

Role of Metal(α -Thiopicoline Anilide) as Sensitizer in the Photo-oxidative Degradation of Polyisobutylene

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The effect of metal *tris*-(α -thiopicoline anilide)manganese(III) (TPAM) and *tris*-(α -thiopicoline anilide)cobalt(III) (TPAC) with (0.01 % wt.) on the photo degradation of polyisobutylene (PIB) film was examined by changes in weight average molecular weight, energy of activation and quantum yield of the photolysis of polymer film with 254 nm light. The photo degradation was affected by the kind of metal and by the temperature. The degree of degradation increases with passage of time confirming the random nature of the chain scission of the polymer. The unsaturation produced is proportional to the time of irradiation. Ultraviolet and infrared absorption spectra have been employed to substantiate a mechanism of the degradation process which does not involve hydrogen abstraction from the polymer, but direct cleavage of the polymer backbone and addition of initiating radicals of *tris*-(α -thiopicoline anilide)cobalt(III) and *tris*-(α -thiopicoline anilide)manganese(III) at the sites of scission *tris*-(α -thiopicoline anilide)manganese(III) was found as a photo sensitizer whereas *tris*-(α -thiopicoline anilide)cobalt(III) merely enhanced the degradation.

Key Words: Effect, Cobalt, Manganese, Degradation, Polyisobutylene, Temperature.

INTRODUCTION

In recent years, a more visible problem is the production of plastics that do not end up ultimately in some form of garbage disposal system. Polyisobutylene was specifically chosen for investigations because it is a primarily commercial molding material whose application are limited by the deterioration of some of its useful properties by solar radiations. Therefore, the photostabilization and degradation of polyisobutylene is a problem of considerable importance and scientific interest. Scott¹ and Andrady and Pegram² have established on the photo-degradation of polymeric materials in connection with the preparation of self disposal packing material. It is well known that trace amount of metallic impurities and additives present in polymers play an important role in photo-degradation of substrates. Some such additives act as photo-sensitizers while other act as quenchers³⁻⁵.

In the present investigation an attempt has been made to study the effect of metal (Co and Mn) *tris*-(α -thiopicolin anilide) in matrix of polyisobutylene film which leads to a reduced molecular weight and random main chain scission of the polymer film when exposed to 254 nm light.

The photo-degradation was followed by light scattering and potassium ferrioxalate actionometry and the data have been processed to calculate the values of weight average molecular weight, degree of degradation, the specific rate constant and

quantum yield. The molecular weight changes and cross linking in case of polydimethylsiloxane was determined by David *et al.*⁶. Likewise the sensitivity of poly(vinyl chloride) in natural environment was found by Hussain *et al.*⁷. In a similar way the changes in carbonyl index average molecular weight on embattlement of enhanced photodegradable was determined by Andrady *et al.*⁸. The chemical and physical changes occurring during UV degradation of high impact polystyrene was found by Gaffar *et al.*⁹. The effect of UV radiation on the thermal parameters of collagen degradation was studied by Kamimska and Sionokowska¹⁰. Kaczmarek and Sionokowska¹¹ studied the influence of transition metal salts on the photo oxidative degradation of polyethylene oxide. Jakubiak *et al.*¹² studied the cross linking polymerization of multifunctional monomers in presence of visible light photo initiator. Likewise Jakubiak *et al.*¹³ also studied amine photo initiating system for the initiation of free radical polymerization.

EXPERIMENTAL

The polyisobutylene (PIB) used throughout was Vistanex-L-140, which was provided by Enjay Chemical Company, New York. The polymer sample was purified by three precipitations from petroleum ether (40-60 °C) with methanol. It had a weight-average molecular weight of 1.95×10^6 g/mol as measured by light scattering photometer. Polyisobutylene film

(80 μm thick) was prepared by blending the polymer with (0.01-0.10 wt. %). *Tris*-(α -thiopicoline anilide)manganese (TPAM) and cobalt (TPAC) was prepared by hot pressing under a pressure of 200 kg cm^2 for 5 min at 50 $^\circ\text{C}$. All films with TPAM and TPAC were prepared under the same processing conditions to avoid different thermal pretreatment of the samples.

