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## Photochemical Behavior of Poly(vinyl Chloride) Stabilized by Dibutyltin Thioglycolate

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### ABSTRACT

The effect of structure and composition changes which occur during processing on the ultimate photochemical stability of PVC samples stabilized with various concentrations of dibutyl tin-bis-isooctylglycolate ( $Y_2SnBu_2$ ) have been studied. The blending operation improves the photostability of the polymer, i.e., induces the destruction of some chromophores which existed after polymerization. The specific effect of some by-products of the stabilizer has been examined; i.e., dibutyltin dichloride, as the stabilizer  $Y_2SnBu_2$ , limits the propagation of the photooxidation reaction and induces the formation of long conjugated polyenes, and thus the coloration phenomena.

## INTRODUCTION

The photochemical behavior of PVC stabilized with organotin compounds has been the subject of many studies. Practitioners make a clear distinction between organotin maleates whose excellent performance is known and organotin mercaptides which may induce a deep coloration phenomenon [1-3]. Wirth [1] and Szabo [2] support the hypothesis of a specific effect of UV radiation on the sulfur moiety of organotin mercaptides. Chauffoureaux [4] imputes the rapid darkening of PVC stabilized with dioctyltin dimercaptide to a strong antioxidant effect. Rabek et al. [5] examined the influence of an organotin thioglycolate on the photochemical stability of PVC and found a contradictory result. This stabilizer decreases the dehydrochlorination rate, increases the photooxidation rate and retards the coloration phenomena.

It has been previously shown that important changes in structure and composition occur during processing of PVC stabilized with various concentration of dibutyltin-bis-isooctyl thioglycolate ( $C_8H_{17}OCO-CH_2S)_2Sn(C_4H_9)_2$  represented as  $Y_2SnBu_2$  [6]. This paper deals with the effect of these changes and especially the specific influence of some by-products of the stabilizer on the ultimate photochemical stability.

## EXPERIMENTAL

Materials

We used a bulk polymer ( $\bar{M}_n = 39,900$ ) with an industrial grade stabilizer Stavinor Sn 3200. The following by-products were studied:  $Bu_2SnCl_2$ ,  $BuSnCl_3$ ,  $Bu_2SnO$ ,  $YClSnBu_2$ , and YH (analytical grades).

Processing, Film Preparation

Blends containing respectively 0.75, 1, 1.25, 1.50, and 1.75% (by weight) of stabilizer were prepared in a Papenmeier at 120°C and then extruded at 180-200°C in the form of rigid sections. Samples were taken before (blends) and after extrusion (extrudates). From each sample, two films are made: one by compression molding at 130°C, to study the influence of residual stabilizer and by-products; the other by film casting of the "pure" polymer in a THF solution, after elimination of the additives by reprecipitation, to study the influence of the structural changes in the PVC macromolecules which appeared during the two steps of the processing. The by-products containing PVC films were also cast from THF solutions as the check sample. The films thicknesses were  $150 \pm 20 \mu m$ .

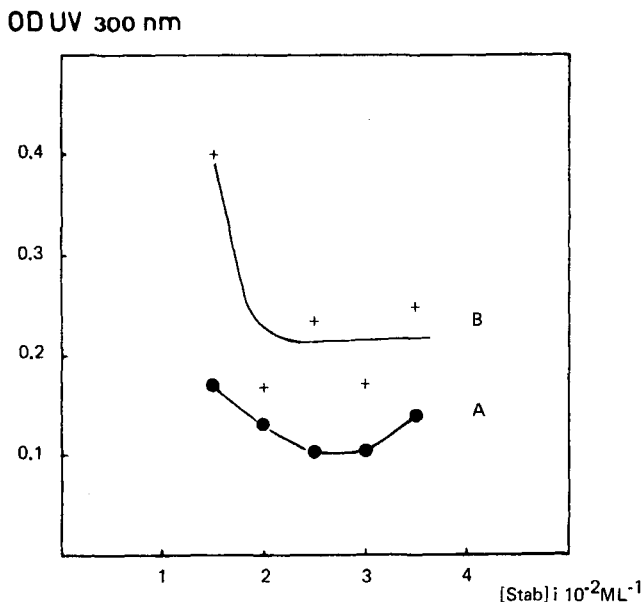


FIG. 1. UV absorbance at 300 nm of polymers extracted versus the initial stabilizer concentration: (A) blends, (B) extrudates.

