Kinetic Studies of the Ring-Opening Polymerization of 1-β-Cyanoethylazetidine

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ABSTRACT

The ring-opening polymerization rate of 1-β-cyanoethylazetidine (CA) with 3-hydroxy-1-propanesulfonic acid sultone (HPSS) as an initiator has been investigated in acetonitrile. The polymerization of CA with HPSS proceeded by way of a zwitterion formed by the addition reaction of CA and HPSS. The course of polymerization involved, as an early stage, slow initiation due to the low reactivity of the zwitterion. The propagation constants were obtained as were the enthalpy of activation for propagation ($\Delta H_p^* = 12$ kcal/mol) and the entropy of activation for propagation ($\Delta S_p^* = -31$ cal/K·mol).

INTRODUCTION

In a previous paper the ring-opening polymerization of 1-β-cyano-ethylazetidine (CA) [1] and 1-benzylazetidine [2], a four-membered cyclic imine, was studied in bulk and in solution (in acetonitrile) with cationic initiators such as 3-hydroxy-1-propanesulfonic acid sultone (HPSS), methyl tosylate, methyl iodide, and trifluoroacetic acid. The polymerization of CA with HPSS provided a high yield of a white powdery polymer. In this report the kinetics of CA polymerization initi-

ated with HPSS in acetonitrile, were studied, and the activation param-
eters obtained were compared with the parameters of the other cyclic
monomers

$N-CH_2CH_2CH_2CN$

$$CH_2CH_2CH_2$$
$$SO_2\!-\!\!O$$
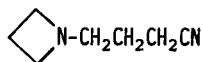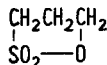
1-β-Cyanoethylazetidine   3-Hydroxy-1-propanesulfonic acid
            (CA)   sultone (HPSS)

EXPERIMENTAL

Materials

1-β-Cyanoethylazetidine (CA) was prepared as described by Chen,
Kato, and Ota [3] as reported in a previous paper [1]. 3-Hydroxy-1-
propanesulfonic acid sultone (HPSS) and acetonitrile were commercial
reagents which were distilled in a dry nitrogen atmosphere before use.

Polymerization of CA

The polymerization rate was measured by gas chromatography
using naphthalene as the internal standard. Acetonitrile, monomer,
and naphthalene were introduced into a 30-mL reaction vessel which
was placed in a thermostatted bath and was stirred by a magnetic
stirrer. Initiator was added to this solution with a microsyringe. The
amount of CA in the polymerization mixture was measured at appropri-
ate intervals, and the rate constant was evaluated from the plot of
Eq. (1).
    Viscosity measurement during polymerization was done with an
Ostwald viscometer which was sealed off with a rubber tube and placed
in a thermostatted bath at 50°C. After the addition of the initiator, the
viscosity of the mixture was measured as a function of time.

RESULTS AND DISCUSSION

The polymerization of CA initiated with HPSS was carried out in
acetonitrile at various temperatures. The time-conversion curves
and the first-order plots of monomer consumption are shown in Figs.
1 and 2. In CA polymerization an S-shaped curve was obtained for
the time-conversion curve, and 100% polymer yield was obtained after
24 h. The first-order plot of polymerization gave a straight line until
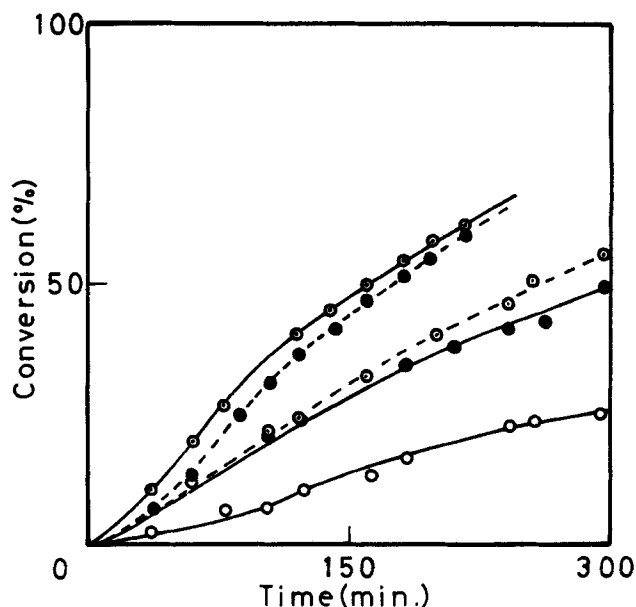60% conversion was obtained, as expected for the early stage. The

FIG. 1. Time-conversion curves for the polymerization of CA in acetonitrile. Monomer CA: 0.05 mol/L. Initiator: HPSS. Conditions as follows: (─⊙─) 0.025 mol/L at 60°C, (--⊙--) 0.015 mol/L at 60°C, (─●─) 0.025 mol/L at 50°C, (--●--) 0.050 mol/L at 50°C, (○) 0.025 mol/L at 40°C.

polymerization of CA with HPSS involves a slow early stage which is probably due both to slow initiation and to a propagation step that is first-order with respect to the monomer concentration.

