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Stereochemistry of the Ring-Opening Polymerization of 2-Methyl-7-oxabicyclo[2.2.1]heptane

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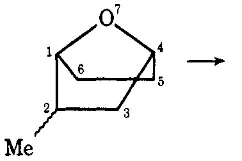
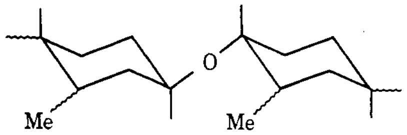
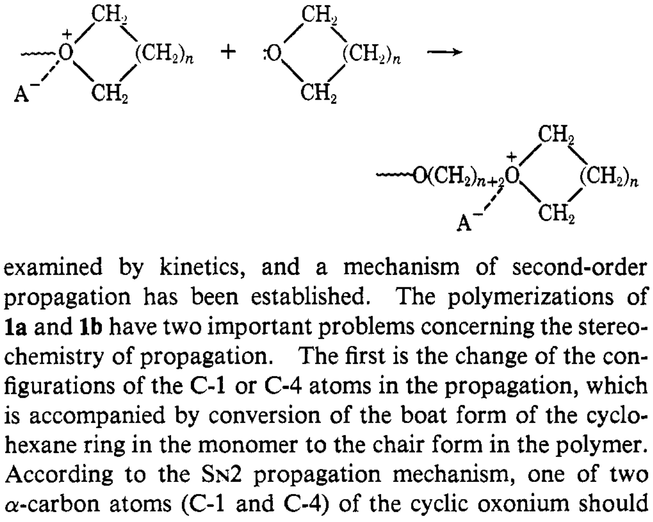
ABSTRACT: Stereochemistry of the propagation of the cationic ring-opening polymerizations of *exo*- and *endo*-2-methyl-7-oxabicyclo[2.2.1]heptane was studied by means of the nmr examination of structure of the product polymers. The *endo*-methyl monomer (**1a**) gave a polymer in which two ether groups as well as a methyl group are placed at the respective equatorial positions of a cyclohexane ring. In the polymer from the *exo*-methyl monomer (**1b**), two ether groups on a cyclohexane ring are trans to each other and the methyl group is cis to the contiguous ether group. An equilibrium mixture of two conformers **4a** and **4b** has been assigned to the polymer from **1b**. From these structure analyses, a stereochemical scheme of SN2 propagation has been presented. In both cases **1a** and **1b**, the nucleophilic attack of monomer is directed selectively to the bridgehead carbon atom (C-4), which is located more remote from the methyl group, from the opposite side of the C–O bond.

The present study is concerned with the stereochemistry of the cationic ring-opening polymerization of 2-methyl-7-oxabicyclo[2.2.1]heptane (**1**). Several kinetic studies[1–6] have shown that the propagation of the cationic polymerization of cyclic ethers having ring sizes more than four is an SN2 process between the cyclic oxonium at the propagating end (electrophile) and the monomer (nucleophile). As to the bicyclic ether monomer, the cationic polymerizations of *exo*-methyl[7] and *endo*-methyl[8] isomers of **1** have already been examined by kinetics, and a mechanism of second-order propagation has been established. The polymerizations of **1a** and **1b** have two important problems concerning the stereochemistry of propagation. The first is the change of the configurations of the C-1 or C-4 atoms in the propagation, which is accompanied by conversion of the boat form of the cyclohexane ring in the monomer to the chair form in the polymer. According to the SN2 propagation mechanism, one of two α-carbon atoms (C-1 and C-4) of the cyclic oxonium should undergo a Walden inversion to produce the polyether in which the two ether groups at C-1 and C-4 of a cyclohexane ring are trans to each other. This problem has been mentioned briefly by Hall, *et al.*,[9] in a paper on the polymerization of bicyclic monomers. But no experiment has yet been done which elucidates this problem of stereochemistry. The second problem is the site of nucleophilic attack, *i.e.*, whether C-1 or C-4 of the bicyclic oxonium at the propagating center is attacked by the monomer nucleophile. In the present study, these two problems have successfully been settled by nmr structure analyses of the product polymers.



