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Syntheses and Ring-Opening Polymerizations of 2, 3- and 2, 5-Dimethyl-7-Oxabicyclo[2. 2. 1]heptanes

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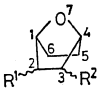
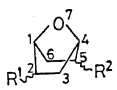
ABSTRACT: New bicyclic ethers, 2,3- and 2,5-dimethyl-7-oxabicyclo[2.2.1]heptanes were synthesized from 2,3- and 2,5-dimethylphenols as starting materials. Each of them was separated by fractional distillation and preparative gas chromatography into the corresponding *exo,exo-*, *endo,exo-*, and *endo,endo*-isomers. Ring-opening polymerizations of these isomeric monomers were carried out in CH_2Cl_2 using cationic initiators such as BF_3—tetrahydrofuran (THF) complex —epichlorohydrin (ECH), $SnCl_4$—ECH, $SbCl_5$—ECH, and $FeCl_3$—$SOCl_2$ systems. The $SbCl_5$—ECH catalyst system brought about high monomer conversions, but it induced a chain-transfer reaction during the polymerization. The *exo,exo-* and *endo,exo-*2,3-dimethyl monomers (**1a** and **1b**) yielded white powdery polymers in yields of 58 and 63%, respectively, using the $SbCl_5$—ECH system. NMR spectroscopic analysis of poly(**1b**) showed that it contained a chair-formed *trans,trans,trans*-1,2,3,4-tetrasubstituted cyclohexane ring in its monomeric unit. Both *exo,exo-* and *endo,endo*-2,5-dimethyl monomers (**2a** and **2c**) yielded grease-like polymers in 16 and 17-% yields, and its *endo,exo*-isomer (**2b**) yielded a highly crystalline polymer, which was insoluble in the usual organic solvents, in 26-% yield using BF_3—ECH. A monomeric unit in poly(**2b**) was assumed to be *trans,cis,trans*-1,2,4,5-tetrasubstituted cyclohexane. In the polymerization of the monomers **1b** and **2b**, it has been shown that the monomer attacks the propagating end at the bridgehead carbon in position 4 (C-4), but not in position 1 (C-1). Nucleophilicities of the monomers **2a** and **2b** were compared based on their copolymerizations with the *exo*-monomethyl analogue (**3a**). The *exo*-methyl group relative to the *endo*-methyl group tends to lower the monomer nucleophilicity. The polymer yield is controlled by three factors; the steric crowding around the bridgehead carbon due to the methyl group, the nucleophilicity, and the ring strain of the monomer.

KEY WORDS Cationic Ring-Opening Polymerization / Bicyclic Ethers / Stereochemistry / Copolymerization /

This paper describes syntheses of six new bicyclic ethers and their ring-opening polymerizations by cationic initiators. These new ether compounds are the *exo,exo-*, *endo,exo-*, and *endo,endo*-isomers of the 2,3- and 2,5-dimethyl-7-oxabicyclo[2.2.1]-heptanes, as shown below:

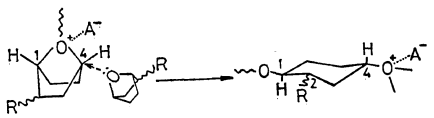


1a, $R^1=R^2=$*exo*-CH_3
1b, $R^1=$*endo*-CH_3, $R^2=$*exo*-CH_3
1c, $R^1=R^2=$*endo*-CH_3



2a, $R^1=R^2=$*exo*-CH_3
2b, $R^1=$*endo*-CH_3, $R^2=$*exo*-CH_3
2c, $R^1=R^2=$*endo*-CH_3

Studies of the kinetics and stereochemistry of ring-opening polymerizations of *exo*- and *endo*-2-methyl-7-oxabicyclo[2.2.1]heptanes (**3a** and **3b**) have been reported by Saegusa and coworkers.[1,2,3] Their polymerizations can be depicted as follows



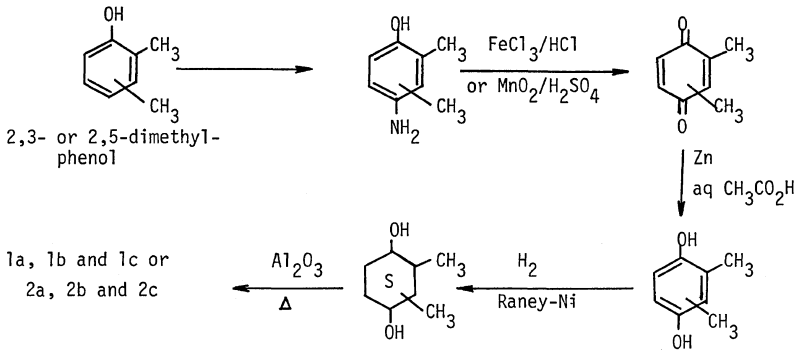
R=*exo*- (**3a**) or *endo*-CH_3 (**3b**)

