Photo-oxidation of Polystyrene in Solution

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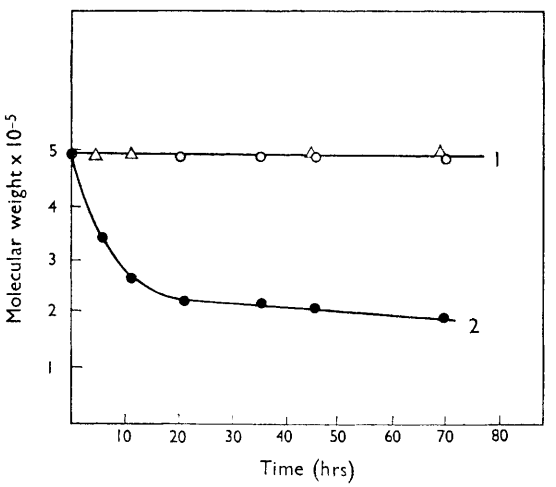
PREVIOUS studies of photo-oxidation of polystyrene have been carried out, almost exclusively on solid polymer samples, like films, and the mechanism of the gas–solid reaction is now fairly well understood.[1] Little is known about the reaction between polystyrene and oxygen in solution, and the object of this work was to investigate possible structural changes accompanying oxidation in solution.

Chloroform solutions of thermally prepared polystyrene (molecular weight $4{\cdot}95 \times 10^5$) were saturated with pure oxygen and irradiated with the output of a medium-pressure mercury arc, a Pyrex filter being interposed to limit the radiation to wavelengths greater than 3000 Å. Molecular-weight changes were investigated viscometrically, samples being withdrawn at regular intervals. The results are shown in the Figure.



FIGURE

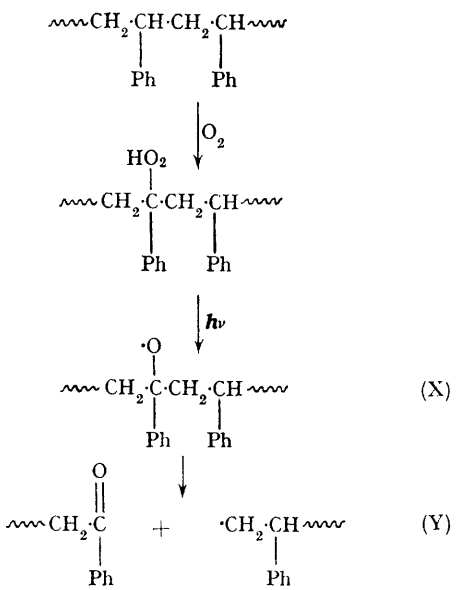
● *Chloroform solution irradiated in presence of oxygen*

△ *Chloroform solution irradiated, no oxygen present*

○ *Chloroform solution, no irradiation, but oxygen present*

It can be seen in Curve 2 that after a rapid initial decrease in molecular weight, the rate of chain scission gradually decreases, suggesting that in the early stages of the reaction, random chain scission occurs. As the reaction proceeds, however, some aggregation of smaller fragments occurs, and this is reflected by a decreased overall molecular-weight change. It can also be seen that oxygen and radiation are required simultaneously to bring about such chain scission, no such scission occurring when either is excluded. Examination of the solutions by infrared spectroscopy showed that carbonyl formation, indicated by absorption at 1740 cm.$^{-1}$, was concomitant with chain scission.

The following reaction scheme accounts for the observed features.



The primary product of oxidation is the hydroperoxide,[2] subsequent photolysis of which yields the radical (X), which in turn decomposes to yield a ketonic compound and a chain radical (Y), chain scission accompanying this reaction. Combination of two radicals like (Y) will constitute an aggregative reaction.

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[1] N. Grassie and N. A. Weir, *J. Appl. Polymer Sci.*, 1965, **9**, 965.
[2] J. L. Bolland, *Quart. Rev.*, 1949, **3**, 1.