four isomers of 2-methyl-4-hydroxycyclohexanol obtained by the hydrogenation of methylhydroquinone with Raney nickel catalyst (glpc conditions PEG 20 M column, carrier gas $H_2$, 1.4 kg/cm$^2$, 127°), mp 103.5–104°. The nmr spectrum is shown in Figure 1c.

**Polymerization Procedure and Polymer Purification.** Under nitrogen, a mixture of monomer, $BF_3$–THF (3.0 mol %), epichlorohydrin (0.5 mol %), and $CH_2Cl_2$ was kept standing at −20° for 4 hr until a 20% yield of product was obtained. Then the polymerization was stopped by alkali, and the solution of polymerization mixture was washed with 5% aqueous NaOH solution. Then the organic layer was dried over $K_2CO_3$ and evaporated. The solid polymer thus obtained was purified by recrystallization with a solvent–precipitant combination of $CH_2Cl_2$–$CH_3OH$. Both polymers were obtained as white powdery materials.

**Nmr Measurement.** Nmr spectra were taken on a $CDCl_3$ solution of polymer using a Varian T-60 at room temperature.

---

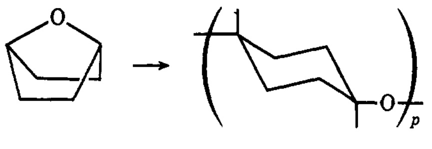
# Kinetic Study of the Polymerization of *exo*-2-Methyl-7-oxabicyclo[2.2.1]heptane

**Takeo Saegusa,* Shu-ichi Matsumoto, Masatoshi Motoi, and Hiroyasu Fujii**

*Department of Synthetic Chemistry, Faculty of Engineering,*
*Kyoto University, Kyoto, Japan.* *Received October 18, 1971*

ABSTRACT: A kinetic study of the polymerization of *exo*-2-methyl-7-oxabicyclo[2.2.1]heptane catalyzed by the $BF_3$-epichlorohydrin system was performed on the basis of the phenoxyl end-capping method. The instantaneous concentration of the propagating species [P*] was determined by converting the propagating chain end into the corresponding phenyl ether whose amount was determined by uv spectroscopy. From the time–[P*] curve, slow initiation and fairly rapid termination reactions were observed. On the basis of the time–[P*] and the time–conversion data, the rate constant of the propagation reaction, $k_p$, was calculated from the equation $\ln([M]_{t_1}/[M]_{t_2}) = k_p\int_{t_1}^{t_2}[P^*]dt$, in which the $[M]_t$'s are the instantaneous monomer concentrations and $\int_{t_1}^{t_2}[P^*]dt$ was obtained by graphical integration. From the $k_p$ values at four temperatures between −10 and −40°, the activation parameters of the propagation reaction were determined; $\Delta E_p^{\ddagger} = 15$ kcal/mol and $A_p^{\ddagger} = 4.1 \times 10^{10}$ l./(mol sec). These values were compared with those for the monocyclic ether polymerizations.

This paper describes the kinetics of the polymerization of *exo*-2-methyl-7-oxabicyclo[2.2.1]heptane (*exo*-MOBH), a bicyclic ether. The ring-opening polymerization of 7-oxabicyclo[2.2.1]heptanes, first reported by Wittbecker, Hall, and Campbell,[1] is characterized by the inversion of the boat form of the cyclohexane ring in the monomer to the chair form in the polymer. Monomers having the bicyclic structure of 7-oxabicyclo[2.2.1]heptane are strained due to the boat form of the cyclohexane ring as well as the bond angle of the five-membered cyclic ether. Therefore, the reactivities of monomers having bicyclic structures are of much interest; especially, the comparison of reactivity between bicyclic and monocyclic ethers is significant.

