

Physico-chemical studies on the photostabilization of poly(1-butene) film

R P SINGH†, R CHANDRA* and A SYAMAL

Department of Applied Chemistry, Regional Engineering College,
Kurukshetra 132 119, India

†Polymer Chemistry Division, National Chemical Laboratory, Pune 411 008, India

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Abstract. Thin films of poly(1-butene) with and without *o*-phenanthroline bis(1,3-diphenyl triazine-1-oxide)-cobalt(II) [*I*] in the temperature range of 233–333° K have been degraded in air from a UV light of 253.7 nm. The changes in weight average molecular weights, degree of degradation, quantum yields, enthalpy and free energy of activation, and carbonyl and hydroperoxide contents, were followed as a function of the time of irradiation. The inhibition effect of *I* is discussed on the basis of the luminescence and UV spectral data. The chelate *I* behaves both as a thermal and UV stabilizer due to a combination of different kinds of activity in the same molecule.

Keywords. Isotactic poly(1-butene); *o*-phenanthroline bis(1,3-diphenyl triazine-1-oxide)-cobalt(II); photodegradation; photo-stabilization.

1. Introduction

Atmospheric oxidation of polymers results in the deterioration in their physico-chemical properties. Addition of commercially available stabilizers to the polymeric formulations results in prolonging the life of these products. However, most such stabilizers are specific and unless the sites of degradation and mechanisms of the oxidative processes are properly understood, the selection of suitable stabilizers remains empirical. In recent years, however, several examples have been given in the literature (Melchore 1962; Schmitt and Hirt 1963; Hormann 1966; Pivovarov *et al* 1967) of a new type of stabilizer, the so-called 'reactive' stabilizer, which is believed to operate by a mechanism of excitation energy transfer from the polymer to the stabilizer. In general, these stabilizers are fairly complex chelates of the transition metals, usually nickel and cobalt, and their exact mode of protective action is not at all clear. It becomes therefore necessary to investigate the process of stabilization for more polymeric systems with a view to ascertain the mechanism of their stabilization.

* To whom all correspondence should be made.

In this paper, we used the light scattering, actinometry and UV-spectrophotometric techniques which clearly demonstrate the effectiveness of a chelate, *o*-phenanthroline *bis*-(1,3-diphenyl triazine-1-oxide)-cobalt(II) [I], that protects poly(1-butene) [PB-1] film. The comparison of weight average molecular weight, degree of degradation, quantum yield, enthalpy and free energy of the activation processes and the changes in carbonyl and hydroperoxide contents of the irradiated samples of PB-1 in the absence and presence of I indicate that I works as a UV absorber and hydroperoxide decomposer towards the degradation of PB-1. In addition, the effect of the concentration of the chelate additive within the polymer film has been discussed. The formation and role of electronically excited oxygen molecules in the photodegradation is also described.

2. Experimental

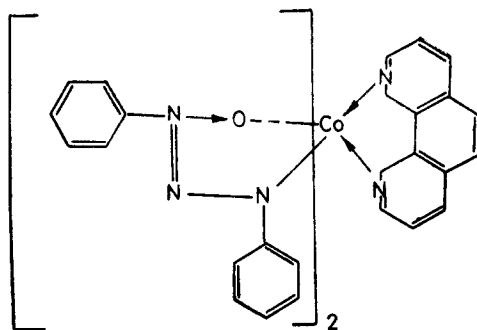
Isotactic poly(1-butene), [PB-1], was supplied by Mobil Chemical Company Metuchem, New Jersey, USA. Traces of atactic polymer in the sample were removed according to the procedure of Natta (Natta *et al* 1956). *o*-Phenanthroline *bis*-(1,3-diphenyl triazine-1-oxide)cobalt(II) [I] was synthesized according to the published procedure (Dutta and Lekha 1975). The preparation of PB-1 film (0.15 mm), the method of incorporation of the stabilizer into the matrix of films and the procedures of photo-irradiation and subsequent dissolution of films in cyclohexane, have been described elsewhere (Chandra *et al* 1980b). The changes in the values of weight average molecular weights and quantum yields of PB-1 due to 253.7 nm light in the temperature range of 233 to 333° K were determined respectively, by a light scattering photometer (Chandra and Singh 1980a) and potassium ferrioxalate actinometer (Chandra and Singh 1979).

