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

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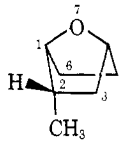
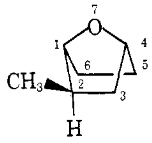
This paper describes a kinetic study on the cationic polymerization of *endo*-2-methyl-7-oxabicyclo[2.2.1]heptane (*endo*-MOBH) in CH_2Cl_2 with an initiator of the BF_3–epichlorohydrin (ECH) system. The cationic polymerizations of *exo*- and *endo*-MOBH were reported,[1-3] in which the kinetic analysis was made on the initial velocity from the time–conversion curve. The propagation rate constants of these two isomeric monomers, however, have not been quantified. In a previous paper by us,[4] the propagation rate constant, k_p, of the cationic polymerization of *exo*-MOBH was successfully determined by using our "phenoxyl end-capping" method.[5-7] In the present study, the kinetic analysis of the polymerization of the endo isomer was made by the same method. Quantitative comparison of the kinetic reactivity between these two isomers has now become possible.



endo-MOBH



exo-MOBH

The *endo*-MOBH monomer was prepared according to the reported procedure.[8] Pure *endo*-MOBH was isolated by repeated fractional distillation using a spinning-band fractionator, bp 136°. The purified monomer was then distilled over benzophenone–disodium prior to use. The purity was over 99.9% by glpc analysis. Other reagents, polymerization procedure, and analytical method were the same as those of the previous study on the *exo*-MOBH polymerization.

Figures 1 and 2 show the course of the polymerization of *endo*-MOBH between −10 and −40°. The molecular weight (vpo) of the product polymer was in the vicinity of 3900 and the melting temperature was 210–252°. Figure 1 shows the time–[P*] profile. The termination reaction is quite noticeable, and becomes significant at −10°. The general shape of the time–[P*] curves is similar to that in the case of *exo*-MOBH,[4] but the rate of the [P*] decrease shown in Figure 1, *i.e.*, the rate of termination, is generally higher than that of the exo monomer. It is also interesting to note that the maximum value of [P*] is only about 6.8% of the initial molar concentration of BF_3 ($[ECH]_0/[BF_3]_0 = 1/6$) at −40°. In the case of *exo*-MOBH, the maximum [P*] was 7.5% of BF_3 at −40°.

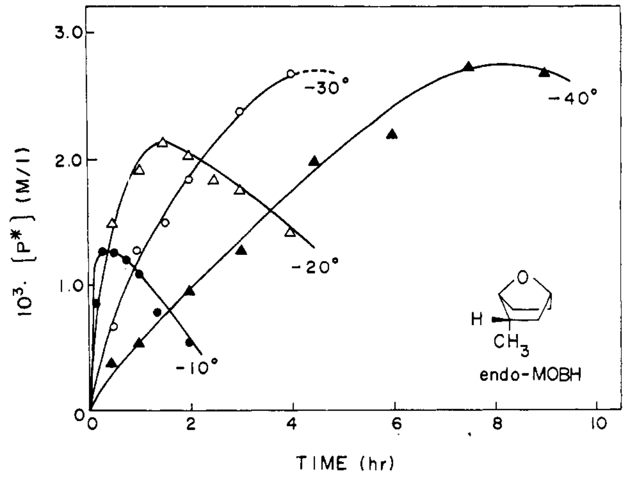


Figure 1. Time–[P*] curve for the polymerization of *endo*-MOBH by BF_3–ECH; solution polymerization in CH_2Cl_2, $[M]_0$ 1.42 *M*, $[BF_3]_0$ 0.039 *M*, $[ECH]_0$ 0.0071 *M*.

