Sensitized Photodegradation of Polyisobutylene Film by Addition of Tris(α-Thiopicolinanilide)–Cobalt(III)

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Synopsis

The photodegradation of polyisobutylene (PIB) film in air at a temperature where volatile formation is negligible was studied by means of light scattering, chemical actinometry, and spectrophotometric techniques. The degradation is accelerated by addition of tris(α-thiopicolinanilide)—cobalt(III) (TPAC). The sensitization and the course of the degradation were determined by weight-average molecular weight, energy of activation, and quantum yield of the photolysis of the polymer film with 254-nm light. The plots of molecular weight, weight-average chain scission, and degree of degradation vs. irradiation time are linear and confirm the random nature of 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 TPAC at the sites of scission.

INTRODUCTION

In recent years, a more visible problem is production of plastics that do not end up ultimately in some form of garbage disposal system. Computer studies have shown[1] that a major factor in the rate of accumulation of litter in the environment is its "lifetime." For this reason, there has been considerable interest in recent years in obtaining procedures for controlling the outdoor lifetime of certain types of plastics. The most convenient and reliable method of doing this is to accelerate the natural processes of degradation induced by the UV rays of the sun.

For this purpose, a chelate complex (I) with Co^{3+}, which is an extremely effective accelerator for the degradation of polyisobutylene (PIB) film, has been chosen:
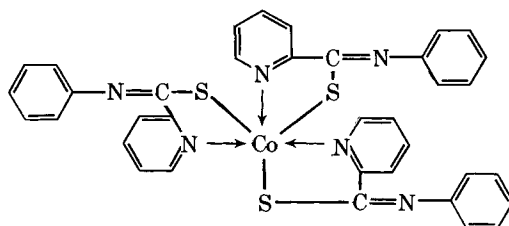
I, TPAC

The incorporation of this chelate complex, tris(α-thiopicolinanilide)–cobalt(III)

(TPAC), in the matrix of PIB film is leading to reduced moleclar weight and random main-chain scission of the polymer film, when exposed to 254-nm light at temperatures from −10 to 110°C in air. In this temperature range, in fact, volatile formation is negligible, and it was hoped that the degradation kinetics would be easier to interpret. Most of the earlier[2,3] studies of PIB have been made in solution at high temperatures (above 200°C) by the viscometric technique which is not an absolute method of molecular weight determination.

The light scattering technique, which enables one to obtain weight-average molecular weight, is an absolute method for such determination and has been used in the present investigations. The changes in quantum yield of chain scission, degree of degradation, and number of ethylenic double bonds were also measured. The absorption spectra of the degraded materials in the ultraviolet and infrared regions were also 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 Enjay Chemical Co., New York. The polymer sample was purified by three precipitations from petroleum either (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.

PIB film (80 μm thick) was prepared by blending the polymer with (0.01–0.1 wt %) tris(α-thiopicolinanilide)–cobalt(III) (TPAC) and hot pressing under a pressure of 200 kg/cm² for 5 min at 50°C. All films with and without TPAC were prepared under the same processing conditions to avoid different thermal pretreatment of the samples.

TPAC was prepared according to the method described by Bohr et al.[4] and was obtained as dark-brown needles.

The PIB films were irradiated with a light flux of 2.38×10^{-9} einsteins sec⁻¹ cm⁻² obtained by monochromatic light of 254 nm for various periods in the temperature range of −10 to 110°C with a General Electric UA-3 medium-pressure Hg lamp in air and nitrogen. The temperature of the system was controlled within ±0.2°C.

The quantum yield ϕ_{cs} values of polymer chain scission were determined[5] from the equation

$$\frac{1}{p_{n,t}} - \frac{1}{p_{n,0}} = \frac{m}{wN} \phi_{cs} I_a t$$

where w is the weight of the irradiated polymer film sample; m is the molecular weight of the monomer; N is the Avogadro number; I_a is the light absorbed in the polymer sample; and $p_{n,0}$ is the number-average degree of polymerization initially and $p_{n,t}$, at any time t during the degradation. 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 ratio can be determined by light scattering measurements and I_a by potassium ferrioxalate actinometry.[6]

The changes in the weight-average molecular weight ($\overline{M}_w$) and in the refractive index increment (dn/dc) for PIB film in isooctane were determined using a light

scattering photometer and a differential refractometer (Phoenix Precision Instrument Co., Philadelphia, Penn.), respectively. Zimm plots were employed to estimate $\overline{M}_w$ as a function of time. Dissymmetry ratios were utilized to calculate the particle scattering factors for correction of the light scattering data.