where A^- is a counteranion. In a propagation step of the polymerization of these monomethyl substituted bicyclic ethers, the monomer attacks the bridgehead carbon of the oxonium end at position 4 (C-4) by S_N2 mechanism so as to avoid the steric hindrance owing to the methyl group. A cyclohexane unit of the polymer takes a chair-formed structure of 1,4-*trans* configuration. On the basis of the kinetic analysis of the polymerization of the monomethyl monomers by means of the phenoxyl end-capping method, it has been established that the propagation rate constant of the *endo* isomer (**3b**) was about 3 to 4 times higher than that of the *exo* isomer (**3a**). The difference of reactivity of these monomers was ascribed to the difference of their ring strains (and also the strains of their oxonium ions). In the polymerizations of the 2,3- and 2,5-dimethyl bicyclic ethers in the present study, geometric positions (*exo* or *endo*) of the two substituents in the monomers (and also their oxonium ions) will influence not only the ring strain of the monomer (and also their oxonium ions) but also the steric hindrance in the propagation process. In this process the bridgehead carbon (either C-1 or C-4) of the propagating oxonium which will be attacked by the monomer nucleophile is blocked more seriously than the bridgehead carbon in the monomethyl monomer **3a** or **3b**. Furthermore, the *endo,exo*-type monomers are of interest, since in these polymerizations there will be two types of propagation processes which give different units of polyethers. The nucleophilicity of the monomer, which will be affected by both the methyl groups, is also one of the important factors of the polymerization.

Recently, Kops and Spanggaard synthesized 2,6-dimethyl analogues, and polymerized the *endo,exo*-isomer by PF_5 initiator to obtain a highly crystalline polymer.[4] It is also possible to discuss the relationship between the polymerization of our new bicyclic ethers and their structures; this may clarify the propagation mechanism and the monomer reactivity.

RESULTS AND DISCUSSION

Two sets of the three isomeric ethers of **1a—1b—1c** and **2a—2b—2c** were prepared from 2,3- and 2,5-dimethylphenols as starting materials according to Scheme I:



Scheme I

The yield of 2,5-dimethylbenzoquinone from 2,5-dimethylphenol by oxidation using $FeCl_3$ and hydrochloric acid was 85%,[5] but that of 2,3-dimethylbenzoquinone from 2,3-dimethylphenol by the same oxidant[6] or CrO_3 and diluted sulfuric acid[7] was not sufficient. The oxidation of the 2,3-dimethyl-4-aminophenol to the corresponding benzoquinone was successfully carried out by use of

MnO_2 and sulfuric acid in a 70-% yield (62%: Arnold and Zaugg[8]). The benzoquinones were reduced by Zn powder and aqueous acetic acid to the dimethylhydroquinones according to the procedure described in the literature.[7] The catalytic hydrogenation products from the hydroquinones were heated with activated alumina to give crude bicyclic ethers, **1a**, **1b**, and **1c** or **2a**, **2b**, and **2c** (purities above 95%) in 11, 16, and 1.4 or 10, 5, and 3-% yields (based on the hydroquinones), respectively, by fractional distillation. Further purifications by preparative gas chromatography gave monomers with purities above 99%. They were identified on the basis of their elemental analyses and NMR spectra. The geometric positions of the methyl groups of these monomers were determined by NMR spectroscopy.

The NMR spectra of **1a**, **1b**, **1c**, **2a**, **2b**, and **2c** are shown in Figures 1a, 1b, 1c, 2a, 2b, and 2c, respectively. In the spectrum of **2b** (Figure 2b), the two doublets at δ 0.92 and 0.95 ppm are assigned to two methyl groups which are located at different geometric positions, *i.e.*, one is at the *exo* and another is at the *endo* position. Therefore, signals due to the methyne protons at the bridgehead carbons must appear at separate chemical shifts. These, in fact, are shown at δ 3.87 and 4.15 ppm as doublet- and a triplet-like signals. The doublet can be assigned to the methyne proton at C-4, and the triplet to that at C-1 bridgehead carbon, since the NMR signals of the methyne protons at C-1 carbons of **3a** and **3b** were observed as doublet- and a triplet-like signals, and the methyne proton of the *exo*-isomer **3a** resonanced at about 0.2 ppm higher field than that of the *endo*-isomer **3b**. In the NMR spectra of **2a** and **2c** (Figures 2a and 2c), doublets at δ 0.92 ppm in Figure 2a and at δ 0.99 ppm in Figure 2c are assignable to the methyl groups of **2a** and **2c**, respectively. A doublet-like signal at δ 3.94 ppm in Figure 2a and a triplet-like signal at δ 4.10 ppm in Figure 2c are due to methyne protons located

