Phthalic (naphthalic) anhydride (0.01 mol) was added to the solution of 0.01 mol of benzamidrazone in DMSO. The reaction solution was stirred overnight at 25–70° and then poured into acetone; the precipitates formed were filtered off, washed with acetone and ether, and dried at 25° (10^{-3} mm). The yields of the products were almost quantitative. The products obtained were treated thermally from 25 to 360° at reduced pressure (10^{-3} mm) for 10 hr and then at 240–360° (10^{-3} mm) for 10 hr. The sublimates formed were collected and sublimed twice more at 240–360° (10^{-3} mm).

The same procedures were employed for the preparation of the model compounds XIV, XVII, XXa–d, and XXIIIa–d.

One-Stage Synthesis of the Model Compounds. Synthesis of XI was carried out following the next procedure. Benzamidrazone (0.01 mol), 0.01 mol of naphthalic anhydride, and 20 cm^3 of 116% PPA were placed in the reaction vessel. The reaction mixture was heated gradually to 180°, stirred at this temperature for 12 hr, and then poured in ice water; the precipitate formed was filtered, washed with sodium bicarbonate solution, and dried. XI was purified by sublimation at 340–360° (10^{-3} mm).

The same procedures were employed for the preparation of the model compounds XVII and XXIIIb–d.

Polymers. Poly(*o*-carboxybenzoylamidrazones) were prepared according to the following general procedure. Solid bis(phthalic anhydride) (0.01 mol) was added portionwise to the stirred solution of 0.01 mol of bisamidrazone in 20 cm^3 of dry DMSO at 25°. The resulting yellow solution became very viscous almost immediately after the addition of anhydride; stirring was continued for 2 hr. The solution of polymer was diluted with DMSO and poured into a large excess of acetone or cast on glass plates. Poly(benzoylene-*s*-triazoles) [poly(isoindolo-*s*-triazolones)] were prepared by heating poly(*o*-carboxybenzoylamidrazones) from 25 to 360° at reduced pressure (10^{-3} mm) for 10 hr and then at 360° (10^{-3} mm) for 10 hr.

Poly(naphthoylene-*s*-triazoles) (poly[benzobis(*s*-triazolo)phenanthrolinediones]) were prepared according to the following general procedure. Naphthalene-1,4,5,8-tetracarboxylic acid (0.01 mol) dianhydride was added to the solution of 0.01 mol of bisamidrazone in 20 cm^3 of 116% PPA. The reaction mixture was heated with stirring up to 180° and this temperature was maintained for 12 hr. The resulting deep-red solution was poured in water, filtered off, washed with water and ethanol, dried, and reprecipitated from sulfuric or methanesulfuric acid in water or ethanol.

Acknowledgment. The authors wish to thank Professor P. M. Hergenrother for the fruitful discussion of the experimental results.

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Kinetic Studies on the Ring-Opening Polymerization of 3-Oxaspiro[3.2]hexane

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ABSTRACT: Kinetics of the cationic polymerization of 3-oxaspiro[3.2]hexane (OSH) has been analyzed by means of the phenoxyl end-capping method. Polymerization proceeded via an S$_N$2 mechanism involving the ring opening of oxetane. The rate constant of propagation (k_p) shows that the spiro cyclopropane ring in OSH does not greatly enhance the polymerization reactivity of OSH. The relatively low $\Delta H^‡$ (favorable) and $\Delta S^‡$ (unfavorable) values were explained by the rigid monomer structure.

In a previous paper we have reported kinetic studies on the cationic ring-opening polymerization of unsubstituted (OX), 3-methyl- (MeOX), and 3,3-dimethyloxetanes (Me$_2$OX) by the phenoxyl end-capping method.[1] Introduction of the methyl group at the 3 position of oxetane ring increased the rate constant of propagation (k_p).[1] In the

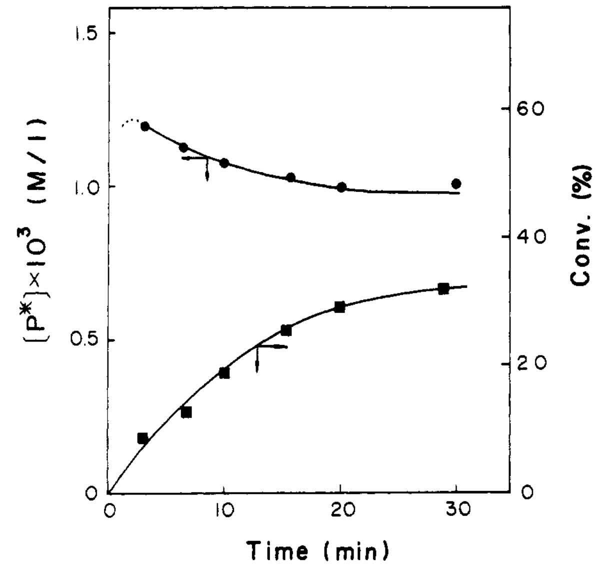


Figure 1. Polymerization of OSH at −20° in methylcyclohexane: $[M]_0$ = 1.09 mol/l., $[BF_3{\cdot}THF]_0$ = 0.01 mol/l.