Photo-degradation: The polyisobutylene films were irradiated with the light flux of 254 nm for various periods in the temperature range -10 $^\circ\text{C}$ to +110 $^\circ\text{C}$. Using a general electric VA-3 mercury lamp in the air temperature of the system was controlled within ± 0.2 $^\circ\text{C}$.

Actionometry: The values of quantum yield of the polymer chain scission were determined from the equation.

$$\frac{1}{P_{n,t}} = \frac{1}{P_{n,o}} + \frac{M}{wN_o \cdot \phi \cdot I_a \cdot t}$$

$P_{n,o}$ = initial number average degree of polymerization; $P_{n,t}$ = number average degree of polymerization after degradation; M = molecular weight of monomer; N_o = Avogadro's number; w = weight of irradiated polymer; t = time of degradation; I_a = intensity of light observed by the polymer film; ϕ = quantum yield of PIB sample.

Thus by plotting $1/P_{n,t}$ versus irradiation time t , one can obtain the quantum yield from the slope of the graph. Here in this case ' $\tan \alpha$ ' would be equal to $M/wN_o \cdot \phi \cdot I_a$. Therefore the quantum yield is given by formula.

$$\phi = \frac{wN_o}{I_a \cdot M \tan \alpha}$$

The value of $\tan \alpha = P_{n,t}/P_{n,o}$ which can be replaced by the ratios of weight average polymerization $P_{w,t}/P_{w,o}$ without making an appreciable error. These ratios have been obtained by light scattering measurement.

Molecular weight determination: The change in weight-average molecular weight (\bar{M}_w) and refractive index increment (dn/dc) of PIB film in isooctane were determined using light scattering photometer and differential refractometer. Zimm plots have been employed to estimate weight-average molecular weight as a function of time. The unsaturation *i.e.*, the presence of ethylenic double bond was determined from iodine number obtained by dissolving the polymer film in chloroform and treating the solution with Wijs reagent (iodine monochloride in acetic acid) for several hours. The iodine number was determined after 1 h in the dark^{14,15}.

Spectrophotometric measurement: The degradation films with 0.01 % wt. TPAM and 0.01 % wt. TPAC were dissolved in isooctane and the reprecipitated with acetone. After separation and drying the polymer was redissolved in isooctane and the UV absorption spectrum measured with a Perkin -Elmer spectra cord (model 4000). The filtrate was washed with distilled water and the isooctane layer which separate was also scanned in the spectrophotometer.

The UV spectrum of the 254 nm irradiated solution of TPAM and TPAC in isooctane (spectro grade reagent) (10^{-4}) was also determined.

The degraded samples dissolved completely in CCl_4 , were therefore in a convenient state for IR analysis. This was carried

out with the Perkin-Elmer (model 21) IR spectrophotometer using a rock salt prism.

RESULTS AND DISCUSSION

An analysis of the relative changes in weight average molecular weight (\bar{M}_w) has been shown to provide a versatile test for random chain scission. Fig. 1.1 and 1.2 shows \bar{M}_w as a function of time of irradiation from PIB film with 0.01 wt. % TPAM and TPAC at various temperatures with a light of flux of 2.38×10^{-9} einstein $\text{s}^{-1} \text{cm}^2$. The plots show a rapid decrease in \bar{M}_w initially which then slows down, suggesting that the initial rapid drop in \bar{M}_w is due to scission of bonds at various weak links that may be distributed along the polymer chain and the initial rate at which the bonds are broken is not sustained. It has been shown that weight average molecular weight values for TPAC shows a decrease when compared with TPAM at different temperatures suggesting that TPAC has various weak links in the polymer chain.

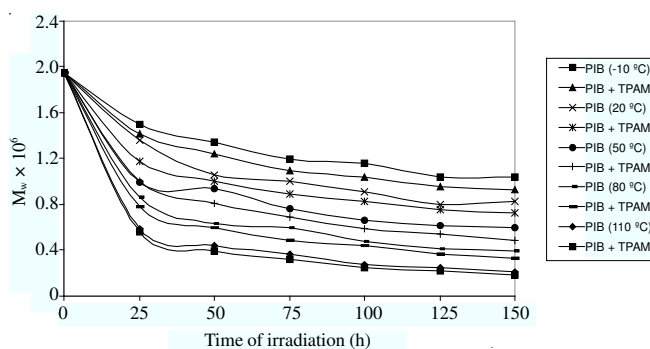


Fig. 1.1. Variation of weight-average molecular weight (\bar{M}_w) during 254 nm irradiation of PIB film with 0.01wt. % TPAM at various temperature

