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Effect of Atmosphere on Radiation-Induced Crosslinking of Polyethylene. Part I. Depressive Effect and Accelerating Effect

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INTRODUCTION

The effect of the atmosphere present during or after irradiation has become an important subject in radiation chemistry. There are many reports on the effect of oxygen alone; all of these show that oxygen reacts readily with radicals, forms carbonyl compounds or peroxides, and reduces the degree of crosslinking. Chapiro[1] showed that in oxygen the amount of radiation necessary to produce crosslinking is more than in vacuum. Furthermore, some of the crosslinks formed in presence of oxygen proved to be thermally unstable. Alexander and Toms[2] found that at a dose rate of 3×10^6 rad/min. the gel content of the polymer decreases by about 10% in the presence of air at 1 atm. in films up to 0.175 mm. thick, while according to St.-Pierre and Dewhurst,[3] at pressures of 10 atm. of oxygen the gel formation is depressed by 64% at a dose rate of 1.4×10^7 rad/min. in a polyethylene film 0.36 mm. thick. The importance of dose rate is strongly emphasized by these latter authors.

In our previous paper, the products due to radiation-induced reactions between polyethylene and several kinds of gases and liquids were analyzed by infrared absorption spectroscopy.[4] From these results, we see that some chemical changes in polyethylene, such as substitution or addition reactions, can occur when the polymer is irradiated in gases or liquids, e.g., air, O_2, Cl_2, SO_2, NO_2, concentrated HCl, concentrated H_2SO_4, aqueous HNO_3, and liquid $CHCl_3$.

In this paper, the effect of atmosphere on radiation-induced crosslinking is investigated in several kinds of gases such as NO_2, O_2, Cl_2, SO_2, NH_3, CO, H_2, and N_2O. The first two, i.e., NO_2 and O_2, are known to be strong radical scavengers. A part of our results was reported previously in this Journal.[5]

EXPERIMENTAL

1. Preparation of Samples

The polyethylene used was Sumikathene L-70 (prepared by Sumitomo Chemicals Co.), low density polyethylene, in a film form 0.03 mm. thick and free from any stabilizer. The molecular weight of film was determined by the melt viscosity method to be 28,000. The purity of commercially available gases such as N_2O, CO, H_2, NH_3, Cl_2, and O_2 was guaranteed as more than 99.9% by mass spectroscopy. SO_2 and NO_2 were prepared in this laboratory.[6,7]

Prior to irradiation, the films in each tube were outgassed at pressures of 1×10^{-4} mm. Hg for two days. Then the gas in question was admitted to the outgassing tube at pressures of about 600 mm. Hg. At the same time, for comparison, a sample in vacuum was also prepared as a standard.

2. Irradiation Procedure

The films were irradiated by gamma-rays from a Co^{60} source at a constant dose rate of 4.7×10^5 r/hr. In each type of atmosphere, these films were irradiated up to doses of 4×10^6–5×10^7 r at room temperature. After irradiation they were stored in sealed tubes for twelve days or more until tested in order to minimize any scatter of data due to post-irradiation effects.

3. Solubility Test

Solubility measurements to determine gel content and swelling ratio were carried out in order to get information about the influences of atmospheres on crosslinking of polyethylene. In our experiments irradiated films were enclosed in a wire mesh container (70 mesh Cu gauze) and the soluble fraction extracted by suspending the containers in a large volume of xylene (80°C.) for 15 hr. Each of these measurements was repeated three times.

RESULTS

1. Irradiations in Various Types of Atmospheres

The changes in gel content as a function of radiation dose are shown in Figure 1 for the films irradiated in various atmospheres. The gel content is usually considered to increase with degree of crosslinking. From the behavior of each curve in Figure 1, it is reasonable to classify effects of atmospheres into the following four groups; the first group includes vacuum as a standard, besides CO and H_2; the second group includes Cl_2, SO_2, and NH_3 by which the gel content is reduced to some extent; the third group includes O_2 and NO_2, by which the gel content is reduced to a marked extent (for example, in NO_2, insoluble material is not produced, even on irradiation up to doses of 5×10^7 r). On the contrary, it is shown that in N_2O the gel content increases in appreciable extent. Although our data show some scatter in Figure 1, more repeated measurements for irradiations in N_2O and in vacuum show more reliable data as following; 80.9 ± 0.52% in N_2O and 73.6 ± 0.52% in vacuum at a dose of 2×10^7 r. This accelerating effect of N_2O gas on crosslinking and the increase in gel con-

