

Mechanism of the Benzophenone-Sensitized Photodegradation of Polypropylene

D. J. HARPER and J. F. McKELLAR,* *Imperial Chemical Industries Ltd.,
Organics Division, Blackley, Manchester M93DA, England*

Synopsis

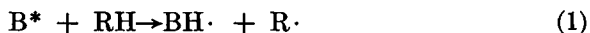
The photodegradation of polypropylene sensitized by benzophenone has been studied under accelerated light-aging conditions using a Xenotest 150. Degradation of the polymer and consumption of the benzophenone was monitored by infrared spectroscopy. The results indicate that hydrogen atom abstraction from the polymer, by photo-excited benzophenone, is the major primary process in the mechanism of sensitized photodegradation.

INTRODUCTION

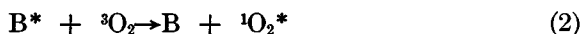
Sensitized photodegradation is a possible method for combating environmental pollution by plastic litter,¹ and one way of achieving this is to add a photochemically active compound to the polymer that promotes its degradation out-of-doors.

The polyolefins are widely used in the manufacture of containers and wrappers for packaging purposes, and in earlier communications^{2,3} we reported that the photosensitized degradation of commercial polypropylene is accelerated when it contains small amounts of a simple aromatic ketone such as benzophenone. This observation is of possible commercial value as many of these ketones are colorless, and there is also evidence⁴ that some are sufficiently nontoxic to permit their use in foodstuff applications.

In this paper we report experiments on the benzophenone-sensitized photodegradation of polypropylene. Our results, we believe, have also considerable significance to the understanding of the more general problem of the sensitized photodegradation of polymers by carbonyl-type compounds. For example, there is currently much debate on the relative importance of the hydrogen atom abstraction.



and singlet oxygen activation,



* Present address: Department of Chemistry and Applied Chemistry, University of Salford, Salford M54WT, England.

as initiating processes in the mechanism of photodegradation.⁵⁻⁸ The important technological problem of the phototendering of cellulosic fabrics by the anthraquinonoid vat dyes is a case in point.⁹

EXPERIMENTAL

Fabrication of Polypropylene Plaques

Polypropylene powder (HF20 manufactured by ICI Ltd.) was slurred with an ethanolic solution of the additives, and the volatiles were evaporated under reduced pressure using a rotary evaporator. The compositions always included calcium stearate (0.4%); dilauryl thiodipropionate (0.25%); and 1,1,3-tris[3-*t*-butyl-4-hydroxy-6-methylphenyl]butane (0.1%).

The dry powder was extruded at 230°C, and the extrudate was compressed using a heated platen press into 0.05-cm-thick plaques at 190°C.

Light Aging of Polypropylene Plaques

These were exposed for measured intervals of time in a Xenotest 150 at a temperature of 45°C and relative humidity of 60%.

The progress of photo-oxidation was monitored by determining the absorbance of the carbonyl band of the carbonyl oxidation products at their λ_{\max} of 5.85 μm , the infrared spectra of the plaque being recorded on a Perkin-Elmer 257 grating infrared spectrometer.

The photolytic destruction of the benzophenone was similarly determined, using the carbonyl band at 5.99 μm .

RESULTS

Initiation of Photo-oxidation of Polypropylene by Benzophenone

Figure 1 compares the progress of photo-oxidation of polypropylene plaques (a) in the presence of 0.1% benzophenone and (b) in its absence.

