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Effect of copper (II) chelate on photodegradation of poly (1-butene)

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Photo-oxidative degradation of isotactic poly(1-butene) in the presence and absence of copper (II) bis-(1,3-diphenyl triazine-*N*-oxide) chelate has been studied, by measuring the weight average molecular weight, measuring changes in the carbonyl groups and by measuring changes in the hydroperoxide contents in the temperature range of 267 to 313 K using monochromatic light of wavelength 253.7 nm. The mechanism leading to the stabilization observed, resulting from the addition of chelate, is discussed.

1. Introduction

Reactions of polymers with oxygen in air are very important processes from both the scientific and industrial point of view. Natural and induced environmental conditions also deteriorate the polymeric materials. Photo-oxidation may result in de-polymerization, chain degradation or cross-linking, processes which change the physical and chemical properties of the polymers. The commercially available ultra-violet stabilizers are less stable and decompose in certain polymers due to evaporation [1]. The effect of copper and its salts on the ageing of polymers was studied by Miller [2].

The thermal degradation of atactic poly(1-butene) has been studied by Stivala *et al.* [3], but very little attention has been given, so far, to the photo-oxidative degradation in the presence of stabilizer of isotactic poly(1-butene). In previous papers [4–6] the effect of stabilizers on the photo-oxidative degradation of isotactic poly(1-butene) has been reported and it has been shown that 2,4-diphenyl-6-(2′-hydroxyphenyl)-s-triazine (PHPT) and 1,3-diphenyl triazine-*N*-oxide (HPTO) reduce the degradation of the polymer. In the present investigation the effect of copper (II) bis-(1,3-diphenyl triazine-*N*-oxide) chelate on the photo-oxidative degradation of isotactic poly(1-butene) has been studied and the mechanism of stabilization has been discussed.

2. Experimental procedure

2.1. Sample preparation and photo-irradiation

Isotactic poly(1-butene) (IPB) was obtained from Mobil Chemical Co., Metuchem, New Jersey, USA. Traces of the atactic form from the sample were removed according to the procedure described elsewhere [7]. Copper (II) bis-(1,3-diphenyl triazine-*N*-oxide) (CPTO) was synthesized according to the literature procedures [8] and dried in vacuum. The method of preparation of IPB films, the incorporation of the stabilizer into the film matrix, the procedure of photo-irradiation with a monochromatic light of wavelength 253.7 nm (using a Hanovia low-pressure mercury lamp) and the dissolution of the films in cyclohexane (spectroscopic grade) was carried out in the manner described by Chandra and Singh [6].

2.2. Quantum efficiency

If all the bonds in the polymer chain may be broken at random, each bond being of equal strength and accessibility, then the following relation holds [9]

$$\frac{1}{p_{n,t}} - \frac{1}{p_{n,0}} = \frac{m}{wN} \phi \, Ia \, t, \tag{1}$$

where w is the weight of irradiated polymer film, m is the molecular weight of the monomer, Ia is the light absorbed in the polymer film, N is

