Evidence for the Reduction of Quinones Added During Thermal Processing of Polypropylene and the Resultant Effect on Polymer Light Stability

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Synopsis

The thermal and photochemical oxidation of anthraquinone- and p-benzoquinone-doped polypropylene has been studied by absorption, luminescence, and infrared spectroscopy. Prior to irradiation, fluorescence and phosphorescence measurements showed that some of the anthraquinone and most of the p-benzoquinone had been converted into their corresponding hydroquinones during processing. The p-benzoquinone, unlike anthraquinone, also imparted a blue coloration to the polymer before irradiation, which is associated with the formation of a quinhydrone complex (or complexes). These results indicate that the quinones are thermally reduced to their corresponding hydroquinones during processing by a mechanism of hydrogen atom abstraction from the polymer substrate. On photo-oxidation, whereas anthraquinone acted as a photosensitizer, p-benzoquinone acted as a photostabilizer.

INTRODUCTION

The sensitized photodegradation of commercial synthetic polymers has been suggested as a method for combating environmental pollution by plastics litter.[1] By this method a small amount of an additive is incorporated in the polymer which results in a much more rapid deterioration of the polymer when it is exposed to sunlight out-of-doors. Of the many additives that can operate in this way, simple aromatic ketones and quinones have been shown to be particularly effective.[2,3] For polypropylene,[4] for example, the primary process of the mechanism whereby these additives initiate photodegradation has been shown to be that of a process of hydrogen atom abstraction from the polymer by the triplet state of the sensitizer (S = sensitizer, R—H = polymer):

$$S^* + R\text{—}H \rightarrow SH\cdot + R\cdot \tag{1}$$

Following the formation of the polymeric macroradical R·, the degradation of the polymer subsequently occurs by the well-known Bolland and Gee[5] mechanism. As to the sensitizer radicals, they may either react with oxygen by[6]

$$SH\cdot + O_2 \rightarrow S + HO_2\cdot \tag{2}$$

or they may dimerize (B = benzophenone or its derivatives),

$$BH\cdot + BH\cdot \rightarrow H\text{—}B\text{—}B\text{—}H \tag{3}$$
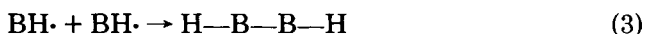
or undergo a process of disproportionation (Q = anthraquinone or derivatives),

$$QH\cdot + QH\cdot \rightarrow Q + QH_2 \tag{4}$$

However, in a recent study of the photosensitizing action of benzophenone and its derivatives in polyethylene,[7] it was concluded that during processing and prior to photodegradation, the presence of the photosensitizer induced the formation of species such as peroxide and carbonyl groups that subsequently contribute to the photodegrading effect of the sensitizer (i.e., the benzophenone acts as a pro-oxidant). However, no mechanism for this pro-oxidant effect was presented.

It was evident, therefore, that for a clearer understanding of the mechanistic action of these technologically important photosensitizers direct evidence of any chemical interaction between sensitizer and polymer during processing was required. To this end we chose for study anthraquinone and p-benzoquinone as sensitizers and polypropylene as a suitable substrate.[6] As can be seen from reaction (4) above, one of the photoproducts is the corresponding hydroquinone (QH_2). These compounds can be readily detected and identified by their characteristic fluorescence and phosphorescence spectra.[8,9]

EXPERIMENTAL

Materials. Polypropylene powder containing no commercial additives was supplied by I.C.I. (Plastics Division) Ltd. The anthraquinone and p-benzoquinone were of Analar quality and, in agreement with the literature, showed no fluorescence.[9]

