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Photochemistry of Benzoin Derivatives in an Oxygenated Polymeric Medium

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SUMMARY

Investigation of the photochemistry of benzoin derivatives in a polymer medium leads to the suggestion that oxygen play an important part in the first processes which occur under U.V. irradiation. This is of interest for the understanding of the photocrosslinking process.

INTRODUCTION

In recent years, the photochemistry of benzoin derivatives has regained its interest owing to the wide use of these substances as photosensitive initiators for photopolymerization or photocrosslinking [1]. However, most of the experiments were often restricted to studies in oxygen free solutions [2][3], which do not always correspond to the usual experimental conditions. This paper is devoted to the behaviour of several benzoin molecules dispersed in an oxygenated reactive medium such as an EPDM elastomer film : poly(ethylene-co-propylene-co-1,4 hexadiene).

EXPERIMENTAL

Four benzoin derivatives have been used : 2,2-dimethoxy-2-phenylacetophenone (I), 2-methoxy-2-phenylacetophenone (II), 2-ethoxy-2-phenylacetophenone (III) and 2-phenylacetophenone (IV). Samples of I, II, III, IV dispersed in EPDM films (10% w/w) were irradiated with a SP 500 W Philips lamp in the 360 nm range. The films were prepared from elastomer solutions either in air or nitrogen atmosphere (it is well known that total outgassing of the solution is difficult and the term "in nitrogen atmosphere" does not mean "really oxygen free system"). After irradiation, the films were extracted for 4 hours by refluxing with methanol, in order to eliminate the reaction products which were not grafted onto the polymer backbone.

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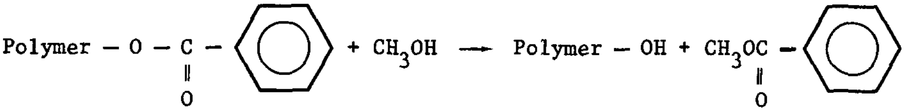
RESULTS AND DISCUSSION

After extraction, the study of several I.R. spectral lines characteristic of well-known functions belonging to the polymeric system led to the following conclusions :

- Peroxide functions appear only when the irradiation is carried out in air atmosphere.

- The band of the ketone group (1690 cm^{-1}) decreases whereas four bands centered about 1730, 1280, 1110, 710 cm^{-1} are enhanced. These latter bands are assigned to o-alkyl aromatic esters. This assumption was checked by performing a reaction on the film (swollen with toluene) with methanol and sodium hydroxide as catalyst (by refluxing at 60°C). After extraction, a decrease of the ester bands was observed, in accordance with the reaction :



- In IV, the amount of ester is significantly lower than in the I, II, III molecules. Moreover, the relative yield between the grafted ester and the soluble alkyl-ester is affected by oxygen since few ester functions are grafted on the polymer in nitrogen atmosphere.

- A weak band at about 1680 cm^{-1} points to the presence of a ketone band with a modified environment, presumably Ph – CO – Polymer ; its intensity seems to be dependent on the presence of oxygen, as this band was not detectable within experimental error upon a film exposed to air.

- A band about 1780 cm^{-1} may be assigned to a perbenzoate function ; it does not occur in irradiated oxygen-free systems.

The major liquid products formed by irradiation both in air and nitrogen atmosphere as revealed by gas chromatography on methanolic solutions were benzaldehyde in all cases, methyl benzoate and acetophenone (with I and II), ethyl benzoate (with III) ; no benzoate was obtained with IV. In the case of I, the ratio benzaldehyde/alkyl ester was lower than in II and III, by an order of magnitude suggesting the formation of a more significant amount of ester since the same efficiency of the hydrogen abstraction reaction leading to benzaldehyde may be assumed.