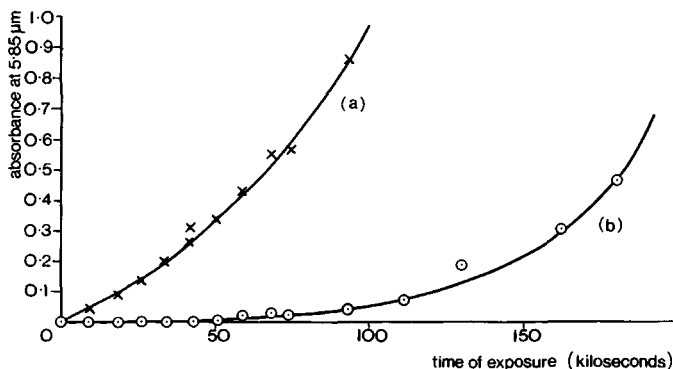


Fig. 1. Progress of photo-oxidation of 0.05-cm-thick polypropylene plaques containing (a) 0.1% benzophenone, (b) no benzophenone.

In the presence of the ketone, the normal induction period (observed in curve b) is absent and the autocatalytic oxidation begins immediately at a (comparatively) very rapid rate.

Photolytic Destruction of Benzophenone

Figure 2 compares the change in absorbance at $5.99 \mu\text{m}$ during light aging in the two plaques described above. It is evident that the aromatic carbonyl is being removed or destroyed. That this was a photochemical process was demonstrated by irradiating two other plaques containing

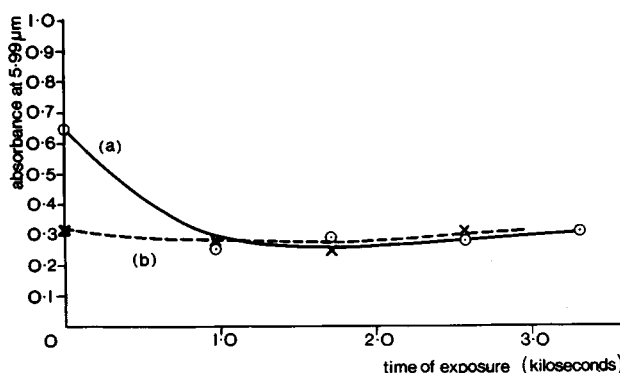


Fig. 2. Change in absorbance at $5.99 \mu\text{m}$ observed in 0.05-cm-thick polypropylene plaques during light aging: (a) plaque containing 0.1% benzophenone; (b) plaque containing no benzophenone.

0.1% benzophenone in the Xenotest, both of which were sealed inside polythene envelopes and one of them protected by black paper. The unprotected sample exhibited a similar loss of benzophenone while the one protected from the radiation showed no loss.

Comparison of Photolysis of Benzophenone in Polypropylene Under Air and Nitrogen

A series of experiments were conducted in which pairs of polypropylene plaques containing either 0.1% or 1.0% benzophenone and contained in separate Pyrex Cells were exposed in the Xenotest 150. One of these cells was left open to the atmosphere and the other was sealed after flushing with pure nitrogen for 15 hr.

Table I compares the extent of the loss of benzophenone under the two sets of conditions. The results indicate a slightly greater loss in an atmosphere of nitrogen than in one of air, for plaques containing 0.1% benzophenone.

TABLE I
Comparison of Extent of Photolysis of Benzophenone
(0.1%) in Polypropylene Under Air and Nitrogen

Environment of plaques	Period of exposure in Xenotest 150, min	Absorbance at 5.99 μm		Benzophenone loss, %
		Before exposure	After exposure	
Air	45	.0804	.0462	42.5
Nitrogen		.0569	.0269	52.7
Air	70	.1086	.0338	68.9
Nitrogen		.0918	.0233	74.6

