

Effect of Atmosphere on Radiation-Induced Crosslinking of Polyethylene. Part IV. Sensitizing Effect of Nitrous Oxide and Xenon

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Synopsis

Low density polyethylene film was irradiated with gamma-rays from Co^{60} in atmospheres of nitrous oxide and xenon. A plot of solubility ($S + S^{1/2}$) against reciprocal of irradiation dose gives a nearly straight line in each case. The probability of crosslinking increases by 44% in N_2O as compared with vacuum irradiation, and increases by 10% in Xe. On the other hand, the probability of main-chain scission is scarcely affected by these gases. Therefore the increase in gel fraction due to these gases is not due to the protection against main-chain scission, but is caused mainly by the sensitization against crosslinking. Furthermore, the formation of *trans* vinylene unsaturation is also sensitized by these gases.

INTRODUCTION

We recently reported that polyethylene film irradiated in atmospheres of N_2O , Xe, etc., shows a decided increase in gel fraction over one irradiated in vacuum.¹⁻⁴

Since polyethylene shows main-chain scission in addition to crosslinking under irradiation,^{5,6} the increase in gel fraction may be due to not only sensitization against crosslinking, but also protection against main-chain scission.⁷

In this paper, we attempted to determine whether N_2O and Xe sensitize the crosslinking or protect against degradation.

In addition, the effects of these gases on the formation of *trans* vinylene unsaturation were observed. Apart from the formation of crosslinks the most noticeable chemical change which occurs when polyethylene is irradiated in the absence of air is the formation of unsaturation. Furthermore there must be some type of relation between the formation of crosslinks and unsaturation, as suggested by several investigators.⁸⁻¹¹

EXPERIMENTAL

Experimental was nearly the same as in the preceding studies.²⁻⁴

In the present work, only the 0.3 mm.-thick film was used, and the gas pressure applied was 600 mm. Hg for N_2O and 4000 mm. Hg for Xe. The

specimens were irradiated at a constant dose rate of 1.07×10^6 r/hr. in vacuum and in Xe, and irradiated at a constant dose rate of 5.1×10^5 r/hr. in N_2O . The relative error of our dosimetry was $\pm 5\%$.

Solubility measurement was somewhat modified. While the irradiated specimens were extracted at $80^\circ C$. continuously for 15 hr. in the previous work, in the present study the extraction was carried out intermittently at $80^\circ C$. during 3 days, i.e., the specimens were heated by day but were cooled by night. The value of gel fraction was reduced by about 1% in the case of present method, probably because the extraction was more severe. It should be stated in this connection that the present method gives nearly the same value if the extraction is carried out at $110^\circ C$. instead of $80^\circ C$.

The formation of *trans* vinylene unsaturation was studied from the infrared absorption at 10.35μ . Since the extinction coefficient of this group is not always known with sufficient accuracy, the absolute concentration of this group could not be obtained.

RESULTS

1. Solubility

Our data were examined in the form of a plot of $S + S^{1/2}$ versus the reciprocal of dose ($1/r$) (Fig. 1). Each of three curves becomes asymptotic to a straight line and tends to a limiting value when the irradiation dose increases, as already shown by Charlesby et al.⁵ for the vacuum irradiation. According to these authors, when the initial distribution of molecular weight is random, the plot gives a straight line and the relation becomes:

$$S + S^{1/2} = p_0/q_0 + 1/q_0u_1r$$

where p_0 and q_0 are the probability(density) of main-chain scission and crosslinking, respectively, and u_1 is the number-average degree of polymerization.

The plot becomes convex upwards, on the other hand, when the initial distribution is broader than a random one¹¹ or when intramolecular crosslinking occurs simultaneously.¹² Low density polyethylenes usually have a very wide molecular weight distribution, and the ratio \bar{M}_w/\bar{M}_n varies in the range 10–20, as against 2 for a random distribution. The ratio p_0/q_0 of degradation to crosslinking is given from the intercept of extrapolated curve at $1/r = \text{zero}$. The relative value of p_0 and q_0 for the vacuum irradiation are calculated from the initial slope and from the ratio p_0/q_0 , as shown in Table I.