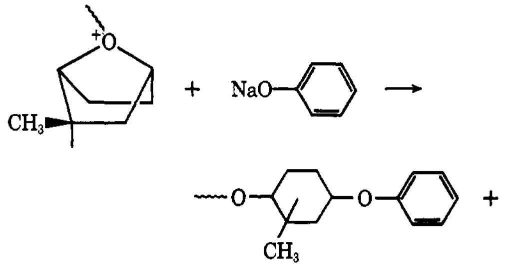


The polymerization of bicyclic ethers has been studied to some extent.[2,3] Baccaredda, *et al.*,[4] reported the results of the kinetics of the polymerization of *exo*-MOBH. In the present study, the polymerization of *exo*-MOBH was studied kinetically on the basis of our "phenoxyl end-capping" method[5–7] which enabled the determination of the concentration of the propagating species [P*]. The methyl-substituted derivative of 7-oxabicyclo[2.2.1]heptane instead of the unsubstituted compound was chosen for this study because the polymer of the unsubstituted monomer is very insoluble and hence the phenoxyl end-capping method is not applicable to the polymerization of 7-oxabicyclo[2.2.1]heptane. The polymer of *exo*-MOBH is sufficiently soluble. The propagation rate, $k_p$, was determined from time–[P*] and the time–conversion data. The $k_p$ values at four temperatures between −10 and −40° gave the activation parameter of this polymerization by means of an Arrhenius plot. Interesting comparisons were made of the propagation rate constant and activation parameters of the *exo*-MOBH polymerization and the corresponding values of the polymerizations of monocyclic monomers.

## Results and Discussion

**Determination of [P*] by the Phenoxyl End-Capping Method.** The phenoxyl end-capping method has successfully been employed in kinetic analyses of polymerizations of a series of monocyclic ethers.[5–7] In the present study, this method was applied successfully to the polymerization of a bicyclic ether, *exo*-2-methyl-7-oxabicyclo[2.2.1]heptane (*exo*-MOBH).

The concentration of the phenyl ether group formed by the reaction of the propagating species at the polymer end



(1)

---

(1) E. L. Wittbecker, H. K. Hall, Jr., and T. W. Campbell, *J. Amer. Chem. Soc.*, **82**, 1218 (1960).

(2) P. Giusti and F. Andruzzi, *Ann. Chim. (Rome)*, **56**, 973 (1966).

(3) P. L. Magagnini, F. Sardelli, F. Andruzzi, and P. Giusti, *ibid.*, **57**, 1493 (1967).

(4) M. Baccaredda, P. Giusti, F. Andruzzi, P. Cerrai, and M. Dimaina, *J. Polym. Sci., Part C*, No. 31, 157 (1970).

(5) T. Saegusa, S. Matsumoto, and Y. Hashimoto, *Macromolecules*, **4**, 1 (1971).

(6) T. Saegusa and S. Matsumoto, *ibid.*, **1**, 442 (1968).

(7) T. Saegusa, S. Matsumoto, T. Shiota, and H. Fujii, to be published.

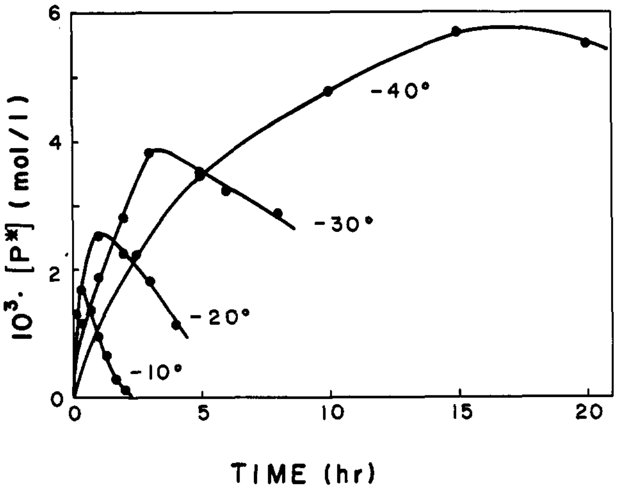
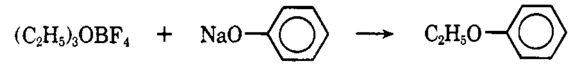


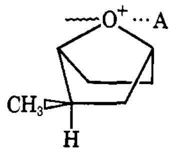
Figure 1. Time–[P*] curve for the polymerization of *exo*-MOBH catalyzed by $BF_3$–ECH; solution polymerization in $CH_2Cl_2$; $[M]_0$, 2.5 *M;* $[BF_3]_0$, 0.075 *M;* $[ECH]_0$, 0.013 *M.*

with sodium phenoxide (eq 1) was analyzed by its uv absorption at 272 mμ.[8] The molar extinction coefficient value of the product phenyl ether in eq 1 was assigned to be $1.93 \times 10^3$ l./(mol cm), as shown in the cases of other cyclic ether polymerizations.[5,7,8]

The quantitative and instantaneous conversion by the above reaction has already been shown by the reference reaction of triethyloxonium tetrafluoroborate with sodium phenoxide (eq 2).[8] A cyclic trialkyloxonium species of type 1, which is the propagating species in the polymerization of *exo*-MOBH, is more strained and is considered to be more reactive toward phenoxide ion than triethyloxonium ion. Therefore, we assume that the reaction of 1 with sodium phenoxide is also instantaneous and quantitative.