The unsturation (i.e., the presence of ethylenic double bonds) was determined from the "iodine number" obtained by dissolving the polymer film in chloroform and treating the solution with Wij's reagent (iodine monochloride in acetic acid) for several hours. The iodometric titer of each solution was determined after 1 h in the dark.[7,8]

The degraded films with and without 0.01 wt % TPAC were dissolved in isooctane and the polymer reprecipitated with acetone. After separation and drying, the polymer was redissolved in isooctane and the UV absorption spectrum measured with a Perkin–Elmer Spectracord (model 4000). The filtrate was washed with distilled water and the isooctane layer which separated was also scanned in the spectrophotometer. The UV spectrum of the 254 nm-irradiated solution of TPAC in isooctane (spectrograde reagent) (10^{-4} M) was also determined.

The degraded samples dissolved completely in carbon tetrachloride and were therefore in a 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

An analysis of the relative changes in $\overline{M}_w$ as recently described by Scott has been shown to provide a versatile test for random chain scission. A random nature of bond scission is necessary when polymer decomposition does not occur in the primary photolysis process. This would be expected from the well-known energy migration by various photophysical processes within polymer until bond rupture occurs at a weak point in the structure. Figure 1 shows a plot of $\overline{M}_w$ as a function of time of irradiation for PIB film with and without 0.01 wt % TPAC at various temperatures in air with a light flux of 2.38×10^{-9} einsteins $\sec^{-1}$ cm^{-2}. The plots show a rapid decrease in $\overline{M}_w$ initially which then slows down, suggesting that the initial rapid drop in $\overline{M}_w$ 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. The process becomes slower and the bond scission may be random. Thus, if the scission of bonds is random, the rate of decrease in $\overline{M}_w$ should be proportional[9,10] to the square of the weight-average molecular weight at that time. Therefore, in order to clarify the type of bond scission, the rate in the decrease of $\overline{M}_w$ with time, $d\overline{M}_w/dt$, was calculated using the relation

$$\frac{d\overline{M}_w}{dt} = \frac{\overline{M}_{w,0} - \overline{M}_{w,t}}{t}$$

where $\overline{M}_{w,t}$ and $\overline{M}_{w,0}$ are weight-average molecular weight at irradiation time t and zero, respectively.

The decrease in the rate of reaction with time (Fig. 1) may, in fact, arise from the formation of some species that favors energy dissipation. The plots (Fig. 2) of $d\overline{M}_w/dt$ vs. $(\overline{M}_w)^2$ were found to be linear. The plots suggest that the weak
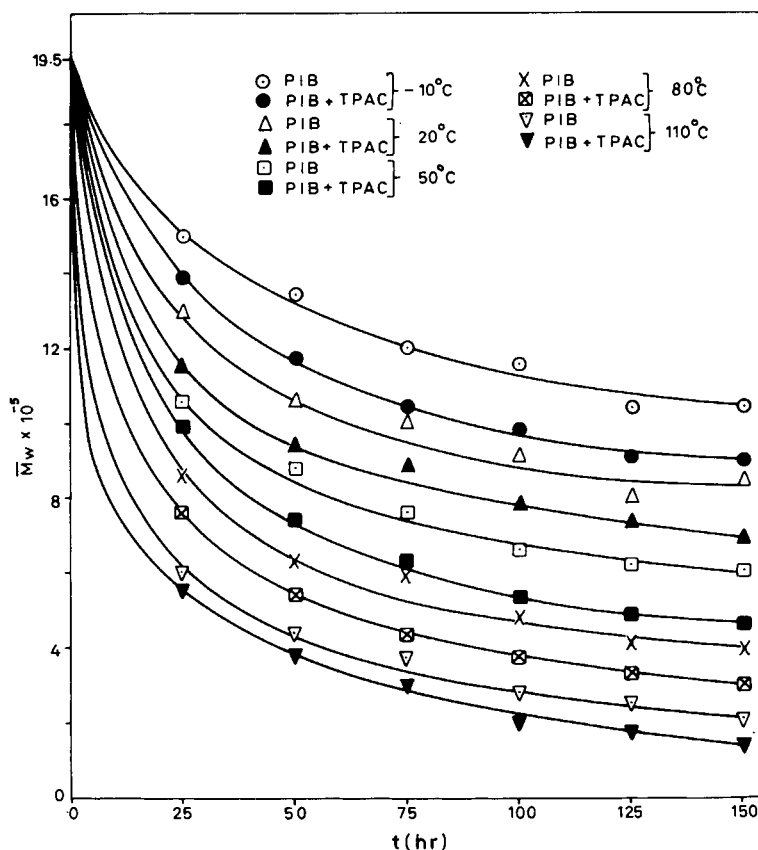
Fig. 1. Changes in weight-average molecular weight ($\overline{M}_w$) during 254-nm irradiation of PIB film with and without 0.01 wt % TPAC at various temperatures.

link is randomly distributed within the polymer chains and that two kinetically independent units are taking part in the scission of bonds in the polymer.   Two similar specimens of PIB film placed on the quartz plates, one open to air and the other in N_2, and both irradiated under similar conditions, subsequently had almost identical molecular weights.