Fig. 1. Fluorescence excitation (EX) and emission (EM) spectra of 9,10-dihydroxyanthracene in n-hexane (deoxygenated) (—) and polypropylene film after thermal treatment with anthraquinone at 190°C for 1 min (- - -).
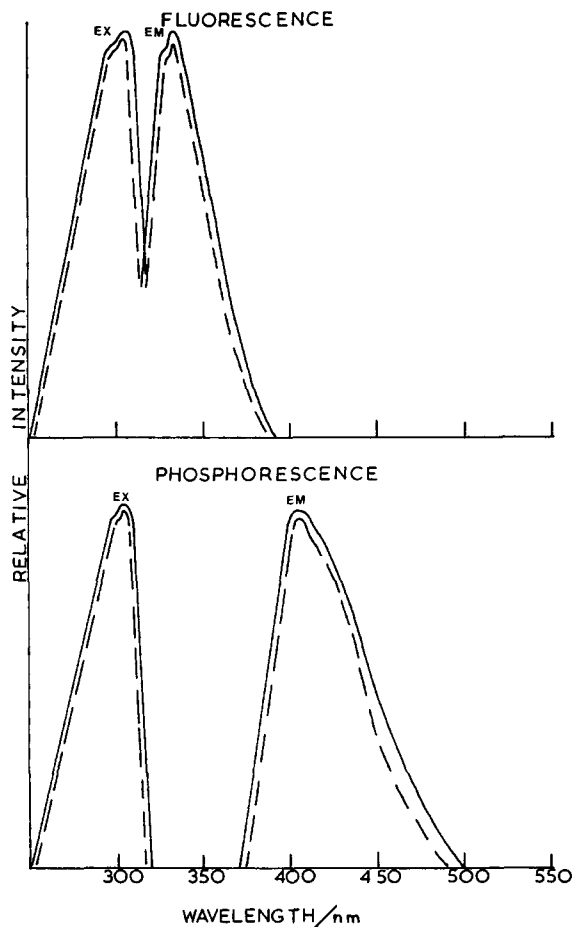
Fig. 2. Fluorescence and phosphorescence excitation (EX) and emission (EM) spectra of hydroquinone (1,4-dihydroxybenzene) in polypropylene film incorporated by solvent blending (0.5%) (—) and by thermal treatment of p-benzoquinone (0.5%) with the polymer at 190°C for 1 min (- - -). Peak heights have been normalized for comparison.

A solution of 9,10-dihydroxyanthracene was prepared by irradiating a nitrogen-saturated 10^{-4} molar solution of anthraquinone in n-hexane for 1 hr using the 365-nm line of a high-pressure mercury lamp (500 W).[8] The corresponding hydroquinone of p-benzaquinone (1,4-dihydroxybenzene) was of Analar quality.

The anthraquinone, p-benzoquinone, and 1,4-dihydroxybenzene (0.5%) were solvent blended into the polypropylene powder with a dichloromethane/isopropanol mixture (50:50 v/v), and the volatiles were removed under reduced pressure using a rotary evaporator. The polypropylene powder was then pressed into film 200μ thick at 190°C for 1 min. A control film containing no additives was similarly prepared as above.

Absorption Measurements. Absorption spectra were obtained using a Unicam SP800 spectrophotometer.

Luminescence Measurements. Corrected fluorescence and phosphorescence excitation and emission spectra were obtained using a double-grating (1200 lines/mm) Hitachi Perkin-Elmer MPF-4 Spectrofluorimeter equipped with two R-446F photomultiplier tubes.

Photo-oxidation. The polymer films were irradiated in a Xenotest-150 Weatherometer set up for natural sunlight-simulated conditions (45°C; 50% relative humidity). The rates of photo-oxidation of the polypropylene films were monitored by measuring the formation of the nonvolatile carbonylic oxidation products absorbing at 1710 cm^{-1} in the infrared using a Perkin-Elmer Model 157G spectrophotometer. Absorption by the quinones did not interfere with the measurements owing to the low concentrations employed. The build-up in carbonyl products was measured using an index:

$$\text{Carbonyl Index} = [(\log_{10} I_0/I_t)/d] \times 100$$

where I_0 = intensity of incident light, I_t = intensity of transmitted light, and d = film thickness in microns.

