Kinetic Study of 1-β-Cyanoethyl Aziridine for Ring-Opening Polymerization Initiated with Alkyl Sulfate

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ABSTRACT

The kinetics of the cationic polymerization of 1-β-cyanoethyl aziridine initiated 3-hydroxy-1-propane sulfonic acid sultone and methyl tosylate have been studied. The course of polymerization involved the propagation stage and termination reaction due to the reaction between the growing chain and imino groups in the polymer chain. The propagation constants and termination constants were obtained. The enthalpies of activation for the propagation and termination reactions are $\Delta H_p^* = 12.9$ kcal/mol and $\Delta H_t^* = 12.4$ kcal/mol, and the entropies of activation are $\Delta S_p^* = -31$ cal/deg·mol and $\Delta S_t^* = -39$ cal/deg·mol. Otherwise, the polymerization initiated with methyl tosylate involved an early stage which was initiated very quickly.

INTRODUCTION

Many studies have been reported by different authors on the ring-opening polymerization of aziridines [1-4]. We described the polymerization of 1-substituted aziridines initiated with such cationic

initiators as 3-hydroxy-1-propane sulfonic acid sultone, methyl tosylate, and methy iodide. The effect of 1-substituted groups of aziridines were very interesting in this polymerization.

For example, in the polymerization of the lower basic monomer 1-β-cyanoethyl aziridine (pK$_a$ 5.45 [5]), a high molecular weight polymer was produced, while a more basic monomer, 1-phenethyl aziridine (pK$_a$ 7.36 [5]), could not produce a high molecular weight polymer. 3-Hydroxy-1-propane sulfonic acid sultone and methyl tosylate were very efficient initiators in this polymerization.

In this study the kinetics of the polymerization of 1-β-cyanoethyl aziridine initiated with 3-hydroxy-1-propane sulfonic acid sultone and methyl tosylate are reported.

EXPERIMENTAL

Materials

1-β-Cyanoethyl aziridine (CA) was synthesized from ethylene imine and acrylonitrile as described by Yoshida et al. [6], and purified by repeated distillation in a nitrogen atmosphere, bp 59-60°C (5 mmHg). 3-Hydroxy-1-propane sulfonic acid sultone (PS) and methyl tosylate (MT), as initiators, were commercial reagents which were distilled under dry conditions. Acetonitrile and tetrahydrofurane were commercial reagents which were dried over P_2O_5 or metallic sodium and then purified by distillation. Tri-methyl amine was a commercial reagent and was 30% in water. It was used without further purification.

Procedure

Polymerization was carried out in a sealed vessel. The monomer and tert-butyl benzene as an internal standard in acetonitrile were placed in a vessel and then left in a thermostat bath for 10 min. Then an initiator was added to this solution with a microsyringe. The rate of polymerization was measured by gas chromatography using an internal standard (Silicon gum SE-30, 2m × 4mmϕ, H_2 gas 60 mL/min at 90°C). The amounts of monomer were measured at appropriate intervals of time. The polymerization of CA was carried out in the same manner and then was stopped by the addition of trimethyl amine. The polymerization mixture was poured into the excess trimethyl amine solution and was shaken vigorously. Then the precipitated polymer was filtrated and washed with methanol and dried in vacuo to a constant weight.
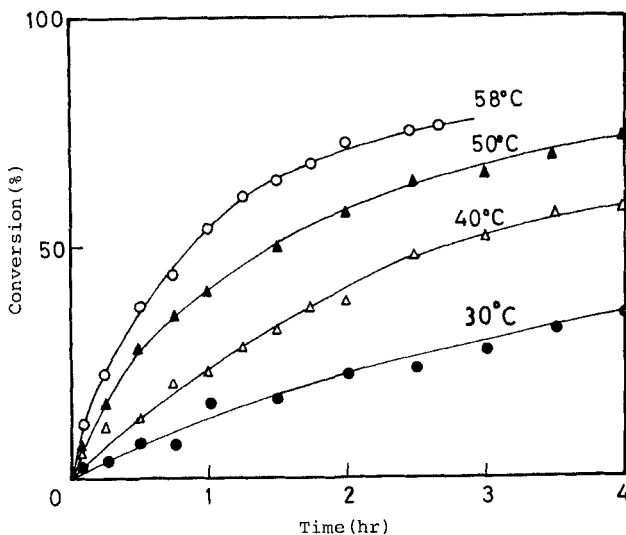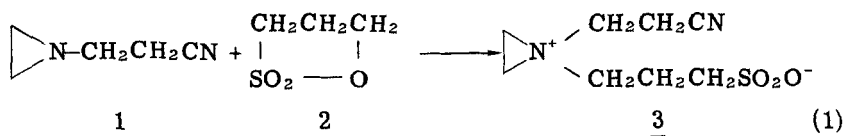
FIG. 1. Polymerization of 1-β-cyanoethyl aziridine by 3-hydroxy-1-propane sulfonic acid sultone at different temperatures. Monomer: 1 mol/L in acetonitrile. Initiator: 0.05 mol/L in acetonitrile.

