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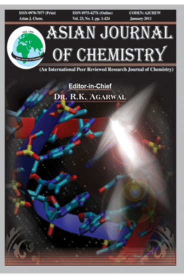

Photodegradation of Polyisobutylene Film by Addition of Tris(α-thiopicoline anilide) with Cobalt(III), Manganese(III) and Iron(III)

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The addition of tris(α-thiopicoline anilide) with manganese(III) (TPAM) cobalt(III) (TPAC) and iron (TPAF) sensitized photo oxidative degradation of polyisobutylene (PIB) film. It was found that photo degradation of the polymer was affected by the kind of metal used. Ultraviolet and infrared absorption spectra have been employed to substantiate a mechanism of degradation process which does not involve abstraction of the polymer, but direct cleavage of the polymer backbone and presence of initiating radicals of TPAM, TPAC at the sites of scission. The chelate TPAF shows the best performance of a photo sensitizer by furnishing the chain initiating free radicals.

Key Words: Photodegradation, Polyisobutylene, Cobalt, Manganese, Iron, Temperature.

INTRODUCTION

In recent years, the plastic articles contribute considerably to solid waste disposal problems and disposal of their wastes from homes, offices and factories is a major problem of the world. The polymeric materials currently used on a large scale are highly resistant to environmental attacks that it increase the plastics-litter problems. Studies[1] have shown that a major factor is the rate of accumulation of litter in environment. Few works has been published[2-4] on the photodegradation of polymeric materials in connection with the elucidation of photo degradation mechanism. There has been considerable interest in recent years in obtaining procedures for controlling the outdoor lifetime to certain types of plastics. The most convenient and reliable method of doing this is to accelerate the natural processes of degradation induced by UV rays of the sun.

In the present investigation, therefore, tris(α-thiopicoline anilide) chelate with Co^{3+}, Mn^{3+} and Fe^{3+} were found to be an effective sensitizer for the photo oxidative degradation of polyisobutylene (PIB) films.

The absorption spectra of the degraded polymer in the UV and IR regions were studied to differentiate between the possible scission reactions and to suggest termination reactions for the radicals formed.

EXPERIMENTAL

The polyisobutylene (PIB) used throughout was Vistanex L-140 which was provided by Enjoy chemical Co., New York. The polymer sample was purified by three precipitations from petroleum ether (40-60 ºC) with methanol. It had average molecular weight of 1.95×10^6 as measured by a light scattering photometer.

Polyisobutylene film (80 µm thick) was prepared by blending the polymer with 0.01-0.10 wt % tris(α-thiopicolinanilide)-manganese(III) (TPAM); cobalt(III) (TPAC) and iron(III) (TPAF) and then hot pressing using pressure of 200 Kg cm^{-2} for 5 min at 50 ºC. All film with TPAM, TPAC and TPAF were prepared under the same processing conditions to avoid different thermal treatment of the samples.

Tris(α-thiopicolinanilide)-manganese(III)- cobalt (III) and -iron(III) were prepared according to the method as described by Bohr and Schoz[5]. The degraded films with 0.01 wt %, TPAC, 0.01 wt % TPAM and 0.01 wt % TPAF were dissolved in iso-octane and the polymer reprecipitated in isooctane and the UV absorption spectrum measured with a Perkin Elmer spectra cord model (Model 4000). The filtrate was washed with distilled water and the isooctane layer separated was scanned in the spectrophotometer. The UV spectrum of 2584 nm irradiated solution of TPAM, TPAC and TPAF in isooctane (spectro grade reagent) (10^{-4} M) was also determined.

The degraded samples dissolved completely in carbon tetrachloride and were therefore in convenient state for infrared analysis. This was carried out with a Perkin-Elmer (Model 21) IR spectrophotometer using a rock salt prism.

RESULTS AND DISCUSSION

To investigate the photosensitization mechanism by TPAM, TPAC and TPAF, the photochemistry in the UV of these materials in PIB were investigated. The changes in UV spectrum of the photochemically induced changes of TPAM, TPAC and TPAF solution in isooctane are presented in Figs. 1-3. The spectra show absorption bands at about 246 and 285 cm^{-1}. After 254 nm irradiation of TPAM, TPAC and TPAF solution (1 cm^3) in an iso octane in oxygen-free atomsphere, the intensity of bands at 246 and 285 cm^{-1} decrease. The 254 nm irradiation of TPAM,TPAC and TPAF solution in presence of oxygen produces a rapid decrease of absorption bands, which disappear almost completely after 50 min of irradiation. These results indicate a photodecomposition of TPAM, TPAC and TPAF.