Changes in carbonyl groups were determined by IR analysis using a Beckmann IR-20 spectrophotometer.

The UV spectra of PB-1 film samples induced by the different light doses by changing the time of irradiation were determined by SP-7000 automatic UV-visible spectrophotometer.

Polymer hydroperoxides produced by UV exposure in PB-1 film were determined by a modified iodometric method (Wagner *et al* 1947).

The emission spectra of each film sample were determined on a Hitachi MPF-2A spectrophotometer with a xenon source and a photomultiplier.



3. Results and discussion

Table 1 gives the values of the time of irradiation, the corresponding values of weight average molecular weights \bar{M}_w , the ratios of the weight average chain length $P_{w,t}/P_{w,0}$, the average number of cuts per original chain lengths and the degrees of degradation a for PB-1 film irradiated with and without 0.1% (by wt) I in air at various temperatures with a light intensity of 2.38×10^{-9} Einstein $\text{sec}^{-1} \text{cm}^{-2}$ for different intervals of time. An inspection of the table reveals that at each temperature, in the initial stages of the photodegradation of PB-1, there is a rapid drop in \bar{M}_w but subsequently it reaches a saturation limit. Such a sharp drop in \bar{M}_w in the initial stages of degradation generally indicates a random breaking of bonds in the polymer chain. These results and those given below can be explained in terms of the theory of Jellinek (1956) for the initial stages of degradation with random initiation. The \bar{M}_w values of the irradiated samples are greater in the presence of I as compared to the corresponding values of PB-1 without I . This indicates that I retards the degradation of the polymer.

In order to avoid complications arising out of branching at high degrees of degradation, the average values of specific rate constants k were evaluated from the initial slope of the curves of a vs irradiation time (figure 1) using the relation, $a = kt$. The value of the Arrhenius energy of activation ΔE and the frequency factor A have been obtained by using the Arrhenius equation (Glasstone *et al* 1941). The plots of $\ln k$ vs $1/T$ are linear and the values of ΔE as well as A so obtained satisfied the equations:

$$\text{PB-1: } k = 1.06 \times 10^{-3} \exp [-662/(RT)] \text{ sec}^{-1},$$

$$\text{and PB-1 + 0.1\% } I, k = 5.80 \times 10^{-4} \exp [-8940/(RT)] \text{ sec}^{-1}.$$

The ΔE may be equated (Bhatnagar and Singh 1968) to the enthalpy (heat) of activation (ΔH^\ddagger) of the activated complex without any appreciable error. As we go from PB-1 to doped sample of the polymer the ΔH^\ddagger value increases from 6.6 to 8.9 kcal mol^{-1} which indicates retardation of degradation reaction of PB-1 by I . As it has been shown (Tkac and Kello 1957), the reaction of the polymer radicals with oxygen is only diffusion-controlled when ΔE is not involved. Because the ΔE of the termination is neglected, our photo-oxidation tests, performed at various low temperatures, give information about the ΔE of the hydrogen abstraction as well as about the energy for transformation of the polymer peroxy radicals to carbonyl and hydroxyl groups. The value (Valko and Marchal 1973) of ΔE of the carbonyl groups formation from the beginning rate of oxidation at low concentration of t-BuOOH in the low thermal range is 8 ± 1 kcal mol^{-1} . This value is in good agreement with that observed by us in the course of these investigations. Irrespective of the variations in the values of ΔH^\ddagger , the values of free energy of activation ΔF^\ddagger remain almost constant around 38 kcal mol^{-1} in both the cases. This leads to the conclusion that the rate-determining step is same for both the systems.

It is observed that the quantum yields ϕ in the range of 2.36×10^{-3} to 18.78×10^{-3} are displayed by neat PB-1 in the temperature range of 233 to 333° K. The smaller ϕ in the range of 0.37×10^{-3} to 4.02×10^{-3} are typical of PB-1 in which the initial UV absorption occurs at I incorporated in the matrix of the

Table 1. Photo-oxidative degradation of poly(1-butene) in the absence and presence of 0.1 wt-% *o*-phenanthroline bis-(1, 3-diphenyl triazine-1-oxide) cobalt(II) [I] in air at different temperatures (Light intensity flux = 2.38×10^{-9} Einstein sec⁻¹ cm⁻², irradiation wavelength $\lambda = 253.7$ nm).

