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Absolute Rate Constants of Radiation-Induced Polymerization of Isobutyl Vinyl Ether

Katsuji Ueno[a]; Koichiro Hayashi[a]; Seizo Okamura[a]
[a] Department of Polymer Chemistry, Faculty of Engineering, Kyoto University, Kyoto, Japan

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LETTER TO THE EDITOR

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In the previous report [1], the authors have been indicating the importance of polymerization techniques for the kinetical analysis of radiation-induced free cationic polymerization. In parallel, spectroscopic observation [2] and the electrical conductivity method [3] were adopted for this purpose. In this report, the pulse-irradiation method, which is based on the same principle as the rotating sector method [4] widely applied for radical polymerization, is applied for the radiation-induced free ionic polymerization of isobutyl vinyl ether (IBVE) by the suggestion of Ka. Hayashi [3], because of half-order dependence of the polymerization rate on the irradiation intensity.

IBVE was dried over Na–K alloy and baked BaO [1]. This extremely dried monomer was distilled in a specially made dilatometer, as shown in Fig. 1. Irradiation was done by X-rays ejected from a Van de Graaff accelerator (1.5 MeV). The control of dose rate was carried out by the change of electric current. Table 1 shows the pulsed beam characteristics of a modified Van de Graaff accelerator.

It has been indicated that the radiation-induced polymerization of IBVE proceeds by a radical mechanism in a "wet" system and by a cationic one in a "dry" system [5]. In this paper, much more effort was made for the drying of IBVE, and better reproducibility was obtained on polymerization. The conversion increased quite linearly as a function of polymerization time up to 10% yield. Figure 2 shows a typical conversion-time curve under the variation of the dose rate. The rate of polymerization (R_p) was proportional to the dose rate (I) approximately in half order, but in the higher dose rate, some saturation phenomena was observed. Figure 3 shows the relative rate of polymerization as a function of pulse repetition time. The ratio (β) between irradiation time and pulse repetition time was 0.42–0.43. The decrease of rate of polymerization was $11.5 \pm 1.0\%$ at the conditions of dose rate (5.3×10^4 rad/hr) and pulse repetition time (0.25 sec). This decrease was confirmed by repeated experiments.

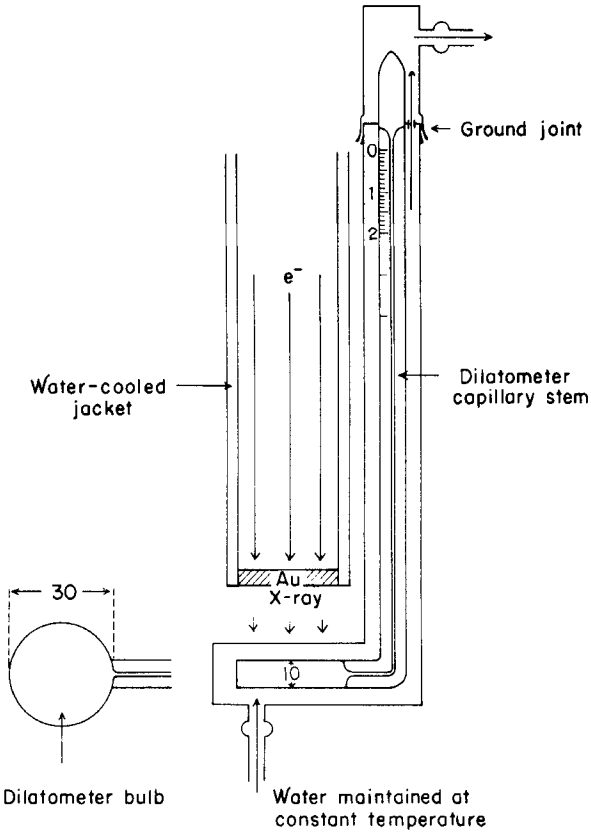

FIG. 1. Dilatometer for X-ray irradiation.

In the extremely dried system, the polymerization mechanism is expressed as follows:

Initiation: $M \longrightarrow M^{\pm} + e$ (1)

$M + e \longrightarrow M^{\cdot}$ (or Y^{-}) (2)

$M^{\pm} + M \longrightarrow \cdot MM^{+}$ (3)

Propagation: $M_n^+ + M \xrightarrow{K_p} M_{n+1}^+$ (4)

Transfer: $M_n^+ + M \xrightarrow{K_{tm}} M_n + M^+$ (5)

Termination: $M_n^+ + Y^- \xrightarrow{K_t} M_nY$ (6)

TABLE 1. Pulsed-Beam Characteristics of a Modified Van de Graaff Accelerator

Accelerating voltage	1.5 MeV
Beam current	1–150 A
Pulse shape	Rectangular wave
Pulse internal	1.0×10^{-3} sec
	1.0×10^{-2} sec
	3.1×10^{-2} sec
	1.2×10^{-1} sec
	2.5×10^{-1} sec
Pulse width	Variable from 1/2 to 1/3 of pulse interval
Pulse rise time	1 sec
Pulse decay time	2 sec

