

## **Concentration Effect of Photostabilizers on Poly(1-Butene) Film**

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### **ABSTRACT**

Effect of addition of various concentrations of stabilizers on poly(1-butene) [IPE] film has been studied, by measuring rate of protection and protective effectiveness through light scattering technique and UV spectral measurements. It has been observed that after a certain percentage of stabilizer addition there was not any further change.

### **INTRODUCTION**

The degradation of polymers on exposure to sunlight in the presence of oxygen has long been recognised an undesirable property. Recently<sup>1</sup> it has been tried to solve this problem by the addition of stabilizers. Because of the many advantages of the polymers to the military, civil and house-hold articles and especially their low cost, considerable efforts have been made to improve their light stability. The incorporation of the ultraviolet absorbers is the most common approach for photostabilizing the polymers. The absorbers compete with the polymer for absorption of the ultraviolet energy responsible for the polymer degradation.

The knowledge of reaction order is necessary for the study of degradation process. Jellinek et al.<sup>2,3</sup> have shown that the degradation of polymer follows a zero order law and is a random process. It has also been proposed that hydroperoxide<sup>4</sup> and carbonyl<sup>5</sup>, the intermediate products of autoxidation, are responsible for the photooxidative degradation. The cross-linking and chain scission occur simultaneously in this type of degradation.

The effect of 0.1 % (w/w) stabilizers on the photooxidative degradation of IPB has been studied by Singh and co-workers<sup>6,7</sup>. In the present paper, we have calculated the protective effectiveness and the optimum concentration of the stabilizers which would impart the saturation photostabilization of IPB. The degree of protection has also been evaluated. It has been shown that the protective influence of the stabilizers remains constant beyond a definite concentration of the stabilizers.

## EXPERIMENTAL

### Materials and Methods

The atactic part was separated from the highly isotactic poly(1-butene) [IPB] (supplied by Mobil Chemical Co., Metuchen, New Jersey, U.S.A. which contains no commercial additives) by dissolution of the sample in benzene followed by precipitation of the isotactic form with ether. The precipitated form was dried under vacuum.

1,3-Diphenyl triazine-N-oxide [HPTO] was synthesised<sup>8</sup> by diazotizing phenyl hydroxylamine (0.202 M) with a solution of benzenediazonium chloride. Benzenediazonium chloride was prepared from 18.6 ml. of aniline, 60 ml. of concentrated hydrochloric acid and 13.8 gm. of sodium nitrite. Copper(II)-bis(1,3-diphenyltriazine-N-oxide) [CPTO]<sup>9</sup> was synthesised by digestion of 1,3-diphenyl triazine-N-oxide and cupric chloride dihydrate solutions in requisite amounts on a water bath. For the synthesis of orthophenanthroline bis(1,3-diphenyltriazine-N-oxide)-cobalt(II) [CPPTO]<sup>10</sup>, a solution of (0.249 gm., 0.001 M) cobalt(II)-acetate tetrahydrate was added to an alcoholic solution of the (0.426 gm., 0.002 M) HPTO. The suspension of the product in acetone was treated with (0.198 gm., 0.001 M) o-phenanthroline. 2,4-Diphenyl-6-(2-hydroxyphenyl)-s-triazine [PHPT] was synthesised according to a literature procedure<sup>11</sup>. These compounds were characterized in our laboratory.

Films of known thickness ( $1.18 \times 10^{-2}$  gm.cm<sup>-2</sup>) were prepared by casting 5 ml. solution of 5 wt.-% IPB on a quartz plate of 5 cm. diameter. The preparation of IPB films, method of incorporation of stabilizers, the procedures of photoirradiation, the subsequent dissolution of films and the

characterisation of weight average molecular weight have been described by Chandra and Bhatnagar<sup>1,2</sup>.

## RESULTS AND DISCUSSION

All the four compounds are very effective ultraviolet stabilizers and can provide comparable protection at 283 K against 253.7 nm wavelength. Increasing the concentration beyond 0.5, 0.6, 0.7 and 0.8 wt.-% of PHPT, CPPTO, HPTO and CPTO respectively, brings a saturation limit in photostabilization of poly(1-butene).