RESULTS AND DISCUSSION

Thermal Oxidation

Figures 1 and 2 demonstrate the fact that a thermally induced chemical interaction occurs between the quinones and polypropylene during processing. This is shown by the fact that their corresponding hydroquinones are present in the polymer after processing and before irradiation. After thermal treatment of polypropylene containing anthraquinone, strong phosphorescence of the anthraquinone was still observed, indicating that only some of the quinone had reacted. In the case of the p-benzoquinone-doped polymer, however, no phosphorescence from the quinone was observed and only the characteristic fluorescence and phosphorescence emissions of the corresponding hydroquinone were observed (Fig. 2). Further, the phosphorescence emission lifetimes for p-benzoquinone- and hydroquinone-doped polymers were also similar ($\tau_{1/e}$ = 1.2 sec). It is evident, therefore, that for the corresponding hydroquinones to
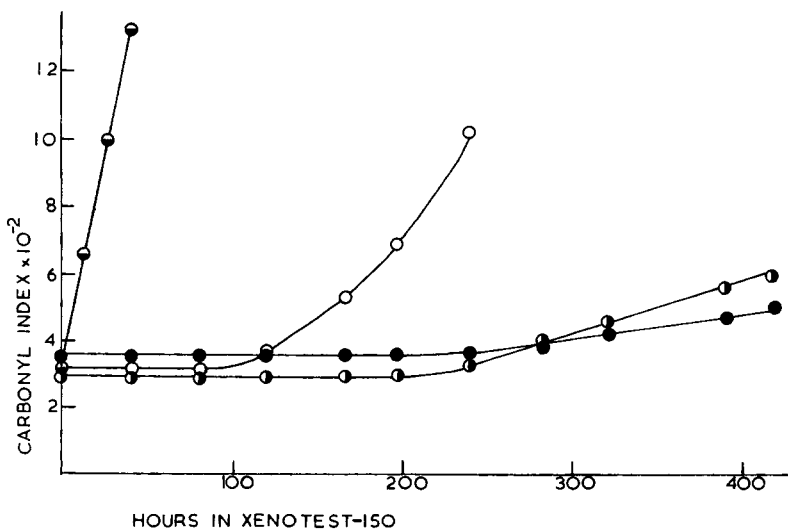
Fig. 3. Rate of photo-oxidation of polypropylene film (200μ thick) containing no additives (O), 0.5% p-benzoquinone (◑), 0.5% anthraquinone (◒), and 0.5% hydroquinone (1,4 dihydroxybenzene) (●).
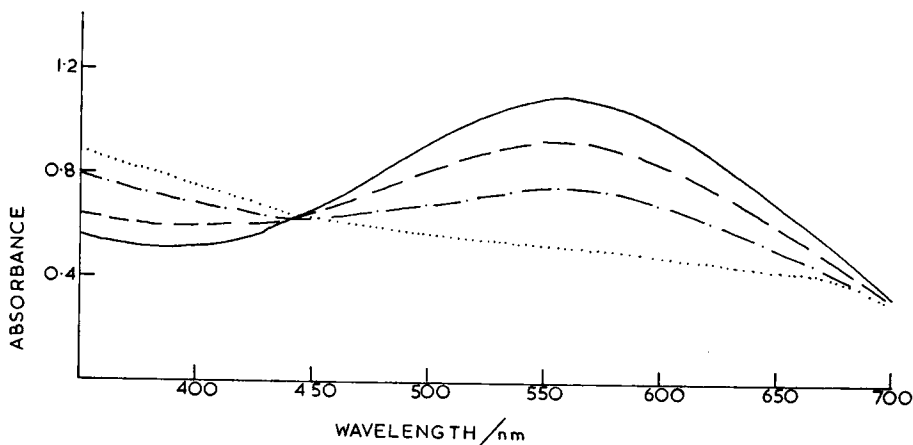
Fig. 4. Visible absorption spectrum of the blue quinhydrone complex in polypropylene film (200μ thick) after 0 hr (—), 15 hr (- - -), 30 hr (-. -.), and 50 hr of irradiation in a Xenotest-150 Weatherometer (. . . . .).

have been formed during processing, a thermally induced chemical interaction must have occurred between the quinones and the polymer by the following reaction processes (where Q = quinone):

$$Q + R\!-\!H \xrightarrow{\Delta H} QH\cdot + R\cdot \qquad (5)$$

followed by reaction (4) or by

$$QH\cdot + R\!-\!H \xrightarrow{\Delta H} QH_2 + R\cdot \qquad (6)$$
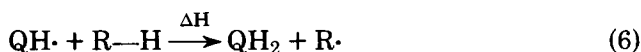
On thermally processing p-benzoquinone into polypropylene, a further interesting observation was the formation of a blue coloration in the polymer which indicates that the quinone must also undergo another thermally induced reaction (see Fig. 4). In contrast, no such effect was observed with anthraquinone. It is well known that p-benzoquinone can form loose, colored complexes with hydroquinone which are known as quinhydrones. These are believed to have the following structures[10]:


