Thermal and Photo-Oxidative Degradation of Poly-1-butene Film in the Presence of Zinc Thiopicoline Anilide

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Synopsis

The photo-oxidative thermal stability of isotactic poly-1-butene stabilized with zinc thiopicoline anilide (ZTPA) was investigated by means of light scattering, chemical actinometry, and spectrophotometric techniques. The inhibition and the course of the oxidative reaction was determined by measuring weight-average molecular weight, heats of activation, and quantum yield of the photolysis of the polymer film with 253.7-nm light at a temperature range of −40 to +60°C. The changes in mechanical, physical, and chemical properties of irradiated polymer film were also examined. The role of ZTPA is discussed on the basis of the luminescence and UV spectral data. ZTPA behaves both as a thermal and UV stabilizer due to a combination of different kinds of activity in the same molecule.

INTRODUCTION

The photo-oxidation of poly-1-butene is a problem of considerable technological importance. Unstabilized poly-1-butene is destroyed rapidly in sunlight, and this has placed a severe limitation on its long-term use out-of-doors. The reason for the irreproducibility of performance of poly-1-butene in the outdoor environment has been shown to be due to the presence of a number of labile tertiary hydrogen atoms in its structure and the introduction of photoinitiating groups during the synthesis, processing, and fabrication operations.[1-3] Some but not all antioxidants which are not UV stabilizers can markedly affect the outdoor behavior of the polymers[4] by controlling the oxidative process occurring during thermal treatment. Others which are both antioxidants and UV stabilizers affect both thermal and photo-oxidation rates.[4,5]

A survey of the literature indicates that very little work has been done on the degradation and stabilization of isotactic poly-1-butene (IPB) film in air. In the present investigations, therefore, the thermal and photostabilizing activity of a new compound, zinc thiopicoline anilide (ZTPA) (I), incorporated in the matrix of isotactic poly-1-butene film at −40 to +60°C by 253.7 nm light has been examined.

I
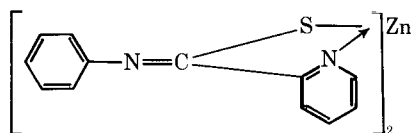
The nature and origin of the photoinitiating groups by studying both the thermal as well as the photo-oxidative degradation were determined. The kinetics were followed by monitoring the rate of chain scission of the polymer. Photo-oxidation of the polymer leads to random chain scission and crosslinking. As a result, the changes in elongation to break, density, and gel fraction were determined. The comparison of weight-average molecular weight, degree of degradation, quantum yield, enthalpy, entropy, and free energy of the activation processes and the changes in carbonyl, hydroperoxide, vinylidene, and hydroxyl contents of irradiated samples of IPB in the absence and presence of ZTPA indicate that ZTPA works as an UV absorber and peroxide decomposer toward the degradation of IPB.

EXPERIMENTAL

Sample Preparation: Traces of atactic polymer in the sample of IPB (Mobile Chemical Co., Metuchem, New Jersey, U.S.A.) were removed by dissolution of the polymer in benzene, followed by precipitation with ether. IPB film (80 μm thick) was prepared by blending the polymer with ZTPA[6] (0.01–0.5 wt %) and hot pressing with a pressure of 200 kg/cm^2 for 10 min at 150°C. All films with and without ZTPA were prepared under the same processing conditions to avoid different thermal pretreatment of the samples.

Photo-irradiation: Photodegradation was carried out in air with a General Electric UA-3 medium-pressure mercury lamp. The IPB films were irradiated by monochromatic light of 253.7 nm for various periods in the range −40 to +60°C. The temperature of the system was controlled within ±0.1°C.

Spectrophotometric Measurements: Absorption measurements were carried out with a Perkin–Elmer Spectracord (model 4000) recording UV spectrometer and a Perkin–Elmer (model 21) IR spectrophotometer.

Luminescence Spectra: Emission spectra of each film sample were determined on a Hitachi MPF-2A spectrophotometer with a xenon source and a photomultiplier.

Molecular Weight Determination: The changes in the weight-average molecular weight ($\overline{M}_w$) and refractive index increment (dn/dc) for IPB film in cyclohexane were determined using a light scattering photometer and differential refractometer (Phoenix Precision Instrument Co., Philadelphia, Pennsylvania, U.S.A.), respectively. Zimm plots were employed to estimate $\overline{M}_w$ as a function of time. The dissymmetry ratios were utilized to calculate the particle scattering factors for correction of the light scattering data.