Time of irradiation sec $\times 10^3$	$\bar{M}_w \times 10^5$	$P_{w,t}/\bar{P}_{w,0}$	s	$a \times 10^{-5}$	Time of irradiation sec $\times 10^3$	$\bar{M}_w \times 10^5$	$P_{w,t}/\bar{P}_{w,0}$	s	$a \times 10^{-5}$
Poly(1-butene), 233 K :									
0.0	9.34	1.000	0.0	9.34	1.000
3.6	8.64	0.925	0.235	1.414	3.6	9.19	0.984	0.048	0.285
7.2	7.94	0.850	0.598	3.052	7.2	9.06	0.970	0.089	0.535
10.8	7.50	0.803	0.695	4.175	10.8	8.94	0.957	0.128	0.770
14.4	7.07	0.757	0.941	5.653	14.4	8.84	0.947	0.165	0.993
18.0	6.51	0.697	1.191	7.154	18.0	8.72	0.934	0.207	1.240
21.6	6.21	0.665	1.369	8.225	21.6	8.58	0.919	0.259	1.558
28.8	5.64	0.604	1.744	10.475	28.8	8.54	0.914	0.272	1.635
36.0	5.22	0.559	2.069	12.425	36.0	8.38	0.897	0.330	1.983
43.2	4.98	0.553	2.273	13.633	43.2	8.46	0.906	0.303	1.818
Poly(1-butene), 253 K :									
0.0	9.34	1.000	0.0	9.34	1.000
3.6	8.39	0.898	0.329	1.975	3.6	9.05	0.969	0.093	0.560
7.2	7.44	0.797	0.724	4.351	7.2	8.89	0.952	0.147	0.880
10.8	6.95	0.744	0.958	5.752	10.8	8.72	0.934	0.207	1.240
14.4	6.35	0.680	1.286	7.725	14.4	8.58	0.919	0.259	1.553
18.0	5.87	0.629	1.586	9.525	18.0	8.41	0.900	0.320	1.920
21.6	5.34	0.572	1.969	11.825	21.6	8.28	0.887	0.371	2.228
28.8	4.86	0.520	2.360	14.175	28.8	8.11	0.868	0.438	2.630
36.0	4.54	0.486	2.686	16.131	36.0	7.97	0.853	0.494	2.968
43.2	4.37	0.468	2.872	17.252	43.2	7.97	0.853	0.493	2.963