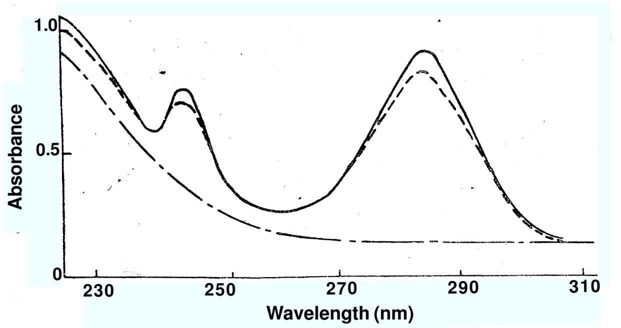


Fig. 1. Changes of UV spectra of TPAM in isooctane (10^{-4} M) during 50 min of 254 nm light irradiation; (—) before irradiation; (----) in oxygen free solution; (-·-·-) in oxygen saturated solution in a cell of 1 cm path

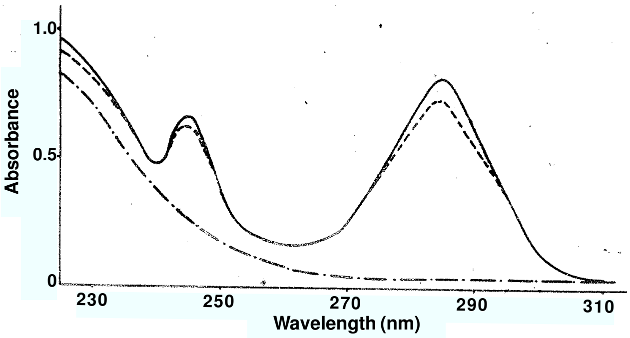


Fig. 2. Changes of UV spectra of TPAC in isooctane (10^{-4} M) during 50 min of 254 nm light irradiation; (—) before irradiation; (----) in oxygen free solution; (-·-·-) in oxygen saturated solution in a cell of 1 cm path

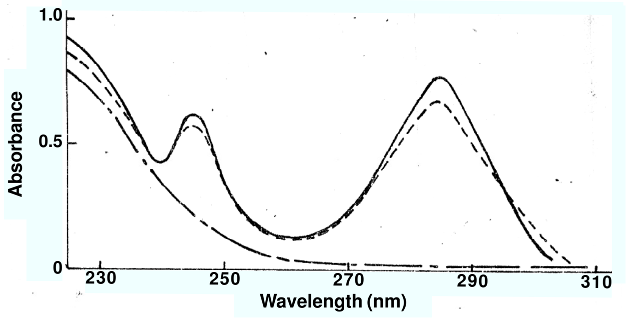


Fig. 3. Changes of UV spectra of TPAF in isooctane (10^{-4} M) during 50 min of 254 nm light irradiation; (—) before irradiation; (----) in oxygen free solution; (-·-·-) in oxygen saturated solution in a cell of 1 cm path

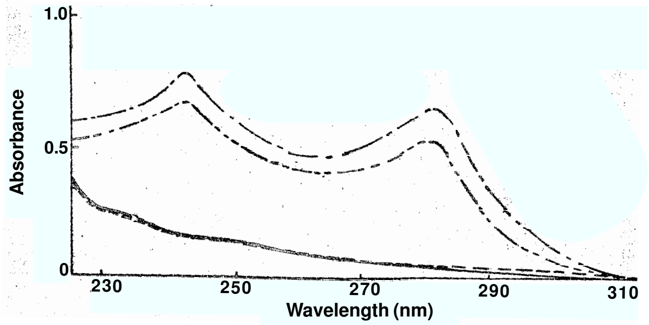


Fig. 4. Change of UV spectra of PIB film (Ca 80 μm) blended with TPAM (0.01 wt %) during 2 h of 254 nm light irradiation; (—) pure PIB film before irradiation; (----) pure PIB film after irradiation; (-·-·-) blended sample before irradiation and (-··-··-) blended sample after irradiation

