

The Photooxidation of Polymers. IV. A Note on the Coloration of Polystyrene

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Synopsis

Yellow coloration develops in polystyrene under 2537 Å. radiation at comparable rates whether or not oxygen is present. Thus the commonly accepted view that coloration is a manifestation of oxidation is wrong. The coloration increases in intensity with time but does not move toward the red end of the spectrum, behavior which is typical of poly(vinyl chloride), polyacrylonitrile, etc., and which is due to the development of long conjugation sequences. It is suggested that the color in polystyrene is due to conjugated carbon-carbon unsaturation in the polystyrene backbone but that the lack of mobility of the molecules within the rigid polymer films prevents long sequences of double bonds becoming coplanar and color consequently moving through the spectrum. The rapid darkening of irradiated polymer which occurs on melting is probably due to relaxation of this rigidity allowing coplanarity of longer sequences.

I. INTRODUCTION

Industrially the most important adverse manifestation of the aging of polystyrene is the development of yellow coloration. This has invariably been associated with oxidation, since in the overall aging process the development of color runs parallel with other evidence of oxidation, principally spectroscopic evidence¹⁻³ for the presence of oxygen containing structures in the aged material. In the photolysis of polystyrene, described in the second paper of this series,⁴ during the progress of which oxygen was rigorously excluded from the system it was found that superficially similar coloration developed at a comparable rate and was accelerated by the presence of nitrogen. Thus an explanation must be sought for the yellow color in terms of chemical structures other than oxygenated chromophones.

Perhaps the most completely understood coloration processes in polymers are those which occur thermally in the chlorine-containing polymers, the nitrile polymers, and in poly(vinyl acetate). In these cases the initial coloration is also yellow but on prolonged exposure the color moves progressively towards the red end of the spectrum. This has been accounted for in poly(vinyl chloride), poly(vinylidene chloride), poly(vinyl acetate), polyacrylonitrile, and polymethacrylonitrile in terms of the progressive

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lengthening of carbon-carbon or carbon-nitrogen conjugated sequences. In polystyrene, however, no comparable bathochromic shift occurs. Instead the initial yellow color simply increases in intensity.

II. EXPERIMENTAL

The extent of coloration of polystyrene films was measured by the optical density at 4400 Å. by use of an E.E.L. Spectra colorimeter. The sample cell of the instrument, in which the polymer film was placed, was fitted with an adaptor provided with a vacuum stopcock and standard socket, so that the film could be alternately irradiated and its absorption measured without upsetting the system. Most important, those films irradiated in vacuum did not have to be exposed to the air during measurement.

III. RESULTS AND DISCUSSION

The characteristics of the coloration of standard films are shown in Figure 1, in which the increase in optical density at 4400 Å. is shown as a function of exposure time.

It was suggested in Part II, on both infrared and ultraviolet spectroscopic evidence, that irradiation in vacuum resulted in carbon-carbon unsatura-

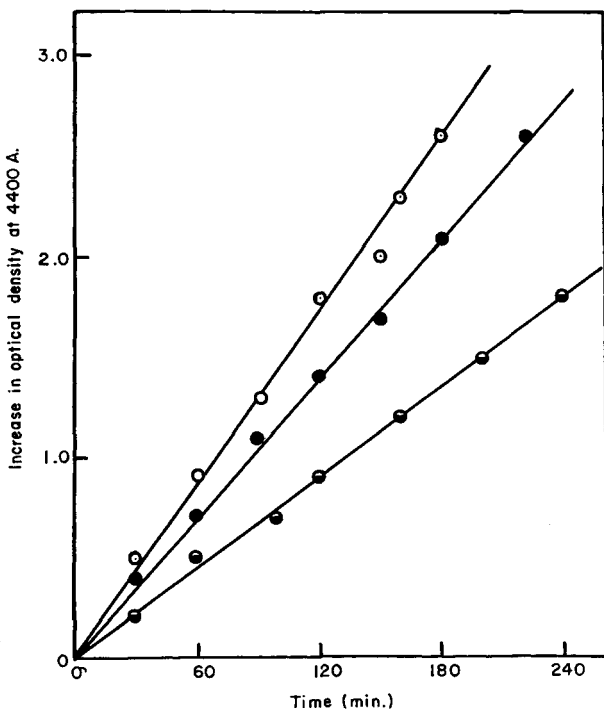


Fig. 1. Development of color in polystyrene films: (⊖) in vacuum; (●) in 600 mm. oxygen; (O) in 600 mm. nitrogen.