Poly(1-butene), 273 K :		Poly(1-butene) + 0.1 wt-% I, 273 K :		Poly(1-butene) + 0.6 wt-% I, 293 K :		Poly(1-butene) + 1.10 wt-% I, 293 K :		Poly(1-butene) + 0.1 wt-% I, 293 K :	
0.0	9.34	1.000	0.0	0.0	9.340	0.0	9.340	0.0	9.34
3.6	7.94	0.850	3.025	3.6	9.336	0.007	9.336	3.6	8.96
7.2	6.81	0.729	6.175	7.2	9.337	0.005	9.337	7.2	8.69
10.8	5.91	0.633	9.325	10.8	9.340	0.000	9.340	10.8	8.43
14.4	5.21	0.558	12.452	14.4	9.340	0.000	9.340	14.4	8.26
18.0	4.62	0.495	15.653	18.0	9.340	0.000	9.340	18.0	7.95
21.6	4.24	0.454	18.125	21.6	9.340	0.000	9.340	21.6	7.71
28.8	3.61	0.387	23.215	28.8	9.340	0.000	9.340	28.8	7.48
36.0	3.44	0.368	24.825	36.0	9.340	0.000	9.340	36.0	7.28
43.2	3.38	0.362	25.513	43.2	9.340	0.000	9.340	43.2	7.20
0.0	9.340	1.000	..	0.0	9.340	1.000	1.000	0.0	1.000
3.6	9.335	0.995	0.042	3.6	9.336	0.996	0.996	3.6	0.959
7.2	9.337	0.997	0.030	7.2	9.337	0.997	0.997	7.2	0.930
10.8	9.340	1.0000	0.000	10.8	9.340	1.0000	1.0000	10.8	0.903
14.4	9.340	1.0000	0.000	14.4	9.340	1.0000	1.0000	14.4	0.884
18.0	9.340	1.0000	0.000	18.0	9.340	1.0000	1.0000	18.0	0.851
21.6	9.340	1.0000	0.000	21.6	9.340	1.0000	1.0000	21.6	0.826
28.8	9.340	1.0000	0.000	28.8	9.340	1.0000	1.0000	28.8	0.801
36.0	9.340	1.0000	0.000	36.0	9.340	1.0000	1.0000	36.0	0.779
43.2	9.340	1.0000	0.000	43.2	9.340	1.0000	1.0000	43.2	0.771
0.0	9.34	1.000	..	0.0	9.34	1.000	1.000	0.0	1.000
3.6	7.50	0.803	4.175	3.6	8.84	0.947	0.947	3.6	0.959
7.2	6.18	0.662	8.325	7.2	8.45	0.905	0.905	7.2	0.930
10.8	5.27	0.564	12.175	10.8	8.04	0.861	0.861	10.8	0.903
14.4	4.35	0.466	17.325	14.4	7.90	0.846	0.846	14.4	0.884
18.0	3.76	0.403	21.613	18.0	7.41	0.793	0.793	18.0	0.851
21.6	3.43	0.367	24.931	21.6	7.07	0.757	0.757	21.6	0.826
28.8	3.09	0.331	28.825	28.8	6.99	0.716	0.716	28.8	0.801
36.0	2.89	0.309	32.075	36.0	6.28	0.672	0.672	36.0	0.779
43.2	2.83	0.303	32.651	43.2	6.15	0.659	0.659	43.2	0.771
0.0	9.34	1.000	..	0.0	9.34	1.000	1.000	0.0	1.000
3.6	7.50	0.803	0.695	3.6	8.84	0.947	0.947	3.6	0.959
7.2	6.18	0.662	1.386	7.2	8.45	0.905	0.905	7.2	0.930
10.8	5.27	0.564	2.027	10.8	8.04	0.861	0.861	10.8	0.903
14.4	4.35	0.466	2.884	14.4	7.90	0.846	0.846	14.4	0.884
18.0	3.76	0.403	3.632	18.0	7.41	0.793	0.793	18.0	0.851
21.6	3.43	0.367	4.151	21.6	7.07	0.757	0.757	21.6	0.826
28.8	3.09	0.331	4.799	28.8	6.99	0.716	0.716	28.8	0.801
36.0	2.89	0.309	5.340	36.0	6.28	0.672	0.672	36.0	0.779
43.2	2.83	0.303	5.469	43.2	6.15	0.659	0.659	43.2	0.771

Table 1 (contd.)

Time of irradiation sec $\times 10^3$	$\bar{M}_w \times 10^5$	$P_{w,1}/\bar{P}_{w,0}$	s	$a \times 10^{-5}$	Time of irradiation sec $\times 10^3$	$\bar{M}_w \times 10^5$	$P_{w,1}/\bar{P}_{w,0}$	s	$a \times 10^{-5}$
Poly(1-butene), 313 K :									
0.0	9.34	1.000	0.0	9.34	1.000
3.6	6.76	0.724	1.051	6.312	3.6	8.60	0.921	0.250	1.503
7.2	4.96	0.531	2.293	13.775	7.2	7.98	0.854	0.493	2.960
10.8	4.08	0.347	3.209	19.275	10.8	7.42	0.794	0.730	4.385
14.4	3.35	0.359	4.299	25.821	14.4	6.83	0.731	1.017	6.108
18.0	2.89	0.309	5.332	32.025	18.0	6.48	0.694	1.205	7.235
21.6	2.66	0.285	5.906	35.475	21.6	6.11	0.654	1.430	8.590
28.8	2.35	0.252	6.839	41.075	28.8	5.54	0.593	1.816	10.908
36.0	2.26	0.242	7.205	43.275	36.0	5.10	0.546	2.162	12.985
43.2	2.26	0.242	7.197	43.227	43.2	4.94	0.529	2.311	13.880
Poly(1-butene), 333 K :									
0.0	9.34	1.000	0.0	9.34	1.000
3.6	5.92	0.634	1.550	9.312	3.6	8.25	0.884	0.379	2.275
7.2	4.22	0.452	3.034	18.225	7.2	7.28	0.779	0.796	4.783
10.8	3.21	0.344	4.554	27.352	10.8	6.69	0.716	1.089	6.543
14.4	2.59	0.277	6.112	36.713	14.4	6.04	0.647	1.475	8.858
18.0	2.18	0.233	7.522	45.177	18.0	5.57	0.596	1.799	10.808
21.6	2.21	0.237	7.405	44.476	21.6	5.08	0.544	2.186	13.130
28.8	2.06	0.221	8.034	48.253	28.8	4.47	0.479	2.761	16.585
36.0	2.02	0.216	8.221	49.376	36.0	4.05	0.434	3.242	19.500
43.2	2.07	0.222	7.999	48.051	43.2	3.86	0.413	3.501	21.030