(2)



1

The absence of a side reaction leading to the formation of phenyl ether was also established by a series of reference experiments.[8]

**Polymerization of *exo*-MOBH.** The *exo*-MOBH polymerization was carried out at four temperatures between −10 and −40°. The molecular weight (vpo) of the product polymer was in the vicinity of 2000 and the melting temperature was 74–88°.

The [P*] change during the polymerization of *exo*-MOBH was examined by means of the phenoxyl end-capping method. Figure 1 shows the time–[P*] profiles of the *exo*-MOBH polymerization catalyzed by the $BF_3$–epichlorohydrin (ECH) system at four temperatures. At −40°, a gradual increase of [P*] is observed until about 17 hr when [P*] begins to decrease. This indicates a fairly slow initiation and the occurrence of a termination reaction. At higher temperatures termination becomes more pronounced and the propagating species is consumed more rapidly. This finding is in marked contrast to the results obtained in the polymerizations of monocyclic ethers by the same catalyst, in which termination is not significant at temperatures below 0°.[5–7] At −40°, the maximum value of [P*] is about 7.5% of the initial concentration of $BF_3$ ($ECH/BF_3$ = 1/6).

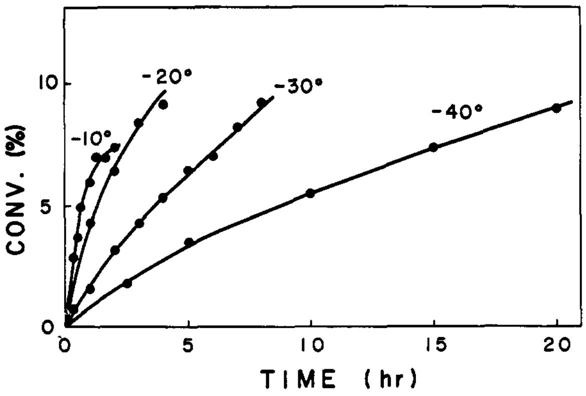
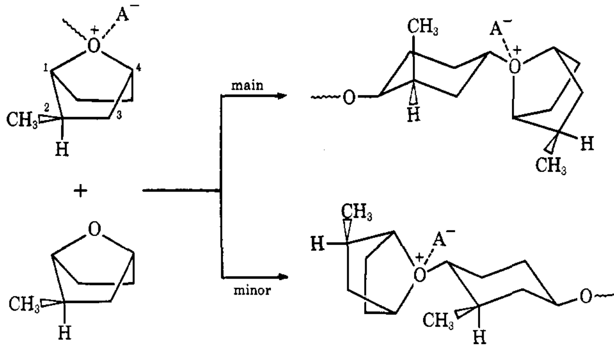


Figure 2. Time–conversion curve for the polymerization of *exo*-MOBH catalyzed by $BF_3$–ECH; conditions are given in Figure 1.

The time–conversion curves at the four temperatures are shown in Figure 2. At −10°, the polymerization ceases after *ca.* 2 hr at a very low conversion because of the destruction of the propagating species by termination (see Figure 1).

From the time–[P*] and the time–conversion data, the rate constant of propagation, $k_p$, for the *exo*-MOBH polymerization was determined by the following procedure.

The first problem of the kinetic analysis is the order of the reaction. The propagation of this polymerization is formulated as an SN2 type of mechanism, where the nucleophilic attack of the monomer on the growing oxonium end occurs mainly at the C-4 carbon atom (eq 3). The configuration of the α-carbon atoms of the propagating cation is inverted.