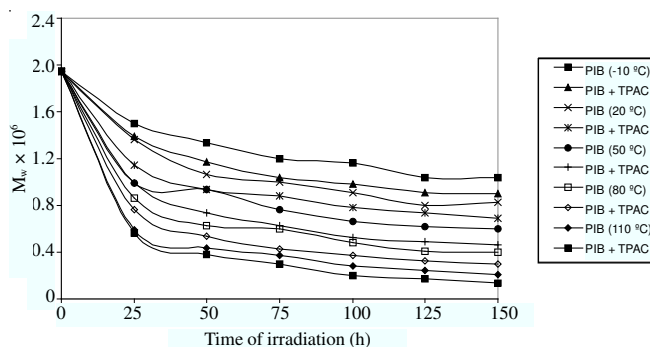


Fig. 1.2. Variation of weight-average molecular weight (\bar{M}_w) during 254 nm irradiation of PIB film with 0.01wt. % TPAC at various temperature

In order to clarify the type of bond scission, the rate in the decrease of \bar{M}_w with time, $d\bar{M}_w/dt$, was calculated using the relation

$$\frac{d\bar{M}_w}{dt} = \frac{\bar{M}_{w,o} - \bar{M}_{w,t}}{t}$$

where $\bar{M}_{w,t}$ and $\bar{M}_{w,o}$ are weight - average molecular weight at irradiation time and zero, respectively.

The decrease in the rate of reaction time may, in fact, arise from the formation of some species that favours energy dissipation. The plots (Fig. 2.1 and 2.2) of $d\bar{M}_w/dt$ versus

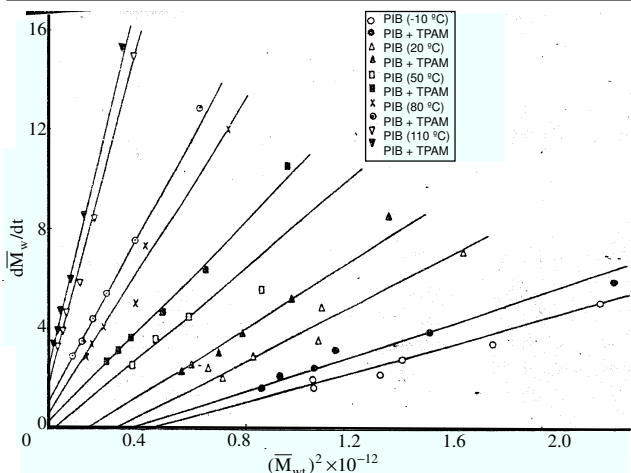


Fig. 2.1. Variation of rate of change of molecular weight ($d\bar{M}_w/dt$) during 254 nm irradiation of PIB film with and without 0.01 wt. % TPAM as a function of $(\bar{M}_w)_t^2$ at various temperatures

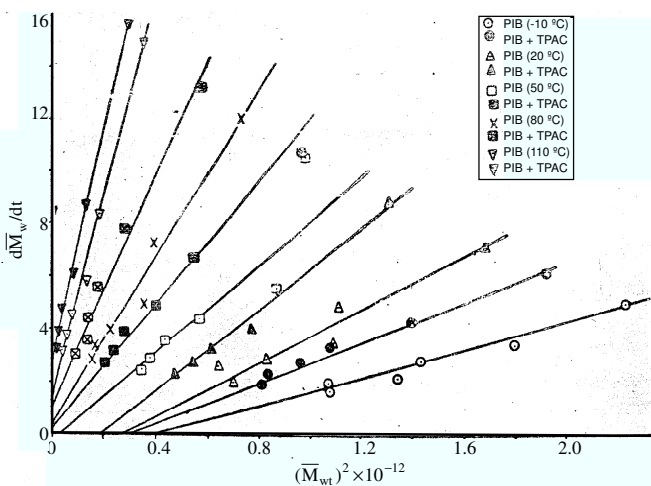


Fig. 2.2. Variation of rate of change of molecular weight ($d\bar{M}_w/dt$) during 254 nm irradiation of PIB film with and without 0.01 wt. % TPAC as a function of $(\bar{M}_w)_t^2$ at various temperatures

$(\bar{M}_w)_t^2$ were found to be linear. The plots suggest that the weak link is randomly distributed within the polymer chains and that two kinetically independent units taking part in the scission of bonds in the polymer.

