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PHOTODEGRADATION BEHAVIOUR OF POLYISOBUTENE OXIDE FOR DISPOSABLE PLASTICS

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Thermally stable polyisobutene oxide was gradually degraded by ultraviolet light and finally converted to volatile compounds. Fundamental photodegradation chemistry of polyisobutene oxide and the possibility of it's application for disposable plastics were discussed.

The thermal degradation of polyethers has been extensively studied.[1] However, few reports on the photodegradation of polyethers appeared.[2] In the course of our studies for the application of polyisobutene oxide, we have found some interesting facts concerning the photodegradation behaviour and degradation products of the polymer.

polyisobutene oxide was prepared using diethyl zinc, water and t-butyl amine (molar ratio $ZnEt_2/H_2O/t\text{-}BuNH_2=3:1:1$) catalyst system in hexane at 75°C. This polymer is highly crystalline, and melts at 172°C.[3]

Polyisobutene oxide film was irradiated by 100 watt high pressure water cooled mercury arc lamp in an air stream, at 50°C and at a distance of 5cm.

In Figure 1, successive weight loss of polyisobutene oxide and the changes of reduced viscosity, $\eta sp/c$, which was measured in the o-dichlorobenzene solution at 110°C, were plotted aginst irradiation time in the process of ultraviolet photodegradation. Polyisobutene oxide film, which contained 0.5 weight percents of ultraviolet absorber, such as 2-(2'-hydroxy-5'-methyl-phenyl)-benzotriazole, was very stable in the course of the irradiation for more than 200 hours. But in the case of the polyisobutene oxide containing no ultraviolet absorber, the marked decrease in $\eta sp/c$, after which successive weight loss has occured, was observed. These facts indicate clearly that the photodegradation of polyisobutene oxide is random scission of main chain and subsequently volatile fragments are produced via reactive radical chain ends.

This phenomena is very interesting indeed from the point of view of application to disposable plastics as well as fundamental photochemistry reaction. Disposed products of polyisobutene oxide would furthermore degrade and convert gradually to volatile compounds by the action of sunlight. Thus the polymer cause no pollution of natural environments.

The photodegradation products of polyisobutene oxide in air were trapped in a cooled vessel at -78°C and were examined by gaschromatograph-mass spectrometry analysis, nuclear magnetic resonance spectroscopy (in Figure 2.), infrared spectroscopy and gas chromatography. It was shown by these analyses that the main photodegradation products were acetone, formic acid and acetic acid. N.M.R. analysis showed that molar ratios of acetone, formic acid and acetic acid were 1 : 0.7 : 0.45. Both NMR and infrared spectra had absorptions assigned to water. But another experiment has shown that water was contained in the air stream during the photodegradation reaction.

On the other hand, in the case of thermal degradation at 400°C in air, main products were acetone (42.8 weight %) and isobutene (34.2 weight %), and in the case of decomposition by concentrated nitric acid, main product was isobutyric acid (about 70 weight %).

Furthermore, under photodegradative conditions mentioned above in high purity nitrogen stream, it was found that the rate of photodegradation reaction was so small that the percentage of weight decrease was one thirteenth of that in air.

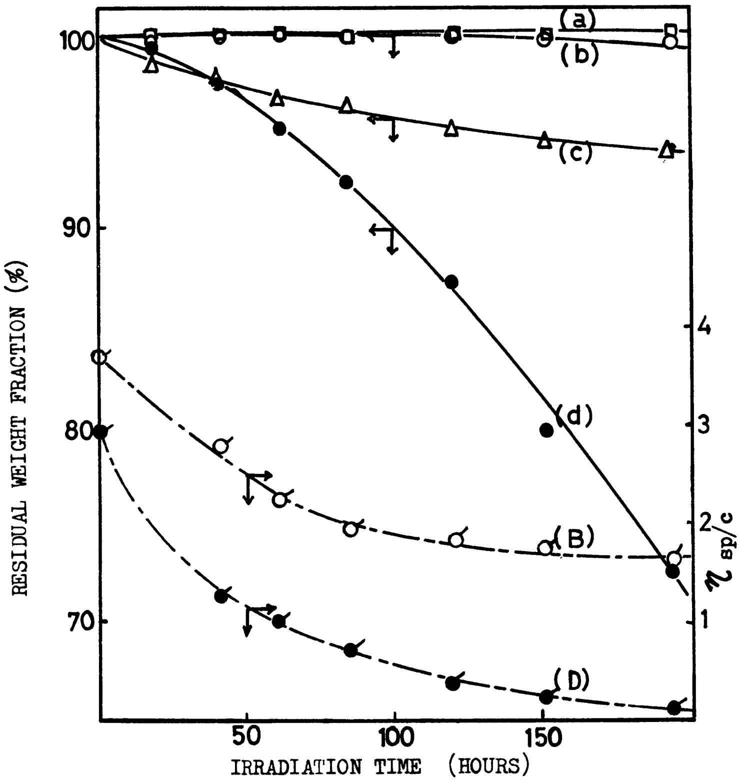

Figure 1. Changes in weight and η_{sp}/c of polyisobutene oxide and other polymers under U.V. irradiation at 50°C in air
(a) □ polystyrene, polypropylene
(b),(B) ○,○ polyisobutene oxide (added U.V. absorber)
(c) △ poly methyl methacrylate
(d),(D) ●,● polyisobutene oxide (not added U.V. absorber)
samples: 70μ thickness

As shown in Figure 1, polypropylene, polystyrene and poly methyl methacrylate, which contained no ultraviolet absorber, gave no or little volatile photodegradative fragments under these conditions. Consequently, this phenomena is apparently considered to be characteristic of ether linkage.[4] The detailed study of the mechanism of photooxidation of polyisobutene oxide is under way.

