Protective Effect of Nitrous Oxide on Radiation-Induced Degradation of Polyisobutylene

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Introduction

We recently reported that polyethylene film irradiated in N_2O atmosphere shows a decided increase in gel content over one irradiated in vacuum.[1–4] We may assume that N_2O not only sensitizes the crosslinking but also protects the main chain fracture to some extent.

This paper is concerned with the effect of N_2O on another type of polymer. The polymer used is polyisobutylene, which is one of the simplest of the long-chain polymers which degrade under irradiation. Moreover, polyisobutylene is one of the most favorable polymers for our investigation, because it has an amorphous structure at room temperature and shows a high gas solubility.[5]

The degradation of polyisobutylene has already been reported by several investigators.[6–9] They showed that the number of main-chain fractures is proportional to radiation dose and that these fractures occur at random in the long-chain molecule. In addition to the fracture, gas evolution and formation of unsaturation were studied.

Experimental

Our samples were Vistanex MML-100, having a viscosity-average molecular weight of 1,000,000. Nitrous oxide was commercial grade and its minimum purity was 99.9%. Prior to irradiation, the specimens in a test tube were outgassed at pressures of 1×10^{-4} mm. Hg for 3 days. Then the N_2O was admitted to the outgassing tube at pressures of 600 mm. Hg. Since polyisobutylene is sensitive to sunlight, the test tube was completely covered with aluminum foil.

After irradiation by γ rays, we measured the intrinsic viscosity of specimens in carbon tetrachloride at 30°C. The equation used to relate the intrinsic viscosity (η) to the viscosity-average molecular weight of polyisobutylene $\bar{M}_v$ was that of Flory et al.:[10]

$$[\eta] = 2.9 \times 10^{-4} \, \bar{M}_v^{0.68}$$

Results and Discussion

Polyisobutylene steadily changes under irradiation from elastic solid to viscous liquid. Thus, we can observe the extent of degradation even from

the appearance of polymer. The specimens irradiated in a nitrous oxide atmosphere are damaged to a lesser extent than those irradiated in vacuum when both are irradiated to the same dose.

Experimental results for the degradation of our specimens are shown in Figure 1. The viscosity-average molecular weight $\bar{M}_v$ was calculated from $[\eta]$ in CCl_4 solution at 30°C. The linearity of two curves over the

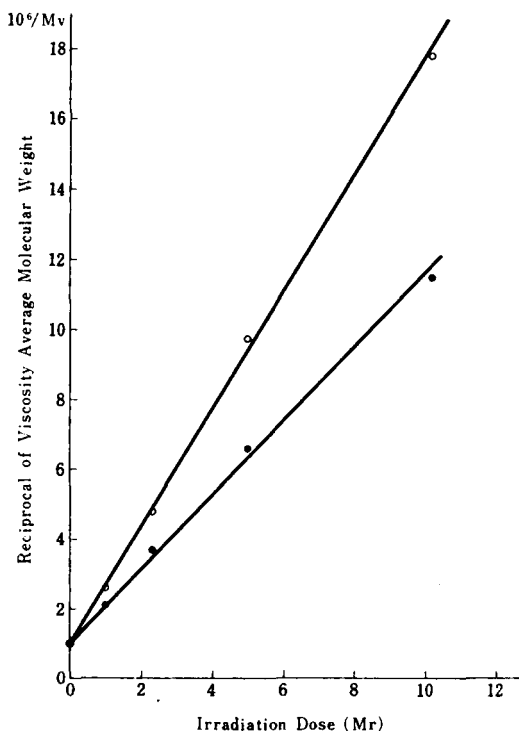Fig. 1. Protective effect for degradation by N_2O on irradiation of polyisobutylene at a constant dose rate of 5.8 × 10⁵ r/hr.: (O) in vacuum; (●) in N_2O; (☉) unirradiated.

range of doses of our experiment (0–1 × 10⁷ r) indicates that the number of fractures produced is proportional to dose in both cases and that these fractures occur at random in the long-chain molecule. Further, it is clear from the data of Figure 1 that N_2O acts to reduce the degradation of polyisobutylene to a certain extent.

In Table I, the values of p_0 and G for main-chain fracture are calculated. According to Charlesby et al.,[6] the relation in Figure 1 can be written in the form:

$$1/\bar{M}_v = (1/1.85 \times 56)p_0(r + r_0)$$

where r_0 is the dose which would be required to produce a polymer with the observed initial distribution from one which is infinitely long and p_0 is the density of main-chain fracture per unit dose.