For randomly distributed weak links, which break rapidly in the initial stages, the degree of degradation is given as

$$\alpha = \beta + kt$$

where β = fraction of weak bonds present in the polymer chain and k = first order rate constant for bond scission and t = irradiation time.

From Fig. 3.1 and 3.2, it is seen that degree of degradation in case of TPAC is more than that of TPAM. This degree of degradation increases with increases in temperature of irradiation. When β is plotted (Fig. 4) as a function of temperature of degradation, a straight line which does not pass through the origin is obtained it means that the weak lines are incorporated into the polymer chain. The frequency of such incorporation increases with temperature.

The activation energy values for the degradation have been calculated from the plots of $\log k$ versus $1/T$ (Fig. 5). The values of activation energies for degradation are 2.33 and 2.22

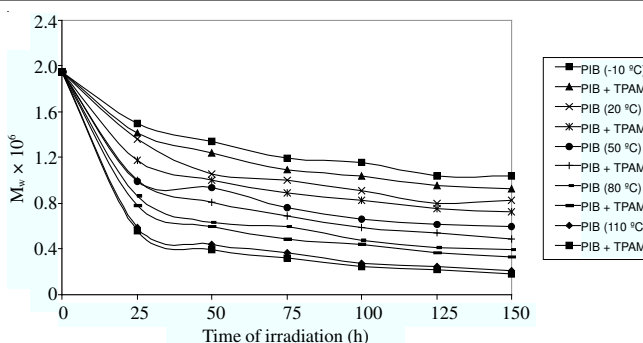


Fig. 3.1. Variation of degree of degradation during 254 nm irradiation of PIB film with 0.01 wt. % TPAM at various temperature

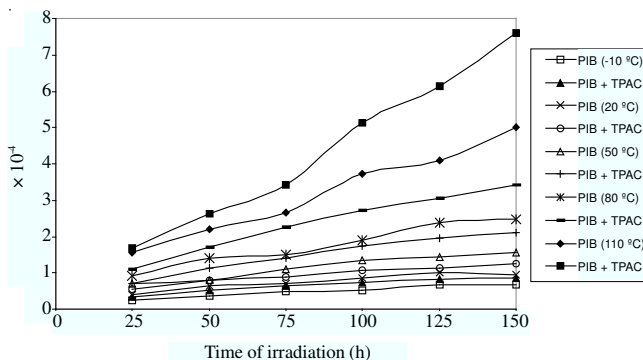


Fig. 3.2. Variation of degree of degradation during 254 nm irradiation of PIB film with 0.01 wt. % TPAC at various temperature

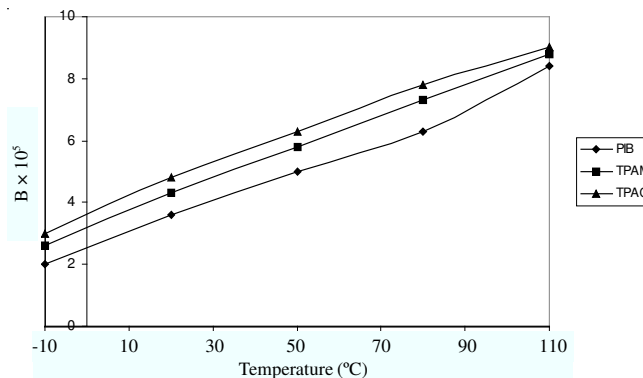


Fig. 4. Variation of fraction of weak bond (β) in PIB film with 0.01 wt. % TPAM and TPAC as a function of temperature during 254 nm irradiation