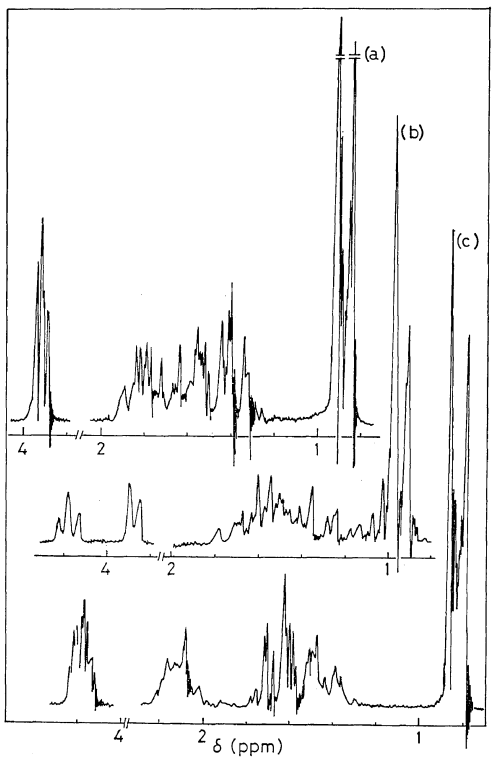


Figure 1. NMR spectra (100 MHz) of (a) **1a**, (b) **1b**, and (c) **1c** in CCl_4.

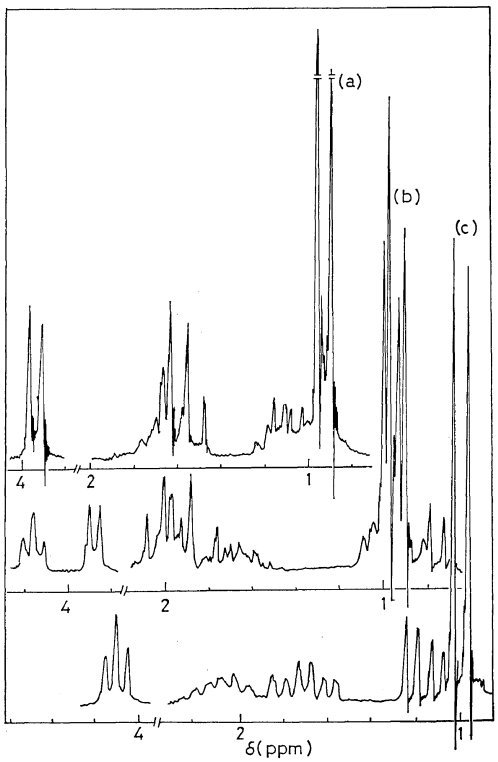


Figure 2. NMR spectra (100 MHz) of (a) **2a**, (b) **2b**, and (c) **2c** in CCl_4.

at the bridgehead carbons of **2a** and **2c**, respectively. From the chemical shifts and the shapes of their signals, it is concluded that **2a** and **2c** correspond to the *exo,exo*- and *endo,endo*-isomers, respectively.

In the spectrum of **1b** (Figure 1b), the triplet- and the doublet-like signals at δ 4.17 and 3.86 ppm are assigned to two methyne protons which are in unequivalent magnetic fields because of the presence of the *endo*- and *exo*-methyl groups. However, two doublets of the methyl groups appear not to be separated sufficiently, probably because their chemical shifts have almost no difference, as will be deduced from the cases of **1a** and **1c**. The spectra of **1a** and **1c** show the multiplet signals, which should be assigned to their methyne protons on the bridgehead carbons, at δ 3.91 and 4.17 ppm, respectively. The doublet signals of the methyl groups of **1a** and **1c** are shown at δ 0.87 and 0.80 ppm, and the difference in these chemical shifts is small.

According to Allinger's rule,[9] the boiling points of these monomers will increase with increasing the number of the *endo*-methyl group. In the series of 2,5-dimethyl monomers, the boiling points of the crude **2a** (*exo,exo*-), **2b** (*endo,exo*-), and **2c** (*endo,endo*-) were 146—148, 152—154, and 157—159°C, respectively. In the 2,3-dimethyl analogues, however, the crude **1b** (*endo,exo*-), **1a** (*exo,exo*-), and **1c** (*endo,endo*-) boiled at 150—151, 156—158, and 158—162°C, respectively. It is interesting that **1a**, with two *exo*-methyl groups, boils at a higher temperature than **1b**, with one *exo*- and one *endo*-methyl groups.

Results of the cationic polymerizations of 2,3- and 2,5-dimethyl ether isomers in CH_2Cl_2 at -20 or 0°C with several catalytic systems are summarized in Table I. The monomers **1a**, **1b**, and **2b** yielded white powdery polymers in fairly good yields with the $SbCl_5$—epichlorohydrin (ECH) system. Poly(**2b**) was insoluble in the usual organic solvents and highly crystalline on the basis of the X-ray diffraction diagram (Figure 3). Poly(**1a**) was rather soluble in hot trichloroethylene. The monomers **1a** and **2b** polymerized heterogeneously with deposition of polymer after about 10 minutes.