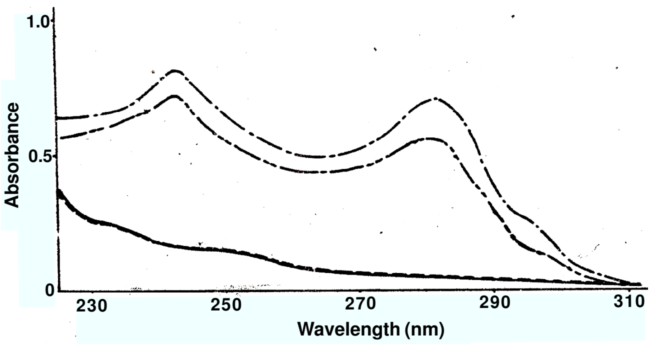


Fig. 5. Change of UV spectra of PIB film (Ca 80 μm) blended with TPAC (0.01 wt %) during 2 h of 254 nm light irradiation; (—) pure PIB film before irradiation; (----) pure PIB film after irradiation; (-·-·-) blended sample before irradiation and (-··-··-) blended sample after irradiation

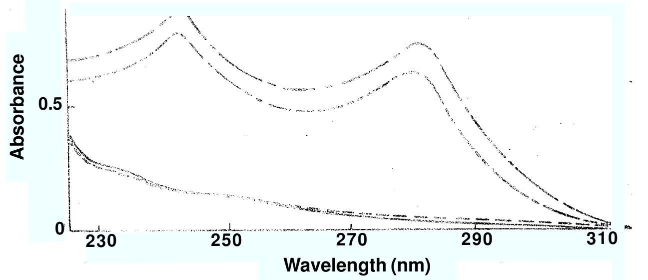
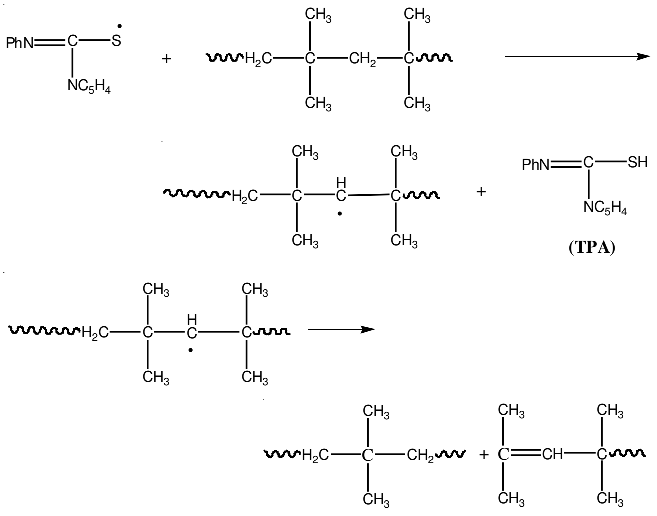


Fig. 6. Change of UV spectra of PIB film (Ca 80 μm) blended with TPAF (0.01 wt %) during 2 h of 254 nm light irradiation; (—) pure PIB film before irradiation; (----) pure PIB film after irradiation; (-·-·-) blended sample before irradiation and (-··-··-) blended sample after irradiation

Polyisobutylene film (80 μm) blended with 0.01 wt % TPAM, TPAC and TPAF exhibits an absorption spectrum (Figs. 4-6) almost similar to the UV absorption spectra of TPAM, TPAC and TPAF in isooctane solutions. Absorptions bands appeared close to 246 and 285 nm. These bands distinctly decrease during the 254 nm irradiation of PIB film.

The acceleration behaviour of TPAM, TPAC and TPAF can be explained by photo chemical decomposition[6,7] of TPAM, TPAC and TPAF absorbing the UV light and free radicals generated effectively initiating the photo degradation of polymer as Zeif[8] has also observed formation of free radical $R^{\cdot}$ during UV light irradiation of TPAM, TPAC and TPAF in solid state in air at room temperature by ESR spectroscopy.

The radicals ($R^{\cdot}$) will abstract hydrogen from PIB chain and the reaction is leading to degradation of PIB. The probable reaction is given in **Scheme-I**:



Scheme-I

The consequences of this mechanism are: (1) α-Thiopicolinanilide (TPA) must be formed. (2) Termination may occur as a result of combination between PIB film radicals, one mode of which would lead to an increase in degree of branching polymer. (3) The $R^{\wedge}$ radicals might enter the polymer as the result of a combination reaction.