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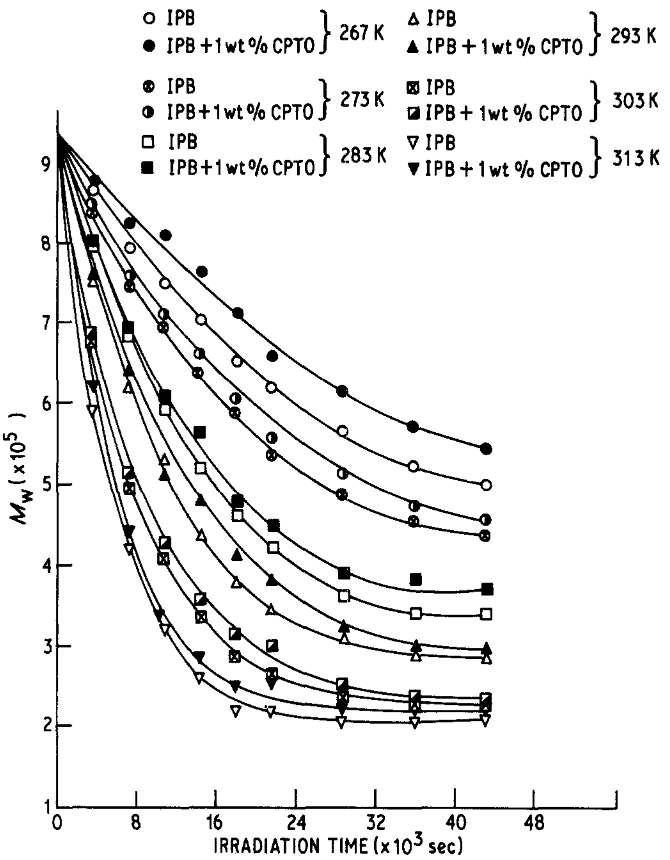


Figure 1 Variation of weight average molecular weight plotted against time of irradiation of IPB film in the presence and absence of 0.1 wt% CPTO.

the Avogadro number, ϕ is the quantum efficiency. $p_{n,0}$ is the initial number average degree of polymerization and $p_{n,t}$ is the number average degree of polymerization at any time t during the photo-degradation process. The quantum efficiency ϕ can be determined from Equation 1 by plotting $p_{n,t}^{-1}$ against t. The ratio $p_{n,t}/p_{n,0}$ can be replaced by the ratio of the weight average degree of polymerization $p_{w,t}/p_{w,0}$, without involving any appreciable error. These ratios can be conveniently determined by light scattering measurements. The value of *Ia* can be determined by potassium ferri-oxalate actinometry [10].

2.3. Spectrophotometric measurements

Infra-red spectra of irradiated samples of IPB were recorded with a Perkin–Elmer Model 21 Infra-red Spectrophotometer; ultra-violet spectra were recorded with an Unicam SP700A Ultra-violet Visible Spectrophotometer in the absence and presence of 0.1 wt% CPTO at a temperature of 283 K.

2.4. Carbonyl groups

Changes in the carbonyl groups were determined using a base-line method [11] from the infra-red spectra.

2.5. Determination of hydroperoxide

The hydroperoxide contents, produced in the irradiated polymer, were determined by a modified iodometric method [12].

3. Results and discussion

Fig. 1 shows the variation of weight average molecular weight, M_w, against time for IPB films irradiated in the presence and absence of 0.1 wt% CPTO in air for different time intervals. An inspection of the plots reveals that at each temperature the value of M_w for the irradiated samples is greater in the presence of CPTO than the corresponding value of IPB in absence of CPTO. This indicates that CPTO retards the photo-oxidative degradation of IPB. Initially there is a rapid decrease in M_w with irradiation time which then levels off and is followed by a slight increase. The tendency to increase in the curve is an indication of cross-linking which predominates at longer irradiation times.