1a, *endo*-Me
b, *exo*-Me





Results and Discussion

Structure of the Polymer of *endo*-2-Methyl-7-oxabicyclo-[2.2.1]heptane (1a). The polymerization of **1a** was done in

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(1) P. Dreyfuss and M. P. Dreyfuss, "Ring-Opening Polymerization," K. C. Frisch and S. L. Reegen, Ed., Marcel Dekker, New York, N. Y., 1969, Chapter 2.

(2) T. Saegusa, H. Imai, and S. Matsumoto, *J. Polym. Sci., Part A-1*, **6**, 459 (1968).

(3) T. Saegusa and S. Matsumoto, *ibid., Part A-1*, **6**, 1559 (1968).

(4) T. Saegusa and S. Matsumoto, *Macromolecules*, **1**, 442 (1968).

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

(6) T. Saegusa, T. Shiota, S. Matsumoto, and H. Fujii, *ibid.*, **5**, 34 (1972).

(7) T. Saegusa, S. Matsumoto, M. Motoi, and H. Fujii, presented at the 24th Annual Meeting of the Chemical Society of Japan, April 1971; *Macromolecules*, in press.

(8) T. Saegusa, M. Motoi, S. Matsumoto, and H. Fujii, presented at the 25th Annual Meeting of the Chemical Society of Japan, Oct 1971; to be submitted for publication.

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

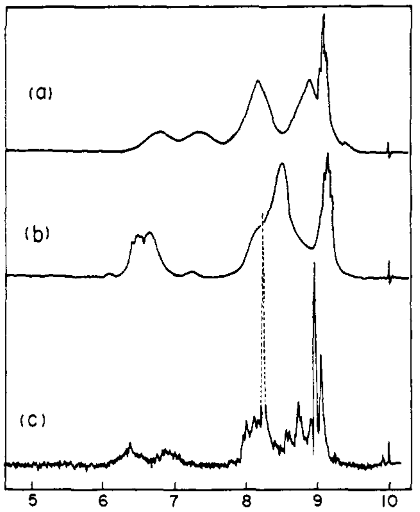
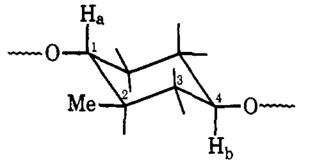


Figure 1. Nmr spectra of (a) polymer from endo monomer, (b) polymer from exo monomer, and (c) *trans*-2-methyl-*trans*-4-hydroxycyclohexanol; 60 MHz, $CDCl_3$ solvent.

CH_2Cl_2 at −20° by means of an initiator system of BF_3–epichlorohydrin.[4-6] The purity of **1a** was shown to be above 99.9% by glpc analysis. The polymer sample was purified by reprecipitation using a solvent–precipitant combination of CH_2Cl_2–CH_3OH. The nmr spectrum of the **1a** polymer in $CDCl_3$ is shown in Figure 1a, from which the polymer structure has been examined. The conclusion from the following analyses is that two ether groups as well as a methyl group are all at equatorial positions of a cyclohexane ring in the polymer.