(3)

In eq 3, A⁻ represents the counteranion derived from the initiator. This stereochemistry has been established by our recent studies in which the structures of the polymers of *exo*- and *endo*-MOBH were investigated by nmr spectroscopy.[9]

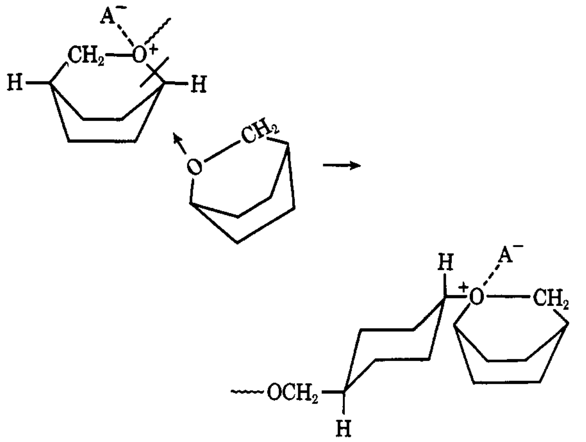
The $k_p$ value obtained in the present study may be taken to represent the value of the propagation rate constant for attack on the C-4 atom of the oxonium end. Also, in the cationic polymerization of 2-oxabicyclo[2.2.2]octane, the SN2 mechanism involving the monomer and the oxonium cation was established in the same manner as above (eq 4).[10]

---

(8) T. Saegusa and S. Matsumoto, *J. Polym. Sci., Part A-1,* **6,** 1559 (1968).

(9) T. Saegusa, M. Motoi, S. Matsumoto, T. Hodaka, and H. Fujii, Presented at the 20th Symposium of High Polymers, Society of Polymer Science, Japan, Nov 1971; *Macromolecules,* in press.

(10) T. Saegusa, T. Hodaka, and H. Fujii, *Polym. J.,* **2,** 670 (1971).



(4)

The second problem is the monomer–polymer equilibrium. The propagation reaction of the cationic polymerization of cyclic ethers is sometimes reversible. In the present study, the reversibility of the *exo*-MOBH polymerization was examined by a depolymerization experiment, in which a purified sample of poly(*exo*-MOBH) was treated with triethyloxonium hexachloroantimonate at −20° for 96 hr. No *exo*-MOBH monomer could be detected in the glpc analysis of the volatile part of the reaction mixture. Therefore, the backward reaction of the propagation, even if it occurs, is negligible, and the propagation is taken to be practically irreversible under the present experimental conditions.

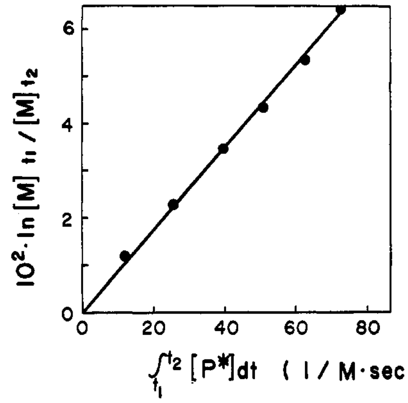


Figure 3. $\int_{t_1}^{t_2}[P^*]dt$ *vs.* ln $[M]_{t_1}/[M]_{t_2}$ plot for the polymerization of *exo*-MOBH catalyzed by $BF_3$–ECH at −30°; solution polymerization in $CH_2Cl_2$; $t_1$, 2 hr.

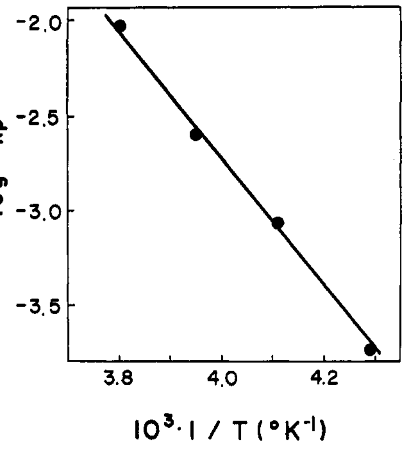


Figure 4. Arrhenius plot of propagation rate constants of the polymerization of *exo*-MOBH; solution polymerization in $CH_2Cl_2$.

Table I
Propagation Rate Constants[a]

| Temp,[b] °C | $10^4k_p$, l./(mol sec) |
|---|---|
| −10 | 94 |
| −20 | 26 |
| −30 | 8.7 |
| −40 | 1.8 |

[a] Solution polymerization in methylene dichloride. Conditions are given in Figure 1. [b] The accuracy of temperature was within ±0.5°.