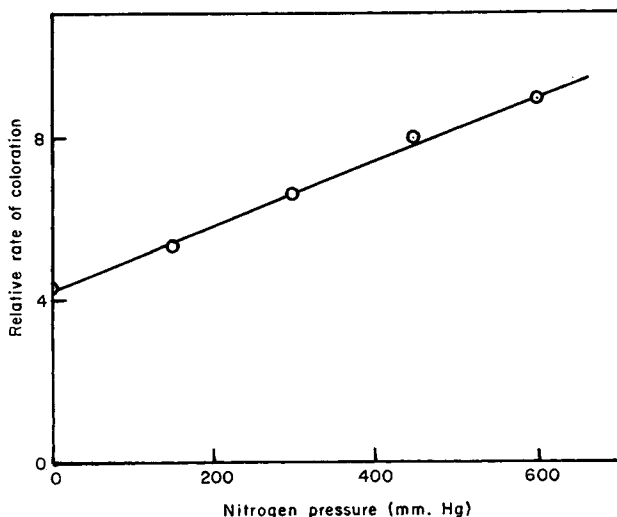
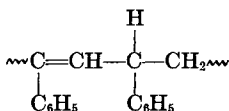


Fig. 2. Effect of nitrogen pressure on the rate of coloration of polystyrene.

tion in the polymer backbone and this was explained as being due to the abstraction by the primarily formed hydrogen atom of a hydrogen atom on an adjacent carbon atom in the same chain. The presence of the double bond will thus render the α hydrogen atom, which is also a tertiary hydrogen atom, more labile by lowering the dissociation energy of the tertiary carbon-hydrogen bond:



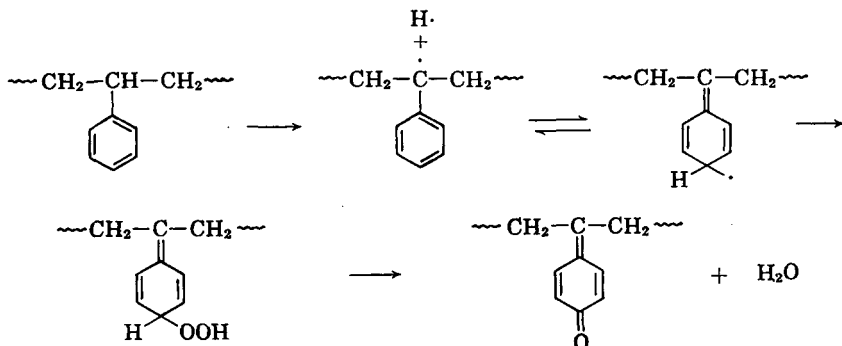
Although the photolytic production of hydrogen from unchanged portions of the polymer chains is essentially a random process by virtue of the random nature of the absorption of radiation quanta by the polymer, the probability of breaking carbon-hydrogen bonds activated in this way must be greater than that for normal tertiary bond scission. If this is so, then conjugation will result. Three double bonds in conjugation in such an environment would be necessary for absorption to move into the visible spectrum.

Further extension of conjugation in this way would result in a bathochromic shift. That it does not occur seems possibly due to the fact that coplanarity of long conjugated sequences is rendered impossible by the lack of mobility of the molecules in the rigid polymer film. When irradiated pale yellow film is heated above its melting point it turns rapidly black, probably due to a relaxation of the rigidity allowing coplanarity of longer conjugated sequences.

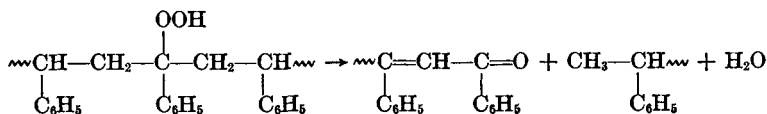
If this mechanism for color production is correct, then the behavior of nitrogen in accelerating coloration can be accounted for qualitatively in

similar terms to the acceleration by nitrogen of the appearance of unsaturation which was discussed in Part II.⁴ Thus the presence of nitrogen restricts the mobility of the primarily formed hydrogen atoms, thereby increasing the probability that they will abstract hydrogen from adjacent carbon atoms. The effect of nitrogen pressure on rate of coloration is illustrated in Figure 2.