Quantum Yield. If bonds in the polymer chain may be broken at random, each bond being of equal strength and accessibility, then the following relation[7] holds:

$$\frac{1}{p_{n,t}} - \frac{1}{p_{n,0}} = \frac{u}{m}\Phi_{cs}Iat \tag{1}$$

where m is the weight of irradiated polymer film, u is the molecular weight of the monomer, I is the light intensity falling on the film, a is the absorbance of the polymer, Φ_{cs} is the quantum yield for chain scission, and $p_{n,0}$ is the number-average degree of polymerization initially and $p_{n,t}$ at any time t during the degradation. The values of the quantum yield Φ_{cs} can be determined from eq.

(1) by plotting $1/p_{n,t}$ vs. t. The ratio $p_{n,t}/p_{n,o}$ can be replaced by the ratio of weight-average degree of polymerization $p_{w,t}/p_{w,0}$, without appreciable error. This ratio can be conveniently determined by light scattering measurements. The values of I and a can be determined by potassium ferrioxalate actinometry.[8]

Under our experimental conditions, the quantity I/m is constant, as the surface area exposed to radiation is proportional to m. Therefore, eq. (1) can be written as

$$\frac{1}{p_{w,t}} - \frac{1}{p_{w,0}} = Kt \qquad (2)$$

with $K = (u/m)\Phi_{cs}Ia$.

Determination of Hydroperoxides: Polymer hydroperoxides produced by either thermal aging or UV exposure of IPB film were determined by a modified iodometric method.[9]

Determination of Mechanical Properties: The elongation-to-break test, according to ASTMD 638, was made using an Instron tensile tester, model TTCM, at an elongation speed of 50 cm/min.

Determination of Gel Fraction: The percent gel fraction was established by determining the amount of IPB insoluble in hot decaline according to ASTMD 2765–68.

RESULTS AND DISCUSSION

The variation of $\overline{M}_w$ vs. time of irradiation of IPB films in the absence and presence of 0.1 wt % ZTPA in air at various temperatures with a light intensity of 2.38×10^{-9} Einstein/s·cm^2 is given in Figure 1. In the case of IPB with the stabilizer, $\overline{M}_w$ shows considerable higher values at all temperatures. In the initial stages of the photodegradation of IPB, there is a rapid drop in $\overline{M}_w$, but subse-
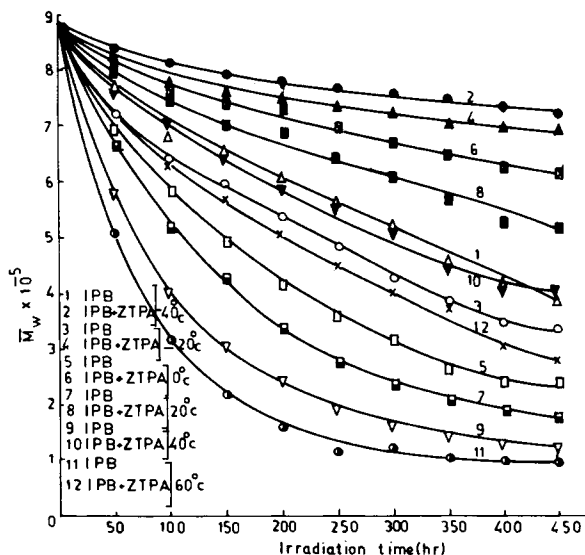

Fig. 1. Change in weight-average molecular weight values of IPB in the absence and presence of 0.1% ZTPA at various temperatures in air.

quently it reaches a saturation limit. Such a sharp drop in $\overline{M}_w$ 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[10] for the initial stages of degradation with random initiation. During the degradation in the absence and presence of ZTPA, it is necessary to consider simultaneous rupture of weak and normal links and also crosslinking.

The average number of cuts (s) per single chain length was determined by using the equation[11]

$$\frac{p_{w,t}}{p_{w,0}} = \left(\frac{2}{s^2}\right)(e^{-s} + s - 1) \tag{3}$$

Values of s were determined from experimental values of $p_{w,t}/p_{w,0}$ by comparing these data with a calculated curve according to eq. (3).

For large values of $p_{w,0}$; $s/p_{w,0} = \alpha$, where α is the degree of degradation. For a random chain degradation process, $\alpha = k_1 t$, and the initial slope of the α vs. t curve (Fig. 2) gives a method of evaluating k_1, the specific rate constant. Figure 2 indicates that the rate of degradation in the initial stages is maximum.

