Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Ring-Opening Polymerization of 1-Benzylazetidine

Shizunobu Hashimoto[a]; Takayuki Yamashita[a]
[a] Department of Applied Chemistry, Doshisha University, Kyoto, Japan

To cite this Article Hashimoto, Shizunobu and Yamashita, Takayuki(1986) 'Ring-Opening Polymerization of 1-Benzylazetidine', Journal of Macromolecular Science, Part A, 23: 3, 295 — 304

To link to this Article: DOI: 10.1080/00222338608063393

URL: http://dx.doi.org/10.1080/00222338608063393

J. MACROMOL. SCI.–CHEM., A23(3), pp. 295-304 (1986)

Ring-Opening Polymerization of 1-Benzylazetidine

SHIZUNOBU HASHIMOTO* and TAKAYUKI YAMASHITA

Department of Applied Chemistry
Doshisha University
Karasuma-imadegawa, Kamikyo-ku, Kyoto 602, Japan

ABSTRACT

The ring-opening polymerization of 1-benzylazetidine (BA) was investigated in bulk and in acetonitrile. The bulk polymerization of BA proceeded with cationic initiators, such as methyl tosylate and 3-hydroxy-1-propanesulfonic acid sultone (PS), at 60°C, and a white, powdery polymer was obtained. The polymer structure was confirmed by elemental analysis and NMR spectroscopy. The polymerization of BA with PS was assumed to proceed via a zwitterion formed by the addition reaction of BA and PS. The polymerization rate was studied in acetonitrile as a solvent. The enthalpy of activation ΔH* and the entropy of activation ΔS* for the propagation were determined.

Much work has been reported by different authors on the ring-opening polymerization of aziridines [1-3]. The ring-opening polymerization of 1-substituted aziridines with methyl tosylate (MT) and 3-hydroxy-1-propanesulfonic acid sultone (PS) has also been studied

---

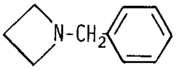
*To whom correspondence should be addressed.

0022-233X/86/2303-0295$3.50/0

[4-6]. The effects of 1-substituted groups are very interesting in this polymerization. For example, in the polymerization of a monomer of weak basicity, e.g., 1-β-cyanoethylaziridine (pK_a 5.45 [7]), a high molecular weight polymer was produced, while a high molecular weight polymer could not be obtained from more basic monomers, e.g., 1-phenethylaziridine (pK_a 7.36 [7]).

On the other hand, very little is known about the ring-opening polymerization of four-membered cyclic immines, except those of azetidine [8], conidine [9], and 1,3,3-trimethylazetidine [10]. The ring-opening polymerization of 1-β-cyanoethylazetidine with alkyl sulfate has been reported [11].

In the present study the ring-opening polymerization of 1-benzylazetidine (BA) as a four-membered cyclic imine was studied.



(BA)

EXPERIMENTAL

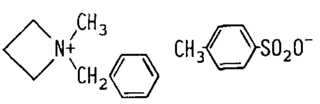
Materials

Acetonitrile (solvent) was a commercial reagent which was dried over P_2O_5 and then purified by distillation. 3-Hydroxy-1-propanesulfonic acid sultone (PS), methyl iodide (MI), and methyl tosylate (MT) (initiators) were commercial reagents which were distilled in a dry nitrogen atmosphere before use. 1-Benzylazetidine (BA) was prepared as described in the literature [12] and purified by repeated distillation in a nitrogen atmosphere, bp 83°C/9 torr (literature, 87°C/10 torr [12]). 1-Methyl-1-benzylazetidinium tosylate (BA-MT) was prepared from BA and MT as follows [13]: A solution of BA (8 mmol) in 3 mL ether was added dropwise at 5°C to a stirred mixture of MT (10 mmol) and 3 mL of ether. The mixture was stirred at 20°C for 3 h. The precipitate of BA-MT was isolated by filtration and washed with a small portion of ether. BA-MT was dried in vacuo (yield 97%, mp 114-115°C, N 4.3% (calculated 4.2), NMR $-N^+-CH_3$ 3.1 ppm, $-N^+-CH_2-$ 4.3 ppm (in D_2O)). 3-(N-Benzylazetidino)propylsulfonate (BA-PS) was prepared by BA and PS in the same manner as described above (yield 98%, mp 210-213°C, N 5.2% (calculated 5.2), NMR, $-N^+-CH_3$ 3.1 ppm, $-N^+-CH_2-$ 4.3 ppm (in D_2O)). The structures of the compounds obtained were confirmed by elemental analysis and NMR spectra.