Figure 3 shows the time dependence of the reduced viscosity of CA polymerization with HPSS. The reduced viscosity of the polymerization mixture increased with the addition of HPSS, and it further increased until the monomer was completely consumed.

Therefore, if there is no termination in this polymerization and if the concentration of the growing chain is equal to the concentration of HPSS, the rate of polymerization is given by

$$k_p t = \frac{1}{[P^*]} \ln \frac{[M]_0}{[M]} \tag{1}$$

where $[M]$ is the monomer concentration, $[M]_0$ is the initial monomer concentration, $[P^*]$ is the concentration of the growing chain (i.e.,
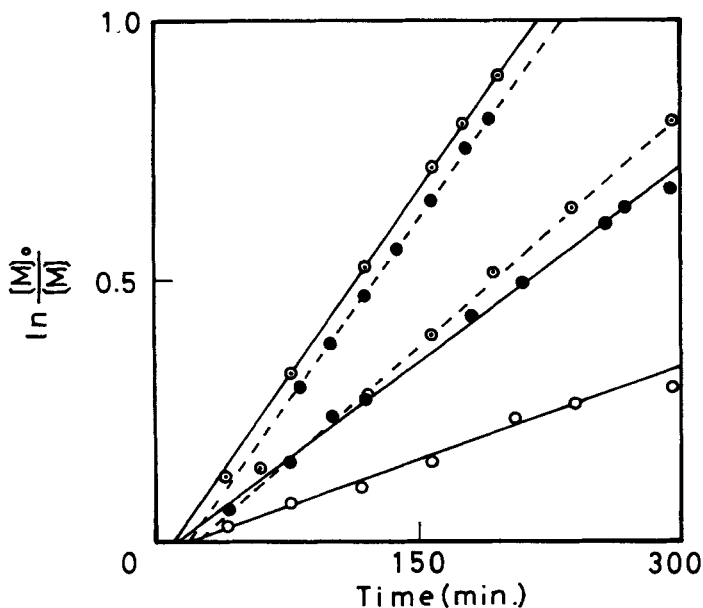
FIG. 2. Plots of ln ($[M]_0/[M]$) against the polymerization of CA in acetonitrile. Monomer CA: 0.05 mol/L. Initiator: HPSS. Conditions as follows: (—⊙—) 0.025 mol/L at 60°C, (--⊙--) 0.015 mol/L at 60°C, (—●—) 0.025 mol/L at 50°C, (--⊶--) 0.050 mol/L at 50°C, (○) 0.025 mol/L at 40°C.
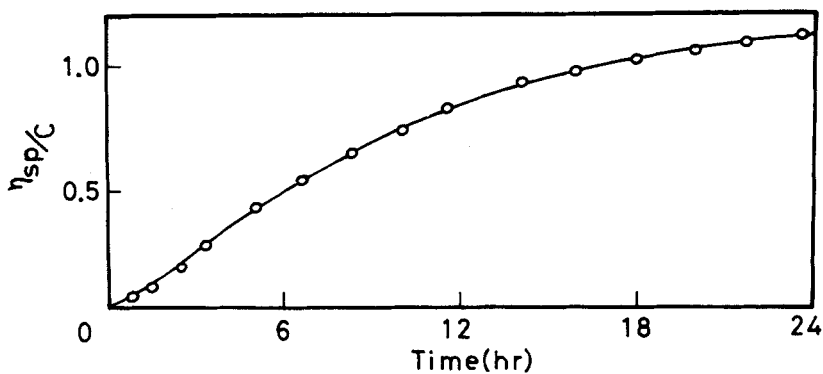

FIG. 3. Viscosity measurement during the polymerization of CA in acetonitrile at 50°C. Monomer A: 0.05 mol/L. Initiator: HPSS, 0.025 mol/L.

TABLE 1. Values of k_p Obtained According to Eq. (1)

| Condition of polymerization[a]		$k_p \times 10^{-3}$, L/(mol·s)
Temperature, °C	Initiator, mol/L	
40	0.025	0.77
50	0.025	1.63
50	0.050	1.65
60	0.015	3.25·
60	0.025	3.34

[a]1-β-Cyanoethylazetidine 0.05 mol/L.

the concentration of initiator HPSS), and k_p is the rate constant of the propagation reaction.

The k_p values obtained from the plot of Eq. (1) are summarized in Table 1. The k_p values at the same temperature were in good agreement with each other. The rate of polymerization of CA was adequately expressed by Eq. (1), as shown by Fig. 2.

The above results suggest that the ring-opening polymerization of CA initiated with HPSS goes by way of a cationic living polymerization without termination.