The value of activation energy ΔE and the frequency factor A have been obtained by using the equation

$$k_1 = A\, e^{-\Delta E/RT} \tag{4}$$

The plots of $\ln k_1$ vs. $1/T$ are linear so that the values of ΔE as well as A can be estimated. The data so obtained satisfied the equations

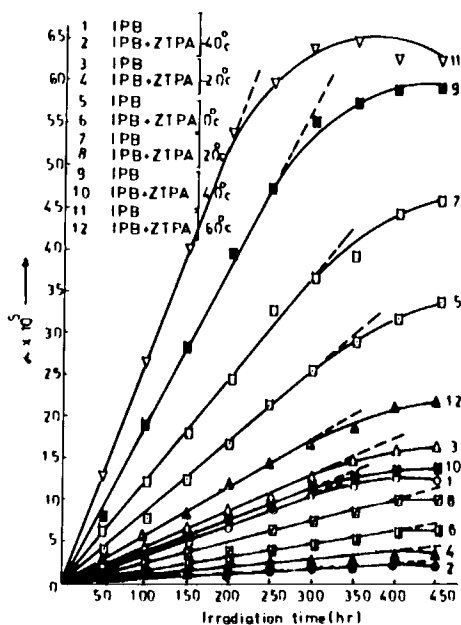$$\text{IPB};\quad k_1 = 1.61 \times 10^{-3} \exp\left(\frac{6.93}{RT}\right) \text{s}^{-1} \tag{5}$$

Fig. 2. Change in degree of degradation of IPB with and without 0.1% ZTPA at various temperatures in air.

and

$$\text{IPB} + 0.1\% \text{ ZTPA}; \quad k_1 = 1.91 \times 10^{-2} \exp\left(\frac{9.81}{\text{RT}}\right) \text{s}^{-1} \tag{6}$$

The values of ΔE and A obtained in the absence and presence of ZTPA are 6.93 ± 0.04 kcal/mol, 1.61 ± 0.02 s^{-1} and 9.81 ± 0.04 kcal/mol, 1.91 ± 0.02 s^{-1}, respectively.

The energy of activation (ΔE) may be equated[12] to the enthalpy (heat) of activation ($\Delta H^{\neq}$) of the activated complex without any appreciable error. As we go from IPB to doped sample of IPB, the $\Delta H^{\neq}$ value increases from 6.93 to 9.81 kcal/mol, which is indicative of retardation of degradation of IPB by ZTPA. As has been shown,[13] the reaction of the polymer radicals with oxygen, P· + O$_2$ = PO$_2^{\cdot}$, is only diffusion controlled when ΔE is not involved. Because the activation energy of the termination is neglected, our photo-oxidation tests, performed at various low temperatures, give information about the ΔE of the hydrogen abstraction from tertiary carbon atoms in the structure of IPB as well as about the energy for transformation of the polymer peroxy radicals POO· to carbonyl groups. The decomposition of the polymer hydroperoxy group at room temperature is very slow (ΔE is ca. 39 kcal/mol),[14] while the oxidation of the polymer proceeds with a relatively high speed (with UV radiation) like a reaction of first order in relation to the increase of the carbonyl groups $d[\text{C}=\text{O}]/dt = k_1[\text{PO}_2^{\cdot}]$. We must also consider, for such low-temperature photo-oxidation, the possibility of a direct attack on the $-\text{C}-\text{C}-\sigma-$ bonds of the IPB chain by primary formed polymer peroxy radicals, according to the concept of intramolecular self-decomposition process of the polymer peroxy radicals proposed by Marchal and others[15,16] and theoretically established by Volko and Marchal.[17] The value[18] of activation energy (ΔE) of the carbonyl group formation at low concentration of t-BuOOH in the low thermal range is 8 ± 1 kcal/mol. This value is in good agreement with that observed by us in the course of these investigations.

The values of the entropy of activation ($\Delta S^{\neq}$) were calculated[18] from $\Delta H^{\neq}$. The $\Delta S^{\neq}$ values lie in the range −58.7 to −75.86 EU. The $\Delta S^{\neq}$ becomes more negative as one goes from IPB to the doped sample of IPB, indicating a slow photochemical reaction in the latter case. Irrespective of the variations in the values of $\Delta H^{\neq}$ and $\Delta S^{\neq}$, the values of free energy of activation ($\Delta F^{\neq}$) remain almost constant around 38.18 kcal/mol in both cases. This indicates that for both systems the rate-determining step is the same.

