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The Non Participation of $^1O_2$ in the Photo-Oxidation of Polybutadiene

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SUMMARY

Experiments performed with polybutadiene (PBD) films containing singlet oxygen quenchers, such as: β-carotene, 1,4-diazabicyclo|2.2.2|octane (DABCO) and 1,3-diphenylisobenzofuran (DPBF), show that the photo-oxidation of PBD is not initiated by singlet oxygen. On the other hand, the oxidation of a film of PBD pre-irradiated under inert atmosphere strongly suggests that it is a free radical initiated process.

INTRODUCTION

The production of hydroperoxides by the reaction of singlet oxygen with alkyl substituted olefins has been known since 1943 (SCHENCK 1943). It has been shown that this reaction also occurs when PBD, in the solid state or in solution, is allowed to react with singlet oxygen produced by chemical reaction or microwave discharge (KAPLAN and KELLEHER 1970, BRECK et al. 1974). A very detailed study of the reaction of PBD and $^1O_2$ was made and reviewed by RABEK and RÅNBY (1978). On the other hand, a quantitative study of PBD which contains dye additives showed that the quantum yield for the formation of hydroperoxides decreases by two orders of magnitude when using films instead of solutions. According to these authors, this reduction cannot be assigned to the reduction in the quantum yield for the formation of $^1O_2$, since under the same conditions the authors observed the sensitized oxidation of an aromatic compound with a high quantum yield (ZOLOTOI et al. 1976). It has also been reported that the presence of singlet oxygen had little effect on the kinetics and mechanism of the photo-oxidation of PBD in the solid state (IVANOV and SHLYAPINTOKH 1978). On the other hand, effective singlet oxygen quenchers, such as carotenoids isolated from plants, were shown to effectivelly stabilize cis-1,4-polybutadiene against photo-oxidation (RABEK and LALA 1980). In light of the above mentioned reports it can be safely concluded that singlet oxygen is susceptible to react with PBD. However, this does not demonstrate that $^1O_2$ really makes any considerable contribution to the photo-oxidation of PBD in the absence of an external source of excited oxygen (GEUSKENS and DAVID 1979).

In this work we have studied the photo-oxidation kinetics of polybutadiene films in the solid state containing well known singlet oxygen quenchers. We present strong evidence to support the non participation of singlet oxygen in the photo-oxidation of commercially available polybutadiene.

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EXPERIMENTAL

PBD furnished by COPERBO was characterized by its i.r. spectrum as a copolymer containing 38, 48 and 14 % of cis-1,4, trans-1,4 and 1,2-vinylic units, respectivelly. It was purified in order to remove anti-oxidants by dissolution in distilled chloroform and precipitation by addition of this solution to methanol. This procedure was repeated three times and the sample was stored in the dark at -10°C prior to use.

Films of ca. 30 μm thickness were obtained by casting a chloroform solution of the purified polymer onto teflon plates. Films containing β-carotene, DABCO and DPBF were prepared by dissolving a weighed amount of the additive together with the polymer and casting this solution. The films were fixed on stainless steel rings.

Irradiations were performed with a Tohwalite TB 20 BLB lamp (maximum of emission centered at 350 nm). The formation of hydroperoxides was monitored by the absorption at 3400 cm^{-1} in the i.r. spectra measured with a JASCO model A-202 spectrophotometer. Absorption of the films at 350 nm were monitored using a MICRONAL model B280 single bean spectrophotometer. In order to avoid errors caused by fluctuation in the light intensity of the source and to obtain comparative results, we irradiated both the film of pure PBD and the films containing the additives at the same time.

RESULTS

The kinetics for the formation of hydroperoxides during the photo-oxidation of films containing 0.0, 0.5 and 2.0 % of β-carotene is shown in figure 1. We observe a drastic reduction of the induction period of the reaction with the increase in β-carotene concentration. This indicates that this compound exerts a strong initiation effect on the formation of

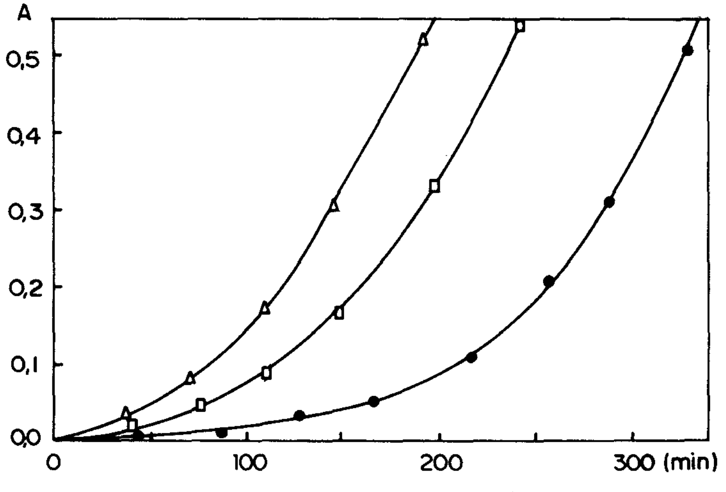

FIG. 1. Changes in the absorption at 3400 cm^{-1} in the i.r. spectra of PBD films containing β-carotene: (●) 0.0%, (□) 0.5% and (Δ) 2.0%

hydroperoxides, hence on the photo-oxidation. Figure 2 shows the effect of DABCO in concentrations of 0.0, 1.0, 2.5, 5.0 and 10.0 %. We observe a small retarding effect for the 1.0 % concentration and a small accelerating effect for 10.0 %. In the intermediate concentrations there is a coincidence of the curves within the experimental error.