RESULTS AND DISCUSSION

The polymerization of CA was carried out at several temperatures using PS or MT in acetonitrile, and the time-conversion curves of CA are plotted in Figs. 1 and 2. In polymerization with MT, very fast initiation was observed and was probably due to the heat produced by the reaction of CA and MT. Polymerization with different amounts of PS at 60°C was carried out, and the time-conversion curves are plotted in Fig. 3. Figure 4 shows that the plot of the initial rate R_0 of polymerization with PS against the amounts of PS which gives a linear relationship.

The reaction of PS and cyclic imines such as 1-substituted azetidine to form the sulfobetain (zwitterion) is known [7]. The polymerization of CA (1) with PS (2) was assumed to be initiated by zwitterion (3) which was formed by the additional reaction of CA and PS, after which cationic polymerization occurred

$$\triangleright N-CH_2CH_2CN + \begin{matrix} CH_2CH_2CH_2 \\ | \quad\quad | \\ SO_2 \underline{\quad\quad} O \end{matrix} \longrightarrow \triangleright N^+ \begin{matrix} \nearrow CH_2CH_2CN \\ \searrow CH_2CH_2CH_2SO_2O^- \end{matrix}$$

$$\underline{1} \quad\quad\quad\quad \underline{2} \quad\quad\quad\quad\quad\quad \underline{3} \quad\quad\quad (1)$$
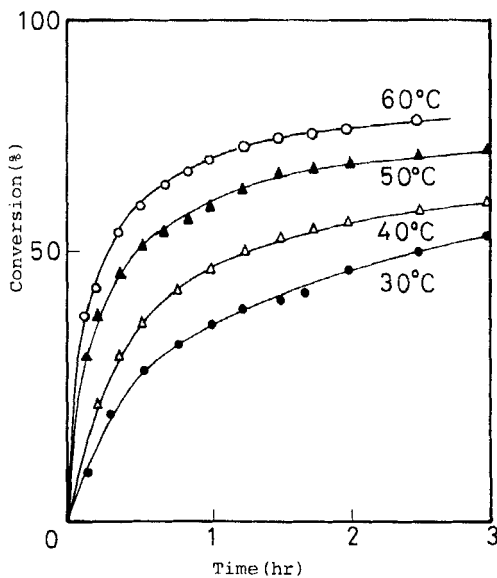
FIG. 2. Polymerization of CA by methyl tosylate at different temperatures. Monomer: 1 mol/L in acetonitrile. Initiator: 0.05 mol/L in acetonitrile.
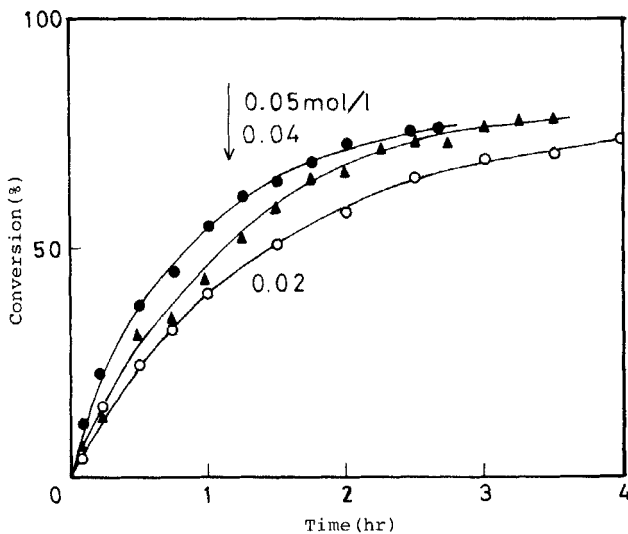