Conversions of the monomers under similar reaction conditions increased in the orders of **1c**$\ll$**1a**$\leq$**1b** and **2a**$\leq$**2c**$<$**2b**. It should be emphasized that these conversion orders are not reflected by the order of the ring strain of these monomers; *i.e.*, the ring strains can reasonably be assumed to increase in the orders of **1a**$<$**1b**$<$**1c** and **2a**$<$**2b**$<$**2c**, since the studies of the heat of combustion of **3a** and **3b** revealed that the ring strain of the bicyclic ethers is increased by an *endo*- more than by an *exo*-methyl substituent.[10]

In addition, the conversion was affected by initiators. Of the initiators used here, the $SbCl_5$—ECH system gave the highest conversions in the polymerization of the dimethyl bicyclic ethers.

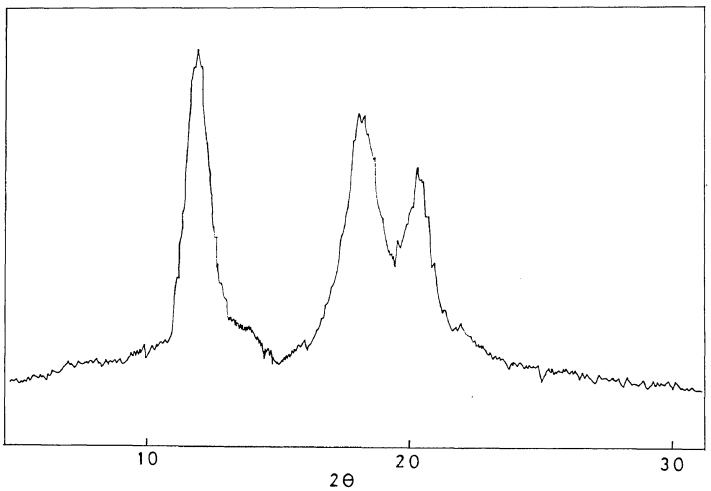


Figure 3. X-ray diffraction intensity pattern for poly(**2b**).

Table I. Cationic polymerizations of 2,3- and 2,5-dimethyl-7-oxabicyclo[2.2.1]heptanes in CH_2Cl_2

Monomer concn, mol l^{-1}	Catalyst, mol %		ECH, mol %	Temp, °C	Time, h	Convn, %	$\bar{M}_n$[a]
exo,exo-2,3-isomer (**1a**)							
1.7	$SbCl_5$	4	2	−20	4	18	
1.7	$SbCl_5$	4	2	−22	94	58	
1.5	$SbCl_5$	4	2	0	48	56	
endo,exo-2,3-isomer (**1b**)							
1.6	$SbCl_5$	4	2	−20	2	35	1438
1.7	$SbCl_5$	4	2	−20	4	42	1194 (3801)[b]
1.7	$SbCl_5$	4	2	−22	94	67	1130
1.3	$SbCl_5$	4	4	−20	2	46	1236
1.6	$SbCl_5$	4	2	0	2	29	716
1.7	$SbCl_5$	4	2	0	4	36	739
2.3	$SbCl_5$	2	2	0	48	56	(1257)[b]
1.7	BF_3THF	4	2	−22	480	24	737 (1795)[b]
1.7	BF_3THF	4	2	0	4	16	876
1.7	BF_3THF	4	2	0	94	21	630
endo,endo-2,3-isomer (**1c**)							
1.7	$SbCl_5$	4	2	0	48	4	
exo,exo-2,5-isomer (**2a**)							
1.7	$SbCl_5$	4	2	−22	94	21	795
1.4	$SbCl_5$	4	2	0	72	28	
1.4	BF_3THF	4	2	0	2	16	493
endo,exo-2,5-isomer (**2b**)							
1.4	$SbCl_5$	1	2	0	72	29	
1.4	$SbCl_5$	2	2	0	72	48	
1.4	$FeCl_3$	1	2[c]	0	72	34	
1.4	$FeCl_3$	2	1[c]	0	72	38	
1.3	$SnCl_4$	1	2	0	72	19	
1.4	$SnCl_4$	2	2	0	72	21	
1.4	BF_3THF	3	2	0	2	26	
1.4	BF_3THF	1	2	0	72	18	
endo,endo-2,5-isomer (**2c**)							
2.8	BF_3THF	2	1	−30	5.5	5	636
1.8	BF_3THF	3	1	0	2	17	1235

[a] Measured by vpo; solvent, $CHCl_3$.
[b] Methanol-insoluble part.
[c] Cocatalyst, $SOCl_2$ in ethyl ether.