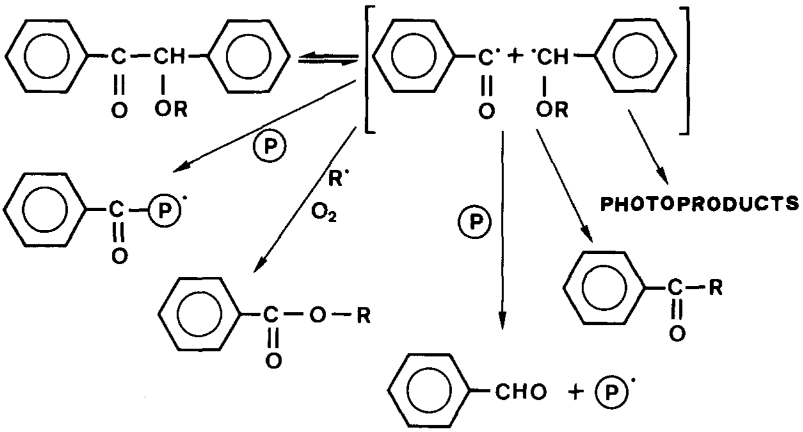
From I.R. quantitative measurements obtained both with the unextracted film and the extracted film (Table 1), some typical points are appeared : no benzoate was observed with IV ; the amount of benzoate was significantly lower in oxygen-free system except for I (this supports the assumption of an intramolecular reaction of the substituted benzyl radical yielding the alkylester, as reported in ref.2 ; moreover a more significant amount of ester is even observed in nitrogen atmosphere related to competiting processes starting from the benzoyl-substituted benzyl radical pair) ; the free/bound benzoate ratios calculated in II and III are dependent upon the oxygen concentration suggesting particular reactivity of the methoxy and ethoxy radicals.

	IRRADIATION			
	in air		in nitrogen	
	bound benzoate	free benzoate	bound benzoate	free benzoate
Dimethoxybenzoin (I)	37	56	23	77
Methoxybenzoin (II)	35	27	10	7
Ethoxybenzoin (III)	40	65	14	26
Deoxybenzoin (IV)	21	-	8	-

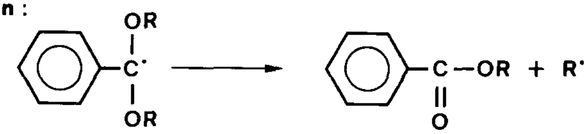
TABLE 1 : Amount of benzoate (in arbitrary units) obtained in irradiation conducted in air and in nitrogen. From I.R. calculations.

Great interest is attached to these results which provide an insight into the first steps of the processes occuring in benzoin molecules when they act as photoinitiators during U.V. curing in air atmosphere. In fact, the influence of oxygen via peroxide formation is clearly established. Since it seems difficult to conceive the formation of soluble methyl benzoate from II in nitrogen atmosphere, it may be assumed that in a really oxygen-free system, no significant reaction should occur between the photofragments and the polymer (excepting a hydrogen abstraction reaction with the benzoyl radical or a direct attack of this radical upon the double bonds of the polymer) so that no subsequent crosslinking of EPDM can occur in this way.

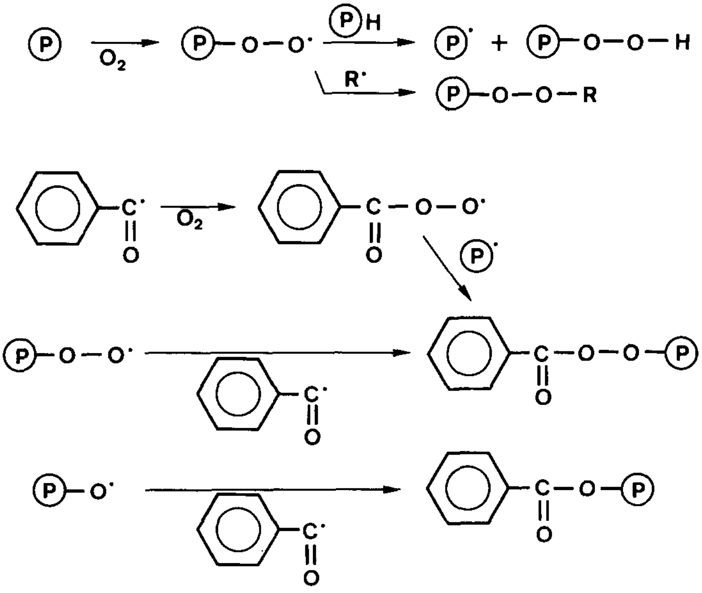
Assuming that Ⓟ represents the polymer, the following reaction schemes may be written :



in addition :



The influence of the oxygen concentration upon the reactions between the polymer and the benzoyl radical may be accounted for by the following processes :



In conclusion, emphasis should be laid on the importance of oxygen in the photochemistry of benzoin in polymer matrix, together with the failure of this surmise in the reaction scheme of deoxybenzoin (IV) as compared with I, II, III benzoin ether, as it appears that the concentration of grafted ester is low in irradiated deoxybenzoin elastomer system. This means that the generation of peroxide functions is not favourable in the case of this initiator. Thus appealing questions arise as to the generation and the decomposition of these functions via a radical mechanism as well as a direct sensitization through energy transfer. Complete results about the evolution of the macroradical and the physical properties of the polymeric samples will be discussed in another report in connection with the photocrosslinking process [4].

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