ^{13}C NMR ($CDCl_3$, 25 MHz) $\delta=24.3$ (C-6), 28.3 (C-5), 34.5 (C-7), 34.8 (C-4), 39.3 (C-3), 40.0 (C-1), and 82.0 (C-2) for the norbornyl group, 26.2 and 70.0 for the tetramethylene groups, and 21.3 (CH_3), 127.5, and 129.5 for the tosyl group. The ^{13}C NMR data for the norbornyl group agree well with those for *exo*-2-(4-phenoxybutoxy)norbornane.6) Saponification of the polymers (0.4086 g) in 10.00 cm^3 90% ethanol containing NaOH (0.00965 M) at 100 °C in sealed tubes for 1 h showed liberation of acid corresponding to 56% of the original tosylate, which was invariant on prolonged saponification time.

Deuterium Scrambling. A solution containing **1**-3-*d* (1.071 g, 0.1002 M) and $LiClO_4$ (1.633 g, 0.3069 M) in THF (40.0 cm^3) was heated to 50.0 °C for 38 min under nitrogen in a sealed tube, and the unchanged tosylate was recovered in the usual manner (0.160 g). The deuterium distribution was determined by the integration of ^{13}C NMR ($CDCl_3$, 25 MHz) signals as previously reported.12)

Rate Measurements. The reaction was conducted under nitrogen in sealed tubes. Aliquots were titrated in acetone with 0.01 M NaOH by using Lacmoid as indicator.

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† 1 Torr = 133.322 Pa.

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