Molecular weights of the soluble polymers were measured by vapor pressure osmometry (VPO) (Table I). Degrees of polymerization of these polymers are generally low. The effect of the initiators on the conversion and the molecular weight may be interpreted by the nature of the counteranions of the oxonium ion. As shown in the time—conversion curves for the polymerization of **1b** by the $SbCl_5$— and the BF_3THF—ECH systems (see Figure 4), the polymerization with BF_3 tends to be terminated at lower conversions than that with $SbCl_5$. When $SbCl_5$ was employed as a catalyst, the conversion increased with the reaction time. The molecular weight, however, did not increase as the reaction proceeded. These findings suggest that a chain-transfer reaction occurred in the polymerization with the $SbCl_5$ catalyst.

In our previous study,[11] the polymerizations of *exo*- and *endo*-2-*t*-butyl-7-oxabicyclo[2.2.1]heptanes using the BF_3THF—ECH system suffered from termination owing to proton elimination in

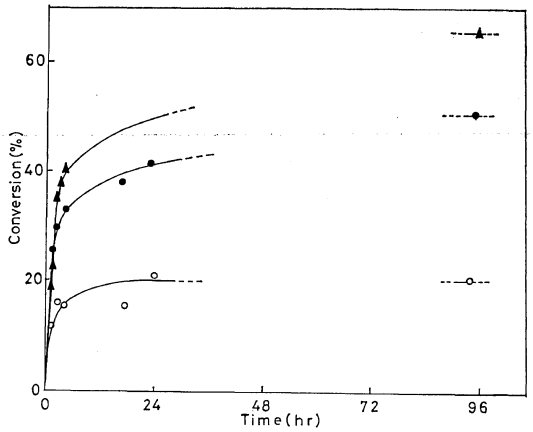
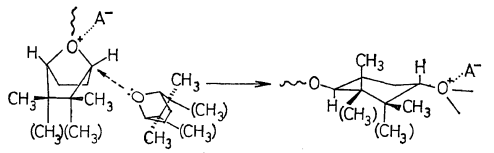


Figure 4. Conversion—time curve in the polymerization of **1b**: ▲, $SbCl_5$ (4 mol %), −20°C; ●, $SbCl_5$ (4 mol %), 0°C; ○, BF_3THF (4 mol %), 0°C; ECH, 2 mol %.

their oxonium end; this resulted in low conversions since the protonic acid (such as HBF_4) could not reinitiate these monomers. However, the polymerization in the present study may be reinitiated by a protonic acid such as $HSbCl_6$ to give polymers of low molecular weights.

Increase of the polymerization temperature (−20 to 0°C) lowers both the conversion and the molecular weight. Probably, at high temperature, another termination, in which the oxonium end reacts with the counteranion, occurred as well.

The stereochemistry of the propagation is an interesting subject of study. First, the propagation of 2,3-dimethyl monomers was examined by NMR spectroscopy of the product polymers. The monomers **1a** and **1c** can attack equally either of two bridgehead carbons of oxonium ions (**4a** and **4c**) to give poly(**1a**) and poly(**1c**), respectively. These are constructed of cyclohexane units of the same conformational structure (Scheme II).



4a or (**4c**) **1a** or (**1c**) poly(**1a**) or (poly(**1c**))

Scheme II

In the NMR spectrum of poly(**1a**) in trichloroethylene (Figure 5a), the two doublets at δ 0.9 and

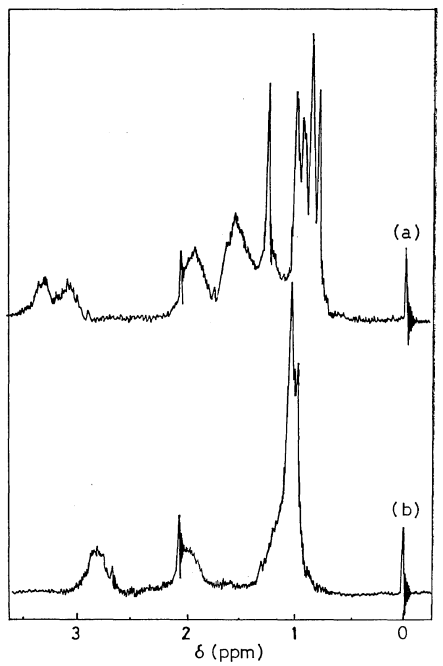
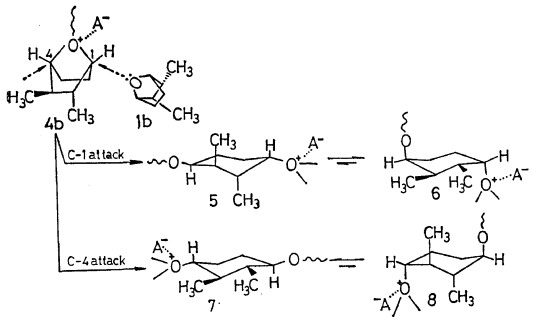


Figure 5. NMR spectra (100 MHz) of (a) poly(**1a**) and (b) poly(**1b**) in $CHClCCl_2$.