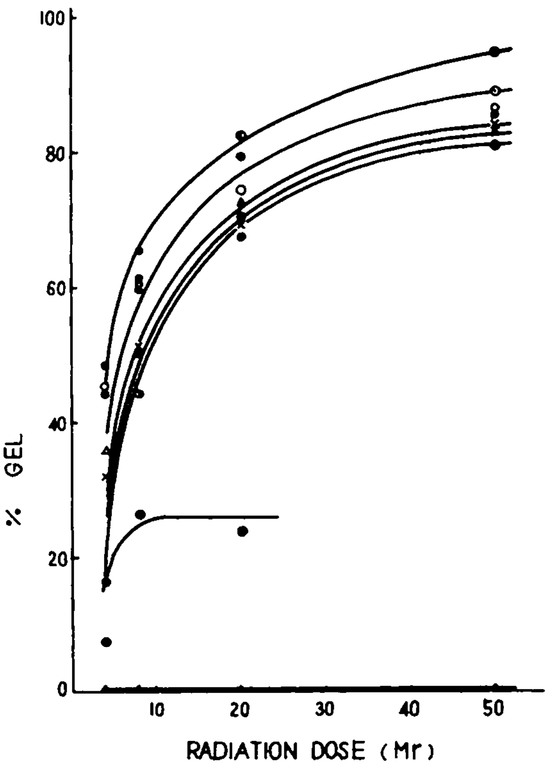

Fig. 1. Per cent gel vs. radiation dose for polyethylene at a constant dose rate of 6.4 × 10^5 r/hr. with irradiation in various atmospheres: (◐) N_2O; (O) vacuum; (⊙) H_2, (●) CO, (△) Cl_2, (×) SO_2; (◑) NH_3; (⊗) O_2; (▲) NO_2.

tent, is believed to be a new and interesting phenomenon. In these experiments, the dose for incipient gel formation cannot be determined since our experiments are limited in the range mentioned above.

The changes in swelling ratio as a function of radiation dose are shown in Figure 2. According to Flory,[8] the molecular weight of crosslinked unit, M_c, changes with swelling ratio; the less the swelling ratio, the higher the degree of crosslinking. From Figure 2 it can be seen that our results support the above conclusion of Figure 1, namely, the swelling ratio for each atmosphere can be arranged in decreasing order as follows, $O_2 > NH_3$, Cl_2, and $SO_2 >$ CO, H_2, and vacuum $> N_2O$.

2. Irradiations in N_2O Gas and in Vacuum

Furthermore, a preliminary examination of influences of N_2O gas pressure and of dose rate on the accelerating effect was carried out. In this examination, USI Petrothene film (0.1 mm. thick) was used for comparison with the Sumikathene film described above. An experiment in vacuum was also carried out as a standard. Figure 3 shows plots of per cent gel vs. dose rate plots for the films irradiated in N_2O and in vacuum at a con-

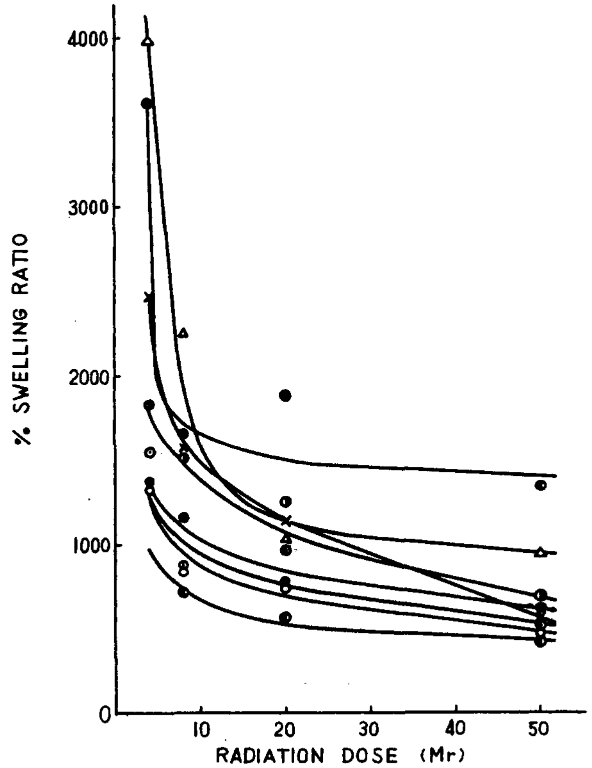

Fig. 2. Swelling ratio vs. radiation dose with irradiations in various atmospheres. Symbols as in Fig. 1.