Another way degradation reaction characterization may be reached is from measurements of quantum yield for chain scission process. The quantum yield (Φ_{cs}) for chain scission was calculated from eq. (1) for IPB films with and without 0.1% ZTPA after different times of irradiation at various temperatures. The Φ_{cs} dependence on temperature for pure IPB and the IPB–ZTPA system is shown in Figure 3. It seems interesting that the Φ_{cs} values for pure IPB films increase with temperature much more than those for IPB with ZTPA. The increase in Φ_{cs} values with increasing temperature may be due to a greater probability of the polymer radicals to recombine at lower temperatures. The Φ_{cs} values decrease with increasing percentage of the stabilizer incorporated in the matrix of IPB films. It is observed that the larger values of Φ_{cs} are displayed by neat IPB film which is internally photosensitized. On the other hand, the smaller values of Φ_{cs} are typical of IPB in which the initial UV absorption occurs
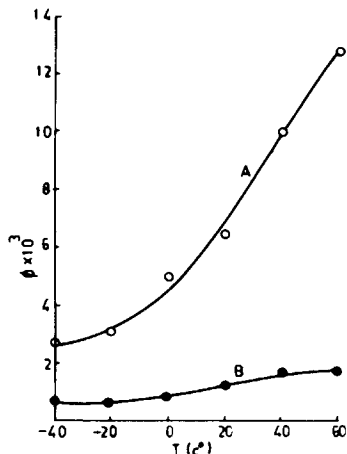
Fig. 3. Effect of temperature on quantum yield Φ_{cs} for chain scission of IPB (A) and IPB + 0.1% ZTPA (B).

at the stabilizer present in the matrix of IPB films. The smaller Φ_{cs} of the degradation process of IPB in the presence of ZTPA is also 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 (0.01 to 0.5%) of ZTPA in the photodegradation of IPB was also examined. The changes in $\overline{M}_w$ and α of IPB must be temperature dependent to some extent, but the constancy of the data indicates the swamping action of the ZTPA. Figure 4 gives the variation of the degree of protection[7] $K(g)/K(0)$ with concentration (g) of ZTPA in IPB at room temperature. The data confirm that the saturation protective action is reached at a value of 0.4% ZTPA in IPB.

During the photo-oxidation of IPB, remarkable changes in IR spectra were observed, at ca. 1730 cm^{-1} due to carbonyl groups, at ca. 3340 cm^{-1} due to hydroperoxides produced by the oxidation of tertiary C–H bonds, at ca. 3400–3500 cm^{-1} due to hydroxyl groups, and at ca. 888 cm^{-1} due to a vinylidene[19] type end group. During the 10 min of processing the film, the thermal oxidation at tertiary carbon atoms of IPB yields predominantly hydroperoxide and vinylidene groups,
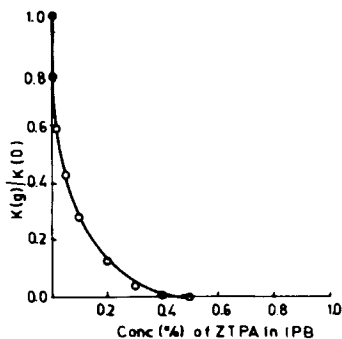

Fig. 4. Change in the rate of protection of IPB with various concentrations of ZTPA during UV irradiation.

and these groups decay with the formation of carbonyl and hydroxyl compounds during UV irradiation. Figure 5 shows the effect of 253.7 nm light on IPB films which have been thermally processed for 10 min at 150°C in the absence and presence of 0.1% ZTPA. The hydroperoxide concentration and vinylidene absorption decay more rapidly, and the rapid formation of decaline-insoluble gel in the neat IPB indicates that hydroperoxide and vinylidene become also involved in a crosslinking process. The crosslinking reaction is not the only reaction consequent upon photolysis; there is also an initial rapid rate of formation of both alcohol and carbonyl bands in the IR spectra. These are formed by alternative reactions of the initially formed alkoxy radical; alcohol by hydrogen abstraction from the polymer and carbonyl by loss of hydrogen. The carbonyl formation rate by hydroperoxide photolysis may be directly related to the hydroperoxide concentration in the initial stages of the reaction. When 0.4% ZTPA is compounded into IPB, no hydroperoxide can be detected and IPB is effectively stabilized. On exposing IPB film containing 0.4% ZTPA to 253.7 nm light, there is an induction period to carbonyl and hydroxyl formation confirming the absence of hydroperoxide. This observation confirms the essential continuity of the thermal and photo-oxidation processes and the key role of hydroperoxides.