TABLE I
Crosslinking and Scission

	p_0/q_0	Relative q_0	Relative p_0
Vacuum	0.22 ₃	1.00	1.00
Xe	0.20 ₀	1.1 ₀	0.9 ₃
N_2O	0.16 ₄	1.4 ₄	1.0 ₆

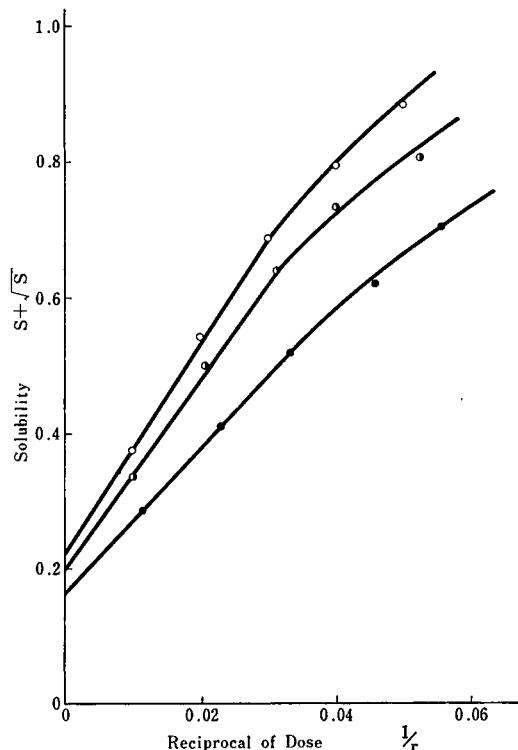


Fig. 1. Sol fraction: (O) irradiated in vacuum; (◐) irradiated in Xe; (●) irradiated in N_2O .

From Table I we see that q_0 is larger for irradiation in N_2O or Xe than in vacuum but p_0 shows a slight change. We can deduce that the increase in gel fraction due to these gases is mainly owing to the sensitization of crosslinking. While p_0 for the irradiation in N_2O is somewhat larger than unity, this can be ascribed to the limited degree of accuracy of our experimental data. Even if p_0 were really to increase on irradiation in N_2O atmosphere, this difference would be due to the effect of radiolytic products of N_2O (O_2 , NO , NO_2).³

TABLE II
 p_0/q_0 for Vacuum-Irradiated Polyethylene

Reference	p_0/q_0
Charlesby et al. ⁵	0.28–0.34
Baskett and Miller ⁶	0.18–0.20
Okada (present work)	0.22

As shown in Table II, the ratio of degradation to crosslinking is not always constant. Moreover, Alexander and Toms¹⁴ and Schmacher¹⁵ found that the sol fraction decreases steadily with dose and tends to zero, which sug-

gests that carbon-carbon bond scissions are of little importance in the process.

2. Swelling Ratio

Figure 2 shows the swelling ratio Q_v plotted against the irradiation dose on a log/log scale. In each case, the plot gives a nearly straight line of slope of -0.6 . Low swelling characteristics of polymer irradiated in N_2O may be due to the high probability of crosslinking above mentioned. On the specimens irradiated in Xe nearly the same characteristics were observed, but the difference from the vacuum-irradiated sample was within the limits of experimental error.