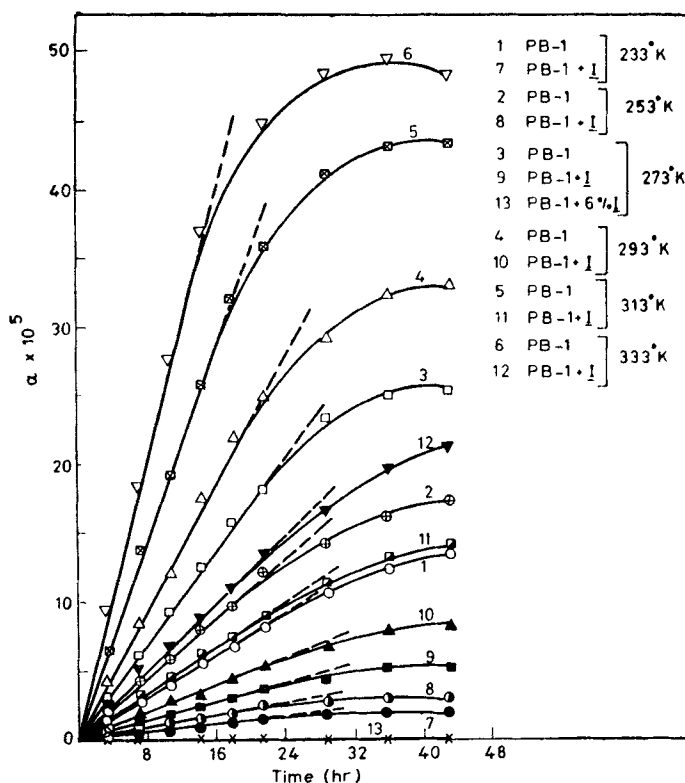


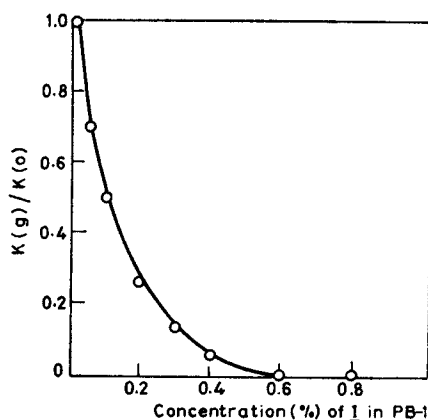
Figure 1. Variation of photodegradation rate (a) in air of 253.7 nm irradiated PB-1 film with 0.1% I .

polymer films. The smaller ϕ of the degradation process of PB-1 in the presence of I is due to the conversion of absorbed energy of light quanta to heat and the low coefficient of light absorption of the polymer molecule.

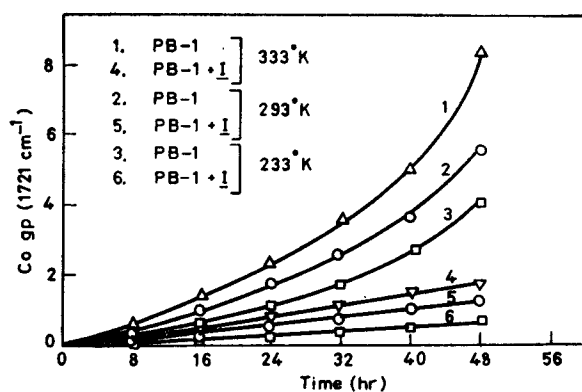
The effect of the concentration (0.1–0.6%) of I in the photodegradation of PB-1 was also examined. The changes in \bar{M}_w and a of PB-1 must be temperature dependent to some extent, but the constancy of the data indicates the swamping action of the I . Figure 2 gives the variation of the degree of protection (Jortner 1959) vs concentration of I in PB-1 at room temperature. The data confirm that the saturation protection action is reached at a value of 0.6% (wt) of I in PB-1.