### Analysis

We used an internal standard for quantitative spectrophotometric determinations (near IR band at  $2.3 \mu\text{m}$ ). The total chloride concentration was measured by coulometry. Details on sample preparation and methods of analysis have been published elsewhere [6].

### Photooxidation

The photochemical reactor was equipped with an OSRAM L 20 W 70 fluorescent lamp emitting in the range 300-450 nm with a maximum at about 365 nm. The total intensity was approximately  $20 \times 10^{14}$  photons  $\text{cm}^{-2} \text{s}^{-1}$ . The sample temperature was  $45^\circ\text{C}$ .

## RESULTS

Chromophores formed during processing are essentially conjugated polyenes. Figure 1 shows the UV absorbance of polymer films at 300

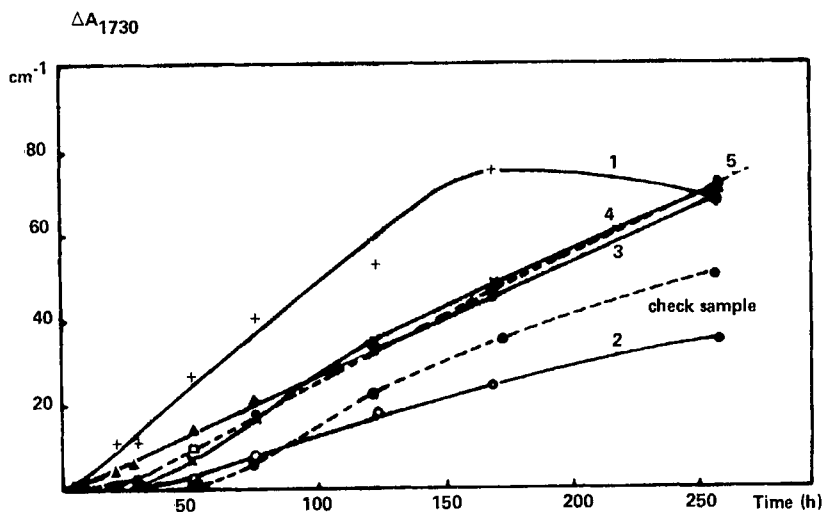


FIG. 2. Absorbance at  $1720\text{ cm}^{-1}$  of polymers extracted from extrudates as a function of irradiation time: (1) 0.75%, (2) 1%, (3) 1.25%, (4) 1.5%, (5) 1.75% dibutyl tin thioglycolate; (●) check sample.