Fig. 2 shows the variation of the degree of

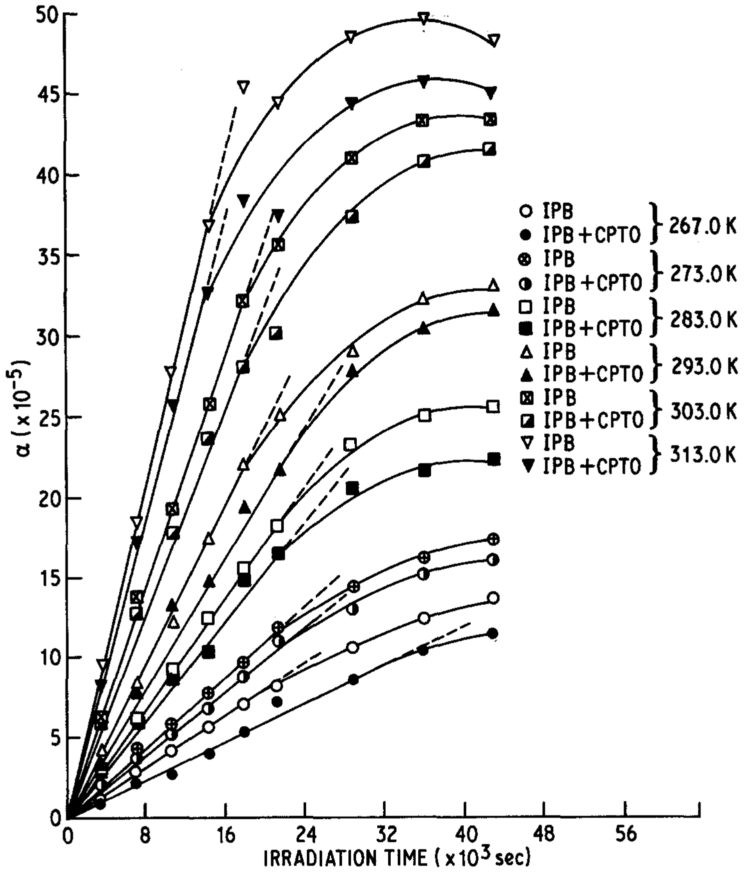


Figure 2 Variation of degree of degradation, α, plotted against time of irradiation of IPB film in the presence and absence of 0.1 wt% CPTO.

degradation, α, against time for the IPB + 0.1 wt% CPTO system. For a random chain degradation process, $\alpha = k_1 t$, where k_1 is the specific rate constant, and the initial slope of the α against t curve gives a method of calculating k_1. If only one kind of atomic links are ruptured, the slope should be linear and if the plot is non-linear, Jellinek [13] has indicated the possibility of more than one rate constant. The degradation kinetics of natural rubber [14], polyethylene [15] and nitrated Egyptian cotton [16, 17] has been studied by this method.

The stabilizing effect of CPTO in IPB was examined by measuring the kinetic parameters, see Table I. The values of k_1 were nearly constant with time indicating the reactions to be of zero order. The plots of $\ln k_1$ against T^{-1} (Fig. 3) are linear and the values of activation energy ΔE, as well as the frequency factor, A, for degradation can be evaluated. These values can be calculated by the method of least-squares fit. The values of A and ΔE for IPB are substituted [18] in

$$k_1 = A \exp(\Delta E/kT), \qquad (2)$$

where k_1 is in units of sec^{-1}, k is Boltzmann's constant and T is the temperature, using $A = 1.06 \times 10^{-3}$ sec^{-1} and $\Delta E = -6.62$ kcal for IPB and $A = 1.56 \times 10^{-3}$ sec^{-1} and $\Delta E = -6.89$ kcal for IPB + 0.1 wt% CPTO.

For a zero-order reaction, ΔE, may be equated to the heat-of-formation of the activated complex, ΔH^*, without any appreciable error. Irrespective of the variations in the values of ΔH^*, the values of ΔF^* (the free energy of activation) remain almost constant in both cases at about 37.29 kcal mol^{-1} at 400 K. This leads to the conclusion that the rate-determining step is the same in both systems. The higher values of ΔH^* indicate that CPTO retards the rate of photo-oxidative degradation of IPB.