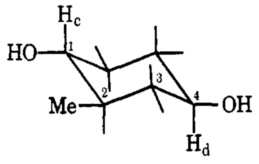


2

Two peaks at τ 8.93 (4 H) and 8.13 (3 H) are assigned to the axial and equatorial hydrogens, respectively, of the trisubstituted cyclohexane ring of the monomeric unit. This assignment is based upon the fact[10] that the τ value of the axial hydrogens of methylcyclohexane is about 0.5 ppm higher than that of the corresponding equatorial hydrogens. Next, two broad peaks (each 1 H) at τ 7.27 and 6.83 are ascribed respectively to the C-1 (H_a) and C-4 (H_b) methyne hydrogens, both of which are placed at axial positions. The assignments of H_a and H_b have been made from the chemical shifts of the methyne hydrogens at the α-carbon of the hydroxyl groups of 2- and 3-methylcyclohexanols.[11] In *trans*- and *cis*-2-methylcyclohexanols, the α-methyne hydrogen appears at τ 7.02 when it is in an axial position and at τ 6.25 when it is in an equatorial position. Similarly, in 3-methylcyclohexanols, the chemical shift of the C-1 methyne hydrogen is τ 6.55 for the axial and τ 6.04 for the equatorial position. The chemical shifts of the α-methyne hydrogens in the axial positions of two model compounds of 2- and 3-methylcyclohexanols (τ 7.02 and 6.55) resemble respectively the C-1 and C-4 hydrogens of the polymer. In addition, the difference in chemical shift between H_a and H_b (7.27 − 6.83 = 0.44 ppm) in the polymer is close to the difference between the chemical shifts of the α-hydrogens of 2- and 3-methylcyclohexanols (7.02 − 6.55 = 0.47 ppm).

The broadness of the H_a and H_b peaks in Figure 1a is also taken to support their axial positions, because, in 4-*tert*-butylcyclohexanol[12] and 2-*tert*-butyl-4-hydroxycyclohexanol,[13] it has been established that the peak for the methyne hydrogen α to the hydroxyl group is broad when the hydrogen is in an axial position (half-width 22 Hz) and sharp when it is in an equatorial position (half-width 7 Hz).

The structure of **2** is further supported by a close resemblance of the nmr spectra of the polymer and another model compound, *trans*-2-methyl-*trans*-4-hydroxycyclohexanol (**3**) (Figure 1c). In the spectrum of **3** (Figure 1c), the doublet at τ 9.00 is due to the C-2 methyl group. The two multiplets at τ 8.5–9.0 and 7.8–8.5 are assigned respectively to the axial and equatorial hydrogens of the cyclohexane ring. The fact that the absorption of the hydrogens of the cyclohexane ring consists of two separate peaks is taken to indicate the stable conformation of the cyclohexane ring without flipping. The singlet at τ 8.23 is due to the hydroxyl groups at C-1 and C-4; this has been shown to disappear by treatment with D_2O. The two wide peaks at τ 6.94 and 6.38 having a half-width of about 20 Hz are assigned respectively to the two axial hydrogens at C-1 (H_c) and C-4 (H_d) on the basis of the τ values of the α-methyne hydrogens in *trans*-2-methylcyclohexanol and *cis*-3-methylcyclohexanol. The assignment of the two axial methyne hydrogens is also supported by the established fact that the absorption peak is broad when the methyne hydrogen is in an axial position and sharp when the hydrogen is in an equatorial position.[12,13] Thus the spectrum of **3** definitely indicates the above conformation. The relative intensities of all peaks agree with the proposed conformation, too. The shapes of two spectra of Figure 1a and 1c resemble each other. The overall slight shifting of Figure 1c downfield may be ascribed to the hydroxyl groups in **3** instead of the ether groups in the **1a** polymer.



3

Structure of the Polymer of *exo*-2-Methyl-7-oxabicyclo[2.2.1]heptane (1b). The polymerization of **1b** and the subsequent polymer purification were carried out similarly to the case of the endo isomer (**1a**). The purity of **1b** was also above 99.9%. The nmr spectrum of the **1b** polymer is shown in Figure 1b. The absorptions due to the hydrogens of the cyclohexane ring of the monomeric unit are not separated into two peaks, but they form a single broad peak having the center at τ 8.65. Two peaks at τ 6.70 and 6.53 are assigned to the C-1 and C-4 methyne hydrogens, which are at lower fields respectively in comparison with the correspond-

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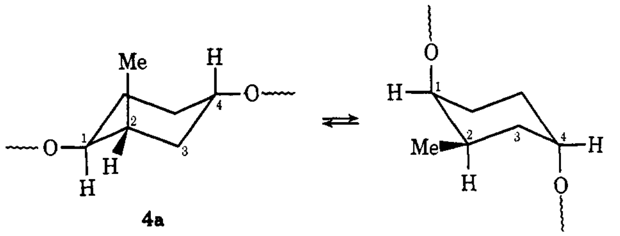
(10) F. A. L. Anet, *Can. J. Chem.*, **39**, 2262 (1961).