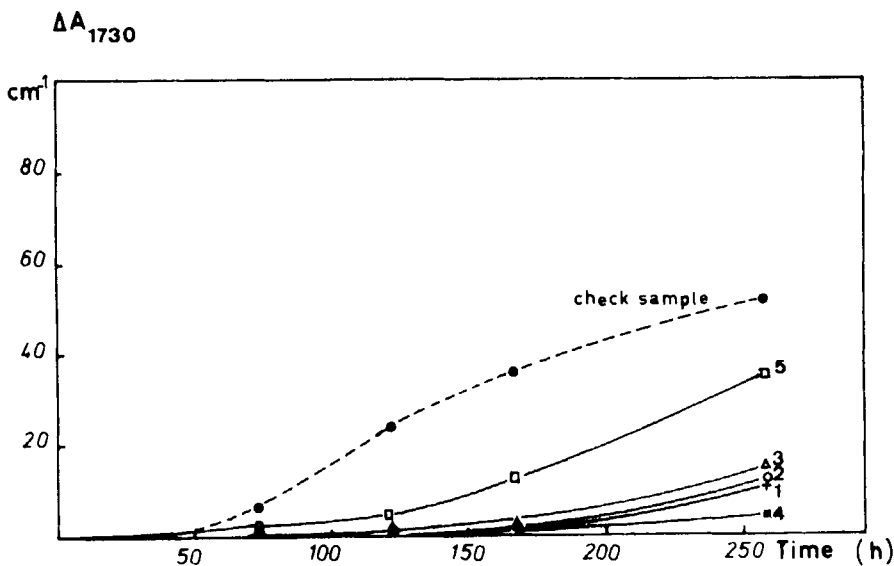


FIG. 3. Absorbance at  $1720\text{ cm}^{-1}$  of polymer extracted from blends as a function of irradiation time.

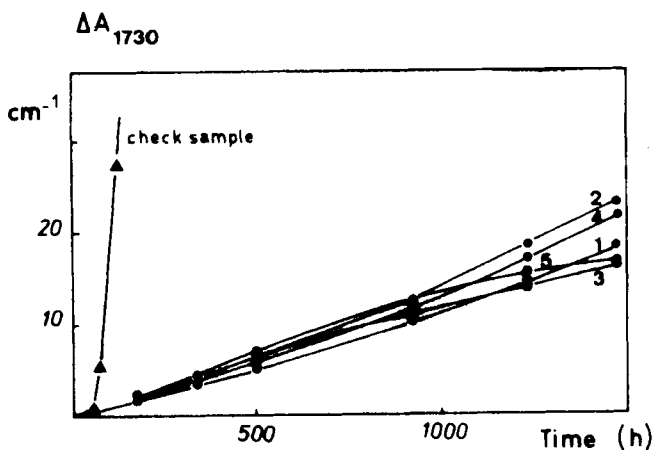


FIG. 4. Absorbance at  $1720\text{ cm}^{-1}$  of extrudates as a function of irradiation time.

TABLE 1. Initial Photooxidation Rates of Blends and Extrudates

Blends	1	2	3	4	5
Vico <sup>a</sup>	0.00	0.00	0.05	0.00	0.03
Extrudates	1	2	3	4	5
Vico <sup>a</sup>	0.03	0.04	0.02	0.01	0.02

<sup>a</sup>Initial photooxidation rate expressed in optical density units per cm thickness per hour.

nm extracted from blends or extrudates. Sample 1 containing the lowest concentration of stabilizer is more degraded than the other samples after extrusion. This is confirmed by visual examination.

However, it seems that a stability threshold exists; in the chosen conditions of processing, it is located between 0.75 and 1% stabilizer concentrations (by weight). The same situation is found in the results of photodegradation of polymers extracted from extrudates; the carbonyl growth (absorbance at  $1730\text{ cm}^{-1}$  versus irradiation time) is shown in Fig. 2. This experiment gave another interesting result. We observed that the blending operation produced a clear improvement of the photochemical stability; i.e., the destruction of some chromophores which initially participated in photoinitiation. The carbonyl growth of polymer extracted from the blend is plotted in Fig. 3. The destruction of these chromophores could be decomposition