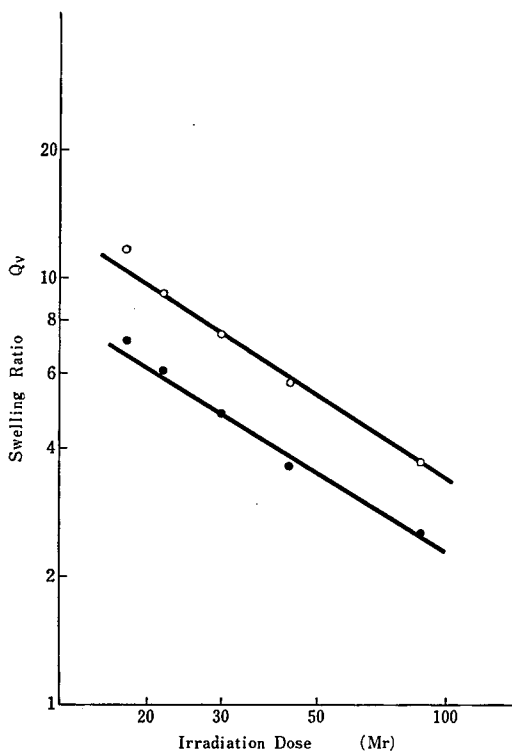


Fig. 2. Swelling ratio of irradiated polyethylene: (O) irradiated in vacuum; (●) irradiated in N_2O .

3. Unsaturation

The absorbance at 10.35μ per unit thickness is plotted against irradiation dose in Figure 3. N_2O and Xe show a marked sensitizing effect. For low irradiation doses, the growth of *trans* unsaturation is linear with dose, but a deviation from the linear relationship is observed for higher dose, as previously reported in the case of vacuum irradiation.^{16,17} The increment of

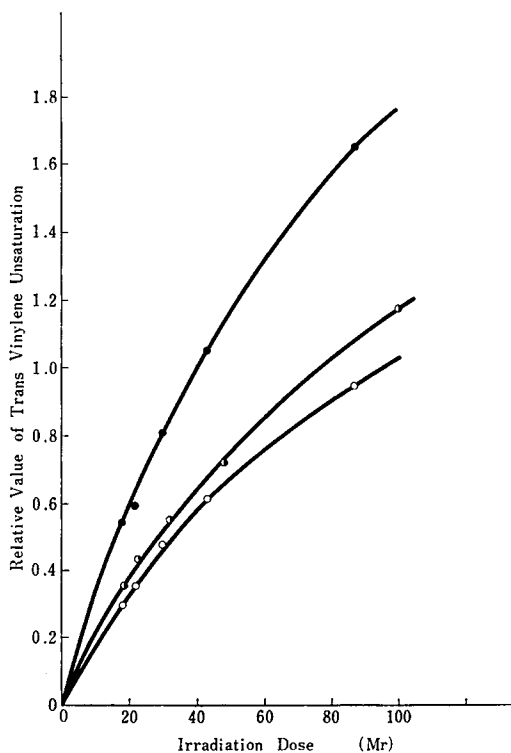


Fig. 3. Formation of *trans* vinylene unsaturation; (○) irradiated in vacuum; (◐) irradiated in Xe; (●) irradiated in N₂O.

trans unsaturation, as calculated from the initial slope of each curve, is 87% for N₂O and 19% for Xe.

In addition, yellow color develops in the specimens irradiated in N₂O up to 1×10^8 r. This color is probably indicative of the presence of the conjugated double bonds.¹⁸

Vinyl and vinylidene unsaturation which exist in the polymer initially are observed to disappear rapidly in each case. However, the thickness of film used was not suitable for detailed study of this unsaturation.

Also, a weak absorption at 5.8μ was observed for polyethylene irradiated in N₂O. The absorbance indicates the presence of carbonyl group formed by reaction with the radiolytic products of N₂O.

DISCUSSION

1. Sensitization against Crosslinking

As mentioned above, the increase in gel fraction is found to be due mainly to the sensitization to crosslinking by N₂O and Xe. We could also expect an increase in gel fraction, if the gases protect against main-chain scission of polyethylene as in the case with polyisobutylene;⁷ however, the probability of scission scarcely changes in this work.

We have never determined whether increased crosslinks due to these gases are composed of carbon-carbon bonds or not. We cannot exclude the possibility of forming a different type of bridge, for example, C—NH—C, C—N(NO)—C, but the possibility may be limited; the existence of a different type of bridge including Xe cannot be expected, and Xe also sensitizes the crosslinking as N₂O does. Furthermore, the simultaneous formation of *trans* vinylene unsaturation would not favor the possibility of forming a different type of bridge, even in the case of N₂O.