Changes in carbonyl groups during the photo-oxidative degradation of IPB have been determined by infra-red spectral analysis. The extent of the degradation, as measured by infra-red spectral analysis, was plotted against irradiation time in Fig. 4. The carbonyl content demonstrates that the amount of carbonyl groups of pure IPB is more than that of the IPB containing 0.1 wt%

TABLE I Photo-degradation of poly(1-butene) in the presence of 0.1 wt% CPTO. (Light intensity flux = 2.38×10^{-9} Einstein sec^{-1} cm^{-2}; irradiation wavelength, λ = 253.7 nm)

Time of irradiation ($\times 10^3$ sec)	Temperature (K)	M_w ($\times 10^5$ g)	$p_{w,t}/p_{w,o}$	s	α ($\times 10^{-5}$)	k_1 ($\times 10^{-9}$ sec^{-1})	k_1 from α against t curve ($\times 10^{-9}$ sec^{-1})
0.0	267.0	9.34	1.000	0.000	0.000	0.000	3.142
3.6	267.0	8.75	0.937	0.200	1.200	3.333	
7.2	267.0	8.25	0.883	0.383	2.300	3.194	
10.8	267.0	8.10	0.867	0.443	2.661	2.464	
14.4	267.0	7.65	0.819	0.631	3.790	2.632	
18.0	267.0	7.10	0.760	0.882	5.298	2.943	
21.6	267.0	6.55	0.701	1.168	7.016	3.248	
28.8	267.0	6.12	0.655	1.421	8.535	2.964	
36.0	267.0	5.72	0.612	1.687	10.133	2.815	
43.2	267.0	5.44	0.583	1.894	11.375	2.633	
0.0	273.0	9.34	1.000	0.000	0.000	0.000	5.313
3.6	273.0	8.40	0.899	0.325	1.950	5.417	
7.2	273.0	7.59	0.813	0.658	3.950	5.486	
10.8	273.0	7.10	0.760	0.882	5.298	4.905	
14.4	273.0	6.60	0.707	1.142	6.859	4.764	
18.0	273.0	6.05	0.648	1.466	8.806	4.892	
21.6	273.0	5.54	0.593	1.820	10.932	5.061	
28.8	273.0	5.11	0.547	2.158	12.962	4.501	
36.0	273.0	4.72	0.505	2.510	15.076	4.188	
43.2	273.0	4.57	0.489	2.660	15.975	3.698	
0.0	283.0	9.34	1.000	0.000	0.000	0.000	8.125
3.6	283.0	8.01	0.858	0.479	2.875	7.986	
7.2	283.0	6.95	0.744	0.957	5.750	7.986	
10.8	283.0	6.10	0.653	1.437	8.631	7.992	
14.4	283.0	5.65	0.605	1.732	10.403	7.224	
18.0	283.0	4.80	0.514	2.435	14.625	8.125	
21.6	283.0	4.50	0.482	2.724	16.362	7.575	
28.8	283.0	3.91	0.419	3.434	20.625	6.162	
36.0	283.0	3.82	0.409	3.548	21.311	5.920	
43.2	283.0	3.71	0.397	3.704	22.250	5.151	
0.0	293.0	9.34	1.000	0.000	0.000	00.000	10.694
3.6	293.0	7.59	0.813	0.661	3.972	11.033	
7.2	293.0	6.37	0.682	1.278	7.675	10.660	
10.8	293.0	5.10	0.546	2.163	12.992	12.030	
14.4	293.0	4.80	0.514	2.432	14.608	10.144	
18.0	293.0	4.08	0.437	3.201	19.225	10.681	
21.6	293.0	3.80	0.407	3.558	21.371	9.894	
28.8	293.0	3.20	0.343	4.578	27.500	9.549	
36.0	293.0	2.99	0.320	5.011	30.100	8.361	
43.2	293.0	2.91	0.312	5.224	31.375	7.263	
0.0	303.0	9.34	1.000	0.000	0.000	00.000	16.840
3.6	303.0	6.87	0.736	1.003	6.025	16.736	
7.2	303.0	5.15	0.551	2.122	12.746	17.702	
10.8	303.0	4.30	0.460	2.946	17.695	16.384	
14.4	303.0	3.59	0.384	3.908	23.475	16.302	
18.0	303.0	3.15	0.337	4.666	28.025	15.569	
21.6	303.0	3.00	0.321	4.999	30.026	13.901	
28.8	303.0	2.53	0.271	6.193	37.199	12.916	
36.0	303.0	2.35	0.252	6.767	40.647	11.291	
43.2	303.0	2.34	0.251	6.909	41.500	9.607	
0.0	313.0	9.34	1.000	0.000	0.000	00.000	
3.6	313.0	6.23	0.667	1.353	8.125	22.569	
7.2	313.0	4.40	0.471	2.835	17.028	23.650	
10.8	313.0	3.37	0.361	2.258	25.575	23.681	

