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Radiation-induced Reaction of Isobutene in the Gas Phase. Effects of Pressure, Temperature and Additives on Polymerization

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In previous papers,[1,2] we have shown that cationic mechanism dominates in the radiation-induced polymerization of isobutene in the gas phase. The propagating rate constant and the mean lifetime of the propagating ion have also been estimated by a quantitative study of the effect of ammonia on the polymerization.[2]

We have investigated the effects of pressure, temperature and some additives to get a deeper understanding of its reaction mechanism.

Experimental

The purification of isobutene was described previously.[1] Research grade oxygen (99.9%) and nitrogen dioxide (99.0%) were dried prior to use. Sulfur hexafluoride was purified by distillation under vaccum. Methyl bromide was purified by passing through a silica gel column and by distillation under vacuum. γ-Irradiation of samples and the analysis of products were described previously[1]. The temperature of samples was controlled using a thermostat.

Results and Discussion

Effect of Pressure. Figure 1 shows the effect of pressure on the polymerization rate of isobutene. We see that the polymerization rate is proportional to the square of pressure below ~800 Torr, and tends to become proportional to the pressure above ~800 Torr.

These results may be qualitatively explained in terms of the competition between fragmentation and deactivation of the excited isobutene ion, provided that a significant fraction of fragment ions do not initiate polymerization. A conventional kinetic treatment leads to the following expression for the polymerization rate:

$$R = \frac{k_\mathrm{p}}{k_\mathrm{t}}\left[\Phi + \Phi' \frac{k_1(\mathrm{M})}{k_2 + k_1(\mathrm{M})}\right](\mathrm{M})I_\mathrm{abs}, \qquad (1)$$

where Φ and Φ' are the quantities proportional to the initial yields of the ground and excited isobutene ions, k_1 and k_2 are the rate constants for deactivation and fragmentation of the excited ion, k_p and k_t are the rate constants for the propagation and termination reactions, I_abs is the dose rate absorbed by isobutene, and (M) is the concentration of isobutene.

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[1] H. Okamoto, K. Fueki and Z. Kuri, *J. Phys. Chem.*, **71**, 3222 (1967)

[2] Y Noro, K. Fueki and Z. Kuri, This Bulletin, **41**, 1737 (1968).

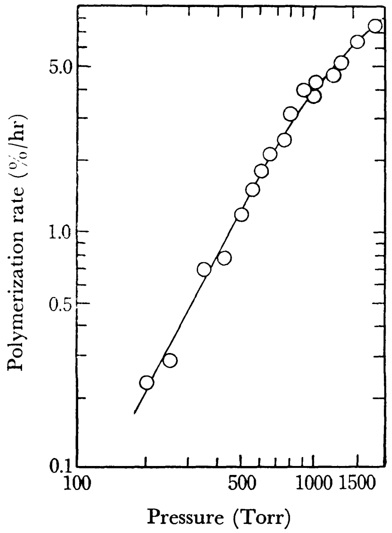

Fig. 1. Dependence of the polymerization rate on the initial pressure of isobutene.
Dose rate, 0.15 Mrad/hr; dose, 0.1—3 Mard; temperature, 20°C

If we assume that $\Phi \ll \Phi' k_1(\mathrm{M})/(k_2+k_1(\mathrm{M}))$,[*1] Eq. (1) is reduced to

$$R \simeq \frac{k_p}{k_t}\Phi' \frac{k_1(\mathrm{M})^2}{k_2+k_1(\mathrm{M})} I_{\mathrm{abs}}. \tag{2}$$

Equation (2) implies that R is proportional to $(\mathrm{M})^2$ at low pressures when $k_2 \gg k_1(\mathrm{M})$ and it is proportional to (M) at high pressures when $k_2 \ll k_1(\mathrm{M})$.

The molecular weight of the polymer produced, when irradiated to 0.3 Mrad at an initial pressure of isobutene of 1000 Torr, was determined to be 11000, and 5700 when irradiated to 1.2 Mrad at 500 Torr.

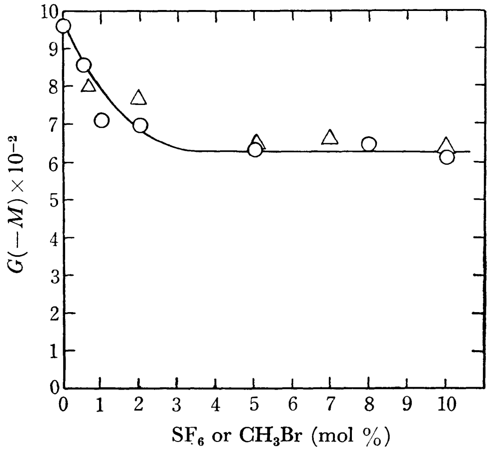

Fig. 2. Effect of sulfur hexafluoride and methyl bromide on the polymerization yield.
SF_6, ○; CH_3Br, △. Initial pressure of isobutene, 500 Torr; dose rate, 0.15 Mrad/hr; dose, 1—2 Mard; temperature, 20°C.

Effect of Temperature. The polymerization rate of isobutene irradiated to 0.3 Mrad at 0°C and at 500 Torr was 1.8 times greater than that at 20°C and at the same pressure and dose. The polymerization did not occur to an appreciable extent when irradiated to 0.3 Mrad at 50°C. At higher temperatures than 50°C, the polymerization was not observed at a dose of 1 Mrad, although a small amount of nonviscous liquid products were obtained when irradiated to 100 Mrad at 100°C. These results indicate the existence of a ceiling temperature between 50°C and 100°C.