In order to further strengthen the view, the weight-average chain scission s defined[11] as in eq. (1) is shown in Fig. 3 as a function of time at various temperatures:

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

where $p_{w,0}$ and $p_{w,t}$ are weight-average degrees of polymerization at times zero and t, respectively.   The linearity of the plots of s vs t gives an indication that no increase in the degree of branching such as might arise from cross linking occurs.

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

$$\alpha = \beta + kt \tag{2}$$

where β is the fraction of weak bonds present in a polymer chain and k is the
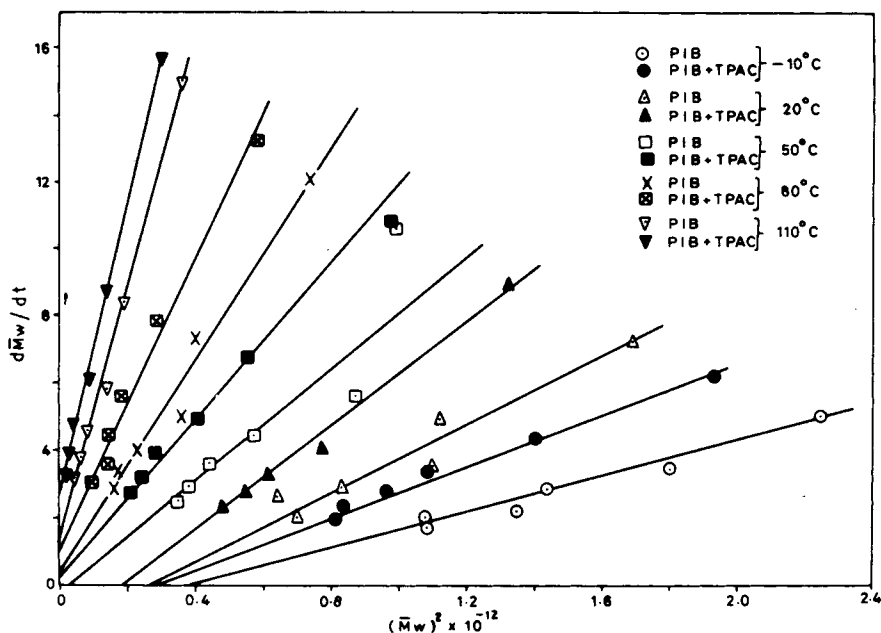
Fig. 2. Variation of rate of change of molecular weight $(d\overline{M}_w/dt)$ during 254-nm irradiation of PIB film with and without 0.01 wt % TPAC as function of $(\overline{M}_w)$ at various temperatures.

first-order rate constant for bond scission. The plots of α as a function of irradiation time at various temperatures are shown in Figure 4. The curves are linear and have an ordinate intercept which depends on the temperature of the irradiation. The presence and the magnitude of the ordinate intercept in the graph indicate the existence and the fraction of weak links (β) in a chain.

When β is plotted (Fig. 5) as a function of temperature of degradation, a straight line which does not pass through the origin is obtained. It means that the weak links are incorporated into the polymer chain. The frequency of such incorporation increases with temperature.

The activation energy of slow chain scission in PIB was determined from a linear plot of log k vs. $1/T$ and yielded a value of 2.33 and 2.10 kcal/mol in the absence and presence of 0.01 wt % TPAC, respectively. The values of k at each temperature for different periods show good agreement; at any rate, there is less than a twofold variation. Even a tenfold variation in the value of k will change the value of the energy of activation by 1.5 kcal/mol only. Therefore, the separate values for activation energy in the absence and presence of 0.01 wt % TPAC do not seem to be very different. The confidence limit for the quoted values is ±0.02.

