The cationic polymerization of tetrahydrofuran initiated by triethylloxonium tetrafluoroborate has been studied kinetically at 0°C up to 2000 kg/cm². The course of the reaction was followed by the thermal method, and the rate constants for the elementary reactions were determined. The volumes of activation for the initiation and propagation reaction were $-5.0 \pm 1.9$ and $-10.5 \pm 2$ cm³/mol in the region from 40 to 1000 kg/cm², respectively. The volume change for the polymerization was $-7.9$ cm³/mol, and the volume of activation for the depolymerization reaction was calculated to be $-2.6 \pm 2$ cm³/mol.

Introduction

The cationic polymerization of tetrahydrofuran (THF) has been well studied thermodynamically and kinetically. The reaction initiated by triethylloxonium tetrafluoroborate (Et₃O⁺BF₄⁻) is characterized as a living polymerization in a dry system at not too high temperature. The initiation reaction is so fast that the polymerization under high pressure cannot be followed by a conventional method. This fact is an essential problem in studies on the ionic polymerization under high pressure. A high pressure technique for the kinetic study of moderately fast reactions in solution was devised previously by the present authors. It was made possible to initiate the reaction after thermal equilibration at desired pressure and temperature and to follow thermally the reaction having half life longer than a few minutes.

This paper deals with the effect of pressure on the elementary reactions of the cationic polymerization of THF initiated by Et₃O⁺BF₄⁻ in dichloromethane.

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4) M. Sangster and D. J. Worsfold, Macromolecules, 5, 129 (1972)
Experimentals

Reagents

Dichloromethane was refluxed over and fractionated from calcium hydride. THF was also purified according to the similar procedure but under nitrogen atmosphere. Both were stored on calcium hydride on a vacuum line.

Epichlorohydrin was dried and distilled by the usual method. Boron trifluoride etherate was distilled under reduced pressure of nitrogen. Triethyloxonium tetrafluoroborate was prepared by the method of Meerwein. The product was washed several times with dry ether under nitrogen atmosphere and stored at low temperature ($< -10^\circ$C). It was purified with dichloromethane and ether immediately before use.

High pressure apparatus

The general layout of the high pressure apparatus is shown in Fig. 1. Temperatures were kept constant within $\pm 1/500^\circ$C. Pressures were determined from the resistance of a manganin wire whose pressure coefficient was determined with the Bourdon gauge calibrated by the free piston gauge in Kobe Steel Ltd.

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Mixing technique and operation

The mixing technique and operation under high pressure were described in the previous paper. The reaction was followed by measuring the differential temperature between the reaction solution and the thermostat, due to the heat of polymerization.

Polymerization procedure

The monomer solution (THF in dichloromethane) was prepared on a vacuum line, and the initiator solution in a dry box under nitrogen atmosphere by dissolving the known weight of the initiator in dichloromethane.

The reaction was initiated by the addition of an aliquot of the initiator according to the method described in the previous paper, and the differential temperature was recorded just after the time of mixing. After the desired time, the polymerization was stopped short by adding the reaction mixture to a methanolic sodium methoxide. The polymer was isolated by liquid extraction. The solution stopped short was poured into a separatory funnel, diluted with dichloromethane and extracted with water to remove all water-soluble components. The final solution was transferred to a preweighed beaker, evaporated and dried in vacuum at room temperature. The conversion was gravimetrically determined.

Measurement of the molar volumes

Compressibilities were measured in a mercury displacement piezometer up to 2000 kg/cm² at 0°C. The compressibility of THF was measured directly. That of the polymer was measured by comparing the compressibility of dichloromethane alone with that of the polymer solution in dichloromethane. The molar volumes were determined by the densities at 1 atm and the compressibilities.

Result and Discussion

Volume change of the polymerization

The volume change of the polymerization (ΔV) was determined from the molar volumes of the polymer and the monomer at 0°C. The results are shown in Fig. 2. As stated in the later section, the ΔV values are necessary in order to determine the equilibrium conversion under high pressure.

Determination of the rate constants from the differential temperature measurement

The cationic polymerization of THF initiated by Et₃O⁺BF₄⁻ in dichloromethane can be characterized as a living system, and proceeds simply as follows;

The chain propagation step is known to occur via not only an ion pair but a free ion. The reactivity of a free ion is thought to be about seven times higher, although its concentration to be much lower. The net effect of free ion on the rate of polymerization is uncertain but small. So in the present treatment the propagation chain is assumed to be in an ion pair.

The temperature of the reaction system changes according to equation (1)\(^8\):

\[
\frac{dT}{dt} = -k_DT + \alpha_p R_p,
\]

where \(k\), \(R_p\) and \(\alpha_p\) are the overall cooling constant, the rate of the polymerization and proportionality constant which is a function of the heat capacity of the system and the heat of the reaction.