TABLE I (*Continued*)

Time of irradiation ($\times 10^3$ sec)	Temperature (K)	M_w ($\times 10^5$ g)	$p_{w,t}/p_{w,0}$	s	α ($\times 10^{-5}$)	k_1 ($\times 10^{-9}$ sec^{-1})	k_1 from α against t curve ($\times 10^{-9}$ sec^{-1})
14.4	313.0	2.86	0.306	5.411	32.500	22.569	23.681
18.0	313.0	2.51	0.269	6.339	38.075	21.153	
21.6	313.0	2.56	0.274	6.181	37.125	17.188	
28.8	313.0	2.23	0.239	7.330	44.027	15.287	
36.0	313.0	2.17	0.232	7.579	45.525	12.701	
43.2	313.0	2.19	0.235	7.463	44.825	10.376	

CPTO, and this behaviour is consistent with the observed decrease in molecular weight. Bell *et al.* [19] have indicated that the radicals $R\dot{O}$, which are formed during degradation, are responsible for the formation of various oxidation products [20, 21]. These results show that CPTO decomposes unstable reaction intermediates to relatively stable products, such as alcohols.

The hydroperoxide contents of the degraded IPB were determined by iodometry and were plotted against irradiation time at different temperatures (Fig. 5). The hydroperoxide content of IPB in the presence of CPTO is lower than that of pure IPB. The results suggest that CPTO decomposes the hydroperoxides which are formed during the oxidative degradation of IPB to stable products, such as alcohols, rather than carbonyl compounds. Therefore, CPTO is an effective stabilizer to inhibit the degradation of IPB.

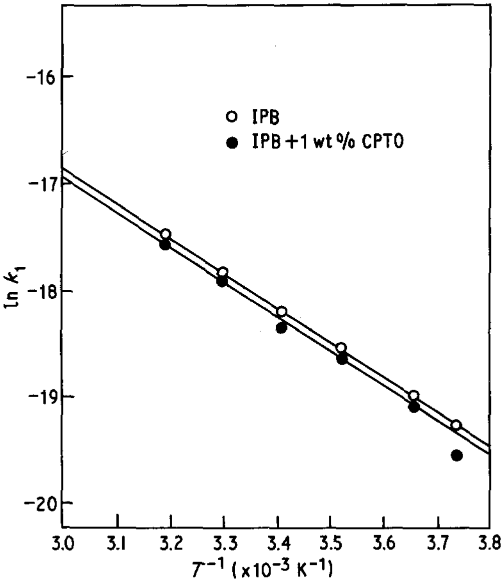


Figure 3 Variation of ln k with T^{-1} for IPB and IPB + 0.1 wt% CPTO.

Ultra-violet spectra of irradiated IPB film in a nitrogen atmosphere at 293 K in the presence and absence of 0.1 wt% CPTO, immediately after irradiation, have been investigated and the results are shown in Fig. 6. A broad band with maximum intensity at 229 nm was assigned to the secondary alkyl free radical, $\text{-(}CH_2-\dot{C}H-CH_2\text{)-}$, the second peak at 272 nm was assigned to the triene group, $\text{-(}CH=CH\text{)-}_3$, and the third very less intense peak at 323 nm was assigned to the trienyl free radical, $-\dot{C}H(CH=CH\text{)-}_3$. The ultra-violet spectrum of irradiated IPB film shows that all the three peaks increases gradually in intensity with time of irradiation. In IPB films containing CPTO, which retards the rate of photo-oxidative degradation, the increase of the intensities of the ultra-violet spectrum at the wavelengths is lower than that observed to occur for IPB films in the absence of CPTO.