1.0 ppm indicate the presence of two methyl groups located at axial and equatorial positions in its cyclohexane ring unit. The multiplets which are constructed of two bands centered at δ 3.1 and 3.4 ppm are assignable to two axial α-methyne protons to the ether groups. The ratio of the integral intensity of these methyne protons to that of the other protons (0.6—2.2 ppm) in the NMR spectrum of poly(**1a**) is about 1 : 7, which is close to the theoretical value (1 : 6).

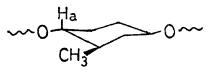
In the polymerization of **1b**, two propagation processes at two bridgehead carbons (C-1 and C-4) of the oxonium ion **4b** must be taken into consideration; *i.e.*, the S_N2 propagation at C-1 yields polymer **5** and the one at C-4 polymer **7** (Scheme III).

The structure **5** is interconverted to the structure **6** in a conformational equilibrium, in which the conformation free-energy difference will favor **6**. This is because the cyclohexane ring unit in **6** has two equatorial methyl groups and two axial ether groups, whereas **5** has two axial methyl groups and two equatorial ether groups. Following the conformational study,[12] it can be generalized that the



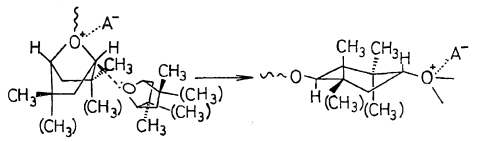
Scheme III

differences in conformational free energy are 1.5—2.1 kcal/mol for methyl and 0.6—0.75 kcal/mol for methoxy or 0.9—1.0 kcal/mol for ethoxy groups. Therefore, when the propagation occurs at C-1, the main conformation of the polymer unit will be **6**, in which α-methyne protons are located at the equatorial position. On the other hand, the ring unit in **7** is conformationally a stable structure, in which all of the four substituents are at equatorial and α-methyne protons are at axial positions. This problem was clarified by an NMR spectroscopic study of the polymer. The NMR spectrum shown in Figure 5b indicates that the methyne proton takes the axial position, as shown by a multiplet signal centered at δ 2.9 ppm. This value of the chemical shift is higher than that of the axial protons of poly(**1a**). The NMR spectrum of poly(**3b**) showed a multiplet signal at δ 2.7 ppm in $CDCl_3$ for the axial methyne proton H_a.



poly(**3b**)

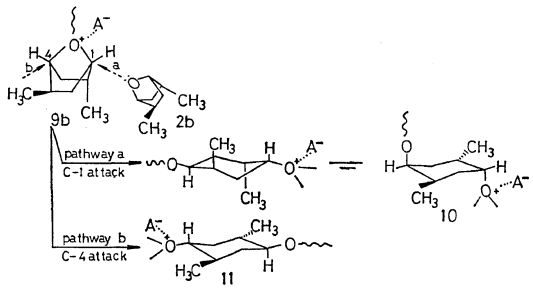
In addition, the axial methyne proton of *trans*-2-methylcyclohexanol resonates at δ 2.98 ppm in CCl_4, whereas the equatorial one of its *cis*-isomer resonates at δ 3.75 ppm.[13] From the above findings, it is concluded that the polymer unit of **1b** takes **7**, but not **6**. This indicates that the steric effect of the *endo*-methyl substituent of the oxonium end **4b** toward the nucleophilic reaction with the monomer is higher than that of the *exo*-methyl substituent. From a molecular model of the monomer **1b**, it is assumed that the back side of the C-1 bridgehead carbon atom is blocked to a larger extent than that of the C-4 atom. The stereochemistry of the polymerizations of 2,5-dimethyl monomers is considered in a similar way. The NMR spectrum of poly(**2a**) coincided with that of poly(**2c**). The following scheme (Scheme IV) of propagation is taken to explain the above finding that the monomers **2a** and **2c** gave the same polymer.



2a or (**2c**) poly(**2a**) or (poly(**2c**))

Scheme IV

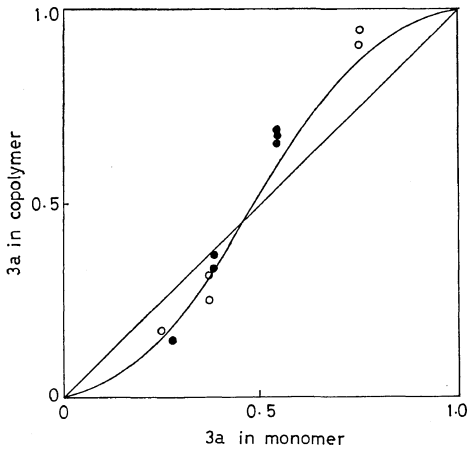
The polymer of **2b** was crystalline and insoluble in common organic solvents. Therefore, the direct analysis of the stereochemistry of the propagation of **2b** could not be made.