Consequently, the initiation reaction and the propagation reaction for this polymerization may be represented as shown in Scheme 1.
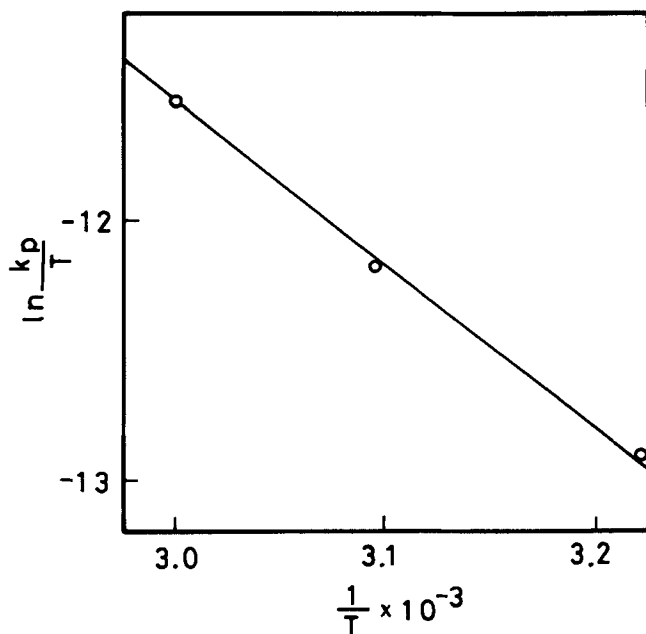
Initiation

Propagation
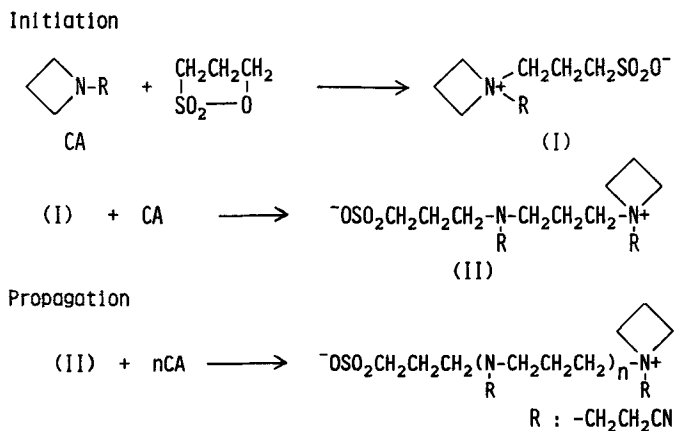
SCHEME 1.

FIG. 4. The determination of the enthalpy and entropy of activation for the polymerization of CA.

In this reaction, Compound (I), 1-methyl-1-β-cyanoethylazetidinium tosylate, a betaine, was isolated as a stable crystal (mp 110°C [4]). However, it was not used as the initiator because when isolated it does not dissolve easily in the monomer.
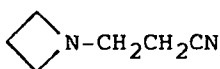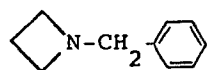
According to Eq. (2) (Eyring [5]), the enthalpy of activation, H_p^*, and the entropy of activation, S_p^*, for propagation were determined by plotting ln k_p/T against 1/t (Fig. 4),

$$\ln (k_p/T) = \frac{k}{h} + \frac{\Delta S_p^*}{R} + \frac{\Delta H_p^*}{R}\frac{1}{T}$$

(2)

where k is Boltzman's constant, h is Planck's constant, R is the gas constant, and T is the absolute temperature.

The ΔH_p^*, ΔS_p^*, and k_p values obtained are summarized in Table 2 together with the activation patameters and k_p values for the ring-opening polymerization of 1-benzylaziridine [2] and 1,3,3-trimethyl-azetidine [6]. From the kinetic parameters shown in Table 2, it

TABLE 2. The Values of k_p and the Activation Parameters for the Ring-Opening Polymerization of Cyclic Imines

	$k_p \times 10^{-3}$ L/(mol·s)	ΔH_p^*, kcal/mol	ΔS_p^*, cal/(K·mol)
N–CH$_2$CH$_2$CN	1.63[a]	12	−31
N–CH$_2$–	17.8[b]	17.8	−35
CH$_3$, CH$_3$ N–CH$_3$	0.68[c]	19	−31

[a]With HPSS in acetonitrile at 50°C.
[b]With methyl tosylate in acetonitrile at 54°C.
[c]With triethyloxonium tetrafluoroborate in nitrobenzene at 60°C.

is concluded that the reactivity of CA for the ring-opening reaction is higher than that for the ring-opening reaction of 1,3,3-trimethylazetidine and 1-benzylazetidine. The low reactivity of the latter two compounds was attributed to the effect of two gem-substituted groups or of its bulky group on the four-membered cyclic conformation.

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