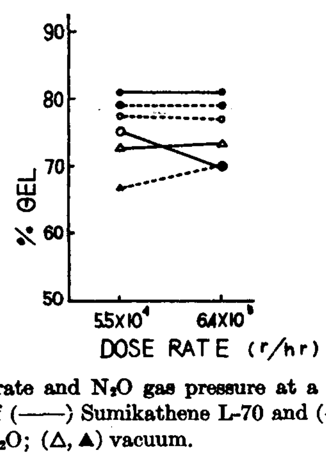

Fig. 3. Effects of dose rate and N_2O gas pressure at a constant radiation dose of 2×10^7 r on irradiation of (——) Sumikathene L-70 and (--) Petrothene 206: (●) $^1/_2$ atm. of N_2O; (O) 4 atm. N_2O; (△, ▲) vacuum.

stant dose of 2×10^7 r. From this examination we may suppose that, first the accelerating effect of N_2O on crosslinking, shows dose-rate independence, and that the effect decreases at higher gas pressure within a range of our experiments.

3. Irradiation in Oxygen

In order to compare the accelerating effect of N_2O with the depressive effect of oxygen on crosslinking, similar examination was carried out in oxygen for reference. Figure 4 shows similar per cent gel versus dose rate plots for the films irradiated in oxygen at a constant dose of 2×10^7 r.

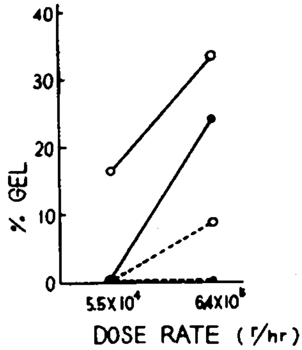

Fig. 4. Effects of dose rate and O_2 gas pressure at a constant radiation dose of 2×10^7 r on irradiation of (——) Sumikathene L-70 and (--) Petrothene 206: (●) 1 atm. O_2; (O) $^1/_4$ atm. O_2.

This result is consistent with the well known results of other authors.[1-3] Our result shows that the higher the gas pressure and the lower the dose rate, the more marked the depressive effect is.

DISCUSSION

1. Depressive Effect on Crosslinking

As shown in Figure 1, five gases show a depressive effect. When additives can act as radical traps, we may have the following relation by the stationary state hypothesis according to Charlesby,[9]

$$k_1 I = k_2[\mathrm{R}\cdot]^2 + k_3[\mathrm{R}\cdot][\mathrm{A}] \quad (1)$$

where I denotes the radiation dose rate; $[\mathrm{R}\cdot]$ and $[\mathrm{A}]$ are the concentrations of the radical and of additives, respectively; k_1, k_2, and k_3 are reaction rate constants. In particular k_2 denotes the reaction rate constant of crosslinking. The rate of crosslinking reduced by the presence of additive in the ratio is given by:

$$Y = k_2[\mathrm{R}\cdot]^2/k_2[\mathrm{R}\cdot]^2_{\mathrm{A}=0} = 1 + X - (2X + X^2)^{1/2} \quad (2)$$

where $X = k_3^2[\mathrm{A}]^2/2k_1k_2I$

Equation (2) will assume the form:

$$Y(Y - 2X - 2) + 1 = 0 \quad (3)$$

It is easily seen that eq. (3) represents a hyperbola in the X, Y system. Since Y cannot exceed 1 on the basis of definition, Y decreases with X monotonically. In other words, the ratio $k_2[R\cdot]^2/k_2[R\cdot]^2_{A=0}$ decreases with $[A]^2/I$. Since [A] in a film is considered to be proportional to the external gas pressure, this is consistent with our results shown in Figure 4, namely, the depressive effect increases with gas pressure and decreases with increase in dose rate. These results will be applicable to other kinds of gases, although not being supported by any experimental investigation.