I

II
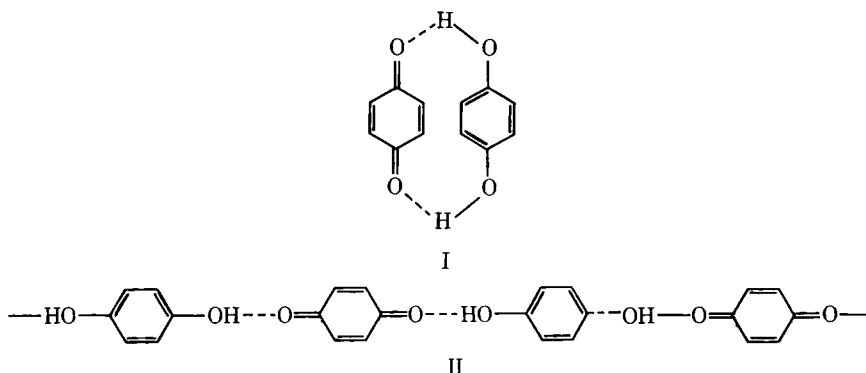
Evidently, where conditions for complexing are favorable, this would explain

the generation of the blue coloration. Hydroquinone formed by the thermal reactions (4) and (6) could complex in this manner with unreacted p-benzoquinone. Indeed, the fact that no phosphorescence was observed from the p-benzoquinone after processing suggests that it must all have reacted to form the hydroquinone and quinhydrone complex (or complexes). The formation of such complexes between anthraquinone and anthrahydroquinone would appear to be unlikely on steric grounds.

Photo-oxidation

The photo-oxidation experiments show two interesting features. First, whereas anthraquinone acts as a strong photosensitizer, p-benzoquinone acts as a light stabilizer (Fig. 3). The results also show that p-benzoquinone exhibits a protective effect similar to that of the hydroquinone (1,4-dihydroxybenzene) itself. The antioxidant mechanisms of phenolic compounds are well established,[11] and the light-stabilizing action exhibited by hydroquinone is probably due to its ability to terminate propagating free-radical species to form nonreactive products, for example:

$$R\cdot + QH_2 \rightarrow R\text{—}H + \cdot QH \text{ (inactive radical)} \qquad (7)$$
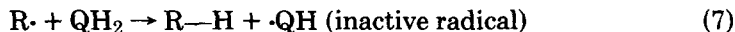
Second, the blue quinhydrone complex (or complexes) is relatively unstable to light and disappears within the early part of the induction period (i.e., long before the onset of carbonyl formation in the polymer (Fig. 4). At present, we have no clear indication of the products formed from the decomposition, but it would seem reasonable that a scission process would occur at the hydrogen bond:

$$(8)$$
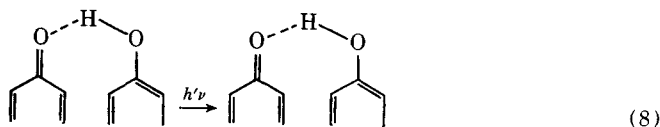
As a consequence of this scission, it may be expected that free photoactive benzoquinone could react by reaction (1). The macroradical $R\cdot$ would thus be available for reaction with oxygen by the Bolland and Gee[5] mechanism:

$$R\cdot + O_2 \rightarrow RO_2\cdot \xrightarrow{R\text{—}H} RO_2H + R\cdot \qquad (9)$$
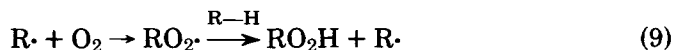
However, it is seen that the free hydroquinone is likely to be in a position close to where the macroradical $R\cdot$ is formed and could thus effectively compete with reaction (9) forming the well-known stable hydroxyquinone radical[11] by reaction (7). In fact, no phosphorescence could be detected from p-benzoquinone during irradiation, indicating that it must undergo further reaction as soon as it is formed.

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