The Figs. 7-9 show the IR absorption spectra of irradiation film of PIB containing 0.01 wt % TPAM, TPAC and TPAF. The overall acceleration behaviour of TPAM, TPAC and TPAF with increasing irradiation time is reflected in the decrease of various bands. The irradiation sample had a new absorption band at 899 cm^{-1}, which can be assigned to vinyl double bond. The total unsaturation was determined by the addition of iodine mono chloride.

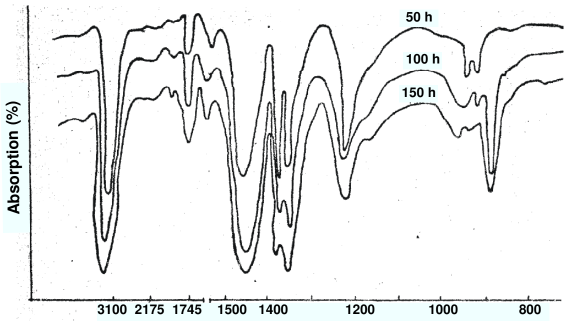


Fig. 7. Change of infra red absorption frequency during 254 nm irradiation of PIB film with 0.01 wt % TPAM

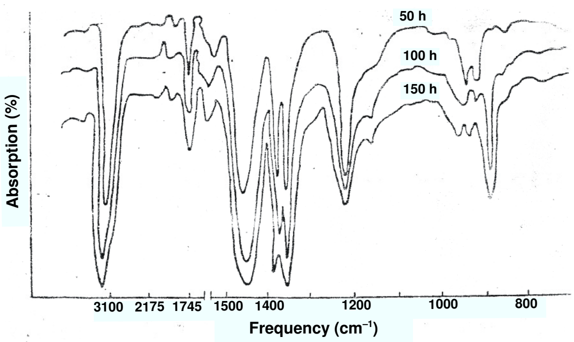


Fig. 8. Change of infrared absorption during 254 nm irradiation of PIB film with 0.01 wt % TPAC

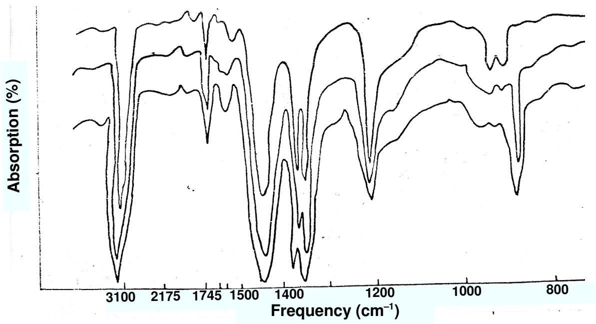


Fig. 9. Change of infrared absorption during 254 nm irradiation of PIB film with 0.01 wt % TPAF

The presence of TPA would be indicated by an absorption in the region 2600-2550 cm^{-1} region corresponding to fundamental S-H stretching frequency. Figs. 7-9 shows that these bands are absent but owing to the fact that TPA absorbs very weekly at the concentration level likely to be unsaturated (2.81 × 10^{-3} mol/L). This cannot be taken as indicative of the complete absence of this compound.

In order to make a precise determination of amount of TPA present, recourse must be made to the UV absorption spectrum (Fig. 10) of the soluble products remaining after precipitation of the degraded polymer from its solution in isooctane. Here, the sensitivity is much greater and the extinction co-efficient for TPA at 246 and 285 nm are 195 and 145 nm, respectively.

