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Yoneho Tabata^a

^a DEPARTMENT OF NUCLEAR ENGINEERING, FACULTY OF ENGINEERING, UNIVERSITY OF TOKYO, TOKYO, JAPAN

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Radiation-Induced Polymerization of Styrene Oxide*

YONEHO TABATA

DEPARTMENT OF NUCLEAR ENGINEERING,
FACULTY OF ENGINEERING,
UNIVERSITY OF TOKYO,
TOKYO, JAPAN

Summary

Radiation-induced polymerization of styrene oxide in the liquid and solid states was carried out by initiating with γ -rays from ^{60}Co and electrons from a Van de Graaff accelerator.

Effects of dose rate, a radical inhibitor, and temperature on the polymerization were examined. Infrared spectra and viscosities of polymers obtained were measured.

From these experiments, the following results were obtained:

1. Apparent activation energies are 6.2 kcal/mole for the liquid-state polymerization and 0.17 kcal/mole for the solid-state polymerization, respectively.

2. The polymerization in liquid state is inhibited and retarded by *p*-benzoquinone.

3. The rate of polymerization is approximately proportional to the dose rate.

4. The viscosity of polymers obtained increases with irradiation dose.

5. Infrared spectrum of polymers obtained varies with the polymerization temperature.

It is emphasized in this paper that the chain-transfer and isomerization reactions are rapid and play an important role in the polymerization of styrene oxide, and that the polymer-forming process is not so rapid, owing to a step-by-step type of growing.

In a previous paper (1), polymerizations of styrene oxide and propylene oxide induced by high-energy electrons were reported by us. It was shown in the paper that a rapid homopolymerization of

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styrene oxide is possible in the liquid state, whereas the polymerization of propylene oxide can mainly take place in the solid state in the presence of styrene oxide.

In this paper, the effects of radical inhibitor and dose rate on the polymerization are reported, and the difference between polymerizations induced with γ -rays and high-energy electrons is discussed.

Recently, the radiation-induced polymerization of 1,2-cyclohexane oxide in the liquid state was reported (2).

EXPERIMENTAL

Styrene oxide was dried and purified by repeating distillation. The melting point of the monomer was -36.6°C . An ampule containing the purified solid monomers was evacuated to $10^{-4} \sim 10^{-5}$ mm Hg. The monomers were irradiated with γ -rays from a ^{60}Co source over the dose-rate range 3×10^3 to 5×10^4 rad/hr and with electron beams from a Van de Graaff generator over the dose-rate range 8×10^4 to 2×10^5 rad/sec. Irradiation was carried out at the Tokyo Branch Institute of the Takasaki Radiation Chemistry Establishment, JAERI. The viscosity of polymers obtained was measured in acetone at 35°C . Infrared spectra of the polymers were also measured. The effect of *p*-benzoquinone on the polymerization was examined.

RESULTS AND DISCUSSION

Effect of Temperature on the Polymerization

The relations between conversion and irradiation time are shown in Figs. 1 and 2 for the liquid- and solid-state polymerizations. It is obvious from the figures that the polymerizations at all polymerization temperatures were not preceded by an induction period. An Arrhenius plot of the polymerization is given in Fig. 3. Apparent activation energies of 6.2 kcal/mole and 0.17 kcal/mole were obtained for liquid- and solid-state polymerizations, respectively.

The Arrhenius plot is different to some extent from that of polymerization induced by high-energy electrons (1). In the case of electron irradiation, the dose rate is extremely high, so the temperature elevation in the irradiated monomer system cannot be avoidable. The effect of impurity on the polymerization may also be

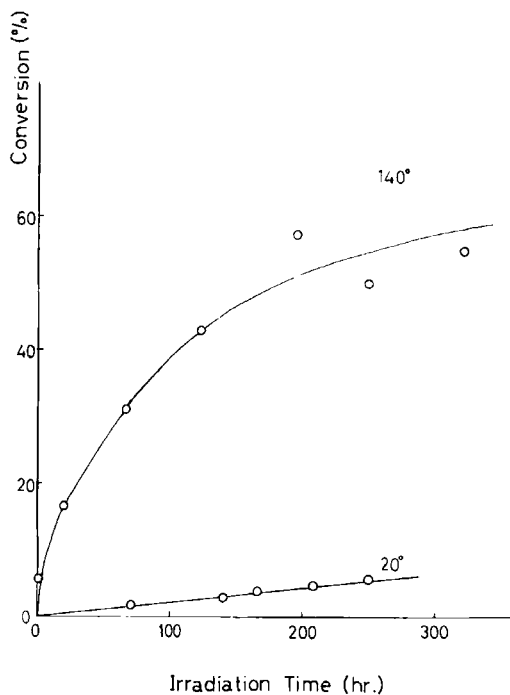


FIG. 1. The relation between conversion and irradiation time in the liquid state. Dose rate, 5.05×10^4 rad/hr.