$R_i[R_i = (G_i/100)I]$ denotes the rates of initiation ($G_i = G_{value}$ of initiation) and Y^- indicates any anion existing in the system. From stationary-state treatment, the following equations are obtained:

$$R_i = K_t[M_n^+][Y^-] \tag{7}$$

$$R_p = K_p[M_n^+][M] \tag{8}$$

$$R_p = K_p/K_t^{1/2} \cdot R_i^{1/2} \cdot [M] \tag{9}$$

Also, the following relation exists between the lifetime of growing cation (τ) and the concentration of growing cation (M_n^+):

$$\tau = [M_n^+]/R_i \tag{10}$$

Assuming $G_i = 0.1$ [1, 3], R_i equals 1.3×10^{-9} mole/liter/sec at

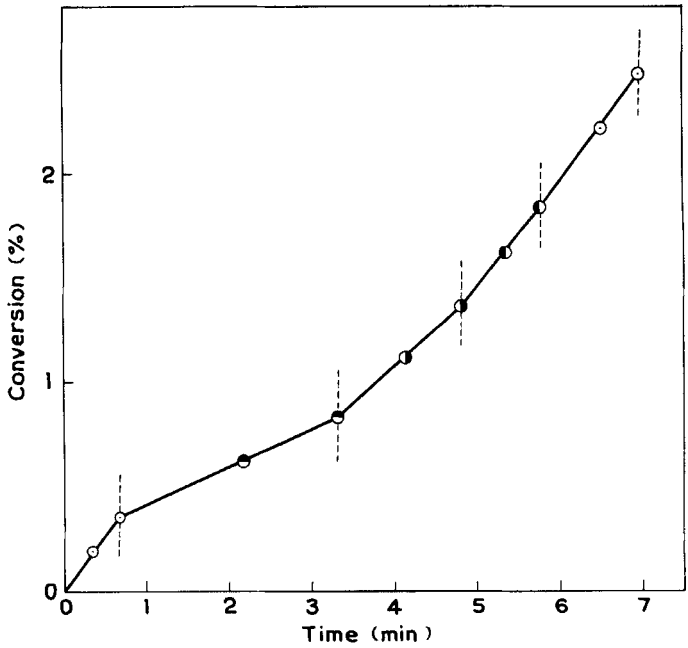

FIG. 2. Time-conversion curve, temp., 42.5 ± 0.07°C. Dose rate: ⊙ 5.3×10^4 rad/hr; ◐, 2.85×10^4 rad/hr; ◑, 1.65×10^4 rad/hr; ◓, 5.2×10^3 rad/hr.

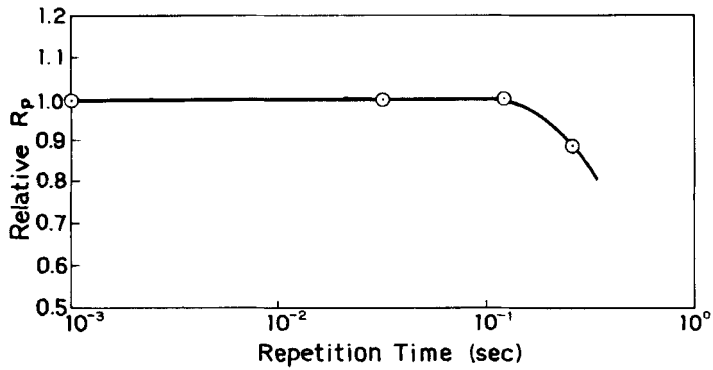

FIG. 3. Relative rates of polymerization vs. repetition time. Temp. 42.5 ± 0.07°C. $\beta = 0.42$–0.43.

5.3×10^4 rad/hr ($= 8.55 \times 10^{14}$ eV/g/sec). τ by this method was 0.2 sec, assuming a theoretical curve [4], so k_p is calculated by

$$k_p = R_p \cdot {k_t}^{1/2}/{R_i}^{1/2}/{R_i}^{1/2}[M] \tag{11}$$

At the conditions of 5.3×10^4 rad/hr and 42.5°C, k_p was estimated to be 1.1×10^6 liter/mole/sec. This value is similar to the value obtained from the conductivity method [3] ($k_p = 3.4 \times 10^5$ liter/mole/sec at 1.32×10^{15} eV/g/sec and 30°C).

Although the measuring lifetime by the pulse-irradiation method under irradiation of X-rays contains some experimentally difficult problems, we believe it should be a powerful method to analyze the polymerization mechanism by free ions. The study is still under way, with some experimental improvements.

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Katsuji Ueno*
Koichiro Hayashi
Seizo Okamura

Department of Polymer Chemistry
Faculty of Engineering
Kyoto University
Kyoto, Japan

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*Present address: Central Research Laboratory, Sumitomo Chemical Co. Ltd., Osaka, Japan.