Dose-rate Dependency of the Radiation-induced Polymerization of Ethylene in an Aqueous Solution of *tert*-Butyl Alcohol

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Recently, Suganuma *et al.*[1,2] have reported the kinetics of the radiation-induced polymerization of ethylene in the presence of *t*-butyl alcohol. Judging from the dose-rate dependency of STY (polymerization rate, mole ethylene/*l*/hr), they concluded that the monomolecular termination process played an important role.

We wish to report an attempt to elucidate the effect of the dose rate on the polymerization of ethylene in the presence of *t*-butyl alcohol and water.

The rate of the polymerization of ethylene was determined by measuring the yield in a 100-cc (internal volume) autoclave in which the pressure was held constant at 400 kg/cm^2 during the polymerization. The differential STY increased with an increase in time at an initial stage of the polymerization, while in the succeeding stage it became constant and was independent of the time. In this region, the reaction seems to be stationary on the concentration of active species. As is shown in Fig. 1, the differential STY in the latter stage was proportional to the square root of the dose rate. This suggests that the active species are mutually terminated.

As has been described above, the bi-molecular termination is assumed for this polymerization. The correlation between the active species concentration, [R·], and the reaction time, *t*, is given as:

$$[\mathrm{R}\cdot] = \frac{\sqrt{K_iI}\{\exp(2\sqrt{K_iIk_t}t)-1\}}{\sqrt{k_t}\{\exp(2\sqrt{K_iIk_t}t)+1\}} \tag{1}$$

From the long-chain approximation, the overall polymerization rate, R, is given as:

$$R = R_p = K_p[\mathrm{R}\cdot] \tag{2}$$

By introducing Eq. (1) into Eq. (2) and integrating it, the polymer yield, M_p, is given as:

$$M_p = \frac{K_p}{k_t}[\ln\{1+\exp(2\sqrt{K_iIk_t}t)\}-\ln 2-\sqrt{K_iIk_t}t] \tag{3}$$

This equation indicates that the differential STY in the latter stage is proportional to the square root of the dose rate, as is shown in Fig. 1. The relationship between M_p and $2\,(K_i I k_t)^{0.5}t$ should be shown as a normalized curve, regardless of the dose rate and the reaction time.

If it is assumed that M_p is proportional to I^α, the dose-rate exponent, α, can be calculated by the use of Eq. (3). As is shown in Fig. 2, α varies with the dose rate and with the reaction time in the range from 0.5 to 1.0. This shows that the type of termination reaction can not be decided simply from the value of α, for this relation is calculated by assuming bi-molecular termination.

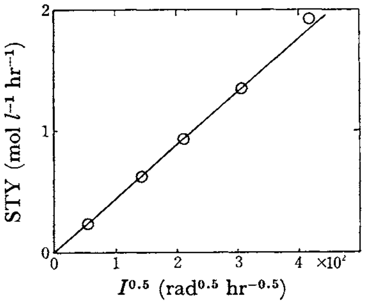

Fig. 1. Dose rate dependency of differential STY in the stationary state.

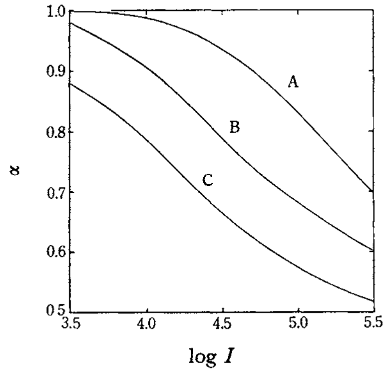

Fig. 2. Dose rate dependency of α.
A: 0.5 hr B: 1.0 hr C: 2.0 hr

The dose-rate exponent, α, shown in Fig. 2, is in good agreement with the experimental results. This fact can not be explained by the monomolecular termination mechanism alone, indicating that the bi-molecular termination process plays an important role.

Precise investigations of reaction mechanism are now under way and will be reported elsewhere.

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[1] F. Suganuma, S. Machi, H. Mitsui, M. Hagiwara and T. Kagiya, *J. Polym. Sci., Part A-1*, **6**, 2069 (1968).

[2] F. Suganuma, H. Mitsui, S. Machi, M. Hagiwara and T. Kagiya, *ibid.*, **6**, 3127 (1968).