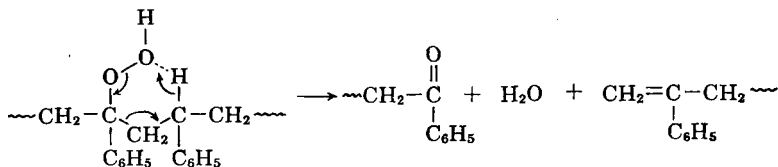
Achhammer⁵ suggested that the color of oxidized polystyrene was due to quinomethanes produced by reaction of the polystyryl radical in an alternative canonical form:



An alternative theory was put forward by Wall and his co-workers^{1,2,6} to account for the changes which occurred in the visible and ultraviolet spectra of photooxidizing polystyrene as well as for certain post-irradiation effects. They suggested that the chromophores are closely related to benzalacetophenone of which hydroperoxide is the precursor:



Since the principal characteristics of coloration in presence and absence of oxygen are similar and the rates of coloration are comparable, it is clear that the mechanisms of coloration and the end products must also be similar. Rather than the direct formation of a substituted benzalacetophenone as formulated above, it seems more probable that the hydroperoxide would decompose by way of a six-membered ring transition state:



These unsaturated centers may then activate the α -methylene groups to propagate the color reaction as in the pure photolysis process.

Clearly a great deal of work will be necessary for the clarification of these reactions. The present experiments have shown, however, that they must not be regarded as straightforward oxidation processes.

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Résumé

Une coloration jaune se développe dans le polystyrène irradié à 2537 Å à des vitesses comparables en présence ou en absence d'oxygène. C'est pourquoi l'idée, généralement admise et suivant laquelle la coloration est une manifestation de l'oxydation, est fautive. La coloration augmente en intensité avec le temps mais ne se déplace pas vers le rouge dans le spectre, comportement qui est typique dans le chlorure de polyvinyle, le polyacrylonitrile etc., et qui est dû au développement de longues séquences conjuguées. On suggère que la couleur dans le polystyrène est due à des insaturations conjuguées carbone-carbone dans la chaîne principale du polystyrène, mais que le manque de mobilité des molécules dans les films de polymère rigide empêche les longues séquences de doubles liaisons de devenir coplanaires et empêche par conséquent la couleur de se déplacer dans le spectre. L'assombrissement rapide du polymère irradié qui accompagne la fusion est probablement dû au relâchement de cette rigidité permettant la coplanarité de plus longues séquences.

Zusammenfassung

In Polystyrol entwickelt sich unter einer 2537-Å-Bestrahlung eine gelbe Verfärbung mit vergleichbarer Geschwindigkeit in An- oder Abwesenheit von Sauerstoff, daher ist der allgemein angenommene Gesichtspunkt, dass die Verfärbung oxydationsbedingt ist, falsch. Die Verfärbung nimmt mit der Zeit an Intensität zu, verschiebt sich jedoch nicht gegen das rote Ende des Spektrums, ein Verhalten, welches typisch für Polyvinylchlorid, Polyacrylnitril etc. und durch die Entwicklung langer konjugierter Sequenzen bedingt ist. Es wird angenommen, dass die Farbe bei Polystyrol durch konjugierte C—C—Doppelbindungen in der Polystyrolhauptkette bedingt ist, dass jedoch die mangelnde Beweglichkeit der Polymermoleküle innerhalb des starren Polymerfilms eine koplanare Anordnung langer Doppelbindungssequenzen und damit eine Bewegung der Farbe durch das Spektrum verhindert. Das beim Schmelzen auftretende rasche Dunkelwerden des bestrahlten Polymeren ist wahrscheinlich auf eine Relaxation dieser starren Anordnungen zurückzuführen, welche eine Koplanarität längerer Sequenzen gestattet.

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