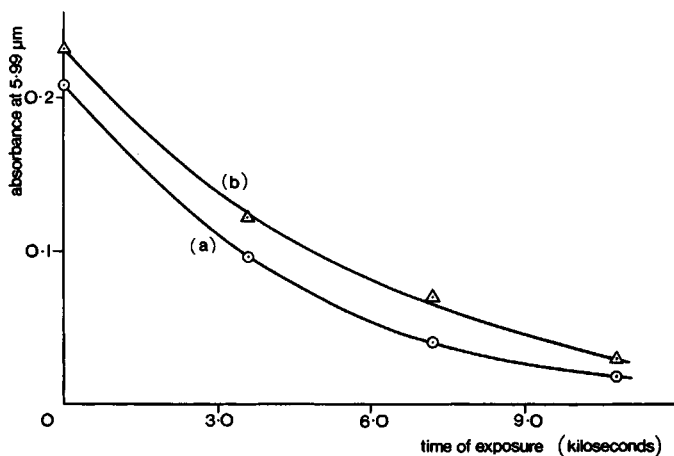


Fig. 3. Progress of loss of benzophenone from 0.05-cm-thick polypropylene plaques during light aging: (a) in an atmosphere of nitrogen (b) in air.

Similar comparisons, in greater detail, for plaques containing 1.0% benzophenone are presented graphically in Figure 3. There is no significant difference in the rate of photolysis of benzophenone evident from these experiments. Duplicate studies using other plaques confirmed this result.

The pairs of samples studied were cut from adjacent areas of large plaques and therefore had the same thermal histories. They were then simultaneously light aged. The samples varied slightly in thickness and moderately in concentration of benzophenone. The latter variation probably arose from incomplete mixing during extrusion. For these reasons results on two pairs of plaques, displaying reversed relative absorbances due to benzophenone, are presented in Table I. The results in the two sets are similar.

Similarly, graphically treated results on pairs of plaques containing 1.0% benzophenone (e.g., Fig. 3) gave the same result independently of the relative absorbances of benzophenone in the plaques.

DISCUSSION

The important observations from this investigation can be summarized as follows:

1. Polymer without added benzophenone exhibited a definite induction period followed by a relatively slow rate of degradation.
2. Polymer containing benzophenone exhibited no induction period and an initially high rate of degradation; the ketone was consumed during this process.
3. The comparison experiments conducted under atmospheres of air and nitrogen clearly indicate little participation by excited singlet oxygen during the sensitized degradation process.
4. The small retarding effect of air on the consumption of benzophenone suggests that oxygen may diminish the rate of the primary photochemical process involving initial abstraction of a hydrogen atom from the polymer, i.e., reaction (1).

However, although our results clearly indicate the importance of the hydrogen atom-abstrating process, the question still remains, "Do singlet oxygen molecules, once generated attack the polymer substrate, and could their presence contribute significantly to the degradation process?" There is now much evidence⁷ to show that singlet oxygen molecules are efficiently generated by reaction such as (2) above. Indeed, workers¹⁰ studying the unsensitized photodegradation of polyolefins have postulated that singlet oxygen molecules, generated by the quenching of photo-excited carbonyl groups native to the polymer (i.e., carbonyls generated for example by oxidation during fabrication), attack the substrate and that this constitutes a major process in the photodegradation mechanism. One interesting aspect here is the observation, reported in our earlier paper,³ that addition of the aliphatic ketone stearone had, compared to that of benzophenone, no significant effect on the rate of polymer degradation.

Of some significance to this question, however, are the recent results of Kaplan and Kelleher¹¹ and their reference to unpublished work by Fahrenholtz.¹² These workers report that when singlet oxygen molecules were generated using a microwave discharge, there was definite evidence of oxidative degradation with the polymers polyethylene and cellulose. Recently, however, it has been pointed out¹³ that in experiments of the type performed by Kaplan and Kelleher¹¹ and Fahrenholtz,¹² there are small amounts of oxygen atoms in the gas stream. These would be highly reactive toward many types of polymer substrate. Thus, a satisfactory answer to the above question cannot be given until the validity of the microwave discharge experiments has been checked. Work of this type is being pursued by one of us (J.F.McK).

CONCLUSIONS

The benzophenone-sensitized photo-oxidation of polypropylene is sensitized by a primary photochemical process of hydrogen abstraction from the

polymer substrate, and even if singlet oxygen is produced in significant amounts, its overall contribution as an initiating process must be small.

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