Thus, the rate of polymerization is expressed by the following bimolecular rate equation which has no term due to depolymerization

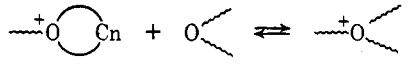
$$-d[M]/dt = k_p[P^*][M] \qquad (5)$$

where [M] is the monomer concentration, $k_p$ is the propagation rate constant, and [P*] is the instantaneous concentration of propagating species. Integration of eq 5 with respect to time gives

$$\ln\frac{[M]_{t_1}}{[M]_{t_2}} = k_p\int_{t_1}^{t_2}[P^*]dt \qquad (6)$$

where $[M]_{t_1}$ and $[M]_{t_2}$ are the monomer concentrations at time $t_1$ and $t_2$, respectively. The cumulative value of [P*] in eq 6 was obtained by graphical integration of the time–[P*] curves in Figure 1. At all four temperatures studied, a plot of ln $([M]_{t_1}/[M]_{t_2})$ *vs.* the integrated value of [P*] from $t_1$ to $t_2$ gave a straight line passing through the origin. Figure 3 illustrates the linear relationship at −30°. From the slope of the straight line, $k_p$ was calculated.

Table I summarizes the $k_p$ values of the *exo*-MOBH polymerization catalyzed by $BF_3$–ECH at four temperatures. In the cationic polymerization of cyclic ether, the reaction of propagating cation with the ether linkages in polymer may occur, which produces less active open-chain oxonium ion (eq 7). The occurrence of this reaction may affect the results of the kinetic analysis. The extent of this reaction depends on the relative basic strengths of the ether linkages of polymer and monomer. Because the basic strength of cyclic ethers is much stronger than that of open-chain ethers,[11] reaction 7 is considered to be unimportant in comparison with the propagation reaction. Furthermore, the present study was carried out at relatively low conversion, where the chain transfer to polymer (eq 7) can be neglected.



(7)

An Arrhenius plot of $k_p$ in Table I gave a straight line (Figure 4), from which the activation energy and the frequency factor were calculated. A kinetic study of the polymerization of the same monomer has been reported by Baccaredda, *et al.*,[4] in which $PF_5$ was used as the initiator and the kinetic analysis was made on the basis of the molar concentration of the initiator with the assumption that the initiator concentration was equal to [P*]. The overall activation energy of 14.2 kcal/mol of the $PF_5$-initiated polymerization[4] might be taken to be close to our result for the activation energy of the propagation (15 kcal/mol, Table II). However, the overall rate of polymerization depends not only on the propagation rate constant but also on [P*]. In fact, [P*] was shown to be much smaller than the molar concentration of $BF_3$ (Figure 1).

---

(11) E. M. Arnett and C. Y. Wu, *J. Amer. Chem. Soc.*, **84**, 1684 (1962).

TABLE II

COMPARISON OF REACTIVITIES OF MONO- AND BICYCLIC ETHERS

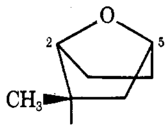
| | *exo*-MOBH[a] ($BF_3$–ECH) | THF[b] ($BF_3$–ECH) | Oxetane[c] ($BF_3$) |
|---|---|---|---|
| $10^3k_p$ (at −10°), l./(mol sec) | 9.4 | 1.7 | 57 |
| $\Delta E_p^{\ddagger}$, kcal/mol | 15 | 12[d] | 14[e] |
| $-10^7/A_p^{\ddagger}$, l.(mol sec) | 4100 | 1.1[d] | 5300[e] |

[a] Present study. [b] T. Saegusa and S. Matsumoto, unpublished data. [c] Reference 5. [d] Temperature range −10 to +10°. [e] Temperature range −27.8 to 0°.

[P*] is controlled by the rates of initiation and termination, both of which are also dependent on the reaction temperature. In the present study, $k_p$ was determined on the basis of the [P*], and hence the activation parameters thus obtained delineate specifically the propagation reaction.

In Table II, the $k_p$ value at −10° and the activation parameters of the *exo*-MOBH polymerization are compared with the corresponding values for the polymerizations of oxetane and THF of monocyclic ethers. The catalyst of the polymerization of THF is the $BF_3$–ECH system. Therefore, the comparison of the kinetics data is being made on the basis of the same counteranion. This is the first case of the quantitative comparison of the polymerization reactivity between monocyclic and bicyclic ethers.

The reactivity toward cationic homopolymerization of *exo*-MOBH is intermediate between the reactivities of four- (oxetane) and five-membered (THF) ethers with monocyclic structures, as is seen from the $k_p$ values at −10°. *exo*-MOBH monomer can be regarded as a THF derivative having a $-CH_2-CH(CH_3)-$ bridge between the 2 and 5 positions (**2**).