The rate of the polymerization can be given by equation (2).

\[
R_p = \frac{d[M]}{dt} = k_p [I]_o [M]_o (y_{\infty} - y)^{1 - \exp(-k[M]_o \int_0^t (1 - y)dt)}.
\]

where \([I]_o\), \([M]_o\), \(y\) and \(y_{\infty}\) are the initial concentration of the initiator, the initial concentration of monomer, the conversion at the reaction time \(t\) and its equilibrium value. The integration of equation (1) gives equation (3).

\[
\int_0^t \left( \frac{dT}{dt} + k_D T \right) dt = \alpha_p ([M]_o - [M]) = \alpha_p [M]_o y.
\]

Combining equation (1) with (2), equation (4) is derived.

\(^8\) M. Okamoto, *This Journal*, 44, 77 (1974)
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\[ \ln \left\{ \alpha_c k_p[I][M_0] - \frac{1}{y_{\text{eq}} - y} \left( \frac{dT}{dt} + k_d T \right) \right\} = \ln \alpha_c k_p[I][M_0] - k_0 \int_0^t (1 - y) dt \]  

The value of \( k \) can be experimentally determined from the cooling process of the compression heat just before initiating the reaction\(^6\). The relaxation of the compression heat is plotted as in Fig. 3. The good linearity was obtained and overall cooling constant \( k \) was determined from the slopes. In Fig. 4 are shown the typical examples of the differential temperature \( (dT) \) in the course of the polymerization reaction. On the base of Figs. 3 and 4, the values of the term, \( (dT/dt) + k_d T \), can be calculated which are plotted as a function of time in Figs. 5, 6 and 7. And since one knows the conversion quenched at a known time and the values of the left hand side of equation (3) at that time, \( \alpha_c \) can be determined. The value of equilibrium conversion \( y_{\text{eq}} \) at 1 atm was cited from literature\(^2,4\) and that at high pressure was calculated using \( (dT) \) in Fig. 2 according to the following equation:

\[ \ln \frac{(1 - y_{\text{eq}})}{(1 - y_{\text{eq}})} = -1/RT \int_0^r \left( \frac{dT}{dT} \right) dP. \]

---

**Fig. 3** The relationship between \(\ln T\) and cooling time

- \(\Delta\) : 40 kg/cm\(^2\)
- \(\bigcirc\) : 1000 kg/cm\(^2\)
- \(\Box\) : 2000 kg/cm\(^2\)

**Fig. 4** Time-course in \(dT\) of the cationic polymerization of THF at various pressures

- \(\bigcirc\) : 40 kg/cm\(^2\), \([M_0]=5.37\text{ mol/kg}, [I]=5.87 \times 10^{-2}\text{ mol/kg}\)
- \(\bigtriangleup\) : 1000 kg/cm\(^2\), \([M_0]=5.23\text{ mol/kg}, [I]=4.84 \times 10^{-2}\text{ mol/kg}\)
- \(\square\) : 2000 kg/cm\(^2\), \([M_0]=5.43\text{ mol/kg}, [I]=4.23 \times 10^{-2}\text{ mol/kg}\)
Fig. 5 Change of \( (d\mathcal{J}/dt) + k\mathcal{J} \) with time at 0° C, 40 kg/cm²
\[
[1] \mathcal{J}_b = 5.87 \times 10^{-2} \text{ mol/kg},
[\mathcal{M}]_b = 5.37 \text{ mol/kg}
\]

Fig. 6 Change of \( (d\mathcal{J}/dt) + k\mathcal{J} \) with time at 0° C, 1000 kg/cm²
\[
[1] \mathcal{J}_b = 3.28 \times 10^{-2} \text{ mol/kg},
[\mathcal{M}]_b = 5.05 \text{ mol/kg}
\]

Fig. 7 Change of \( (d\mathcal{J}/dt) + k\mathcal{J} \) with time at 0° C, 2000 kg/cm²
\[
[1] \mathcal{J}_b = 4.23 \times 10^{-2} \text{ mol/kg},
[\mathcal{M}]_b = 5.43 \text{ mol/kg}
\]

Fig. 8 Plots of equation (4) at various pressures
\( \triangle : 40 \text{ kg/cm}^2, \bigcirc : 1000 \text{ kg/cm}^2, \Box : 2000 \text{ kg/cm}^2 \)
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Table 1: Numerical values of $k_1$ and $k_2$ for the cationic polymerization of THF initiated by $\text{EtO}^+\text{BF}_4^-$ in CH$_2$Cl$_2$ at high pressure (0°C)