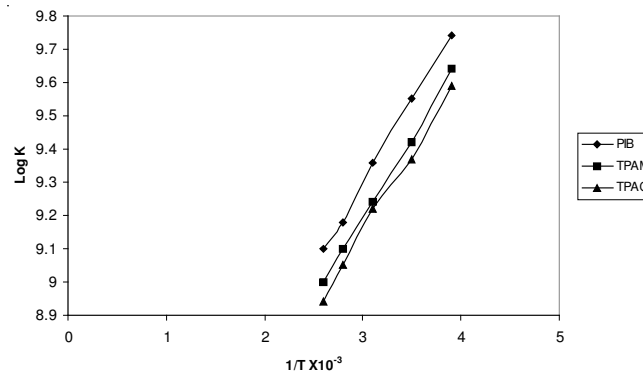


Fig. 5. Variation of $\log K$ versus $1/T$ of photodegradation of PIB in the presence of 0.01 wt. % with TPAM and TPAC

Kcal mol⁻¹ for TPAM and TPAC, respectively. The value of TPAC is lower as compared to TPAM. A lower value of activation

energy means fast degradation reaction. It means that TPAC degrades faster as compared to TPAM. This is further confirmed by degree of degradation in which TPAC has a higher value of degradation when compared with TPAM at different temperatures. A greater value of degree of degradation generally indicates a random breaking in polymer chain. Further the values of k at each temperature for different periods show good agreement, at any rate there is less than two fold variation.

$$\text{PIB} + 0.01\% \text{ TPAM}, k = 1.995 \times 10^{-9} \exp^{(-222/RT)}$$

$$\text{PIB} + 0.01\% \text{ TPAC}, k = 1.928 \times 10^{-9} \exp^{(-210/RT)}$$

The unsaturation *i.e.*, presence of ethylenic double bond (C=C) was determined by measuring iodine number. The original specimens (Fig. 6) already showed small degrees of unsaturation which is subtracted from the total unsaturation of PIB film due to 254 nm irradiation at 110 °C. In both TPAC and TPAM the unsaturation does increase linearly with time, it is therefore suspected that weak links are formed in PIB structures due to intermolecular unsaturation.

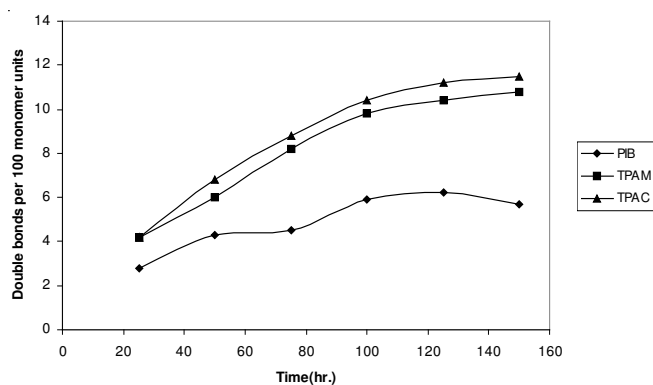


Fig. 6. Variation of unsaturation during 254 nm irradiation of PIB film with 0.01 wt. % TPAM and TPAC at 20 °C

Another way of degradation reaction characteristics is measurement of quantum yield for chain scission process (Fig. 7). The values of quantum yield are more in TPAC than in TPAM and they increase with temperature. The explanation of low value in TPAM is that the energy is absorbed at one site, so that the probability of a single bond breaking is small.