TABLE I
p_0 and G Value for Main-chain Fracture

| | Atmosphere | | |
	Vacuum	N₂O	Ratio
p_0	1.7×10^{-4}	1.1×10^{-4}	0.63
G	2.9	1.9	0.63

Although our values for the vacuum irradiation are somewhat lower than Charlesby's[6] ($p_0 = 2.9 \times 10^{-4}$, $G = 5$), ours coincides with the data of Henglein's data[8,9] ($G = 1.5$–2.8) and those of Sebban-Donon[9] ($G = 3.0$).

Thus, in N_2O atmosphere only 63% of the energy absorbed is used for the degradation of polymer and the remaining 37% is dissipated due to the presence of N_2O.

Alexander and Charlesby[11] irradiated copolymers of isobutylene and styrene and determined the effect of protection conferred by benzene ring. As the amount of styrene in the copolymer is increased, the rate of degradation drops far more rapidly than can be explained by the reduced proportion of isobutylene present. The G value at a styrene content of 20% is half that of polyisobutylene. Furthermore, a study[12] of the protective effect of various additives such as aniline, thiourea or benzoquinone in polymethylmethacrylate during irradiation indicates that the addition of 10% of these reduces the amount of degradation by a factor of about two or three. On the other hand, Henglein and Schneider[8] irradiated solutions of polyisobutylene and studied the effect of solvent at a concentration of 10 g./l. G values for main-chain fracture decrease by a factor of 1.5–2.8 in the solutions of benzene–heptane (1:1), diisobutylene, and cyclohexane.

In our case, we may assume that the dissolved gas in the polymer plays a main role in the protection of main-chain fracture, in the same way as in the case of polyethylene.[3,4] While we have no information on the gas solubility in polyisobutylene, we can roughly estimate it from the data in polyethylene,[4] if the solubility of N_2O runs parallel to known solubility of propane in polyethylene[13] and polyisobutylene.[5] According to our estimation, N_2O at 600 mm. Hg dissolves in polyisobutylene to about 0.2 wt.-%.

Although the concentration of N_2O in the polymer is extremely low as compared with the additives or solvents above mentioned, the protective effect of N_2O reaches nearly to the same extent. Thus, we see that N_2O is extremely effective for protection. We do not know whether the gas itself is so powerful or the uniform and microscopic (molecular) distribution of gas molecules in the polymer is so favorable for the protection. However, it is sure that the gas in question is a very powerful agent practically.
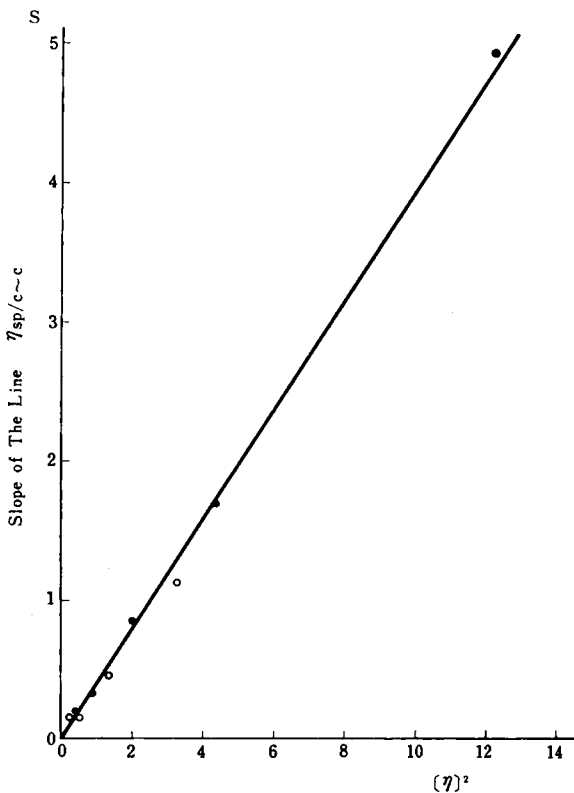
Fig. 2. Huggins' constant k' of the specimens.