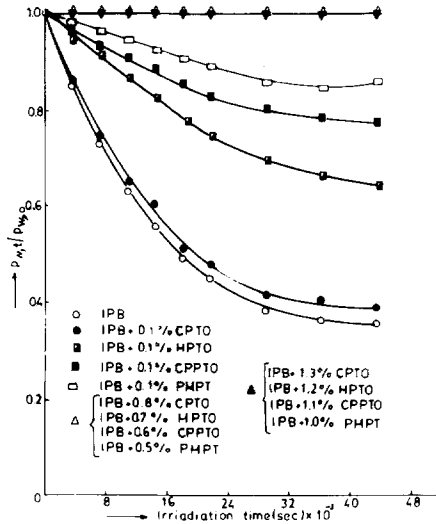


FIG. 1 SHOWS THE VARIATION OF WEIGHT AVERAGE DEGREE OF POLYMERIZATION OF POLY(1-BUTENE) vs IRRADIATION TIME

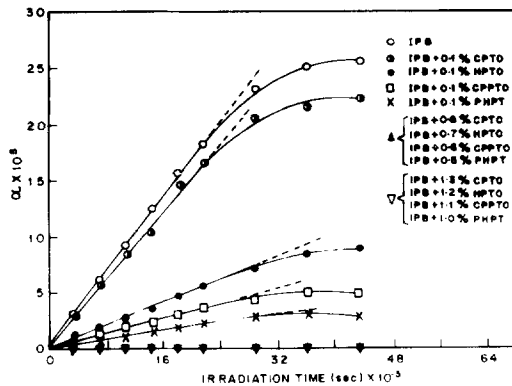


FIG. 2 SHOWS THE VARIATION OF PHOTODEGRADATION RATE WITH TIME

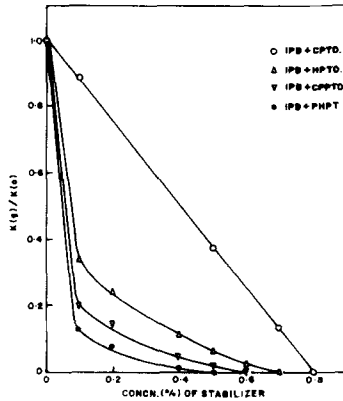


FIG. 3 SHOWS THE VARIATION OF RATE OF PROTECTION OF IPB WITH CONCENTRATION OF STABILIZERS

Figure 1 gives the values of  $p_{w,t}/p_{w,0}$  versus irradiation time for IPB with and without the stabilizers at the intensity flux of  $2.38 \times 10^{-9}$  einstein  $\text{sec.}^{-1} \text{cm.}^{-2}$  where  $p_{w,t}$  and  $p_{w,0}$  are weight average chain length at time  $t$  and zero respectively. Fig. 2 gives the variation of the degree of degradation per original chain length ( $\alpha$ ) of IPB with and without the stabilizers at 283 K versus irradiation time. The values of  $k_{1(g)}/k_{1(0)}$  obtained from Fig. 2, represent quantitatively the degree of protection of IPB, where  $k_{1(g)}$  and  $k_{1(0)}$  being the rate constants with and without the stabilizers (Table 1). These data and Figs. 1, 2 and 3 confirm that the saturation protective action is reached at 0.5, 0.6, 0.7 and 0.8 wt.-% of PHPT, CPPTO, HPTO and CPTO on the weight of IPB. These results are also supported by the values of the specific rate constant ( $k_1$ ) at different concentrations of the stabilizers. The values of  $k_1$  are negligible beyond saturation concentration of the stabilizers.