The oxidative changes described above are paralleled by corresponding changes in the physical properties of IPB. The chemical crosslinking reaction associated with vinylindene decay in IPB is accompanied by an increase in gel formation, and this is reflected in changes in the mechanical properties of the polymer (Fig. 6). The measuring of the elongation to break of polymeric materials in weathering tests often proves to be a more reliable method than the determination of breaking strength. In Figure 6, all samples—stabilized and unstabilized—showed a slight initial elongation gain which may be due to the slight increase of crystallinity of the polymer caused by thermal treatment. The stabilized samples are showing the characteristic delayed aging curves. The gel fraction curves show that the ZTPA-free IPB film has a relatively strong tendency
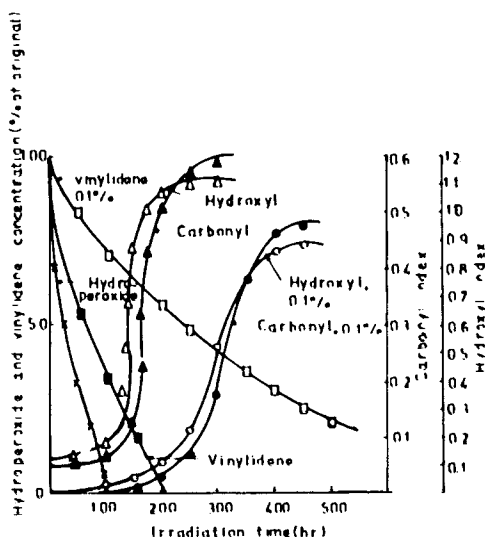

Fig. 5. Effect of 253.7 nm light on functional group concentration in IPB film with and without 0.1% ZTPA.
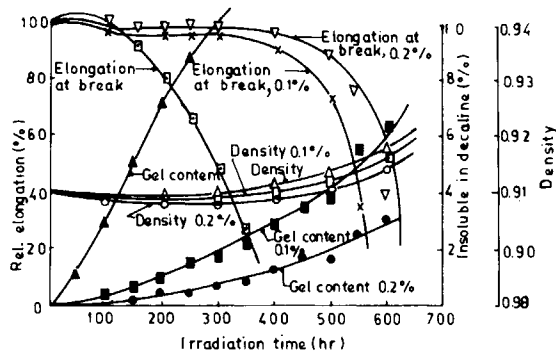
Fig. 6. Effect of 253.7 nm light on the physical and mechanical properties of IPB film containing various concentration of ZTPA.

for crosslinking. The samples containing UV absorber are, however, adequately more resistant to this process.

In order to investigate the protection mechanism of ZTPA, the UV spectra (Fig. 7) of irradiated IPB film at room temperature in the presence and absence of 0.1% ZTPA were investigated. The broad band with a maximum at ca. 236 nm was assigned to the allyl free radical. An intense band at ca. 280 nm which is due to the carbonyl group was observed. The UV spectrum of neat irradiated IPB film gradually increases with time of irradiation. On the other hand, with IPB film containing ZTPA, the increase in the spectrum is slower than the increase in that of neat IPB film.

The UV spectrum of neat ZTPA possesses a strong absorbance in the UV region where photodegradation of IPB occurs, and it shows an intense absorption peak at ca. 280 nm. The kinetics of the photochemically induced change of ZTPA solution in cyclohexane ($4.5 \times 10^{-3}M$), at 253.7 nm in air are presented in Figure 8. The increase in absorption is linear with the dose, indicating the absence of reverse reactions. When a solution of ZTPA saturated with CO_2 was irradiated with 253.7 nm light, an increase of absorption was observed which was somewhat smaller than that obtained in the presence of air. A similar effect was also found in case of irradiated film of neat ZTPA. These experiments indicate
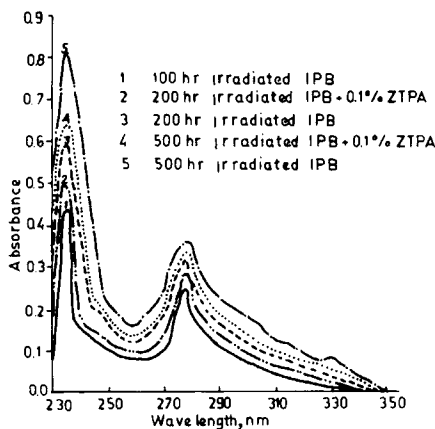