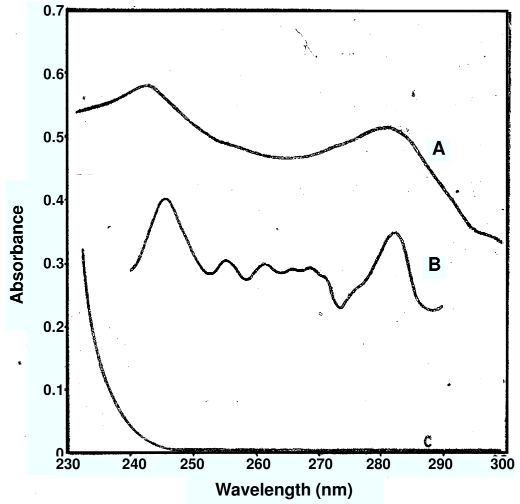


Fig. 10. Ultra-violet absorption spectra of (A) photodegraded PIB precipitated from isooctane (B) a-thiopicolinanilide (C) isooctane layer after precipitation of PIB and washing with water

The spectra in Fig. 10 were obtained from a sample which had undergone the same treatment as that used for IR analysis. A known wt. of degraded films were dissolved in 100 mL isooctane and after precipitation and washing, the volume of filtrate was 20 mL. A study of the same composition showed that for a concentration of 2.5 × 10^{-5} mol TPA in 10 mL isooctane, the final distribution.

TPA was isooctane layer 60 % and water + acetone layer 40 %. If TPA radicals $R^{\wedge}$ in this weight (0.2143 g) of polymer film all abstracted hydrogen, the concentration of TPA in 10 mL isooctane would be 2.52 ×10^{-5} mol. The optical densities at 246 and 285 nm of the isooctane layer,taking of the distribution, would then be 0.281 and 0.202, respectively. Fig. 10 shows that no TPA type absorption occurs in 240 and 290 nm region by isooctane layer.

The optical density at 246 nm is 0.004 and at 285 nm is 0.002 and if this were due to TPA, the amount present was corresponding to that 1.5 % of the TPA radicals $\hat{R}$ produced in the system. This is in good agreement with the figure obtained from IR analysis.

It must be concluded (Fig. 10) that the majority of TPA radical $\hat{R}$ (at least 95 %) become attached to the degraded polymer. Fig. 10 shows that the degraded polymer film absorbs strongly in the 240-285 nm region and this can only result from the attachment of TPA radicals $\hat{R}$ to the degraded PIB chains. The exact position of maximum would appear to depend upon the irradiation time. This suggests that the absorption group is itself further changed by further irradiation. The optical density of PIB film is directly proportional to irradiation time. Comparison for the spectrum for TPA reveals that as wavelength shift has occurred, the absorption maxima 241 and 280 nm appearing to correspond to maxima at 246 and 285 nm in the free TPA. It is interesting to note that if a calculation is made assuming the extinction coefficient to be unchanged, all the radicals of TPAM, TPAC and TPAF in the system appear to have become attached to the polymer.

These absorption spectra show exclusively that degradation result mainly from attack upon the polymer chain by $\hat{R}$ radicals. They also show that first stage in the reaction is not hydrogen abstraction from the polymer and that the $\hat{R}$ radicals responsible for degradation combine with the degraded material. It is apparent that these results are inconsistent with the simple degradation mechanism already[9] outlined.

The fact was also interpreted on the assumption that during 254 nm irradiation, the interaction of free radicals of PIB occurred predominantly by disproportion rather by combination. This assumption was further sustained by the fact that the yield of double bond formation sharply increased as a result of irradiation. Such a view agree with the fairly low activation energy found for the degradation, since the difference between the activation energies of disproportionate and combination of hydrogen free radical is order of 2-3 kcal/mol. Thus, the experimental activation energy do not relate to the primary photolysis process but rather to subsequent chemical reactor of species produced in the primary event.

The 254 nm exposure of PIB alone causes only a small change in UV spectra in comparison with UV spectra obtained in presence of TPAM, TPAC and TPAF. Hence the photosensitization begins with absorption of light by TPAM, TPAC and TPAF. The maximum UV absorption occurs at the surface of polymeric film containing a uniform distribution of TPAM TPAC and TPAF. The excess energy of TPAM, TPAC and TPAF may be lost in any of the several ways, reemission of radiation, radiation less conversion in the ground state an energy transfer or it can lead to the formation of free radicals which are responsible for further free radical generation and sensitization of photo degradation of PIB.

Conclusion

It is found that the chelates of TPAF show the best performance as a best sensitizer by furnishing the chain initiating free radicals. Therefore, the role of metal tris(α-thiopicolinanilide) on photo degradation is greatly dependent on the kind of metal, wavelength of irradiated light and based on these, the metal tris(α-thiopicolinanilide) shows various effects on photodegradation of polymers.

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