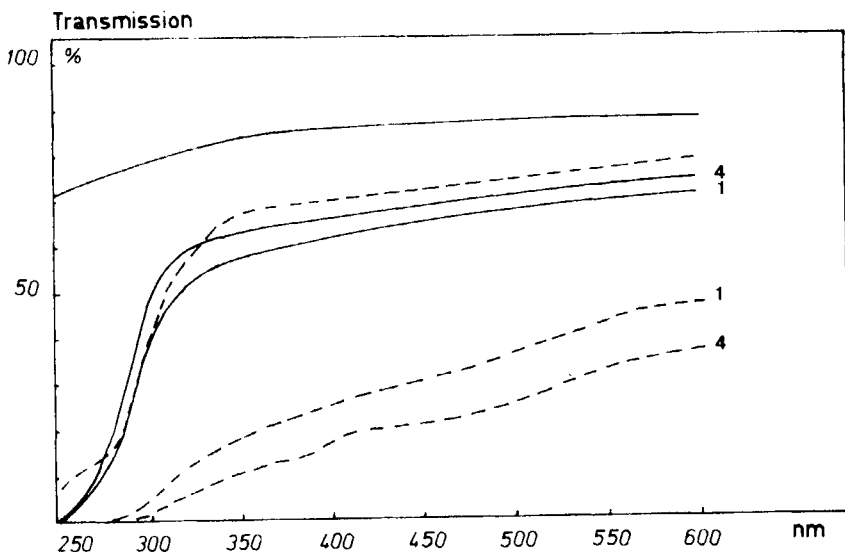
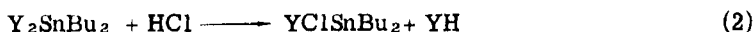
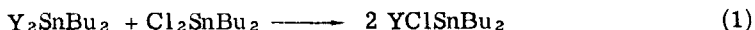


FIG. 5. UV spectra of extrudates: (—) before irradiation, (---) after 1000 h of irradiation; (1) 0.75%, (4) 1.5% dibutyl tin thioglycolate.

of peroxides or transformation of short conjugated polyenes into long conjugated polyenes which are less photosensitive.

Concerning blends and extrudates containing residual stabilizers and by-products, our experiments gave the following results:

1. The photooxidation reaction is slower for stabilized samples than for a nonstabilized (check) sample (Fig. 4). We do not observe an induction time, and the photooxidation rate (Table 1) seems to be unconnected with the initial stabilizer concentration. The autocatalytic effect of HCl on the photooxidation reaction which we observe for the check sample disappears in the case of the stabilized samples.
2. Analysis in UV spectrophotometry (Fig. 5) shows that the presence of stabilizer or by-products induces deep colorations, which is in good agreement with the observations made by practitioners.
3. The stabilizer is consumed during irradiation. The concentration of  $YClSnBu_2$  first increases and then decreases owing to the disappearance of  $Y_2SnBu_2$  which could reclaim it from other chlorides by the following reactions:



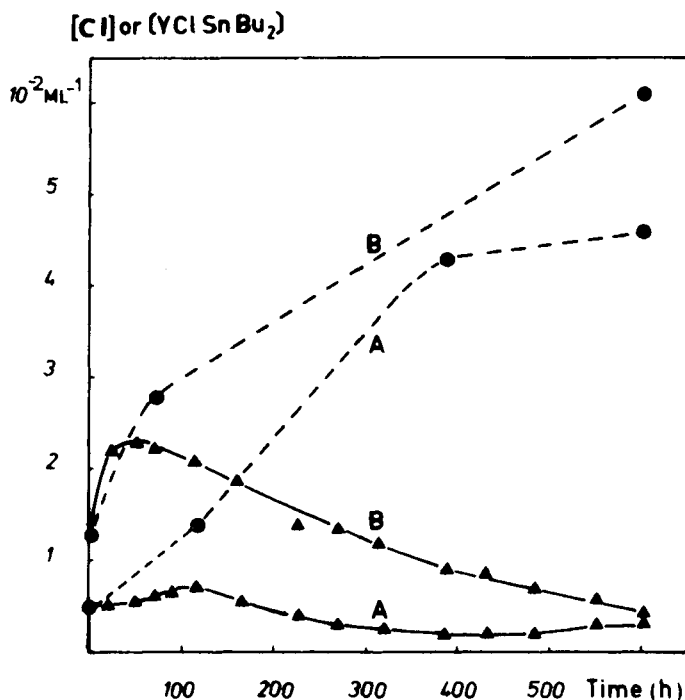


FIG. 6. Concentration of chlorides in Sample 3 as a function of irradiation time: (●)  $(Cl^-)$  total, (▲)  $YClSnBu_2$ , (A) blends, (B) extrudates.