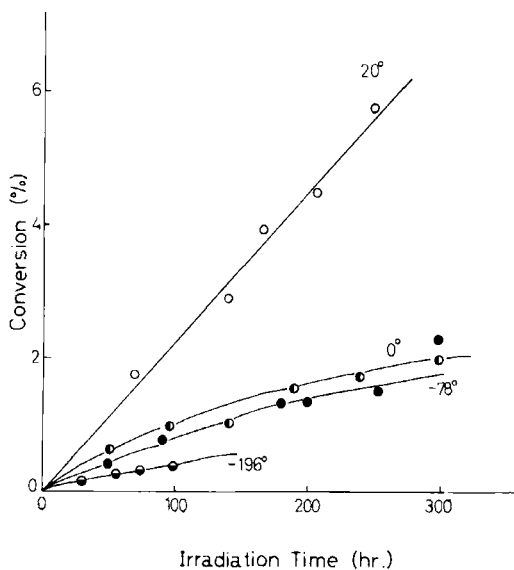


FIG. 2. The relation between conversion and irradiation time in both liquid and solid states. Dose rate, 5.05×10^4 rad/hr.

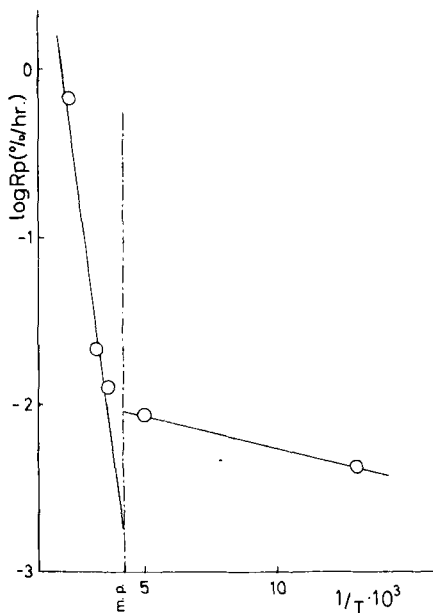


FIG. 3. Arrhenius plot of the polymerization of styrene oxide in liquid and solid states.

influenced by the radiation intensity, because the diffusion of impurity is in competition with the initiation reaction. These may be the main reasons for the difference.

The difference in the activation energies between the liquid and solid states suggests that the polymerization mechanisms differ from each other, as was observed in many cases (3).

Effect of Radical Inhibitors

The effect of *p*-benzoquinone on the polymerization of styrene oxide in the liquid state is shown in Fig. 4. As is obvious from the figure, the polymerization is inhibited and retarded by the radical inhibitor. This indicates that polymerization in the liquid phase proceeds by a radical mechanism.

The induction period is about 150 hr, so that it corresponds to an irradiation dose of $(5.05 \times 10^4 \text{ rad/hr} \times 150 \text{ hr})$ 7.6 Mrad. As the absorbed energy is $6.24 \times 10^{13} \text{ eV/g}$ for unit rad, the deposited energy per one monomer molecule for the induction period can easily be estimated; the value is 0.1 eV/molecule. Assuming that 5

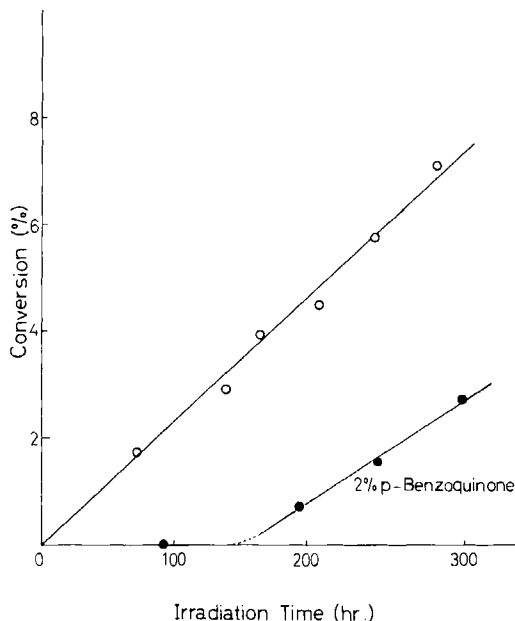


FIG. 4. The effect of a radical inhibitor on the polymerization in liquid state at 20°C.

to 10 eV is required to produce a radical, the radicals produced in the induction period are calculated to be 1 to 2 mole-%. On the other hand, the concentration of benzoquinone in monomers is 1.5 mole-%.

This suggests that the radical inhibitor scavenges all the radicals produced in the induction period, and after the consumption of the inhibitor by the monomer radicals, polymerization begins to take place.