The tensile strength and elongation of bi-axial four fold stretched polyisobutene oxide films, which were irradiated carbon-arc by weather meter at a temperature of 60°C, were measured successively. These results were shown in Figure 3. The decrease of tensile strength of the polyisobutene oxide film seems to be controlled by changing the weight fraction of added ultraviolet absorber.

Formic acid, acetic acid and so on, which are photooxidation products of polyisobutene oxide, will be enclosed into the recycle system between living organism and environment, such as, for example, "tricarboxylic acid cycle", or will be furthermore degraded by the action of becteria, soil, sunlight, air and so on, to carbon dioxide and water.

Thus, the application of the photodegradable property of polyisobutene oxide to desposable plastics is very prospective as a solution of the problem of environmental pollution by synthetic polymers.

A further detailed discussion will be reported in near future.

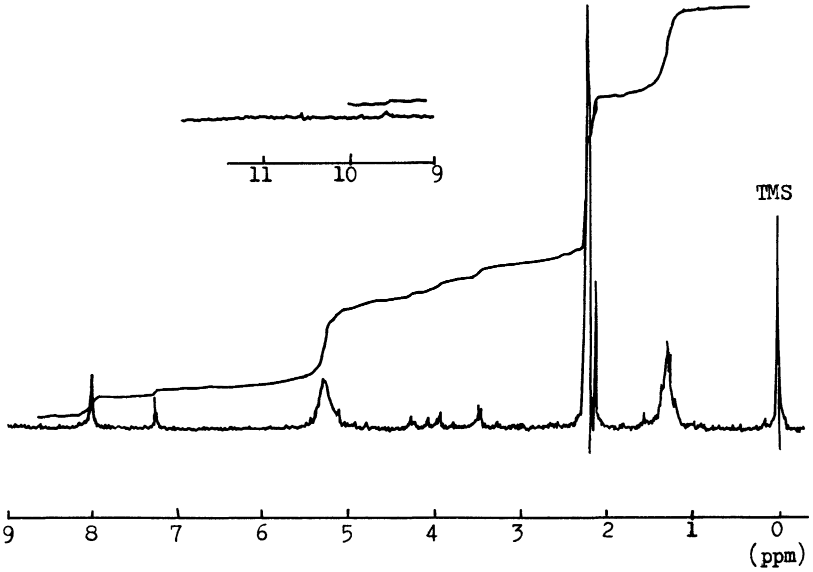

Figure 2. NMR (60MHz) spectrum of volatile products photodegradated from polyisobutene oxide at 50°C in air. The spectrum was taken at 20°C in $CDCl_3$ solution.

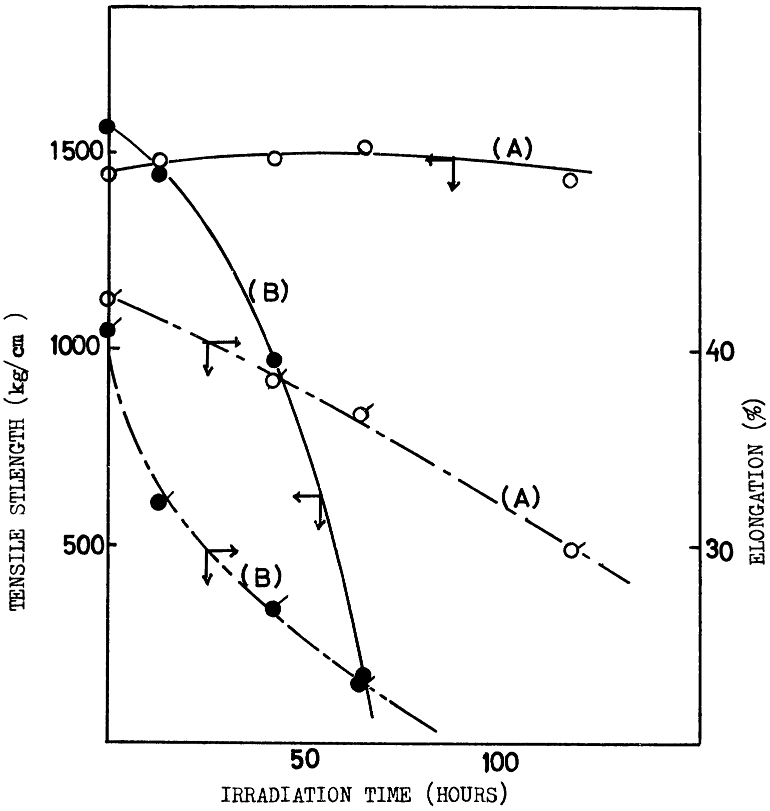

Figure 3. Changes in mechanical properties of polyisobutene oxide film (25 μ thickness) under U.V. irradiation at 60°C in air
sample: (A) ○ ○⁄ (added U.V. absorber)
(B) ● ●⁄ (not added U.V. absorber)
U.V. : carbon arc (sunshine weather meter)

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