<table>
<thead>
<tr>
<th>Pressure, kg/cm$^2$</th>
<th>$k_1$, kg/mol min$^{-2}$</th>
<th>$k_2$, kg/mol min$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 atm</td>
<td>$9.2 \times 10^{-3}$</td>
<td>$0.233 *$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$0.097$ (for ion pair)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$0.69$ (for free ion)</td>
</tr>
<tr>
<td>40</td>
<td>$9.60 \times 10^{-3}$</td>
<td>0.148</td>
</tr>
<tr>
<td>1000</td>
<td>$1.18 \times 10^{-2}$</td>
<td>0.228</td>
</tr>
<tr>
<td>2000</td>
<td>$1.29 \times 10^{-2}$</td>
<td>0.299</td>
</tr>
</tbody>
</table>

$[M]_0 = 5.05 - 5.49$ mol/kg, $[I]_0 = 2.83 \times 10^{-2} - 5.87 \times 10^{-2}$ mol/kg

Once $k_0$ is determined, the left hand side of equation (4) can be plotted against $\int_0^t (1 - y)dt$.

The value of $k_2$ giving a good linearity of the plot, and consistent with the calculated value from the intercept was found by the trial and error. The value of $k_1$ was determined from the slope. The plots thus obtained at 40, 1000 and 2000 kg/cm$^2$ are shown in Fig. 8. The values of the rate constants are given in Table 1. The rate constants at 40 kg/cm$^2$ were close to the values reported by other workers at 1 atm$^{-1}$.

Effect of pressure

The kinetic studies of cationic polymerization at high pressure are, to the authors' knowledge,
only on the systems of styrene initiated by perchloric acid\(^9\) and isomallyl vinyl ether by iodine\(^{10}\), where the activation volume is \(-20\) to \(-25\) \(\text{cm}^3/\text{mol}\) and \(-22\) to \(-25\) \(\text{cm}^3/\text{mol}\), respectively. Those large negative volumes of activation were considered to arise from the strong electrostriction around the highly polar transition state compared with the initial one.

The activation volumes which were calculated based on the pressure dependences of \(k_i\) and \(k_p\) which were shown in Fig. 9, were \(-5.0 \pm 1.9\) and \(-10.5 \pm 2\) \(\text{cm}^3/\text{mol}\) for the initiation and propagation steps, respectively, in the region from 40 to 1000 \(\text{kg/cm}^2\), and \(-2.1 \pm 2\) and \(-6.4 \pm 1.5\) \(\text{cm}^3/\text{mol}\) in the region from 1000 to 2000 \(\text{kg/cm}^2\). Those values are considerably more positive than those of vinyl compounds.

The volume of activation for the initiation reaction seems to be reasonably understood, taking into account that the initiation is a type of ionic exchange reaction, because the values so far reported for the ionic exchange reactions are in the range \(-5\) to \(-13\) \(\text{cm}^3/\text{mol}\)\(^{11}\).

The propagation of polymerization of THF can be regarded to proceed by a \(S_2\) mechanism in which THF acts as a nucleophile attacking the \(\alpha\)-carbon atoms of propagating oxonium ion. Matyjaszewski et al. studied the rate of polymerization of THF as a function of dielectric constant \(D\) in THF/CCl\(_4\) mixtures and obtained the following relationship\(^{12}\):

\[
k_p = 1.78 \times 10^{-5} \exp(4.9/D).
\]

The contribution of electrostriction term \(\Delta V_{\text{est}}\) to the activation volume can be estimated from the equation,

\[
\Delta V_{\text{est}} = (RT/D^2)(\partial \ln k_p/\partial (1/D))_{T_p} (\partial D/\partial P)_{T_p} \Delta P_{\text{comp}}
\]

Using Eckert's value for \(\partial D/\partial P\)\(^{13}\), we found \(\Delta V_{\text{est}} = +1.5\) \(\text{cm}^3/\text{mol}\) which is unimportant for this reaction as usually pointed out for \(S_2\) reactions\(^{11}\). Therefore, the volume loss \(-10.5 \pm 2\) \(\text{cm}^3/\text{mol}\) may arise mainly from the structural term.

The volume change for the polymerization (Fig. 2) was \(-7.9\) \(\text{cm}^3/\text{mol}\) at 0\(^\circ\) C and 1 atm, and so the activation volume for the depolymerization reaction was calculated to be \(-2.6 \pm 2\) \(\text{cm}^3/\text{mol}\). The depolymerization reaction occurs by a nucleophilic attack by the penultimate oxygen atom followed by the expulsion of monomer. Therefore, we should expect a greater decrease in volume than this. It seems likely that the formation of empty space in the middle of the ring in the transition state partly compensates the decrease of volume that occurs when the transition state is formed, as discussed in the acid-catalyzed lactonization of \(\gamma\)-hydroxybutyric acid\(^{10}\).

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