Next, it seems to us very reasonable to classify the five gases into two groups in compliance with their reactivity shown in Figure 1. The one group includes Cl_2, SO_2, and NH_3, and the other group NO_2 and O_2. The former shows rather mild reactivity, but the latter rather marked activity. According to our study by infrared spectroscopy,[4] it is found that each of the gases Cl_2, SO_2, NO_2, and O_2 reacts with polyethylene on irradiation and produces specific substitution groups. Only with NH_3, do we find hardly any spectral changes due to radiation-induced reaction. In relation to our experiments, Kuri, Ueda, and Shida[10] reported on the electron spin resonance of polyvinyl chloride irradiated in various atmospheres. According to their investigation, each of the gases H_2S, NO, NO_2, and Br_2 acts as a scavenger for the polymer radicals, O_2 and SO_2 convert the polymer radicals into other types of radical, and the gas pressure of NH_3 decreases during irradiation.

Although gas permeability into polyethylene may be one of the most important factors in our experiments, it is excluded in this report because we did not measure it sufficiently.

2. Accelerating Effect of Nitrous Oxide

The depressive effect of certain gases is known to some extent, but an accelerating effect appears to be a phenomenon not previously reported.

The effect of N_2O increases with radiation dose, as shown in Figures 1 and 2. If the effect is not due to radiation, it may be independent on radiation dose. Moreover, we found that the solution viscosity of polyethylene irradiated in N_2O increases with dose over the range of 3.8×10^4–6.08×10^5 r.

Even in the case of so-called vacuum irradiation, the trace oxygen remaining in the tube may diffuse to polymer radicals or to other active sites and may inactivate them. In this case, if a foreign gas is present in the tube, the diffusion of oxygen may be depressed by the foreign gas; this gas may then appear to be an accelerator of crosslinking. This is not, however, the case so far as N_2O is concerned, because the accelerating effect of N_2O increases with radiation dose, is rather small at higher gas pressure, and is independent of dose rate.

The next subject is, therefore, what is the reaction mechanism of this effect? Although we have few data on the subject for the present, it seems to us the effect must be due to some intermediates in the radiolysis of N_2O.

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Synopsis

Polyethylene films were irradiated in various atmospheres by gamma-rays from a Co^{60} source, and solubility measurements against xylene were carried out at 80°C. In NO_2 and O_2, the crosslinking of polyethylene is depressed markedly but in NH_3, Cl_2, and SO_2 not so much. On the other hand, N_2O accelerates the crosslinking appreciably. In CO and H_2, neither the depressive nor the accelerating effect is observed within a limit of error. In O_2, the depressive effect is more considerable at higher gas pressure and at lower dose rate; however, in N_2O the accelerating effect is reduced at higher gas pressure, and shows dose-rate independence within the range of our experiments.

Résumé

On a irradié des films de polyéthylène sous diverses atmosphères au moyen de rayons-gamma du $Co;^{60}$ les solubilités dans le xylène ont été mesurées à 80°C. Sous NO_2 et O_2, le pontage du polyéthylène est fortement diminué; sous NH_3, Cl_2 et SO_2 l'effet est moins prononcé. Par contre, N_2O accélère le pontage de façon appréciable. Sous CO et H_2, il n'y a aucun effet ralentisseur ou accélérateur observable aux limites d'expériences près. Sous O_2, l'effet est plus prononcé sous pression élevée, et à dose moins forte; toutefois sous N_2O l'effet accélérateur est réduit par une élévation de pression de gaz, et est indépendante de la dose dans les limites de nos expériences.

Zusammenfassung

Polyäthylenfilme wurden in verschiedenen Gasen mit Gammastrahlen von Co^{60} bestrahlt und Löslichkeitsmessungen in Xylol bei 80°C durchgeführt. In NO_2 und O_2 wird die Vernetzung von Polyäthylen merklich, in NH_3, Cl_2 und SO_2 jedoch nicht im gleichen Ausmass verlangsamt. Andererseits beschleunigt N_2O die Vernetzung beträchtlich. In CO und H_2 wurde innerhalb der Fehlergrenzen weder eine Verlangsamung noch eine Beschleunigung gefunden. In O_2 ist der hemmende Einfluss bei höherem Gasruck und geringerer Dosisleistung stärker, in N_2O wird hingegen der beschleunigende Einfluss bei höherem Gasrcuck vermindert und erweist sich innerhalb des untersuchten Bereichs als unabhängig von der Dosisleitsung.

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