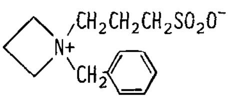
Polymerization

Bulk polymerization was carried out in sealed tubes. BA was placed in a glass tube. Then an initiator was added with a microsyringe, and the mixture was shaken vigorously. The reaction mixture was thermostated at 60°C for 24 h. After that, the reaction mixture was poured into excess ether, and the precipitated polymer was filtered and then washed with ether and dried in vacuo.

Polymerization in acetonitrile was carried out in the same manner as described above after the addition of acetonitrile (2 mL). The rate of BA polymerization was measured by gas chromatography using an internal standard, nitrobenzene (column, Silicon OV-17 2 m × 4 mm, H_2 gas 80 mL/min at 110°C). The amount of monomer was measured at appropriate time intervals.



(BA-MT)



(BA-PS)

RESULT AND DISCUSSION

The bulk polymerization of BA was carried out at 60°C. The results are shown in Table 1. BA could be polymerized under the influence of such cationic initiators as MT, PS, and methyl iodide (MI). In the bulk polymerization of BA with PS, quantitative conversion was attained in about 24 h. The polymer yield of solution polymerization of BA in acetonitrile decreased compared to that of bulk polymerization, due to precipitation of polymer which was formed at the end of the polymerization acetonitrile.

The polymer obtained was a white, powdery substance. It was soluble in chloroform, DMF, and DMSO, and insoluble in water, methanol, and acetonitrile. The structure of the polymer obtained was confirmed by NMR spectra and elemental analysis. The NMR spectrum of the polymer and the assignments of the NMR signals are given in Fig. 1. Elemental analysis of this polymer showed the same composition as the BA monomer.

Analysis: Calculated for $(C_{10}H_{13}N)_n$: C, 81.6; H, 8.9; N, 9.5%. Found: C, 82.0; H, 9.0; N, 9.1%.

These results confirm the structure of this polymer as that shown in Fig. 1.

TABLE 1. Ring-Opening Polymerization of 1-Benzylazetidine[a]

	Polymer		
Initiator,[b] mol%	Yield, %	mp, °C	η_{sp}/C[c]
MT (2)	83.7	48.0-51.5	0.15
MT (5)	81.0	48.5-52.0	0.15
PS (2)	94.9	46.0-48.0	0.11
PS (5)	97.9	36.0-45.0	0.09
PS (5)[d]	79.8	Viscous polymer	0.08

[a] Monomer 5 mmol, 24 h at 60°C.

[b] MT = methyl tosylate, PS = 3-hydroxy-1-propanesulfonic acid sultone.

[c] C = 0.5 g/100 mL dimethylformamide at 30°C.

[d] Solution polymerization in CH_3CN (2 mL).

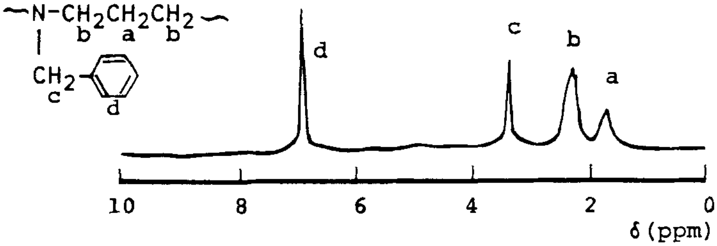


FIG. 1. NMR spectrum of poly(1-benzylazetidine) (60 MHz in $CDCl_3$).

The time-conversion curves and the first-order plots of the monomer consumption for BA polymerization follow Eq. (1) up to a conversion of 60%, except for the early stage (Figs. 2 and 3). In this polymerization, if there is no termination and if the concentration of the growing chain is equal to the concentration of the initiators, the rate of polymerization is given by

$$k_p t = \frac{1}{[P^*]} \ln \frac{[M]_0}{[M]}, \qquad (1)$$

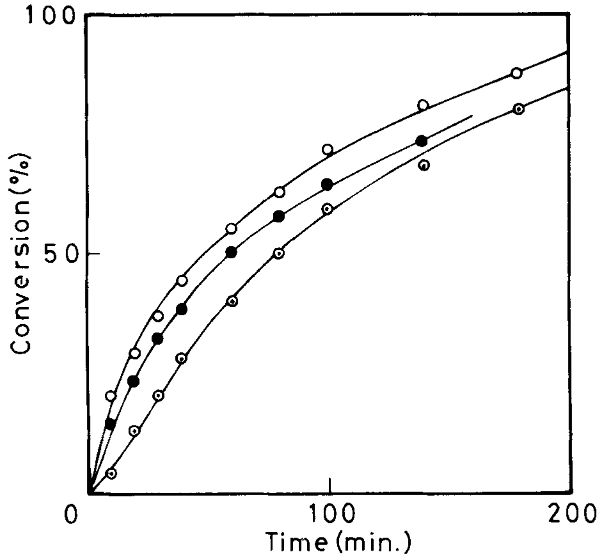


FIG. 2. The polymerization of BA with various initiators in acetonitrile at 60°C. Monomer (BA): 0.5 mol/L. Initiator: 0.025 mol/L. (○) Methyl tosylate, (●) Methyl iodide, (⊙) 3-Hydroxy-1-propanesulfonic acid sultone.