In addition to the decrease in $\overline{M}_w$ following irradiation, there is an increase in the amount of unsaturation in the polymer sample. This unsaturation, i.e., the presence of ethylenic double bonds C=C, was determined for unirradiated and irradiated specimens with and without 0.01 wt % TPAC by measuring the iodine number. The original specimens already showed small degrees of unsaturation (Fig. 6) which were not directly related to the initial $\overline{M}_w$ and were subtracted from the total unsaturation of PIB due to 254-nm irradiation in air at 110°C. It is also seen that the increase in unsaturation above its initial value
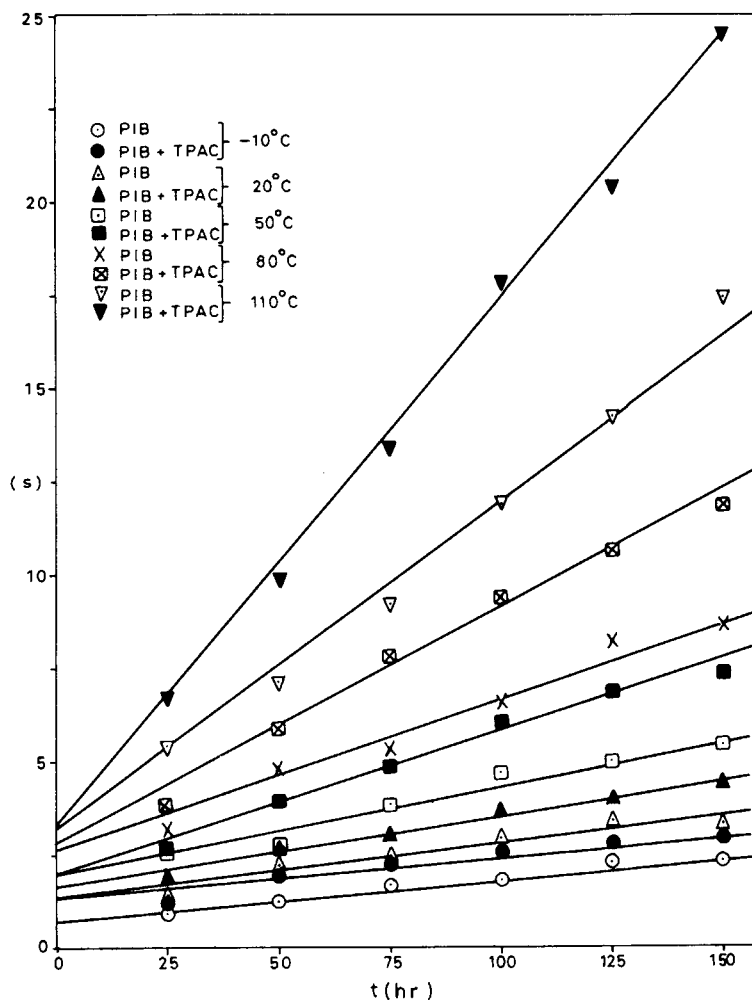
Fig. 3. Changes in weight-average chain scission(s) during 254-nm irradiation of PIB film with and without 0.01 wt % TPAC at various temperatures.

is directly proportional to the irradiation time. After high irradiation, the unsaturation does not increase linearly with irradiation time. It is suspected that weak links are formed in PIB structure due to the intramolecular unsaturation.

Another way of degradation reaction characterization is measurements of the quantum yield (ϕ_{cs}) for the chain scission process. The quantum yield for chain scission was calculated[12] for PIB films with and without 0.01 wt % TPAC after different times of irradiation at various temperatures and by plotting $1/p_{w,t}$ vs. irradiation time (Fig. 7). The calculation of ϕ_{cs} is based on the light absorbed by the polymeric film. The ϕ_{cs} dependence on temperature for neat PIB and the PIB + TPAC system is shown in Figure 8. The ϕ_{cs} values for PIB films with TPAC increase with temperature much more than those for neat PIB films. The explanation of low values (Fig. 8) of ϕ_{cs} is that in a large molecule of PIB the energy is absorbed at one site, but then the electronic excitation is distributed over many bonds so that the probability of a single bond breaking is small, or
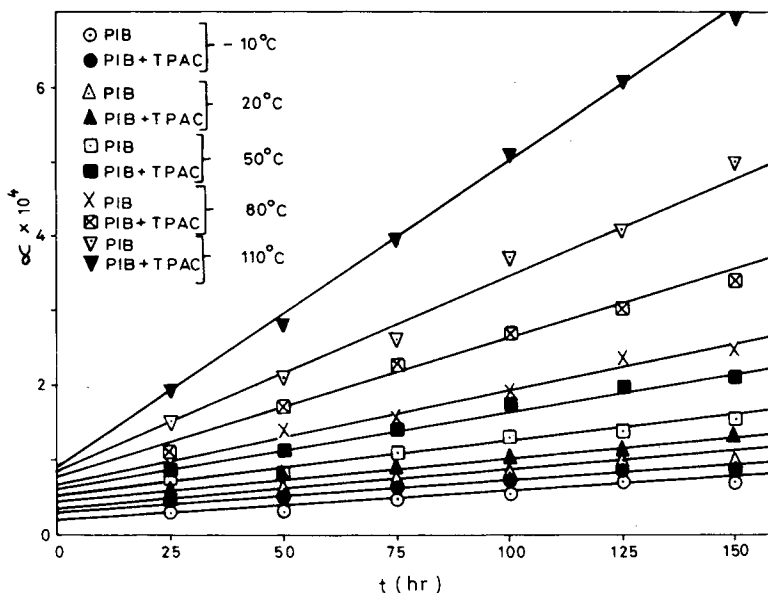
Fig. 4. Changes in degree of degradation (α) during 254-nm irradiation of PIB film with and without 0.01 wt % TPAC at various temperatures.