During the degradation of PB-1 the remarkable changes in IR spectra were observed in the regions *ca.* 1721 cm^{-1} due to carbonyl groups, *ca.* 3340 cm^{-1} , due to hydroperoxide by the oxidation of tertiary C-H bonds and *ca.* 3400–3500 cm^{-1} , due to hydroxyl groups. The carbonyl bands at *ca.* 1721 cm^{-1} of the photo-oxidized PB-1 film appear sharper (figure 3) throughout their term of exposure. At the same time of irradiation the content of carbonyl groups of pure polymer is higher than that of the polymer containing I and this behaviour is consistent with the observed decrease in molecular weight.

The hydroperoxide content of the oxidized polymer was plotted against time in figure 4. The hydroperoxide content of the polymer sample containing I is



(2)



(3)

Figure 2. Variation of rate of protection in air of PB-1 film with various concentrations of I during 253.7 nm irradiation.

Figure 3. Variation of carbonyl content in air of 253.7 nm irradiated PB-1 film with 0.1% I .

lower than that of pure polymer. The hydroperoxide was rising to a maximum concentration but the carbonyl showed an induction period.

Figure 5 shows the UV spectra of irradiated PB-1 film in the presence and absence of 0.1% I . A band with maximum at *ca.* 229 nm was assigned to the allyl free radical. An intense band at *ca.* 272 nm which is due to the carbonyl group has been observed. The UV spectrum of heat irradiated PB-1 film gradually increases with the time of irradiation. On the other hand, PB-1 film containing 0.1% I , the increase of the UV spectrum is slower than neat PB-1 film.

The value of the protective effectiveness (Miller 1958) for PB-1 of 0.1% I is found to be *ca.* 210 nm.

The free radical mechanism of PB-1 photo-oxidation by light and molecular oxygen has been described in the previous studies (Chandra *et al* 1980b). But it has recently been proposed that the oxidative photodegradation of the polymer is also promoted by electronically excited molecular oxygen (commonly called

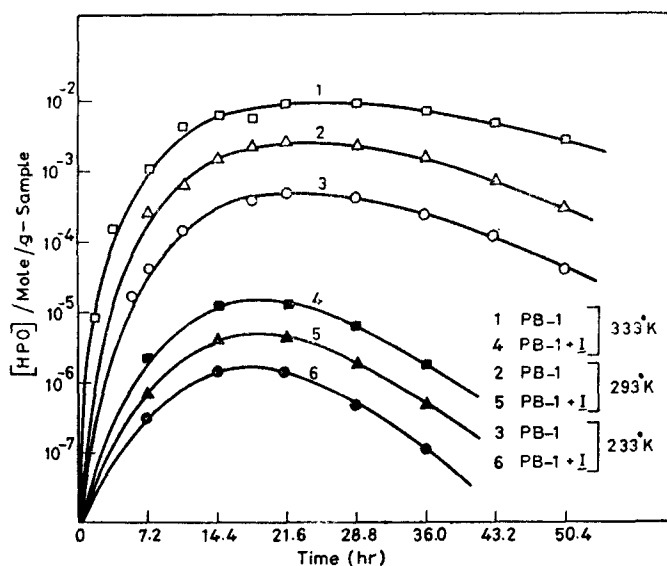


Figure 4. Variation of hydroperoxide content in air of 253.7 nm irradiated PB-1 film with 0.1% I.