where [M] is the monomer concentration, $[M]_0$ is the initial monomer concentration, [P*] is the concentration of the growing chains (taken to be equal to the concentration of the initiator), and k_p is the rate constant of the propagation reaction.

For polymerization of BA with MT or MI, first-order plots by Eq. (1) show a fairly linear fit, except in the early stage, owing to a very fast initiation which was probably due to the heat produced by the reaction of BA and the initiator. On the other hand, in the polymerization of BA with PS, an S-shaped curve was obtained for the time-conversion curve. The first-order plot by Eq. (1) shows a fair linear fit, except for the slow initiation as shown in Fig. 3.

To explain the fast initiation for the MT initiator and the slow initiation for the PS initiator, the polymerizations of BA with 1-methyl-1-benzylazetidinium tosylate (BA-MT) and with 3-(N-benzylazetidino)-propyl sulfonate (BA-PS) were examined. The results are plotted in Fig. 4 in terms of Eq. (1). The polymerization of BA could be expressed completely by Eq. (1). The early stage for the MT initiator may be negligible.

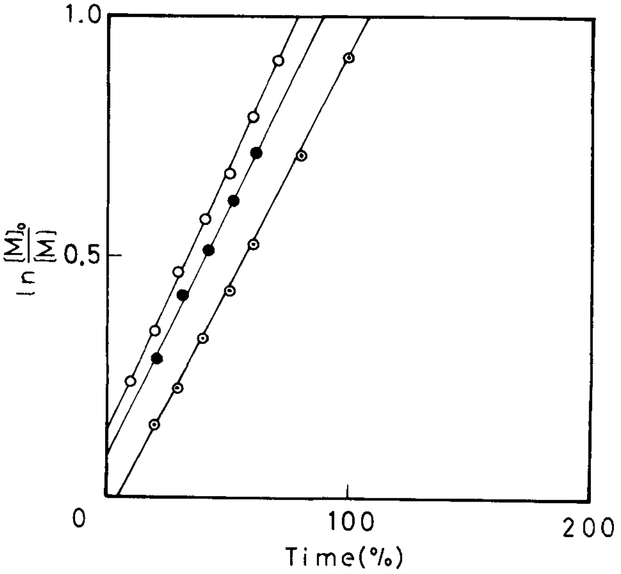
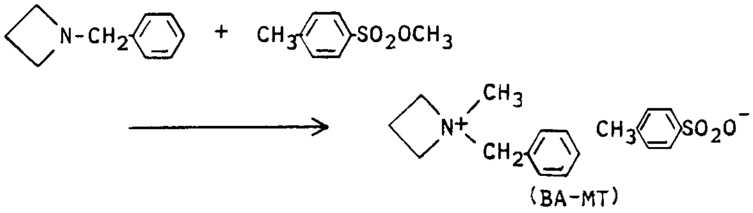


FIG. 3. Plot of the experimental data (Fig. 2) according to Eq. (1). (○) Methyl tosylate, $k_p = 7.29 \times 10^{-3}$ L/(mol·s); (●) methyl iodide, $k_p = 7.10 \times 10^{-3}$ L/(mol·s); (⊙) 3-hydroxy-1-propanesulfonic acid sultone, $k_p = 6.76 \times 10^{-3}$ L/(mol·s).

These results are compatible with a polymerization scheme involving initiation with a cyclic immonium cation formed from BA and MT (Eq. 2). Then the propagation continues by the consecutive reaction between BA and the cyclic immonium cation of the polymer end-group as shown in Eqs. (3) and (4).