(11) E. L. Eliel, *et al.*, *Tetrahedron Lett.*, 741 (1962); J. I. Musher, *J. Chem. Phys.*, **35**, 1159 (1961).

(12) R. U. Lemieux, R. K. Kullnig, H. J. Bernstein, and W. G. Schneider, *J. Amer. Chem. Soc.*, **80**, 6098 (1958).

(13) R. D. Stolow, T. Groom, and D. I. Lewis, *Tetrahedron Lett.*, 913 (1969).

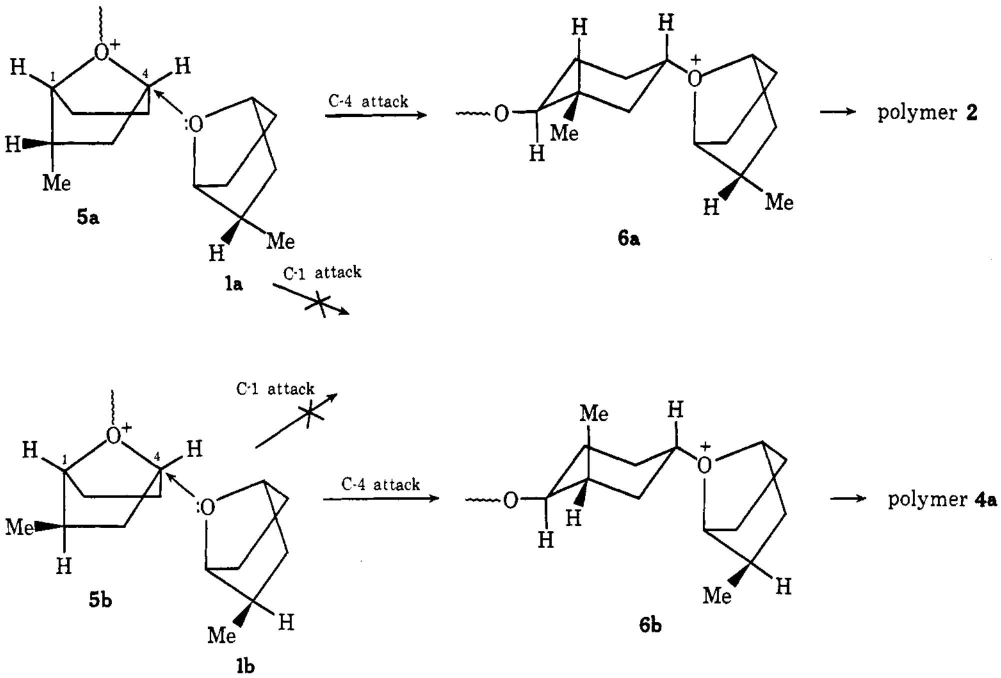


4a ⇌ **4b**

ing peaks of the **1a** polymer. These nmr observations are well explained by assuming a rapid equilibrating mixture of two conformers, **4a** and **4b**, having comparable concentrations. In these conformers, two ether groups are trans to each other, and the methyl group is cis to the contiguous ether group at C-1. In **4a**, the two ether groups are equatorial and the methyl is axial, whereas in **4b** the ether groups are axial and the methyl group is equatorial. The equilibrium free energy difference between **4a** and **4b** is assumed to be quite small from the energy difference values between the equatorial (more stable) and axial (less stable) conformers for the methyl (ΔG = 1.5–1.9 kcal/mol) and methoxyl (ΔG = 0.5–0.7 kcal/mol) substituents of the cyclohexane ring.[14] Therefore, the assumption of comparable concentrations of the two conformers is reasonable.

Stereochemistry of Propagation. On the basis of the structure analyses of the two polymers from **1a** and **1b**, two important facts have been disclosed as to the stereochemistry of propagation. First, the two ether groups are trans to each other in both polymers. This means that one of two carbon atoms (C-1 or C-4) at the bridgeheads of the monomer has suffered from inversion in propagation (see also Scheme I).