4. Mechanism of photo-oxidative degradation and stabilization

Photo-oxidative degradation is the most common type of deterioration mechanism. According to

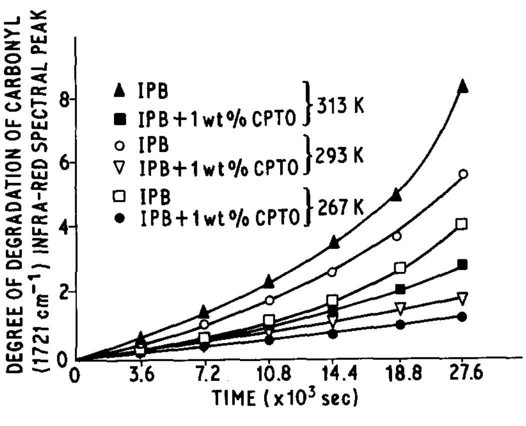


Figure 4 Variation of carbonyl content plotted against irradiation of IPB film in the presence and absence of 0.1 wt% CPTO.

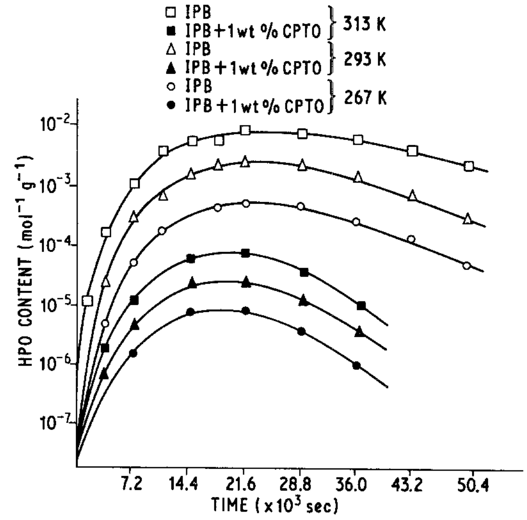


Figure 5 Variation of hydroperoxide content plotted against time of irradiation of IPB film in the presence and absence of 0.1 wt% CPTO.

Chandra and Singh [6] the photo-oxidative degradation is a radical chain reaction comprising initiation, propagation, hydrogen transfer and termination reactions. The reaction sequence is initiated by light energy. As a result of autoxidation, there is formation of oxygenated functional groups in the polymer backbone as a result of which many peroxides and hydroperoxides are formed which decompose with chain scission rather than by cross-linking. The value of $\Delta F^* \approx 37.29 \text{ kcal mol}^{-1}$ obtained experimentally is quite close to the 40 kcal mol^{-1} required for the decomposition of the O–O bond in PO–OH. In this reaction, polymer oxy and hydroxy radicals are also formed:

$$\mathrm{POOH} \rightarrow \mathrm{P\dot{O}} + \mathrm{\dot{O}H}; \qquad (3)$$

polymer oxy radicals are very reactive and can abstract hydrogen [22] from the neighbouring molecules to form hydroxyl groups:

$$\mathrm{P\dot{O}} + \mathrm{PH} \rightarrow \mathrm{P{-}OH} + \mathrm{\dot{P}}, \qquad (4)$$

where $\mathrm{PO\dot{O}}$, $\mathrm{P\dot{O}}$ and PH represent a polymer peroxy radical, polymer oxy radical and a polymer molecule, respectively. The observed data can be satisfactorily explained on the basis of this mechanism. Photo-oxidation normally occurs mostly in the surface regions of the polymer because of combinations of such effects as oxygen diffusion and the opacity of the polymer to the radiation. Light provides the energy for scission of hydroperoxide bonds but the thermal source accelerates the process.