(2)

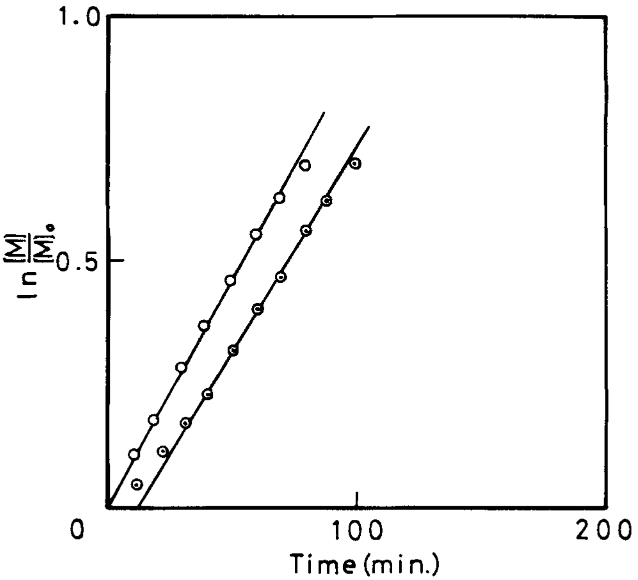
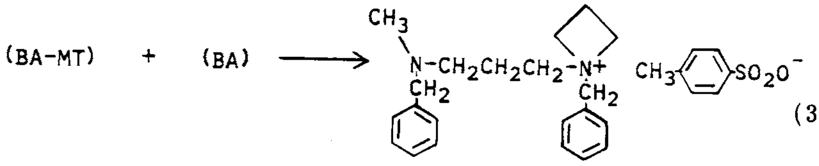
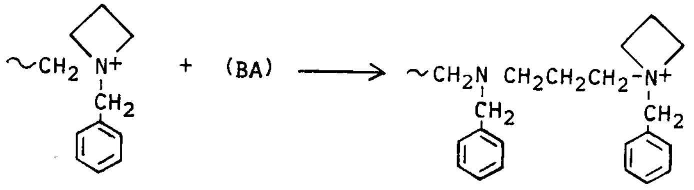


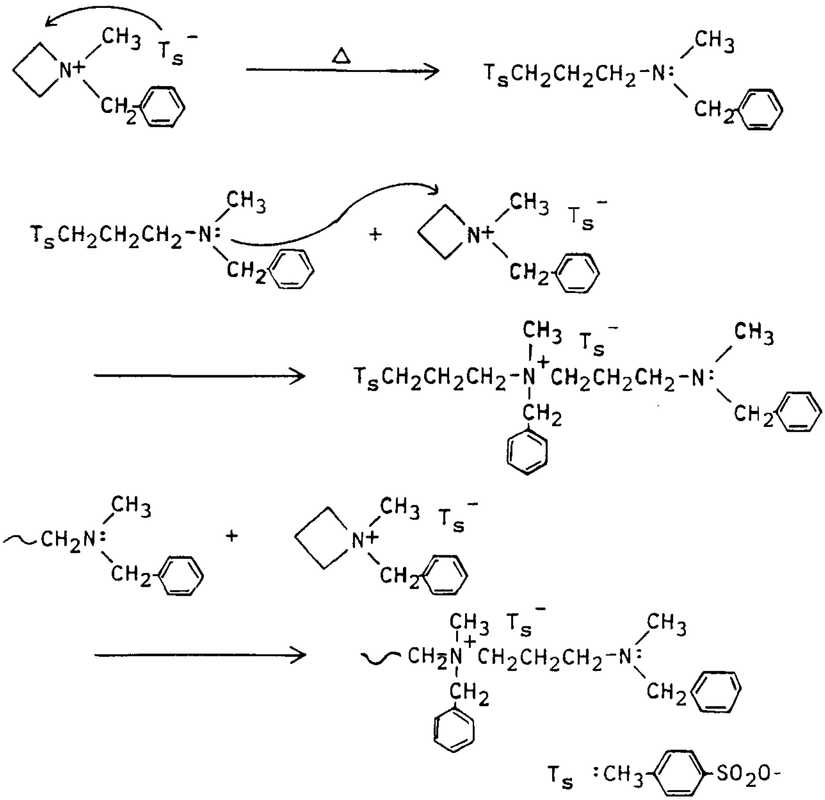
FIG. 4. The polymerization of BA with 1-methyl-1-benzylazetidinium tosylate and 3-(N-benzylazetidino)propyl sulfonate in acetonitrile at 60°C and the application of Eq. (1) to the data. Monomer: 0.5 mol/L. Initiator: 0.025 mol/L. (○) 1-Methyl-1-benzylazetidinium tosylate, $k_p = 6.3 \times 10^{-3}$ L/(mol·s); (⊙) 3-(N-benzylazetidino)-propyl sulfonate, $k_p = 6.2 \times 10^{-3}$ L/(mol·s).