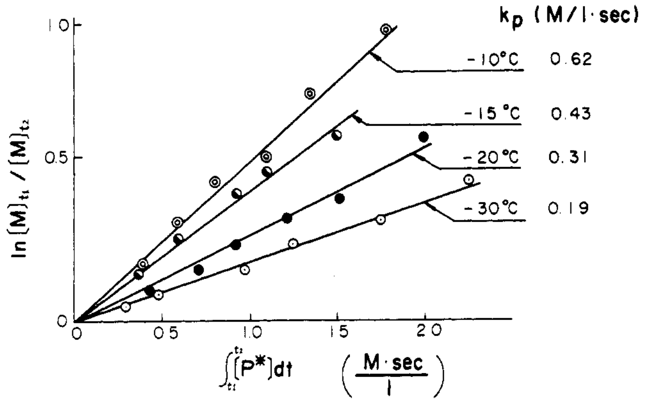
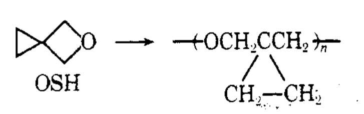


Figure 2. Plots of eq 4 in the polymerization of OSH.

ring-opening polymerization, the ring strain of monomer is considered to be an important factor in the polymerization reactivity of the monomer. Among oxetanes 3-oxaspiro[3,2]hexane (OSH) is the smallest spiro compound, and hence, the strained spiro cyclopropane may influence the ring-opening reactivity of the oxetane ring. The purpose of the present study is to examine the kinetics of the cationic



OSH 1 (1)

ring-opening polymerization of OSH by means of the phenoxyl end-capping method.[2-4] Before the present study semiquantitative studies showed that the cyclopropane ring did not affect the polymerization rate of OSH.[5]

Experimental Section

OSH was prepared by the cyclization of 3,3-bis(chloromethyl)oxetane with zinc dust in molten acetamide, according to Searles and Lutz.[6] It was purified by repeated distillation using a spinning-band column over sodium metal under nitrogen: bp 97° (yield 15%); NMR (neat) δ 4.75 (s, 4 H, $-CH_2O-$), 0.60 (s, 4 H, $-CH_2CH_2-$). The purity of OSH was higher than 99.9% by GLPC analysis. Methylcyclohexane and methanol-*d* were purified as previously reported.[1] The catalyst $BF_3{\cdot}THF$ complex was prepared and purified in the same manner as described previously.[2]

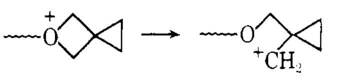
Polymerization was carried out in methylcyclohexane solution under nitrogen, using the established procedures of the phenoxyl end-capping method,[1,2] in which $[M]_0$ and $[BF_3{\cdot}THF]_0$ were 1.09 and 0.01 mol/l., respectively.

The basicity of OSH was determined according to the ir method of Iwatsuki et al.[7] in which the O–D band of methanol-*d* was measured with a Hitachi grating ir spectrometer, Model EPI-G3. The cell was 0.010 cm thick. The concentration of methanol-*d* was 0.1 mol/l. in benzene solution.

Results and Discussion

The polymerization of OSH was carried out with $BF_3{\cdot}$THF catalyst.

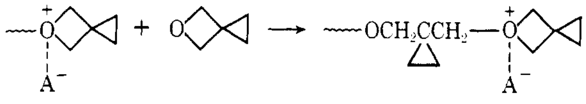
First, the structure of the polymer was examined by NMR spectroscopy. The NMR spectrum of the solid polymer in $CDCl_3$ shows two sharp singlets at δ 3.32 and 0.45. They are assigned respectively to $-CH_2OCH_2-$ and to cyclopropane methylene protons of the structure 1. This indicates that OSH did not undergo any isomerization and that polymerization occurred at the oxetane ring. This result is quite compatible with the SN2 mechanism of propagation as discussed later. The SN1 propagation via the cyclopropylcarbinyl ion 3 would have caused some rearrangements.



2 3

The instantaneous concentration of the propagating species [P*] was determined by means of the phenoxyl end-capping method.[1-4] Figure 1 shows the relationships of [P*] and of the monomer conversion as a function of the reaction time at −20°. [P*] reached the maximum value in 2 min or less, and then diminished gradually. The highest value of [P*] measured is only 12 *M* % of the charged catalyst.

The propagation reaction of the cationic ring-opening polymerization of OSH can be formulated as an SN2 mechanism



2 (2)

where A^- is the counteranion derived from the catalyst. The rate equation of polymerization is

$$-d[M]/dt = k_p[P^*][M] \tag{3}$$

where k_p denotes the rate constant of propagation. The integrated equation, therefore, is given by

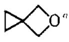
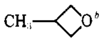
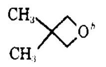
$$\ln\frac{[M]_{t_1}}{[M]_{t_2}} = k_p\int_{t_1}^{t_2}[P^*]dt \tag{4}$$

where $[M]_{t_1}$ and $[M]_{t_2}$ are the monomer concentrations at time t_1 and t_2, respectively.