SCHEME I



5a **1a** **6a** **5b** **1b** **6b**

The Walden inversion is consistent with the SN2 mechanism given by our previous kinetics studies.[7,8]

The second finding is that the C-4 carbon atom but not the C-1 carbon atom selectively undergoes inversion of configuration, as is shown in Scheme I. According to the SN2 mechanism of the cationic polymerization of cyclic ethers, the propagating species are the cyclic oxonium ions **5a** and **5b** in the polymerization of **1a** and **1b**, respectively. The monomer nucleophile attacks exclusively the C-4 atom of **5a** and **5b** from the back side to cause configuration inversion at C-4. Thus, **5a** propagates into **6a**, which gives rise to a polymer having structure **2**. This scheme is in accord with the experimental results. If the C-1 atom of **5a** were attacked by monomer, a polymer whose structure consists of two equilibrating conformers, **4a** and **4b**, would have been produced. On the other hand, **5b** propagates to **6b**, which leads to a polymer of structure **4a** ⇌ **4b**. Again the scheme satisfied the experimental facts. If the C-1 atom of **5b** were attacked by monomer, a polymer of structure **2** would have been formed.

Now it has become clear that the monomer normally attacks the C-4 atom of the cyclic oxonium. There is another element for the formation of the so-called "stereoregular polymer," *i.e.*, the stereoselective polymerization of the racemic mixture of each monomer. Both **1a** and **1b** have molecular asymmetry, and each of them is a mixture of two antipodes. In the present study, no indication has been recognized as yet for the stereoselective polymerization.

Experimental Section

1a and **1b** were prepared by procedures similar to those given in the literature,[9] except for the employment of Raney nickel in the place of ruthenium dioxide as the catalyst for hydrogenation (H_2 pressure 125 kg/cm^2, 120–140°) of methylhydroquinone. Each monomer was purified by repeated fractional distillation under nitrogen, bp 136 (**1a**), 132° (**1b**). The monomers were distilled from benzophenone–disodium prior to use. The purities of both monomers were found to be above 99.9% by glpc analyses.

Polymerization Reagents. BF_3–THF complex (catalyst), epichlorohydrin (promoter), and CH_2Cl_2 (polymerization solvent) were purified similarly to the procedures of a previous study.[6]

***trans*-2-Methyl-*trans*-4-hydroxycyclohexanol (3).** A model compound for the **1a** polymer was isolated by glpc from a mixture of

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[14] E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill, New York, N. Y., 1962, p 236.

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

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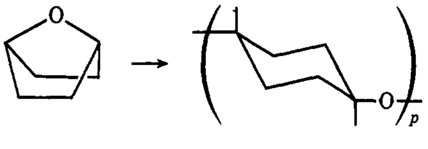
ABSTRACT: A kinetic study of the polymerization of *exo*-2-methyl-7-oxabicyclo[2.2.1]heptane catalyzed by the BF_3-epichlorohydrin system was performed on the basis of the phenoxyl end-capping method. The instantaneous concentration of the propagating species [P*] was determined by converting the propagating 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.

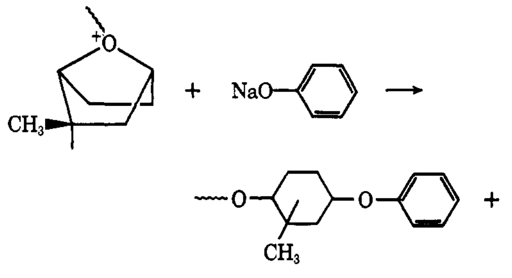


The polymerization of bicyclic ethers has been studied to some extent.[2,3] Baccaredda, *et al.*,[4] reported the results of the kinetics of the polymerization of *exo*-MOBH. In the present study, the polymerization of *exo*-MOBH was studied kinetically on the basis of our "phenoxyl end-capping" method[5–7] 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



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[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.