These facts indicate clearly that the polymerization is initiated by the radicals produced by high-energy radiation in the liquid state of monomers.

Effect of Radiation Intensity on the Polymerization

The effect of dose rate on the rate of polymerization was examined in a wide range. The result is shown in Fig. 5. From the figure it is obvious that the rate of polymerization is approximately proportional to the dose rate. This suggests that the termination is a unimolecular process.

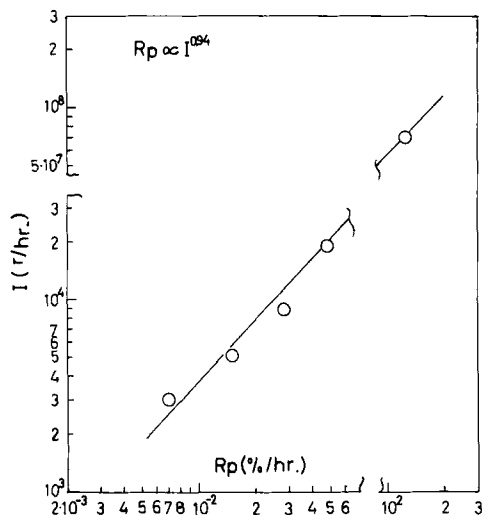


FIG. 5. Dose-rate dependency of the rate of polymerization in liquid-state polymerization at 20°C.

Viscosity of Polymer Solutions

The result of viscosity measurement of polymers obtained at various irradiation doses is shown in Fig. 6. The relation between the intrinsic viscosity and irradiation dose is shown in Fig. 7.

The polymerization of styrene oxide using SbCl_5 , AlCl_3 , FeCl_3 , and ZnCl_4 was carried out by Colclough et al. (4). They got a mixture of dimers. The intrinsic viscosity was in a region of 1.1 to 1.8×10^{-2} $[\eta]$ (g/100 ml). These coincide with those of our experiments.

From the viscosity measurements it is obvious that the degree of polymerization is rather small, and increases with the irradiation time. It suggests that the polymer-forming process is not so rapid, owing a step-by-step type of growing, and so the molecular weight increases gradually with the irradiation time. The polymer chain seems to be degraded by further irradiation, as shown in the figure.

Infrared Spectra of Polymers Obtained

Infrared spectra of polymers obtained at various temperatures are shown in Fig. 8. It is obvious from the figure that the spectrum varies depending on the polymerization temperature. Absorptions

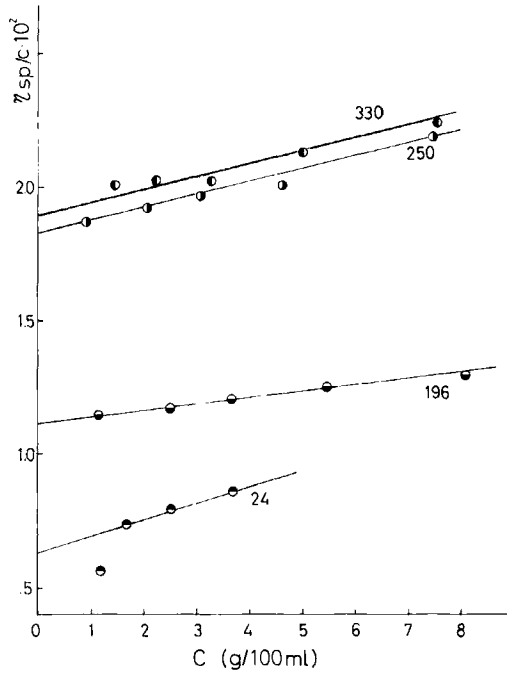


FIG. 6. Viscosities of polymers obtained in acetone at 35°C. The number indicates the irradiation time in hours.

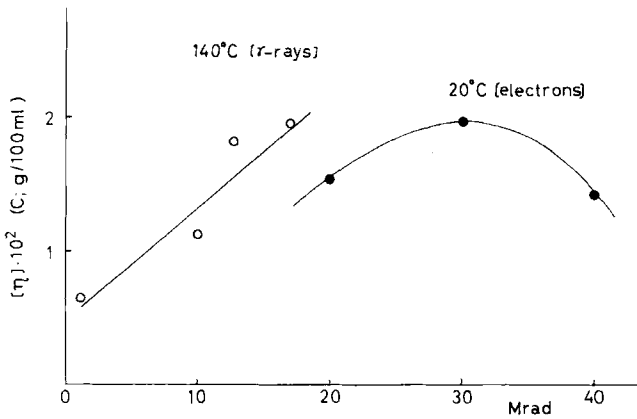


FIG. 7. The relation between intrinsic viscosity $[\eta]$ of polystyrene oxide and irradiation dose.