Figure 2 illustrates the plots of eq 4 carried out at four different temperatures, whose slopes gave k_p values. The Arrhenius plot of k_p values was linear and activation parameters were calculated. Table I lists the k_p value at −20° as well as the activation parameters. For the sake of comparison Table I includes also those values of OX, MeOX, and Me_2OX.

The reactivity of polymerization is in the order Me_2OX > MeOX > OSH > OX at −20°. OSH polymerized slightly faster than OX, the unsubstituted monomer. This indicates that the spiro cyclopropane ring does not much affect the polymerization reactivity of OSH. However, the general

Table I
Kinetic Data in the Polymerization of Four Oxetanes by $BF_3 \cdot THF$ Catalyst at −20° in Methylcyclohexane

	 [a]	 [b]	 [b]	 [b]
k_p, l./(mol sec)	0.31	0.18	0.92	3.4
$\Delta H^{\dagger}$, kcal/mol	7.3	10.7	11.3	12.1
$\Delta S^{\dagger}$, eu	−28.0	−18.6	−14.6	−8.5

[a] This work. [b] Taken from ref 1.

Table II
Position of ν_{O-D} in Benzene

	ν_{O-D}, cm^{-1}	$\Delta\nu_{O-D}$, cm$^{-1\,a}$
CH_3OD	2664	0
CH_3OD + OSH	2562	102[b]
CH_3OD + OX	2561	103[c]
CH_3OD + MeOX	2558	106[c]
CH_3OD + Me_2OX	2565	99[c]

[a] $\Delta\nu_{O-D} = \nu_{O-D}$(benzene) − ν_{O-D}(monomer in benzene). [b] This work. [c] Taken from ref 1.

character of the activation parameters of the propagation of OSH is different from the characters of other oxetane monomers (Table I). The $\Delta H^{\ddagger}$ value of OSH is extremely low (favorable for k_p) in the series of four oxetane monomers and the $\Delta S^{\ddagger}$ value is also low (unfavorable). The reason probably relates to the particular structure of OSH monomer. Thus, the low $\Delta H^{\ddagger}$ value may be ascribed to the increased ring-opening reactivity of the propagating oxonium ion having a higher strain. On the other hand, the explanation as to the more negative value of activation entropy (unfavorable) is not simple. The rigid structure of the SN2 transition state due to the spiro ring may possibly be assumed, which gives rise to a decreased freedom of mobility, and hence the unfavorable entropy factor. The desolvation due to the charge dispersion at the transition state contributes to the favorable entropy gain. A lower contribution of desolvation may be explained either by the decreased solvation of the initial species of spiro oxonium ion **2** or by the decreased extent of desolvation at the transition state. At present a conclusive explanation is not given for the unfavorable entropy of activation.

The $\Delta\nu_{O-D}$ value obtained by the ir method has been taken as a measure of the monomer basicity.[7-9] Although the $\Delta\nu_{O-D}$ values are in a narrow range (Table II), the order of basicities is not the same as that of k_p values. Thus the monomer basicity is not the decisive factor in the polymerizability of these monomers.

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Stereochemical Configuration of Polypropylene by Hydrogen Nuclear Magnetic Resonance

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Received March 28, 1975

ABSTRACT: An investigation of the stereochemical structure of deuteriopolypropylene and polypropylene (PP) has been made using ^{1}H NMR. Our assignments of the tetrad methylene hydrogen bands in this polymer, determined from various deuteriopolypropylenes and epimerized PP, agree with previously published assignments for five of the possible six tetrads. Although we were not able to make a firm *mrm* assignment, our results favor the Flory-Fujiwara assignment of this tetrad. This tetrad absorbs in the *r* methylene region of the spectrum, and the uncertainty in its precise location does not limit the accuracy of stereoregularity determinations. Determinations made on the heptane insoluble fraction of several PP and deuteriopolypropylene samples gave a range of 1 to 5% for the *r* dyad content. We disagree with the interpretation of the ^{1}H NMR spectra of highly isotactic commercial PP published by other investigators. Such spectra are not inconsistent with the structures that we and others have found in highly isotactic deuteriopolypropylene fractions.

Numerous theoretical and experimental investigations of the stereoregularity of polypropylene (PP) have been made using ^{1}H NMR[2-15] and, more recently, ^{13}C NMR.[16-22] These investigations have been directed mainly to determining the degree of stereoregularity of PP and to obtaining more detailed information about the structure of the polymer chain. In ^{1}H NMR investigations the methylene portion of the spectrum has been most thoroughly studied. Numerous bands have been resolved in this region,[10,12,13,15] and much information about stereochemical structure can be deduced therefrom if the bands can be correctly assigned.

A complete ^{1}H NMR assignment of the six possible tetrads was first given by Flory and Fujiwara.[3a] Using conformation considerations, they calculated the expected chemical shifts of the various tetrad bands. Comparison of the calculated spectrum with experimental spectra showed sufficient similarity to allow them to assign the bands in the experimental spectrum. Subsequently, Heatley and Zambelli (HZ) made an assignment based on experimental ap-