Fig. 7. Change in UV spectrum of IPB upon irradiation by light of wavelength 253.7 nm.
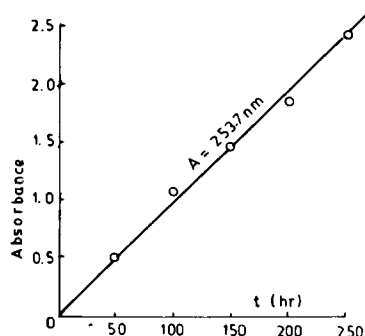
Fig. 8. Change in the absorption of aerated solution of 4.5 × 10⁻³ M ZTPA in cyclohexane induced by 253.7 nm light.

that under the effect of 253.7 nm light, ZTPA is converted into a strongly absorbing product which acts as inner filter for UV light.

The emission spectra of IPB films irradiated with and without 0.1% ZTPA are shown in Figure 9. In the case of neat IPB film, an emission spectrum observed at ca. 360 nm in unirradiated sample gradually disappears and a new emission spectrum appears at ca. 480 nm and gradually increases. IPB film containing 0.1% ZTPA shows no emission spectra at ca. 360 nm with excitation of 300 nm; instead, an emission spectrum is observed at ca. 430 nm with excitation of 300 nm. The decay of the emission is slower than the decay of emission at ca. 360 nm in neat IPB. The decrease in emission at ca. 360 nm may result from the quenching of fluorescent species by oxidation products; and oxidation products showed luminescence at about 480 nm.

From the luminescence spectra data, it is clear that energy was transferred from the excited state of the polymer molecules to ZTPA, which has an unsaturated chromophore. In the absence of ZTPA, the polymer is excited by 300 nm light and emits 360 nm light to a ground state (S_0) and takes part in photochemical reactions. But in the presence of ZTPA, the excitation energy of the polymer transfers to the ZTPA present in the matrix of the film. The energy is utilized for the electronic transitions (d–d) and metal–ligand charge transfer
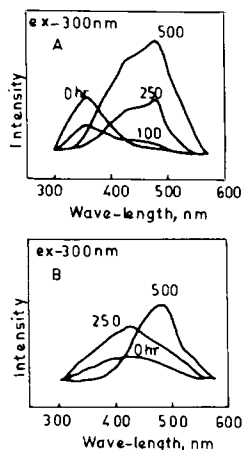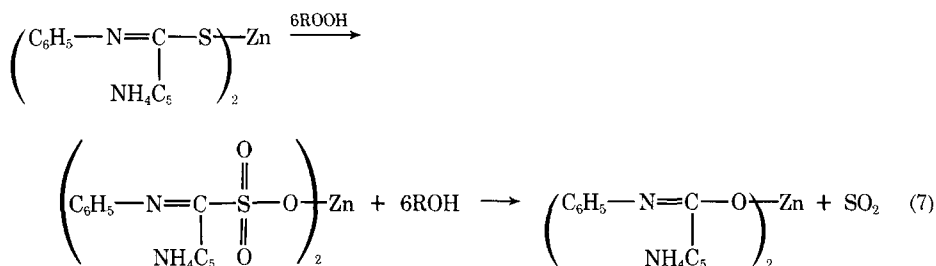

Fig. 9. Change in emission spectra of IPB film during 253.7 nm photoirradiation: (A) IPB; (B) IPB + 0.1% ZTPA.

in this complex. The absence of 360 nm emission and the appearance of 430 and 480 nm emissions might suggest that this assumption is sound (ZTPA itself emits 370 and 480 nm light).

It is clear from Figure 5 that a minor amount of hydroperoxide in the substrate plays an important role in the degradation of the polymer and that the hydroperoxide decomposer ZTPA inhibits this degradation:

$$\left(C_6H_5 - N = \underset{\underset{NH_4C_5}{|}}{C} - S \right)_2 Zn \xrightarrow{6ROOH}$$

$$\left(C_6H_5 - N = \underset{\underset{NH_4C_5}{|}}{C} - \underset{\underset{O}{\overset{O}{\|}}}{S} - O \right)_2 Zn + 6ROH \longrightarrow \left(C_6H_5 - N = \underset{\underset{NH_4C_5}{|}}{C} - O \right)_2 Zn + SO_2 \quad (7)$$

Gaseous SO_2 can act as an acid catalyst for the ionic decomposition of hydroperoxide groups to alcohols and ketones.[20,21] Therefore, the function of ZTPA might be that of hydroperoxide decomposer, conventional UV absorber, and energy acceptor from excited polymer.

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