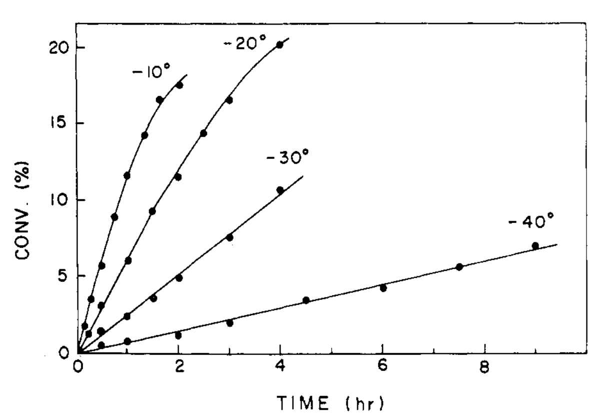


Figure 2. Time–conversion curve of the polymerization of *endo*-MOBH by BF_3–ECH; conditions are given in Figure 1.

Table I
Kinetic Data

	°C	*endo*-MOBH	*exo*-MOBH[a]
$k_p \times 10^3$, l./(mol sec)	−40	0.85	0.18
	−30	4.0	0.87
	−20	8.4	2.6
	−10	27	9.4
$\Delta E^{\ddagger}$, kcal/mol		14	15
$10^9 A_p^{\ddagger}$, l./(mol sec)		7	41

[a] From ref 4.

From the time–[P*] and the time–conversion curves, the k_p of *endo*-MOBH was determined by the same procedure as that employed in the polymerization of the exo monomer (Table I). An Arrhenius plot of k_p gave a straight line, from which the activation parameters were calculated.

In the S_N2 propagation of *endo*-MOBH, the nucleophilic monomer attacks predominantly the C-4 atom of the oxonium ring **1** to cause inversion of configuration at the C-4 atom. The above stereochemistry has been established by us on the basis of nmr analyses of the product polymer.[9] In addition, the same conclusion was given in the polymerization of *exo*-MOBH. Therefore, the k_p values in Table I are taken to represent the rates of ring opening of the cyclic oxoniums by

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

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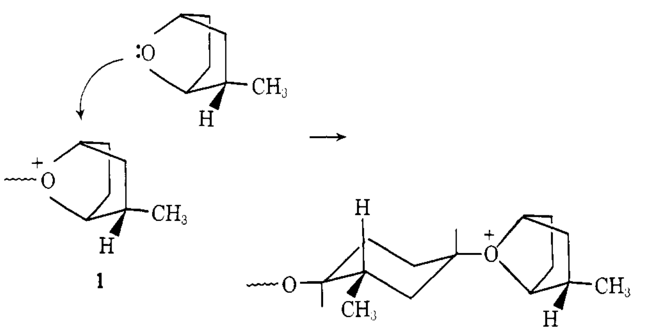
(9) T. Saegusa, M. Motoi, S. Matsumoto, and H. Fujii, *Macromolecules*, **5**, 233 (1972).



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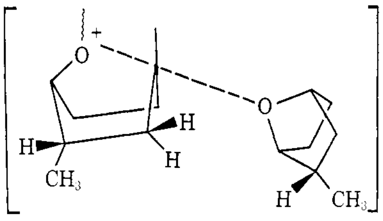
the attack of monomer on C-4. Table I shows that the k_p value of endo monomer is higher than that of exo monomer, and that the difference in this kinetic reactivity is ascribed mainly to the activation energy rather than the frequency factor.

From the heat of formation, Bedfoad, *et al.*,[10] reported that *endo*-MOBH is less stable (more strained) than *exo*-MOBH due to more severe interaction of the C-2 methyl group with the hydrogen atoms at C-3, C-5, and C-6. Therefore, it is not unreasonable to assume that the cyclic oxonium derived from *endo*-MOBH in the ground state is more strained than that derived from *exo*-MOBH. In the transition state **3** of the SN2 propagation, the steric interaction of C-2 methyl group with the neighboring hydrogen atoms will be relieved due to the stretch of C-4–O-7 bond. Thus, the increased strain energy in the ground state serves to decrease the activation energy, $\Delta E_p^{\ddagger}$.