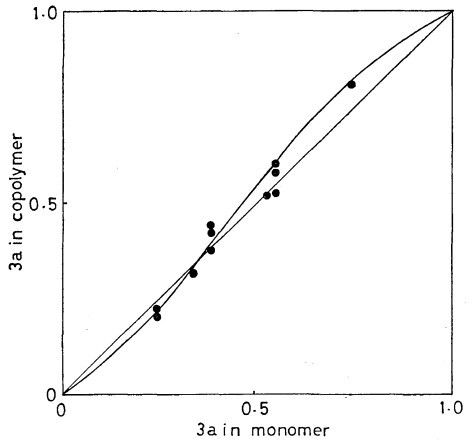
Scheme V

Nevertheless, a possible propagation through pathway **b** in the Scheme V is reasonably suggested on the basis of the fact that the back side of C-1 atom in **9b** is more blocked by steric hindrance of the *endo*-methyl substituent, as deduced from the result of the polymerization of **1b**. The polymer prepared from **2b** through the pathway **b** has the structure **11**, in which four substituents at 1, 2, 4, and 5 positions take equatorial positions.

In order to examine the nucleophilic reactivity of monomers, **2a**, **2b** and **3b** were subjected to cationic copolymerization with **3a** (M_1). The reactivity ratios in these three systems were determined according to the Mayo—Lewis equation (Table II). The monomer nucleophilicities towards the common oxonium ion of **3a** were compared



(a)



(b)

Figure 6. Copolymerization curves of **3a** with the 2,5-dimethyl bicyclic ethers by BF_3THF—ECH in CH_2Cl_2.
(a) Copolymerization of **3a**—**2a** at −20°C (●) and 0°C (○).
(b) Copolymerization of **3a**—**2b** at 0°C.

Table II. Cationic ring-opening copolymerizations of **3a** with **2a**, **2b**, and **3b** by BF_3THF—ECH at 0°C in CH_2Cl_2

Comonomer		Reactivity ratio		$1/r_1$
M_1	M_2	r_1	r_2	
	2a	6.0	5.5	0.17
3a	**2b**	2.0	1.5	0.50
	3b	0.9	1.4	1.11

by the reciprocals of the reactivity ratios, $1/r_1$. The $1/r_1$ values increase in order of **2a**<**2b**<**3a**<**3b**. This fact indicates that the presence of the *exo*-methyl group which is located at the front of the monomer is less favorable for its nucleophilicity. In the two series of the 2,3- and 2,5-dimethyl monomers, it is assumed that the nucleophilicity increases in the order of *exo,exo-*<*endo,exo-*<*endo,endo*-isomers.

It is concluded that the reactivities of the dimethyl monomers in the present study are governed by the following factors: (1) the steric crowding around the bridgehead carbon atom of the propagating oxonium, (2) the monomer nucleophilicity, and (3) ring strain. The *endo,exo*-isomer will be the best situation among the dimethyl monomers. The position of the substituents in the monomer, of couse, affects its polymerization, and the *exo,-exo*-2,3-dimethyl monomer gave a higher yield of polymer than the *exo,exo*-2,5-dimethyl monomer did. This may be interpreted as increased steric interaction of the substituents in the orientation of the 2,5-dimethyl monomer to its oxonium end.

Since the conversion should be influenced by the initiation and termination reactions, the direct comparison of monomer reactivity may be made by the kinetic study of the propagation reaction.

EXPERIMENTAL

Materials

exo,exo-, endo,exo-, and endo,endo-2,3-Dimethyl-7-oxabicyclo[2.2.1]heptanes (**1a**, **1b**, *and* **1c**). Dimethylaminophenol, which was prepared from 2,3-dimethylphenol (100 g, 0.82 mol) according to the ordinary method described by Fieser,[14] was dissolved in a mixture of 45 m*l* of concentrated H_2SO_4 and 890 m*l* of water, and filtered through a pad of active carbon. The filtrate was added to a suspension of MnO_2 (assay 65%) in a mixture of concentrated H_2SO_4 and 890 m*l* of water below 45°C and stirred at 45—50°C for 1 h. Yellow crystals of 2,3-dimethylbenzoquinone was separated from the reaction mixture by steam distillation at 40—42°C under the reduced pressure of 70 mmHg: mp 54.5—57.5°C [lit.[7] 54.5—55.5°C], yield of 70% based on the dimethylphenol. The benzoquinone was reduced with Zn powder in aqueous acetic acid to give 2,3-dimethylhydroquinone in a 90-% yield: mp 221.5—224°C [lit.[7]