Figure 2 shows Huggins' constant k' of each specimen for Huggins' viscosity equation:[14]

$$\eta_{sp}/c = [\eta] + k' [\eta]^2 c$$

In Figure 2, $[\eta]^2$ is plotted against S, where S is the slope of the line relating η_{sp}/c and c. Since $k' = S/[\eta]^2$, there will be a linear relation between $[\eta]^2$ and S when k' remains constant. On the other hand, k' is supposed to be dependent on solvent, temperature, and degree of branching, but not on molecular weight. All of our experimental values are scattered along the line of $S = 0.40 [\eta]^2$. We see that the degree of branching is nearly the same for all of the specimens. If some crosslinking occurred in addition to main-chain fracture, polymer molecules would become increasingly branched. Therefore, we can conclude that the effect of N_2O is literally the protection against main-chain fracture in the case of polyisobutylene.

It is difficult to explain the mechanism of protection by N_2O from our experiment. In order to explain our results, however, it may be necessary to assume that a type of energy transfer occurs in the presence of N_2O under irradiation, for a small quantity of N_2O can protect the degradation

markedly as mentioned above. On the other hand, N_2O is regarded[15] as a resonance hybrid of the following structures:

$$^-:\overset{..}{N}\!=\!\overset{+}{N}\!=\!\overset{..}{O}: \quad \leftrightarrow \quad :N\!\equiv\!\overset{+}{N}\!-\!\overset{..}{\underset{..}{O}}: ^-$$
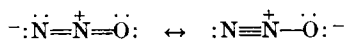
This may be helpful for the explanation of our results.

I wish to acknowledge the many helpful suggestions from Professor A. Amemiya (University of Tokyo). I am also indebted to T. Ito for his eager assistance.

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Synopsis

Polyisobutylene was irradiated by γ-rays from a Co^{60} source in vacuum and in nitrous oxide atmosphere. The irradiated specimens in N_2O were damaged to a lesser extent than those in vacuum. Irradiated specimens were dissolved in CCl_4 and their viscosity was measured at $30°C$. A plot of reciprocal of viscosity-average molecular weight against dose gives a straight line in each case for specimens irradiated in vacuum and in N_2O. Moreover, the presence of nitrous oxide reduces the extent of main-chain fracture to 63%. The degree of branching is nearly the same for all of the specimens, since Huggins' constant k' is constant ($k' = 0.40$) throughout our experiments. It can be concluded that the N_2O has a protective effect for main-chain fracture of polyisobutylene.

Résumé

On a irradié du polyisobutène par des rayons-gamma de Co-^{60} sous vide et sous atmosphère d'oxyde nitreux. Les échantillons irradiés sous N_2O sont endommagés dans une proportion moindre que sous vide. Les échantillons irradiés sont dissous dans CCl_4 et leur viscosité est mesurée à $30°C$. Un diagramme de l'inverse du poids moléculaire moyen viscosimétrique en fonction de la concentration donne une ligne droite dans chacun des cas d'irradiation, sous vide et sous N_2O. De plus, la présence d'oxyde nitreux réduit le nombre de scissions de la chaine principale à 63%. Le degré de ramification est presque le même pour tous les échantillons, de sorte que la constante de

Huggins k' est constante et égale à 0.40 dans le domaine de nos expériences.   On conclut que l'effet de N_2O est littéralement la protection contre la scission de la chaine principale dans le cas du polyisobuténe.

Zusammenfassung

Polyisobutylen wurde mit Co-60-γ-Strahlen im Vakuum und unter einer Stickoxydul-atmosphäre bestrahlt.   Die in N_2O bestrahlten Proben wurden in geringerem Ausmass angegriffen als die im Vakuum bestrahlten.   Die bestrahlten Proben wurden CCl_4 gelöst und ihre Viskosität bei 30° gemessen.   Die Auftragung des Reziprokwertes des Viskositätsmittelwertes des Molekulargewichts gegen die Dosis ergibt in allen Fällen für Bestrahlung im Vakuum und in N_2O eine Gerade.   Über dies setzt die Gegenwart von Stickoxydul die Zahl der Hauptkettenspaltungen auf 63% herab.   Der Verzweigungsgrad ist bei allen Proben etwa der gleiche, da die Huggins-Konstante bei allen Versuchen den gleichen Wert 0,40 besitzt.   Man kommt zu dem Schluss, dass die Wirkung von N_2O im Falle des Polyisobutylens buchstäblich in einem Schutze gegen Hauptkettenspaltung besteht.