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Communications to the Editor

Stereoregularity of Polystyrene Determined by Carbon-13 Nuclear Magnetic Resonance Spectroscopy

We wish to report the preparation of polystyrenes with various tacticities, especially with random (atactic) configurations, and the determination of the stereoregularity by ^{13}C nmr spectroscopy. To our knowledge, all the reports on the stereoregularity of polystyrene have been concerned with isotactic- and syndiotactic-rich polymers.

The determination of the stereoregularity of polystyrene was first attempted by Brownstein, *et al.*,[1] using proton nmr spectroscopy. The three peaks in the methine proton spectrum of poly(styrene-β,β-d_2) were assigned to isotactic, heterotactic, and syndiotactic triads from a lower magnetic field. The authors concluded that polymers prepared by usual methods have syndiotactic-rich configurations. Bovey and coworkers studied in detail the proton nmr spectra of isotactic polystyrene.[2,3]

Recently, Segre and coworkers[4] observed six peaks in the methine proton spectrum of poly(styrene-d_7) and assigned the second peak from the lower magnetic field (216 Hz from TMS) to the *mmmm* pentad. They suggested the possibility of the presence of different heptads.

The ^{13}C nmr spectrum of polystyrene was first measured by Bovey, et al.,[5] revealing that the aromatic C-1 spectrum is similar to the α-methine proton spectrum. Recently, Nishioka and coworkers[6] determined ^{13}C nmr spectra of radically polymerized polystyrene. The aromatic C-1 spectra were analyzed in terms of triads, and they found that the observed triads did not obey Bernoullian statistics.

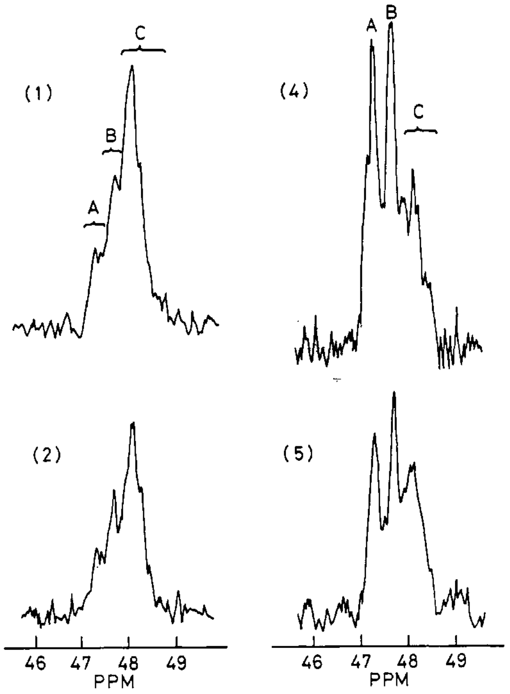

Figure 1. ^{13}C nmr spectra of aromatic C-1 of polystyrenes prepared with (1) BPO in toluene at 80° (256 scans), (2) *n*-butyllithium in *n*-heptane at 40° (400 scans), (4) BF$_3$ etherate in toluene at 30° (256 scans), and (5) BF$_3$ etherate in toluene at 0° (256 scans) (^{13}CS$_2$ as reference zero).

Polystyrenes were prepared under various conditions by using a high-vacuum technique. The results are shown in Table I. The 25.14-MHz ^{13}C nmr spectra were obtained at 60° with a JEOL PS-100 spectrometer equipped with an IS-100 proton irradiation sweep unit and an SD-HC heterospin decoupler. Polymers were dissolved in *p*-xylene–chloroform (2 : 3 v/v) or benzene–chloroform (1 : 4 v/v) to give about 20–40% solutions. The spectra obtained were the same in both solvent mixtures.

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[4] A. L. Segre, P. Ferruti, E. Toja, and F. Danusso, *ibid.*, 2, 35 (1969).

[5] L. F. Johnson, F. Heatley, and F. A. Bovey, *ibid.*, 3, 175 (1970).

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