221°C]. Catalytic hydrogenation of the hydroquinone (50 g) was carried out with Raney Ni (W-2) (15 m*l*) in CH_3OH (100 m*l*) at 140—150°C under initial H_2 pressure of 110 atm. The solution was freed from the catalyst by filtration. Removal of the solvent gave a residue of an isomeric mixture of 2,3-dimethylcyclohexane-1,4-diols almost quantitatively. The diols (102 g) was mixed with 153 g of activated alumina (after being heat-treated at 450—500°C for 4 h) and the mixture was heated gradually to 260°C. The volatile fraction was distilled to a trap cooled in icewater under reduced pressure (90—100 mmHg). The distillate was extracted with ether and dried over anhydrous K_2CO_3. After removal of the solvent, a residue was separated onto the desired bicyclic ethers, **1b**, **1a**, and **1c**, in yields of 16.5, 11.2, and 1.4%, respectively, by means of a fractional distillation using a column (100 cm) equipped with a spinning band. Their boiling points were 150—151, 156—158, and 158—162°C; their purities were about 95% by gas-chromatographic analyses. Final purification of the ethers was successfully achieved with High Vacuum Oil or PEG 20M on Celite (60—80 mesh) at 100°C under H_2 pressure of 1.0 kg/cm^2. The monomers had purities above 99%. Their NMR spectra are shown in Figures 1a—1c. Elemental analyses for **1a** and **1b** were as follows:

Anal. Calcd for $C_8H_{14}O$: C, 76.14; H, 11.18. Found: C, 76.23; H, 11.07, and C, 75.95; H, 11.20, respectively, for **1a** and **1b**. The analytical value for **1c** could not be determined because its weight decreased gradually during weighing of a sample.

exo,exo-, endo,exo-, and endo,endo-2,5-Dimethyl-7-Oxabicyclo[2.2.1]heptanes (**2a**, **2b**, *and* **2c**). These were synthesized by procedures similar to those for 2,3-dimethyl monomers, with the exception of the oxidation procedure. The oxidation of 2,5-dimethylaminophenol to the corresponding benzoquinone was carried out with $FeCl_3 \cdot 6H_2O$ and hydrochloric acid to yield a yellow crystal: mp 121.3—123.5°C [lit.[15] 123—125°C]. The catalytic hydrogenation of 2,5-dimethylhydroquinone, mp 213—214°C [lit.[16] 212—213°C], followed by treatment with active alumina produced **2a**, **2b**, and **2c** in yields of 9.6, 4.9, and 3.2%; their boiling points were 146—148, 152—154, and 157—159°C, respectively. By the preparative gas chromatography, they were purified to above 99%. Their NMR spectra are shown in Figures 2a—2c.

Anal. Calcd for $C_8H_{14}O$: C, 76.14; H, 11.18. Found: C, 76.06; H, 11.34 for **1a**, C, 76.39; H, 11.19 for **1b** and C, 75.87; H, 10.91 for **1c**.

Initiators and Solvents

BF_3THF complex was prepared according to the literature,[17] bp 88°C (11 mm). $SnCl_4$, $SbCl_5$, and $FeCl_3$ were purified by distillation or sublimation under nitrogen. $FeCl_3$ was dissolved in dry ether, and the other salts in CH_2Cl_2. ECH and $SOCl_2$ were distilled over CaH_2 and P_2O_5, respectively, under a nitrogen atmosphere. Solvent CH_2Cl_2 was purified according to the procedure described previously.[18] Ether was purified by the ordinary method.[19]

Polymerization Procedure

The polymerization was carried out under dry nitrogen. The monomer was weighed in a reaction tube, which was dried and flushed with N_2 gas, and the catalyst and cocatalyst or promotor solutions were added successively into the monomer at the desired temperature. The polymerization was quenched by addition of 0.5-*N* sodium methoxide in methanol, and the amount of the remaining monomer was determined by gas chromatography after adding dioxane as an internal standard (3 mm × 3 m glass column packed with PEG 6000/Shimalite F; 100°C; carrier gas, N_2; detector, FID). The polymer solution was extracted with CH_2Cl_2, washed successively with aqueous NaOH and water, and dried over K_2CO_3. Evaporation of the solvent and the unreacted monomer from the solution left a polymer. Poly(**1b**) was purified further by reprecipitation using CH_2Cl_2 (solvent)—methanol (precipitant), and poly(**2a**) and poly(**2c**) were purified by methanol—water. The insoluble polymers, poly(**1a**) and poly(**2b**), were separated from the polymerization mixture by centrifuging, washed with 3-*N*HCl and water successively, and dried *in vacuo*. The monomer reactivity ratios were determined by the curve fitting method (Figure 6).

NMR and X-Ray Measurements

Nuclear magnetic resonance spectra were determined on a PS-100 (Jeol Ltd.) at 23°C. X-ray diffraction used Cu—Kα rays on a SG-7 (Rigaku Denki).

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