The photostabilization mechanism of IPB by

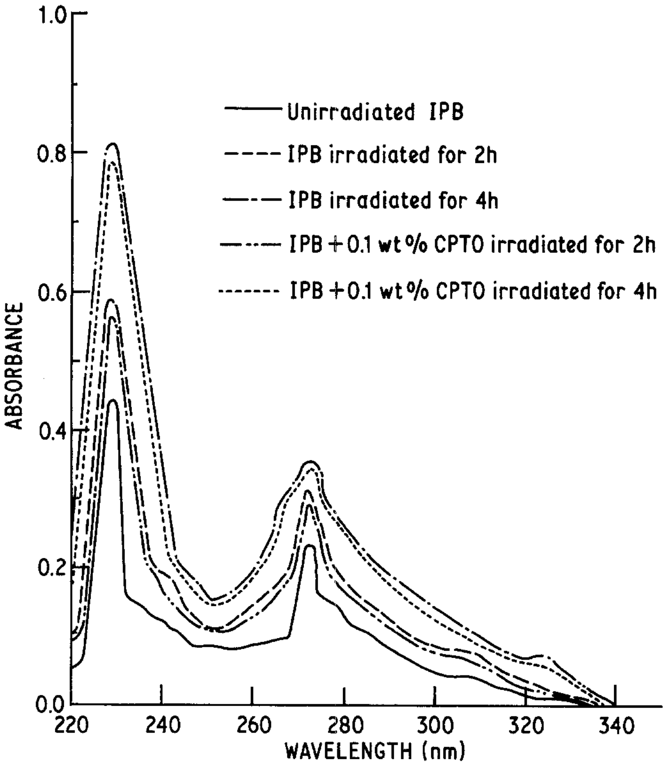
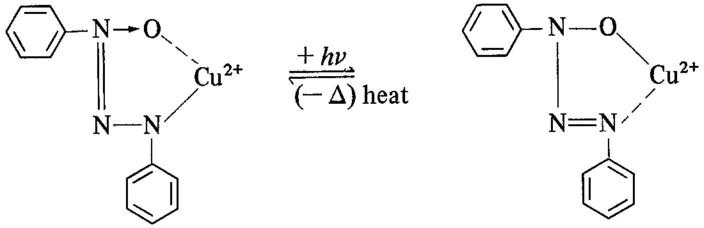


Figure 6 Ultra-violet spectra of irradiated IPB film in the presence and absence of 0.1 wt% CPTO.

CPTO involves both interference with the propagation reaction of the oxidative chain and decomposition of the polymer peroxides and hydroperoxides. CPTO is represented by the following resonating structures:



(5)

The stabilization of IPB by CPTO can be effected in several stages. The chelate stabilization process operates by interfering with the photoinitiation process through the absorption of light. By minimizing the amount of ultra-violet energy absorbed by the polymer the primary photochemical processes are prevented. The chelate is able to dissipate the radiation harmlessly as heat through resonating structures. Thus the chelate acts as light shielding agent, absorber and quencher. The quencher, as a result of the absorption of energy, is raised to an excited state which dissipate its accumulated energy harmlessly so reducing the photodegradation.

The chelate is effective at the chain-branching stage and decomposes the hydroperoxide into inert products. Carlsson and Wiles [23] have confirmed that the stabilizer slowly migrates through the solid polymer destroying the –OOH groups. CPTO may introduce additional terminal steps by acting as $\dot{P}$, $P\dot{O}$ or $PO\dot{O}$ scavengers. Thus CPTO also acts as a free radical scavenger. The radicals of the chelate are stabilized by resonance and no further reaction occurs to initiate the new oxidative chain. In addition to this, CPTO inhibits such a process by electron transfer and the formation of the inert complexes. Photostabilization does not occur through a single process but results from a combination of all the above proposed processes. The relative importance of each mechanism depends on the nature of the additive.

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