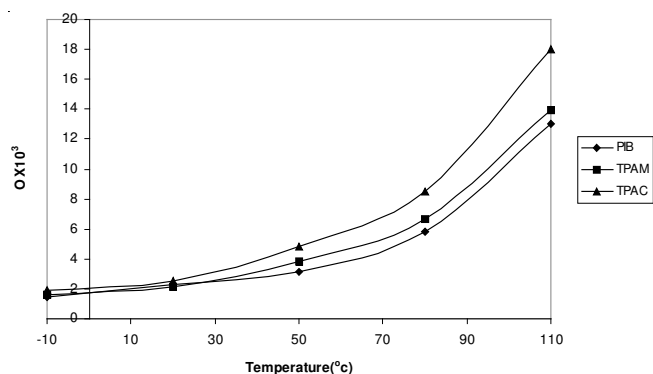
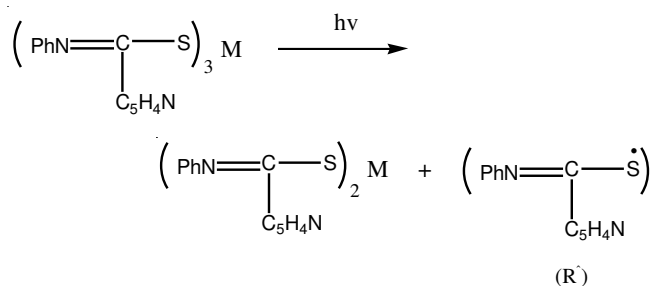
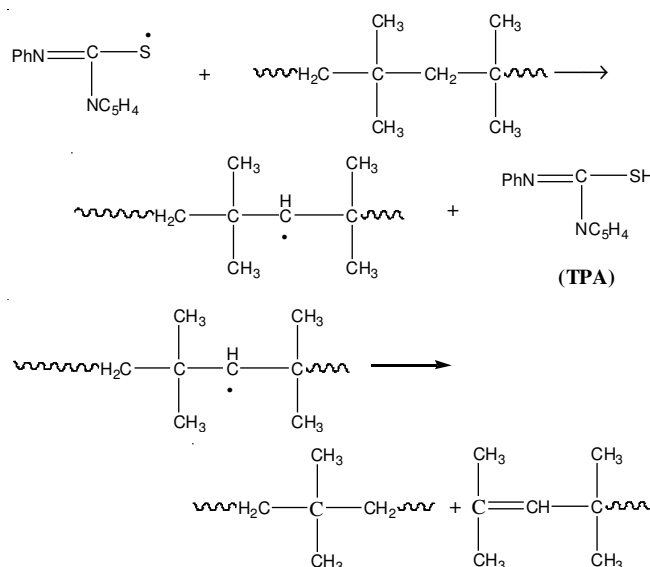


Fig. 7. Variation of quantum yield during 254 nm irradiation of PIB film with 0.01 wt. % TPAM and TPAC as a function of temperature

The acceleration behaviour of TPAM and TPAC is explained by the photochemical decomposition of TPAM and TPAC into free radical (R^\cdot) which initiate the photo-degradation of the polymer.



The free radical (R^\cdot) will abstract hydrogen from the PIB chain and the reaction is leading to degradation in PIB the most probable reaction scheme would be:



To clarify the degradation mechanism, the UV spectra of PIB film at 254 nm light in presence of 0.01 wt. % TPAM and 0.01 wt. % TPAC have been investigated. This can only result from the attachment of TPA radical R^\cdot with the degrade films. The exact position of maximum would appear to some extent upon irradiation time. This suggest that the absorbing group is itself changed by further irradiation. Comparison with the spectrum for TPA reveal that a wavelength shift has occurred, the absorption maxima at 240 and 280 nm appearing to correspond at 246 and 285 nm in free TPA. It is be unchanged, all the radical of TPAM and TPAC in the system appear to have become attach to the polymer.

These absorption spectra shows conclusively that degradation results mainly from attack upon the polymer chain by radicals R^\cdot . They also show that the first stage in the reaction is not hydrogen abstraction from the polymer and that the radicals R^\cdot responsible for degradation combines with degraded material. It is apparent that these results are inconsistent with the simple mechanism already outlined.

The 254 nm exposure of PIB film alone causes only a small change in UV spectra in comparison with UV spectra obtained in presence of TPAM and TPAC. The UV spectra (Figs. 8 and 9) gradually increases with the time of irradiation. However with TPA film containing TPAC, the increase of UV spectrum is lower as compared to TPAM. *Tris*-(α -thiopicolin anilide)cobalt behaves as an UV absorber whereas TPAM enhances the degradation of the polymer.

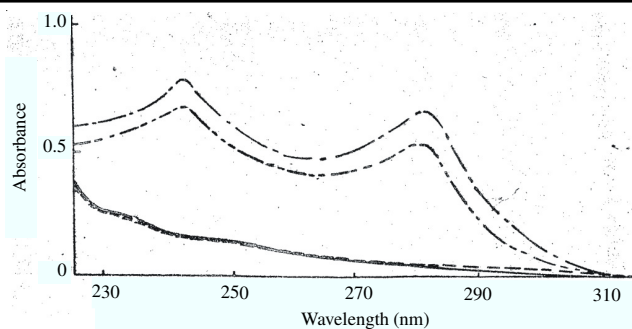


Fig. 8. Change of UV spectra of PIB film (Ca 80 μm) blended with TPAM (0.01 wt. %) during 2 h of 254 nm light irradiation; (—) pure PIB film before irradiation; (---) pure PIB film after irradiation; (· · · ·) blended sample before irradiation and (- · - · - ·) blended sample after irradiation