FIG. 3. Polymerization of CA by various concentrations of initiator at 58°C. Monomer: 1 mol/L in acetonitrile. Initiator: PS, mol/L.
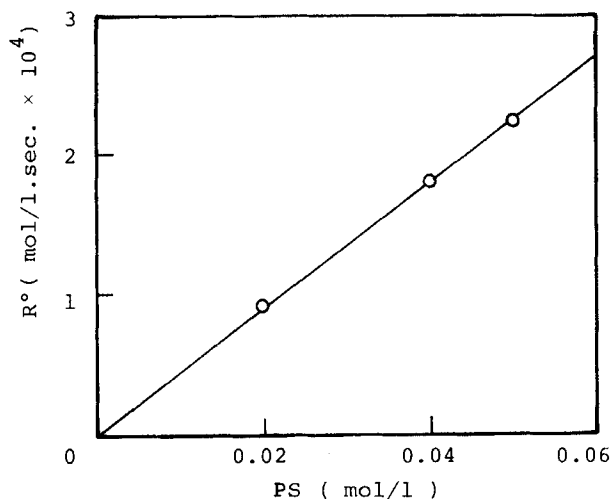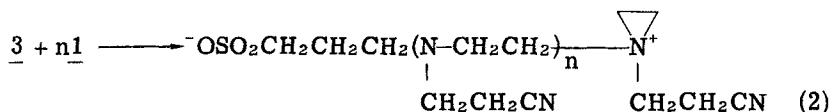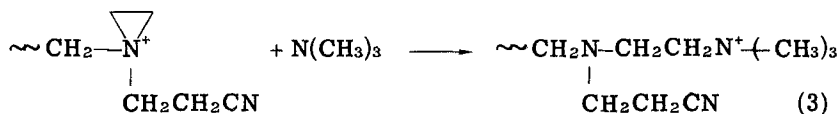
FIG. 4. Relationship between the initial rate of polymerization and initiator concentration at 58°C. Monomer: 1 mol/L. Initiator: PS, mol/L in acetonitrile.

$$\underline{3} + n\underline{1} \longrightarrow {}^-OSO_2CH_2CH_2CH_2(N-CH_2CH_2)_n \overset{\triangle}{N^+} \qquad (2)$$
$$\underset{CH_2CH_2CN}{|} \qquad \underset{CH_2CH_2CN}{|}$$

However, a termination reaction was assumed from the time-conversion curve. To obtain some clarification of the termination, the polymerization of CA with PS was stopped by adding trimethyl amine at different times. The results are shown in Table 1. The NMR spectrum of the polymer which formed with PS and was stopped by trimethyl amine shows a NMR peak due to the trimethyl immonium group, $-N^+-CH_3$, 3.4 ppm, at the end of the polymer chain which was derived by the termination reaction (Fig. 5):

$$\sim CH_2-\overset{\triangle}{N^+} \qquad + N(CH_3)_3 \longrightarrow \sim CH_2N-CH_2CH_2N^+(CH_3)_3$$
$$\underset{CH_2CH_2CN}{|} \qquad \qquad \underset{CH_2CH_2CN}{|} \qquad (3)$$

The molecular weight of the polymer obtained was increased linearly with the reaction time.

From the above, the termination in this polymerization was assumed to be as follows:

TABLE 1. Polymerization of 1-β-Cyanoethy Aziridine with PS and Termination with Trimethyl Amine [Monomer, 1 g; PS, 2 mol% of monomer; Solvent THF, 2 mL; N(CH₃)₃, 2 mL)

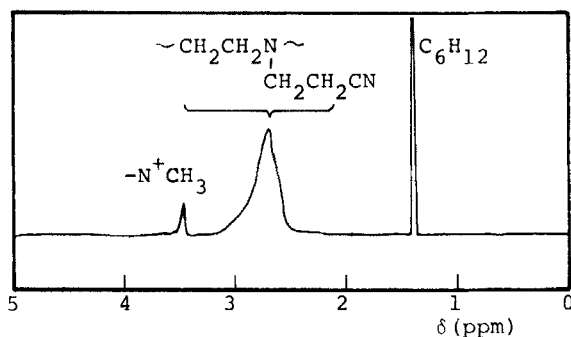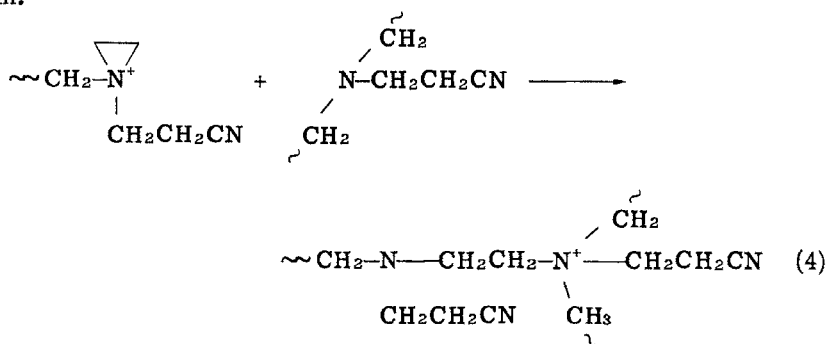| Time of polymerization (min)	Yield (%)	mp (°C)	η_{sp}/C [a]
10	14.6	96–104	0.031
20	21.3	102–104	0.035
40	28.5	96–102	0.076
120	51.9	95–101	0.137