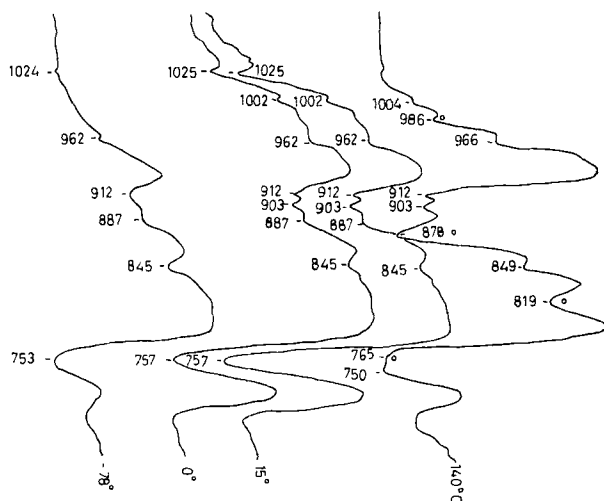


FIG. 8. Infrared spectra of polymers obtained at various temperatures.

at 986, 878, 819, and 765 cm^{-1} were observed only in the polymers obtained at 140°C . The relative absorption intensity at 845 and 1716 cm^{-1} increases with decreasing polymerization temperature. On the other hand an absorption at 903 cm^{-1} was not observed in the polymer obtained at -78°C .

The absorption spectrum of the polymer obtained at 140°C is quite similar to that of the polymer obtained with electron irradiation at 20°C . These facts suggest that a thermal effect on the polymerization is very important in this case.

Absorptions at 878 and 1260 cm^{-1} are due to the epoxide ring; therefore, the polymers obtained at higher temperatures include small amounts of epoxide ring. On the other hand, the carbonyl ($\text{C}=\text{O}$) contents increase with decreasing polymerization temperature. The mechanism of termination reaction may be suggested by the spectra.

The author believes that the chain-transfer and isomerization reactions play an important role in the polymerization of styrene oxide in the liquid state, as pointed out in a previous paper (1).

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Zusammenfassung

Die strahlungsinduzierte Polymerisation von Styroloxid im flüssigen als auch im festen Zustande wurde durch Initiierung mit γ -Strahlen einer Kobalt-60 Quelle und mit Elektronen aus einem Van de Graaff Beschleuniger durchgeführt.

Der Einfluss der Bestrahlungsintensität, eines Radikalinhibitors und der Temperatur in Bezug auf die Polymerisation wurde untersucht. Die Infrarotspektren und Viskositäten der erhaltenen Polymeren wurden gemessen.

Aus diesen Experimenten ergeben sich folgende Ergebnisse:

1. Die scheinbaren Aktivierungsenergien sind 6.2 kcal/Mol für die im Flüssigkeitszustand erfolgte Polymerisation und 0.17 kcal/Mol für die Polymerisation im Festzustand.

2. Die Polymerisation im flüssigen Zustand wird durch p-Benzochinon inhibiert und verlangsamt.

3. Die Polymerisationsgeschwindigkeit ist ungefähr der eingestrahnten Intensität proportional.

4. Die Viskosität der erhaltenen Polymeren steigt mit zunehmender Strahlungsdosis an.

5. Die Infrarotspektren hängen von der Polymerisationstemperatur ab.

Es wird weiterhin in dieser Arbeit betont, dass die Kettenübertragungs- und Isomerisierungsreaktionen schnell verlaufen und eine wichtige Rolle bei der Polymerisation von Styroloxid spielen und dass die eigentliche Bildungsgeschwindigkeit des Polymeren nicht so schnell verläuft auf Grund eines stufenweise vor sich gehenden Aufbaumechanismus.

Résumé

La polymérisation, induite par irradiation, de l'oxyde de styrolène à l'état solide et liquide a été amorcée avec des rayons du Co^{60} et avec des électrons d'un accélérateur de Van de Graaff.

On a examiné l'influence du débit de dose de l'inhibiteur radicalaire et de la température. On mesuré les spectres infrarouges et les viscosités de ces polymères.

Les résultats suivants ont été obtenus:

1. Les énergies apparentes d'activation pour les polymérisations à l'état liquide et solide sont 6.2 kcal/mol et 0.17 kcal/mol, respectivement.

2. La benzoquinone inhibe et retarde la polymérisation à l'état liquide.

3. La vitesse de polymérisation est approximativement proportionnelle au débit de dose.

4. La viscosité des polymères obtenus augmente avec la dose d'irradiation.

5. Le spectre infrarouge des polymères obtenus avec la température de polymérisation.

L'auteur souligne dans cette note l'importance du transfert des chaînes et des réactions d'isomérisation dans la polymérisation de l'oxyde de styrolène et le fait que le processus formant les polymères n'est pas si rapide en raison de sa progression par paliers.

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