In our preceding papers,² it was suggested that the radiolytic intermediates of N₂O probably play a main role in the sensitization (accelerating effect). However, such a simple idea must be modified to some extent, for the energy absorbed by gas molecules dissolved in polymer would be extremely little as compared with the energy absorbed by polymer itself if the sensitization is a homogeneous reaction in the solid phase between the dissolved gas molecules and polymer, as assumed earlier.³ Since the features of the sensitization have been clarified to a certain extent, we will discuss the mechanism of the sensitization in a forthcoming paper.

2. Sensitization against Formation of Unsaturation

The formation of *trans*-vinylene unsaturation sensitized by any irradiation atmosphere has never been reported. The formation of unsaturation has been found to be practically independent of temperature^{17,19,20} and of crystallinity of polymer.²⁰ In addition, Prober²¹ found that a number of additives which act as free radical scavengers, do not affect the formation of unsaturation in polyethylene. Most authors assumed that the mechanism of formation of unsaturation involves a molecular detachment process of a hydrogen molecule from main chain.

A certain relation between the formation of unsaturation and crosslinks has been discussed by several investigators.⁸⁻¹¹ Both crosslinks and unsaturation increase proportionally with dose and are independent of dose rate. Also, Snow and Moyer⁸ irradiated *n*-paraffin wax, mainly C₂₆-C₂₇, and separated the dimer produced. It was confirmed that the disappearance of the initial paraffin was linear with dose and the unsaturation was more likely to occur in the dimer fraction. The formation of both crosslinks and unsaturation is considered to be a result of a dehydrogenation reaction of polyethylene. Crosslink formation is an intermolecular reaction but the unsaturation results from an intramolecular reaction. Some investigators suggest that both reactions can be explained by the same reaction mechanism, a "molecular" mechanism.²²⁻²⁴

Our results indicate that the increment of crosslinks is 44% for N₂O and 10% for Xe, and the increment of unsaturation is 87% for N₂O and 19% for Xe. We can assume that some type of intimate relation exists certainly between the formation of crosslinks and unsaturation.

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Résumé

On a irradié un film de polyéthylène de faible densité avec des rayons gamma à partir de ^{60}Co dans une atmosphère d'oxyde nitreux et de xénon. La solubilité ($S + S^{1/2}$) par rapport à la dose d'irradiation donne une ligne quasi droite dans chaque cas. La probabilité de ramification augmente de 44% dans le N_2O par rapport à l'irradiation sous vide, et augmente de 10% dans le Xe. D'un autre côté, la probabilité d'une scission de la chaîne principale est rarement affectée par ces gaz. Dès lors l'augmentation de la fraction de gel due à ces gaz n'est pas imputable à la protection contre la scission de la chaîne principale mais est causée principalement par la susceptibilité à la ramification. De plus la formation d'insaturation *trans*vinylène est également sensible à ces gaz.

Zusammenfassung

Eine Folie aus Polyäthylen niedriger Dichte wurde mit ^{60}Co - γ -Strahlen in einer Stickoxydul- und einer Xenonatmosphäre bestrahlt. Die Vernetzungswahrscheinlichkeit nimmt im Vergleich zur Bestrahlung im Vakuum in N_2O um 44% und in Xe um 10% zu. Andererseits wird die Wahrscheinlichkeit für die Spaltung der Polymerkette durch diese Gase kaum beeinflusst. Es ist daher die Zunahme an Gelfraktion unter diesen Gasen nicht eine Folge einer Schutzwirkung gegen Polymerkettenspaltung sondern hauptsächlich einer Sensibilisierung für Vernetzung. Ausserdem wird durch diese Gase auch die Bildung von *Trans*vinylidoppelbindungen sensibilisiert.

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