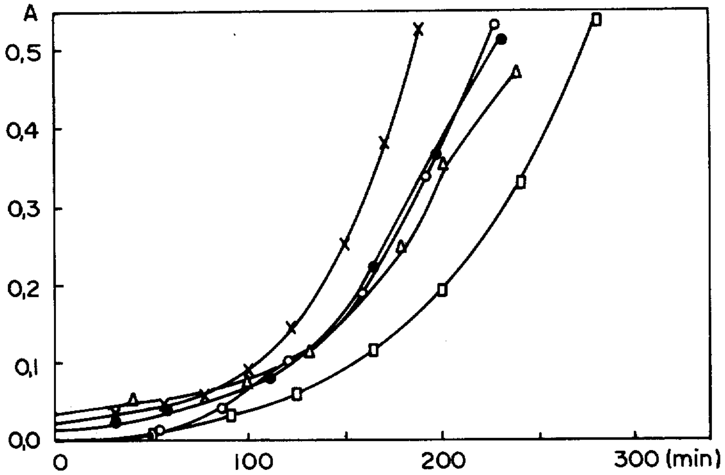

FIG. 2. Changes in the absorption at 3400 cm^{-1} in the i.r. spectra of PBD films containing DABCO: (o) 0.0%, (□) 1.0%, (Δ) 2.5%, (●) 5.0% and (X) 10.0%

Figure 3 shows the effect of DPBF in concentrations of 0.5, 2.0 and 4.0 %. In this case the time necessary to observe complete oxidation of the films containing the additive is not sufficient to initiate the photo-oxidation of the pure polymer sample. Also, the additive-containing films show no induction period in the kinetic curves, evidencing a lack of inhibiting effect.

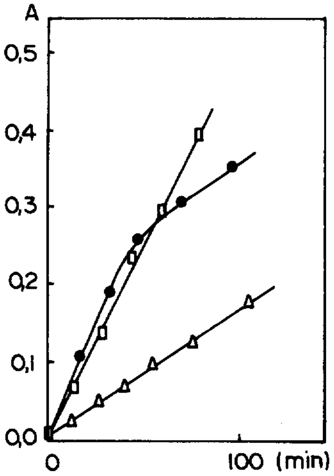

FIG. 3. Changes in the absorption at 3400 cm^{-1} in the i.r. spectrum of PBD films containing DPBF: (Δ) 0.5%, (□) 2.0% and (●) 4.0%

DISCUSSION

The deactivation of $^1O_2$ can occur by energy transfer to a quencher or by chemical quenching. The rate constant for the quenching reaction (kq) is a measure of the effectiveness of the quencher to deactivate $^1O_2$ to the $^3O_2$ ground state. A great number of compounds are known to quench singlet oxygen. Among them, β-carotene has the highest kq (1.4 to 3.0 x 10^9 $mol^{-1}.sec^{-1}$, depending on the solvent) and in a polystyrene matrix it was shown to quench $^1O_2$ with a kq of 4.3 x 10^8 $mol^{-1}.sec^{-1}$ (NOVAKOWSKA 1978). Another class of compounds that quenches $^1O_2$ efficiently are the amines. DABCO has a kq three orders of magnitude lower than β-carotene but it has the advantage of not absorbing light at wavelengths longer than 300 nm. According to BELLUS (1978) these two compounds are widely used as a diagnostic test for the participation of $^1O_2$ in oxygenation reactions. DPBF is reported to be an efficient chemical quencher of $^1O_2$. Because of the readiness with which it is converted to o-dibenzoylbenzene by $^1O_2$, this reaction has also been used as a diagnostic for the presence of $^1O_2$ in both chemical and biological processes (CHAN 1970). For these reasons we performed our experiments with polymer films containing these compounds.

For both energy transfer and chemical quenching, we should expect an increase in stability of the polymer upon the addition of a quencher, if the photo-oxidation is singlet oxygen initiated. This stabilization effect should be proportional to the quencher concentration. The opposite is observed for β-carotene and DPBF and no net effect is observed for DABCO. On the other hand, in a complementary experiment we compared the thermal oxidation at 90°C of a film of PBD pre-irradiated with uv light under an inert atmosphere with a non irradiated film. The former oxidizes to a large extent after 15 minutes while the second, in exactly the same conditions, shows no change in the i.r. spectrum. This experiment provides support for the assumption that the initiation step of the photo-oxidation is the photochemical production of free radicals. The crosslinking of a film irradiated for a longer period with uv light under an inert atmosphere also corroborates this conclusion.

We believe that our results provide strong evidence for the non participation of excited singlet oxygen in the photo-oxidation of commercial polybutadiene.

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