The total concentration of chlorides increases in a regular way with the irradiation time (Fig. 6).

From these data it would be rather easy to build a mechanistic scheme based on two properties of the stabilizer, i.e., efficient capture of hydrogen chloride even at moderate temperature ( $45^\circ C$  in the present case) and the Reaction (1) of polychloride elimination involving the formation of  $YClSnBu_2$ . We attribute to  $HCl$  first the initial autocatalytic effect and second the limitation of lengths of conjugated polyenes by readdition [7]. Its capture eliminates these effects and involves the observed behavior. Another possibility for the limitation of polyenes lengths is the photooxidation of these structures. Therefore a possible antioxidant effect of the stabilizer or of its by-products cannot be excluded. Reaction (1) (autoelimination of polychlorides) could explain the change in the concentration of  $YClSnBu_2$  during exposure, increasing or decreasing concentration depending on the quantity of free dithioglycolate  $Y_2SnBu_2$  at the beginning of



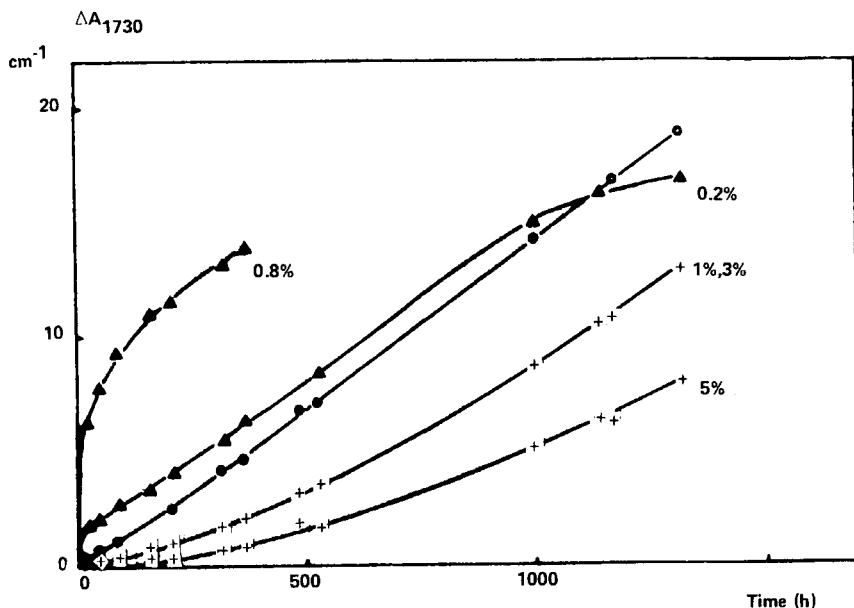


FIG. 7. Carbonyl growth in polymer films containing  $\text{YClSnBu}_2$  or  $\text{Cl}_2\text{SnBu}_2$  versus irradiation time: ( $\blacktriangle$ )  $\text{YClSnBu}_2$ , ( $+$ )  $\text{Cl}_2\text{SnBu}_2$ , ( $\circ$ ) check sample.

exposure. This approach is rather speculative, and we tried to complete the analysis by studying the specific influence of some supposed or identified by-products of the stabilizer.

Figure 7 demonstrates the carbonyl growth in cast PVC films containing  $\text{YClSnBu}_2$  or  $\text{Cl}_2\text{SnBu}_2$ . The first one has a photosensitizing effect, but on the contrary the second one shows a nonnegligible stabilizing effect.

Figure 8 shows the influence of  $\text{Bu}_2\text{SnO}$  and  $\text{Cl}_3\text{SnBu}$  which may be formed in a later step from  $\text{Cl}_2\text{SnBu}_2$ .  $\text{Bu}_2\text{SnO}$  photosensitizes the polymer to photooxidation. The effect of  $\text{Cl}_3\text{SnBu}$  is less clear: one observes initially an induction time and then a fast start of the reaction with a rate higher than the check sample rate. This suggests an important catalytic effect of one by-product of  $\text{Cl}_3\text{SnBu}$ . ThiolyH is quickly destroyed, which is not surprising taking into account the radical reactivity of these compounds, but it is difficult to reach conclusions about its influence on the photochemical behavior of the polymer.