[a]$C = 0.5$ g/100 mL DMF at 30°C.

FIG. 5. NMR spectrum of poly(1-β-cyanoethyl aziridine) which was stopped with trimethyl amine (CDCl₃). Polymerization time: 40 min.

Consequently, the rate of initiation is given as

$$-d[I]/dt = k_i[I][M] \tag{5}$$

In Eq. (5), $[I]$ is the concentration of the initiator, $[M]$ is the concentration of the monomer, and k_i is the rate constant of the initiation. The rates of propagation R_p and termination are given by Eqs. (6) and (7), respectively:

$$R_p = -d[M]/dt = k_p[P^*][M] \tag{6}$$

$$-d[P^*]/dt = k_t[P^*]([M]_0 - [M]) \tag{7}$$

Here, $[P^*]$ is the concentration of the growing chain and $[M]_0$ is the concentration of the initial monomer.
Integration of Eq. (7) gives

$$-\ln[P^*] = k_t \int_0^t ([M]_0 - [M]) \, dt + C \tag{8}$$

For $t = 0$, $[M] = [M]_0$, and then $-\ln[P^*] = C$.

Thereupon, if the zwitterion 3 as a propagation species $[P^*]$ is formed rapidly in good yield in Eq. (1), $[P^*]$ at $t = 0$ is equal to the concentration of initiator $[I]_0$. Thus $C = -\ln[I]_0$. Equation (8) can be written as

$$-\ln[P^*] = k_t \int_0^t ([M]_0 - [M]) \, dt \tag{9}$$

$$[P^*] = [I]_0 \, e^{k_t \int_0^t ([M]_0 - [M]) \, dt} \tag{10}$$

Combining Eq. (10) and Eq. (6) gives

$$\ln \frac{R_p}{[M][I]_0} = \ln k_p - k_t \int_0^t ([M_0] - [M]) \, dt \tag{11}$$

Here, $\int_0^t ([M]_0 - [M]) \, dt$ is equal to the area under a time-conversion curve up to time t, and R_p is obtained from the tangent at various points of the time-conversion curves. An equation similar to Eq. (11)
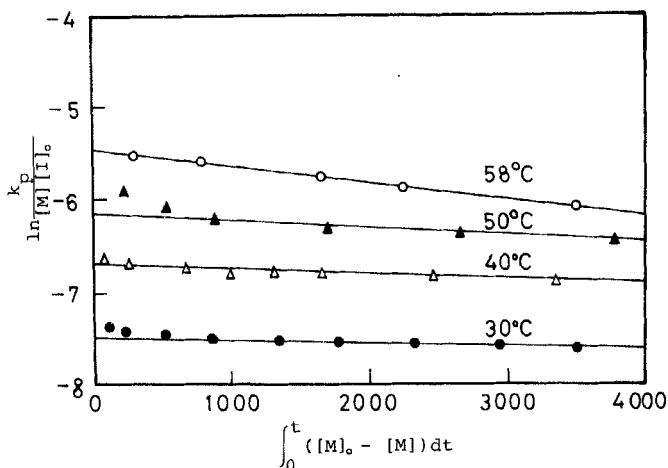
FIG. 6. Application of the experimental data (Fig. 1) to Eq. (11). The effects of temperature. Monomer: CA, 1 mol/L in acetonitrile. Initiator: PS, 0.05 mol/L.
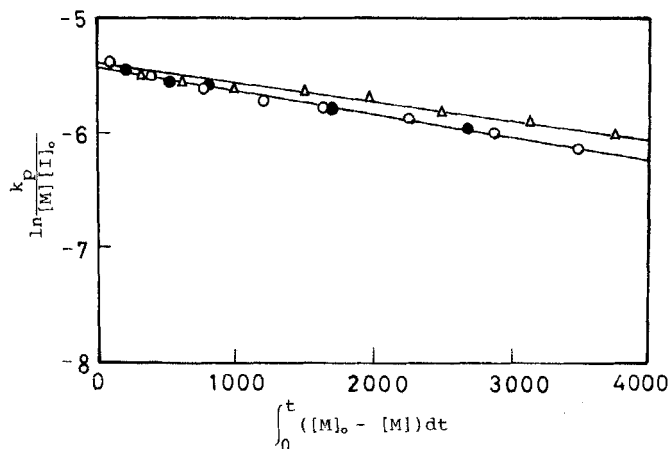
FIG. 7. Application of the experimental data (Fig. 3) to Eq. (11). The effect of initiator concentration. Monomer: CA, 1 mol/L in acetonitrile. Initiator: PS in acetonitrile at 58°C.