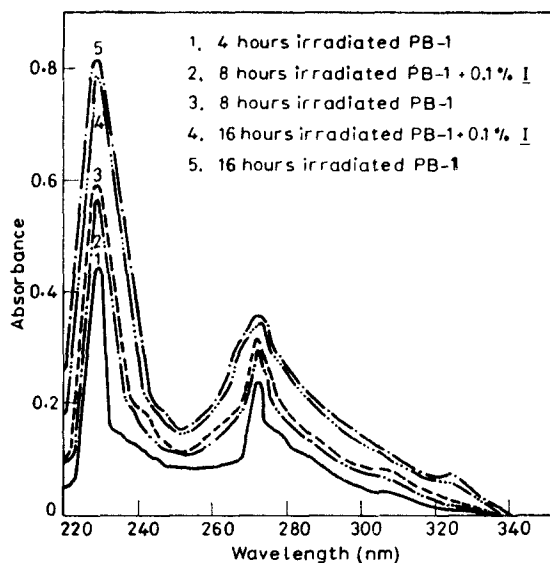


Figure 5. Variation of UV spectrum in air of 253.7 nm irradiated PB-1 film with 0.1% I.

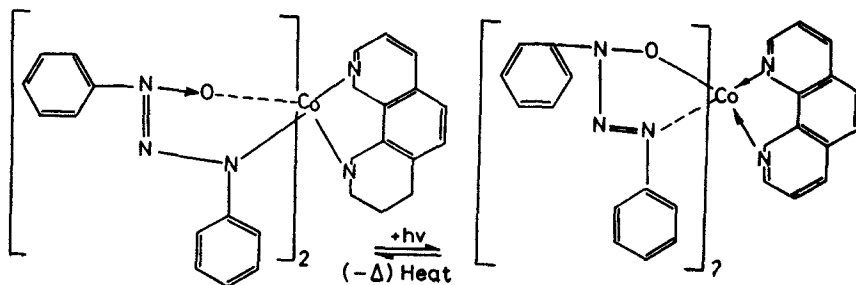
singlet oxygen) formed in the polymer (Trozzolo and Winslow 1968). The UV radiation is absorbed by carbonyl groups causing their excitation and some of the electronically excited carbonyl groups may transfer energy to dissolved molecular oxygen forming singlet oxygen in the $^1\text{O}_2$ ($^1\Delta_g$) state (Kaplan and Kelleher 1971).

Such photo-processes leading to the formation of singlet oxygen are well documented (Kearns 1971). The absorption of UV energy by some of the carbonyl groups results in the formation of vinyl groups. The degradation is subsequently accelerated by reaction of singlet oxygen with vinyl groups and even saturated carbon atoms in the polymer chain to form hydroperoxides (Mill *et al* 1968; Kaplan and Kelleher 1970). The decomposition of hydroperoxides, on exposure to light, causes the formation of macro-radicals which by disproportionation leads to degradation of the polymer. The value of $\Delta F^\ddagger \approx 38 \text{ kcal mol}^{-1}$ obtained by us is quite close to 40 kcal mol^{-1} required (Ranby and Rabek 1975) for the decomposition of oxygen-oxygen bond in the polymer hydroperoxide (PO-OH).

The stabilizer *I* which is a chelate of cobalt is believed to function primarily as quencher of electronically excited polymer molecules (probably excited carbonyl species) by an energy transfer process (Carlsson and Wiles 1974; Rabek and Ranby 1975). The UV stabilizer *I* is also believed to quench the singlet oxygen and stabilized PB-1 from oxidative photodegradation.

From the luminescence spectral data of PB-1 film it is clear that in the absence of *I*, the polymer is excited by 310 nm light and emits 360 nm light to a ground state (S_0) and takes part in photochemical reaction. But in the presence of *I* the excitation energy of the polymer transfer to *I* which has an unsaturated chromophore and can take up harmful UV radiation and dissipate this energy as harmless IR radiation or heat. Due to the energy difference of *d* orbitals in *I*, it may also absorb visible and UV incident light. These energies are utilized for the electronic transitions (*d-d*) and metal-ligand charge transfer in the chelate *I*. In the presence of *I* in the polymer, the absence of 360 nm emission and the appearance of 430 and 480 nm emissions might suggest that this assumption is sound.

Thus, *I* is a powerful UV stabilizer at all concentrations and this has been shown to be due to the ability of *I* to behave as UV absorber. The *I* also produces a minimal amount of adventitious photosensitizers such as hydroperoxide and derived carbonyl and hydroxyl compounds during the irradiation. Therefore, it is much more effective than UV stabilizers whose main function is only to screen the UV light.



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