From equation (1), it is possible to compare the protective ability<sup>1)</sup> of 0.1 wt.-% concentration only of the various stabilizers and determine the effect of the stabilizer concentration on the effectiveness of the stabilizer (Table 2).

$$PE = \frac{I_{O\lambda} (1 - 10^{-b_1 a} p_\lambda)}{I_{O\lambda} \left[ 1 - 10^{-b_2 (a_{p_\lambda} c_p + a_{B_\lambda} c_B)} \right] \frac{a_{p_\lambda} c_p}{a_{p_\lambda} c_p + a_{B_\lambda} c_B}} \quad \dots (1)$$

TABLE 1

The optimum concentrations of the stabilizers for the protection of IPB in air at 283°K  
 Light intensity =  $2.38 \times 10^{-9}$  einstein  $\text{sec.}^{-1} \text{cm.}^{-2}$   
 Irradiation wavelength ( $\lambda$ ) = 253.7 nm

IPB + CPTO system		IPB + HPTO system		IPB + CPPTO system		IPB + PHPT system	
conc. $\frac{k_1(g)}{\text{gm. \%}} \times 10^{-9}$ (CPTO)	$k_1(g) / k_1(o)$	conc. $\frac{k_1(g)}{\text{gm. \%}} \times 10^{-9}$ (HPTO)	$k_1(g) / k_1(o)$	Conc. $\frac{k_1(g)}{\text{gm. \%}} \times 10^{-9}$ (CPPTO)	$k_1(g) / k_1(o)$	Conc. $\frac{k_1(g)}{\text{gm. \%}} \times 10^{-9}$ (PHPT)	$k_1(g) / k_1(o)$
$\text{sec.}^{-1}$		$\text{sec.}^{-1}$		$\text{sec.}^{-1}$		$\text{sec.}^{-1}$	
0.0	8.653	1.000	0.0	8.653	1.000	0.0	8.653
0.1	8.125	0.939	0.1	2.647	0.306	0.1	0.995
0.8	0.000	0.000	0.7	0.000	0.000	0.5	0.000
1.13	0.000	0.000	1.12	0.000	0.000	1.0	0.000
2.25	0.000	0.000	2.00	0.000	0.000	1.50	0.000

TABLE 2

Average values of protective effectiveness for IPB at 0.1 wt. -% concentration of the stabilizers. Light intensity =  $2.38 \times 10^{-9}$  einstein  $\text{sec}^{-1} \text{cm}^{-2}$ , Irradiation wavelength ( $\lambda$ ) = 253.7 nm.

<u>Stabilizer</u>	<u>Protective effectiveness</u>
CPTO	1.2
HPTO	1.4
CPPTO	1.7
PHPT	1.9

where PE = protective effectiveness,  $I_0$  = incident intensity at  $\lambda$ ,  $b_1$  = thickness of unprotected IPB film in millimeters,  $b_2$  = thickness of protected IPB film in millimeters,  $a_{p\lambda}$  = absorptivity of polymer at  $\lambda$ ,  $a_{B\lambda}$  = absorptivity of stabilizer at  $\lambda$ ,  $c_p$  = concentration of polymer in percentage, and  $c_B$  = concentration of stabilizer in percentage. Therefore, the protective effectiveness of the stabilizers was determined experimentally by comparing the rate of photochemical degradation of unprotected and protected films.

The data in the Table-2 indicate that the protective effectiveness is least for IPB in the presence of CPTO and highest in the presence of PHPT. In the earlier studies<sup>6,7,14</sup>, it has been experimentally estimated that the enthalpy of activation is least for IPB in the presence of CPTO ( $6.89 \text{ K cal mole}^{-1}$ ) and highest in the presence of PHPT ( $7.72 \text{ Kcal mole}^{-1}$ ). The protective effectiveness and enthalpy of activation clearly show that the stabilizing actions of these stabilizers are in the order CPTO < HPTO < CPPTO < PHPT.

This study indicates that the optimum stabilization can probably be achieved by incorporating of 0.5, 0.6, 0.7 and 0.8 wt.-% or more of PHPT, CPPTO, HPTO and CPTO respectively in the matrix of IPB film irradiated with 253.7 nm wavelength.

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