TABLE 2. Value of k_p and k_t for the Polymerization of 1-β-Cyano-ethyl Aziridine ($[I]_0$ = PS, $[M]_0$ = 1.00 mol/L)

Temperature (°C)	$[I]_0$ (mol/L)	k_p (L/mol·s)	k_t (L/mol·s)	k_p/k_t
30	0.05	0.599×10^{-3}	0.028×10^{-3}	21
40	0.05	1.347	0.057	23
50	0.05	2.029	0.101	20
58	0.05	4.516	0.195	21
58	0.04	4.516	0.195	21
58	0.03	4.600	0.140	32
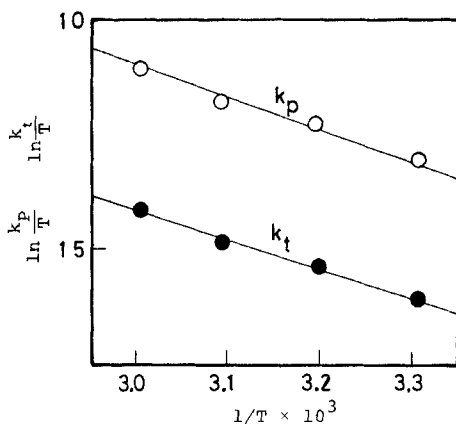
FIG. 8. Determination of ΔH_p^*, ΔH_t^*, ΔS_p^*, and ΔS_t^0 according to Eq. (12).

has been used by others for the ring-opening polymerization of 3,3-bis-(chloromethyl)oxetane [8] and 3,3-dimethyl thietane [9].

Figures 6 and 7 show the data in Figs. 1 and 3, and give a linear relationship of ln $R_p/([M][I]_0)$ against $\int_0^t ([M]_0 - [M])$ dt, as expected from Eq. (11). The polymerization of CA with PS could be expressed by Eq. (11). However, in polymerization with MT, the linear relationship in Eq. (11) could not exactly be obtained due to the explosive reaction in the early stage of polymerization.

In the polymerization of CA with PS, values of k_p and k_t at different temperatures are obtained by plotting as shown in Fig. 5 and Table 2, and some values of k_p and k_t at polymerization with different concentrations of initiator, PS, are obtained as well (Table 2). However, the value of k_t initiated with a lower concentration on initiator PS was decreased more than usual.

According to Eq. (12) shown by Eyring, the enthalpy of activation ΔS^* and the entropy of activation ΔS^* for the propagation and termination reactions were determined by plotting ln (k_p/T) or ln (k_t/T) against 1/T (Fig. 8).

$$\ln \frac{k}{T} = \ln \frac{k}{h} + \frac{\Delta S^*}{R} - \frac{\Delta H^*}{R} \frac{1}{T} \qquad (12)$$

where $k = k_p$ or k_t, k = Boltzmann constant, and h = Planck constant.

The enthalpy and entropy were obtained and are shown as follows:

Propagation:

$$\Delta H_p^* = 12.9 \text{ kcal/mol}, \qquad \Delta S_p^* = -30.9 \text{ cal·deg}^{-1}\text{mol}^{-1}$$

Termination:

$$\Delta H_t^* = 12.4 \text{ kcal/mol}, \qquad \Delta S_t^* = -40.0 \text{ cal·deg}^{-1}\text{mol}^{-1}$$

The enthalpy of activation of propagation and termination were similar to each other, and coincided with the values of k_p/k_t (Table 2) which were almost constant at various temperatures.

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