**2**

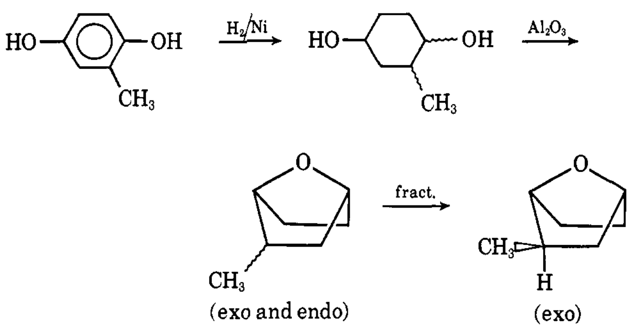
The presence of the bridge increases the reactivity ($k_p$) and the ring strain of the monomer. This is a sharp contrast to the fact that the presence of alkyl substituents at the $\alpha$ (2 or 5) position of THF decreases the polymerization reactivity; *e.g.*, 2-methyltetrahydrofuran has no polymerization reactivity.[1] The increased ring strain of *exo*-MOBH in comparison with that of THF is evident from the lower value of the equilibrium monomer concentration (~0) in the present polymerization as compared with that of the THF polymerization (~2 *M* at 0°).

Table II also includes the activation parameters of the three monomers. In spite of higher reactivity of *exo*-MOBH, the activation energy ($\Delta E^{\ddagger}$) for *exo*-MOBH is even higher than that of THF. On the other hand, the frequency factor of the *exo*-MOBH polymerization is much larger than that of the THF polymerization and very close to the value in the oxetane polymerization. Thus, the higher reactivity of *exo*-MOBH is essentially ascribed to the larger value of the frequency factor. In addition, the activation parameters suggest that the character of the transition state of the *exo*-MOBH polymerization resembles that of the oxetane polymerization. It is also interesting to compare the reactivity of *exo*-MOBH with that of the endo isomer. The results on the latter will be reported in a subsequent paper.

## Experimental Section

**Materials. Monomer.** The *exo*-MOBH monomer was prepared by the reactions shown in Scheme I, according to the reported procedure.[1] Commercial methylhydroquinone was hydrogenated over Raney nickel catalyst at 140° and 120 atm to give an isomer mixture of methylcyclohexanediol in a quantitative yield. Treatment of this mixture with an equal amount of activated alumina (Alcoa F-20) gave a mixture of the exo and endo isomers of MOBH together with small amounts of methylcyclohexadienes. Pure *exo*-MOBH was isolated by repeated fractionation on a spinning-band fractionator (Taika Kogyo, Japan), bp 132° (lit.[1] 133–134°). The yield of *exo*-MOBH from the mixture of methylcyclohexanediol was 20%. The purified monomer was then distilled over benzophenone–disodium prior to use. The purity of the monomer was over 99.9% (glpc analysis).

SCHEME I



**Methylene Dichloride and ECH.** Commercial reagents were purified as described in the previous papers.[8,12]

**Catalyst.** The $BF_3$–THF complex was prepared as reported previously.[6]

**Sodium Phenoxide Solution.** The solution of sodium phenoxide in THF was prepared from a solution of phenol in THF and metallic sodium (concentration *ca.* 0.1 *M*).[8]

**Polymerization Procedure and Determination of [P*].** Polymerization was carried out in methylene dichloride solution under nitrogen. $BF_3$ was used as its THF complex. The reaction was initiated by the addition of a small amount of precooled catalyst solution to a monomer–solvent mixture containing ECH which had been kept at the polymerization temperature. After the desired time of reaction, the polymerization was stopped short by adding an appropriate amount of sodium phenoxide solution. The work-up procedure and the method of [P*] determination were the same as those reported previously.[6,8] Conversions were determined from the amount of polymeric product.

**Depolymerization.** Purified *exo*-MOBH polymer (0.24 g, equivalent to 2.14 mmol of *exo*-MOBH) and triethyloxonium hexachloroantimonate (0.12 mmol) were allowed to react in 2 ml of methylene dichloride at −20° for 96 hr. The reaction was stopped by the addition of a small amount of aqueous sodium hydroxide solution, the volatile product was distilled *in vacuo*, and the distillate was collected at −78°. The distillate was then analyzed for *exo*-MOBH by glpc.

---

(12) H. Imai, T. Saegusa, S. Matsumoto, T. Tadasa, and J. Furukawa, *Makromol. Chem.*, 102, 222 (1967).