(3)



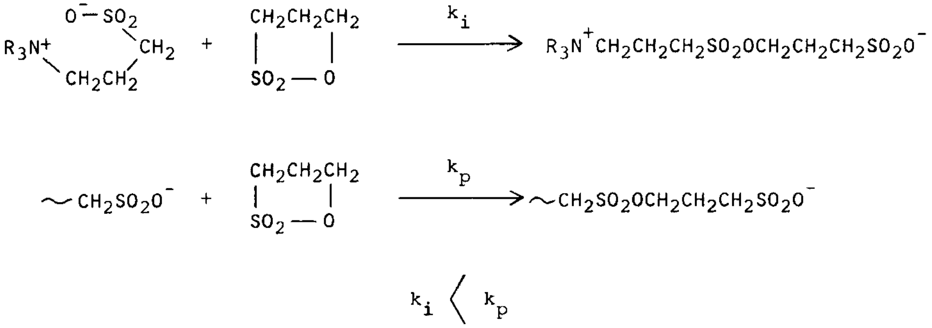
(4)



SCHEME 1.

However, the rate constant k_p for polymerization with BA-MT is smaller than that with MT. This deactivation was assumed to be due to a decrease in the concentration of initiator BA-MT which is polymerized spontaneously by heating because it would be unstable, as shown in Scheme 1 [13].

On the other hand, in the polymerization of BA with BA-PS, slow initiation appeared along with polymerization with PS initiator. This slow initiation can be explained in the following manner: The low reactivity of the quaternary ammonium cation of the zwitterion can be expected from the effect of the neighboring anion site, and the coulombic energy of the charge separation would be higher than that in the propagation step. It has been reported that the early step of polymerization was affected by the low reactivity of the zwitterion formed from the monomer and the initiator for the ring-opening polymerization of PS with quinoline (Scheme 2) [14].



SCHEME 2.

TABLE 2. Propagation Rate Constant for the Ring-Opening Polymerization of 1-Benzylazetidine with Methyl Tosylate at Different Temperatures[a]

Temperature, °C:	65	60	54	42
k_p, 10^{-3} L/(mol·s)	8.42	7.29	4.23	1.50

[a] Monomer, 0.5 mol/L in CH_3CN; initiator, 0.025 mol/L.

The polymerization mechanism for BA with MT can be expressed by Eqs. (2), (3), and (4). The first-order plot by Eq. (1) shows a fairly linear fit except for the early stage. Values of k_p at different temperatures obtained by Eq. (1) are shown in Table 2. According to Eq. (5), given by Eyring [15], the enthalpy of activation ΔH* and the entropy of activation ΔS* for the propagation were determined as follows:

$$\ln (k_p/T) = \frac{k}{h} + \frac{\Delta S^*}{R} + \frac{\Delta H^*}{R}\,\frac{1}{T}, \qquad (5)$$

where k is Boltzmann's constant, and h is Planck's constant. Application of Eq. (5) leads to $\Delta H^* = 17.8$ kcal·mol^{-1} and $\Delta S^* = -35$ cal·deg^{-1}·mol^{-1}.

REFERENCES

[1] W. G. Berg, J. Chem. Soc. p., 2564 (1955).

[2] T. Kagiya and Y. Sumida, Bull. Chem. Soc. Jpn., 41, 767 (1968).

[3] G. D. Jones, J. Org. Chem., 9, 125, 484 (1944).

[4] S. Hashimoto, T. Yamashita, and M. Ono, Kobunshi Ronbunshu, 33, 83 (1976).

[5] S. Hashimoto and T. Yamashita, J. Macromol. Sci.–Chem., A17(4), 559 (1982).

[6] S. Hashimoto and T. Yamashita, Ibid., A21(6&7), 875 (1984).

[7] C. R. Dick, J. Org. Chem., 32, 72 (1957).

[8] E. H. Shacht and E. J. Goethals, Makromol. Chem., 175, 3447 (1974).

[9] E. F. Rasvodovskii et al., J Macromol. Sci.–Chem., A8, 241 (1973).

[10] E. H. Shacht and E. J. Goethals, Makromol. Chem., 167, 155 (1973).

[11] S. Hashimoto, T. Yamashita, and J. Hino, Polym. J., 9, 19 (1977).

[12] W. R. Vaughan, J. Org. Chem., 26, 138 (1961).

[13] S. Hashimoto and T. Yamashita, Polymeric Amines and Ammonium Salts (E. J. Goethals, ed.), Pergamon, Oxford, 1980), p. 79.

[14] S. Hashimoto and T. Yamashita, Polym. J., 8, 15 (1976).

[15] W. F. K. Wynne-Jones, and H. Eyring, J. Chem. Phys., 3, 492 (1935).

Received December 15, 1984
Revision received February 11, 1985