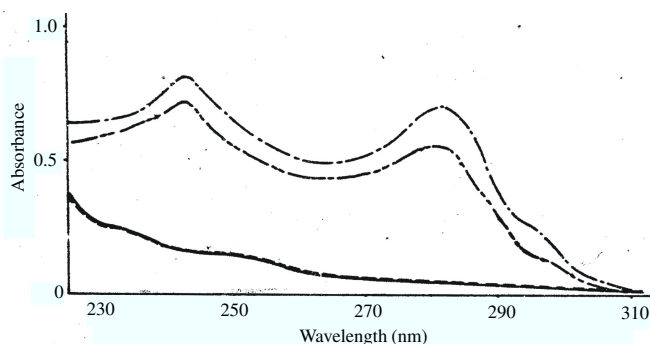


Fig. 9. Change of UV Spectra of PIB film (Ca 80 μm) blended with TPAC (0.01 wt. %) during 2 h of 254 nm light irradiation; (—) pure PIB film before irradiation; (---) pure PIB film after irradiation; (· · · ·) blended sample before irradiation and (- · - · - ·) blended sample after irradiation

Relative effect of TPAC and TPAM on photo-degradation of TPA were compared by the simultaneous irradiation of TPAM and TPAC with light of 253 nm wavelength, IR spectra of both the samples are shown in Figs. 10 and 11. The figure shows that the IR absorption spectra of irradiated film at PIB containing 0.01 wt. % of TPAM and TPAC, the overall acceleration behaviour of TPAM and TPAC with increasing irradiation time are reflected in the decrease of various bands. Under similar conditions of irradiation-time, temperature, wavelength *etc.*, the contents of polymer film with TPAC are higher whereas with TPAM are lower. Specifically, TPAM accelerates the photodegradation whereas TPAC retards it.

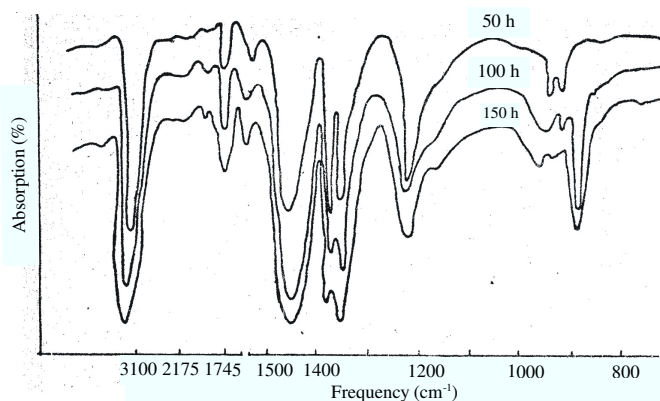


Fig. 10. Change of infra red absorption frequency during 254 nm irradiation of PIB film with 0.01 wt. % TPAM

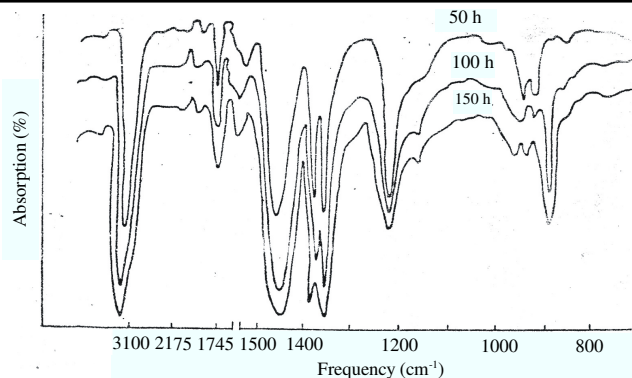


Fig. 11. Change of infrared absorption during 254 nm irradiation of PIB film with 0.01 wt. % TPAC

Therefore, the role of metal (α -thiopicoline anilide) on photodegradation are greatly dependent on the kind of metal used as shown in the case that TPAC is degrading faster than TPAM in this study.

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