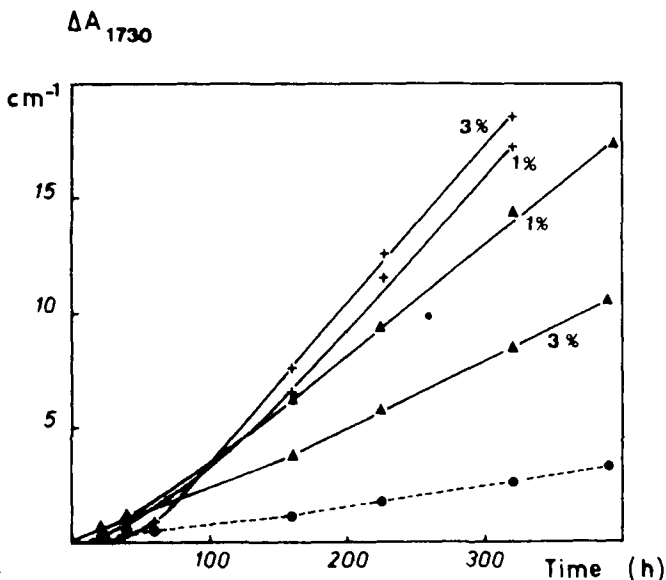


FIG. 8. Carbonyl growth in polymer films containing  $\text{Bu}_2\text{SnO}$  or  $\text{Cl}_3\text{SnBu}$  versus irradiation time: ( $\blacktriangle$ )  $\text{Bu}_2\text{SnO}$ , ( $+$ )  $\text{Cl}_3\text{SnBu}$ , ( $\bullet$ ) check sample.

## DISCUSSION

These results are somewhat in contradiction with the results of a previous study on the influence of organotin mercaptide stabilizers on the photochemical stability of PVC [5]. According to those authors, these stabilizers decrease the dehydrochlorination rate, retard the coloration phenomena, and increase the photooxidation rate. However, their experimental conditions were different. A mercury lamp emitting mainly outside the solar range was used. Samples were cast films obtained by solvent evaporation. The authors did not indicate the way in which they extracted the residual solvent which could have a photosensitizing effect [8]. Our results, i.e., during irradiation the stabilizer reacts mostly by HCl capture, do not support the hypothesis of a specific effect of UV radiation on mercaptide moieties of the stabilizer [1, 2].

Vesely [9] imputes the stabilizing effect of organotin compounds during photochemical aging to the property of hydrogen chloride capture. Our results show that we have a more complex mechanism. On the one hand, HCl capture is not necessarily suitable insofar as the autoinhibition mechanism may stop working. On the other hand, the total effect of any stabilizer should be dependent on the nature of the

by-products as much as on its initial properties. In addition, a conventional antioxidant effect is not necessarily suitable in the case of PVC. 1) In general, a possible stabilizing effect of antioxidants in photooxidation remains to be established. 2) In the case of PVC, if this effect really exists, it would induce the inhibition of oxidation reactions responsible for the limitation of conjugated polyene lengths and therefore of coloration phenomena. Recent work [10] shows clearly that dibutyl tin diisooctyl thioglycolate and dibutyl tin dichloride react quickly in a hydrocarbon matrix (polyethylene) in thermooxidation. These results seem to open a relatively important field of research overlaying photophysical properties of these compounds as well as their interference mechanisms in radical oxidation chains. Finally, there are specific aspects of PVC possibly bound to the interaction between polyenes (which can easily give  $\pi$  complexes) and organotin compounds. It may also be supposed that the destruction of conjugated polyenes which already exist is carried out by addition reactions to double bonds. Scott [11] supports this kind of mechanism in the case of dialkyl tin maleate (Diels-Alder addition).

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