Effect of Additives. *a) Sulfur Hexafluoride and Methyl Bromide.* Figure 2 shows the effect of SF_6 or CH_3Br on the *G*-value for isobutene consumption at an initial pressure of isobutene of 500 Torr at 20°C. The *G*-value decreases with increasing concentration of SF_6 or CH_3Br, approaching a plateau value which is about 65% of the *G*-value obtained for pure isobutene, at ~3 mol% of these additives.

Both SF_6 and CH_3Br are known as electron scavengers, *viz.*, they capture electrons to form negative ions:

$$SF_6 + e^- \longrightarrow SF_6^-,$$

$$CH_3Br + e^- \longrightarrow CH_3 + Br^-.$$

The retarding effect of these additives on the polymerization may be interpreted in terms of the acceleration of charge neutralization forming the negative ions. In the absence of these scavengers, the propagating ions would disappear by diffusion to the wall of the reaction vessel[2)] and possibly by reacting with a trace of impurities.

If the polymerization terminates by the neutralization between the propagating cation and the negative ion in the presence of SF_6 or CH_3Br, it can be expected that the termination will be of the

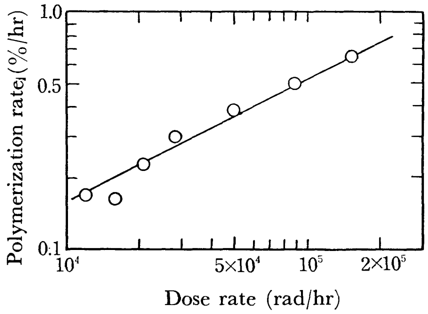

Fig. 3. Dependence of the polymerization rate on the dose rate.
Initial pressure of isobutene, 500 Torr; pressure of SF_6, 50 Torr; dose, 0.1—1 Mrad; temperature, 20°C.

[*1] Abundance of the parent ion of isobutene is relatively small in its mass spectrum (E. Collinson, F. S. Dainton and H. A. Gillis, *J. Phys. Chem.*, **63**, 909 (1959)).

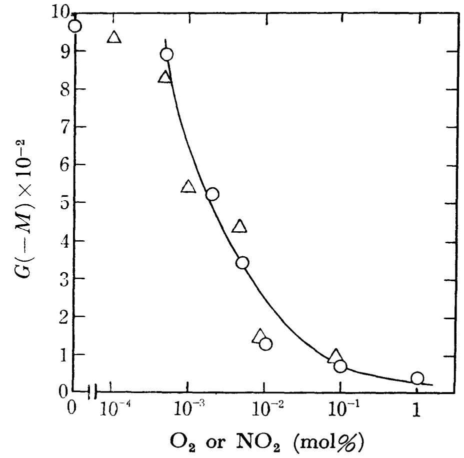

Fig. 4. Effect of oxygen and nitrogen dioxide on the polymerization yield.
O_2, ○; NO_2, △. Initial pressure of isobutene, 500 Torr; dose rate, 0.15 Mard/hr; dose, 1—5 Mrad; temperature, 20°C.

second-order with respect to the concentration of the ions. As shown in Fig. 3, it is found that the polymerization rate is proportional to the square root of dose rate, indicating a second-order termination reaction. This is in contrast with a first-order dependence of the polymerization rate on the dose rate for the case of pure isobutene in the gas phase.[1]

b) Oxygen and Nitrogen Dioxide. Figure 4 shows the effect of O_2 or NO_2 on the *G*-value for isobutene consumption at an initial pressure of isobutene of 500 Torr at 20°C. Polymerization is retarded remarkably by the presence of O_2 or NO_2, and almost completely at a concentration of ~1 mol% of these additives. Such an effect of O_2 or NO_2 on the polymerization is quite different from that of SF_6 or CH_3Br, and it cannot be explained simply by electron capture by O_2 or NO_2. A similar result was obtained for N_2O.[1] This might explain the retarding effect of oxygen-containing compounds such as O_2, NO_2 and N_2O on the polymerization of isobutene in the gas phase where these compounds*[2] capture electrons to form O^- (at least, as a fraction of negative ions), which will subsequently react with isobutene to produce water,[3] a cation scavenger.

Conclusion

(1) The pressure effect on the polymerization of isobutene in the gas phase has been investigated over a wider range of pressure than in the previous studies. It has been interpreted in terms of the competition between fragmentation and deactivation of the excited isobutene ion.

(2) It has been found that there exists a ceiling temperature between 50°C and 100°C.

(3) The present study of the effect of electron scavengers such as SF_6 and CH_3Br has further confirmed the role of ionic processes in this polymerization. Termination of polymerization by ion neutralization has been verified by investigating the dose-rate dependence of the polymerization in the presence of electron scavengers.

(4) It has been found that the oxygen-containing compounds such as O_2, NO_2 and N_2O retard remarkably the polymerization, perhaps by producing water.

[*2] Since the ionization potentials of O_2, NO_2 and N_2O are higher than that of isobutene, the positive charge transfer from isobutene to these compounds is unlikely to occur.

3) W. J. Holtslander and G. R. Freeman, *Can. J. Chem.*, **45**, 1661 (1967).