the absorbed energy is dissipated by quenching reactions. The low ϕ_{cs} values also indicate that most of the light energy is dissipated by nonreactive processes. The larger ϕ_{cs} values are displayed by PIB film which is internally photosensitized by TPAC. The values of ϕ_{cs} increase with increase in the percentage of TPAC incorporated in the matrix of PIB films.

The effect of the concentration (0.01–0.5 wt %) of TPAC in the photodegradation of PIB was also examined. Figure 9 gives the variation of the degree of sensitization,[13] $k(g)/k(0)$ vs concentration (g) of TPAC in PIB film at 20°C.
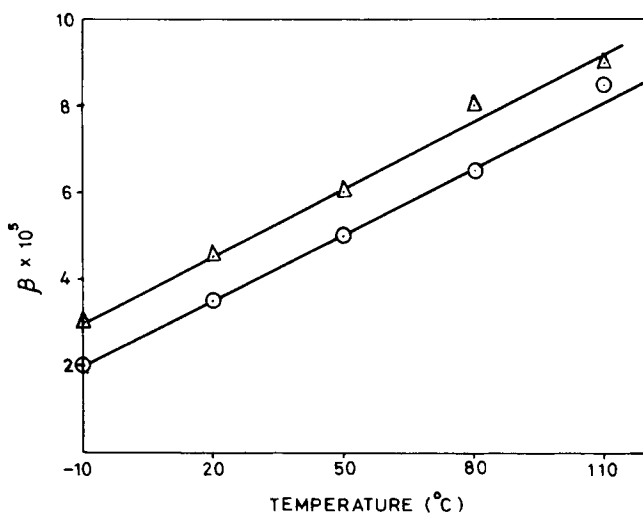

Fig. 5. Variation of fraction of weak bonds (β) in PIB film with and without 0.01 wt % TPAC as function of temperature during 254-nm irradiation: (⊙) PIB; (△) PIB + TPAC.

Fig. 6. Variation of unsaturation during 254-nm irradiation of PIB film with and without 0.01 wt % TPAC at 20°C: (⊙) PIB; (●) PIB + TPAC.

To investigate the photosensitization mechanism by TPAC, the photochemistry in the UV of this material and in PIB was investigated. The changes in the UV spectrum of the photochemical-induced change of TPAC solution in isooctane are presented in Figure 10. The spectrum shows absorption bands at 246 and 285 cm^{-1}. After 254-nm irradiation of TPAC solution (1 cm^3) in isooctane in an oxygen-free atmosphere, the intensities of the bands at 246 and 285 cm^{-1} decrease. The 254-nm irradiation of TPAC solution in the presence of oxygen produces a rapid decrease of the absorption bands, which disappear almost completely after 50 min of irradiation. These results indicate a photodecomposition of TPAC.

Polyisobutylene film (80 μm) blended with 0.01 wt % TPAC exhibits an absorption spectrum (Fig. 11) almost similar to the UV absorption spectrum of TPAC in isooctane solution. Two absorption bands appeared close to 246 and 285 cm^{-1}. These bands distinctly decrease during the 254-nm irradiation of PIB film.

The acceleration behavior of TPAC thus can be explained by the photochemical decomposition[14,15] of TPAC absorbing the UV light and the free radicals (R·) generated effectively initiating the photodegradation of the polymer as

$$(PhN=C\!\!-\!\!S)_3Co \xrightarrow{\ +\ h\nu\ } (PhN=C\!\!-\!\!S)_2Co\ +\ PhN=C\!\!-\!\!S\cdot \qquad (3)$$

$$\underset{H_4C_5N}{\big|} \qquad\qquad \underset{H_4C_5N}{\big|} \qquad\qquad \underset{N_4C_6N}{\big|}$$

initiating radical, R·

Zeif[16] has also observed formation of a free radical R· during UV light irradiation of TPAC in the solid state in air at room temperature by ESR spectroscopy.
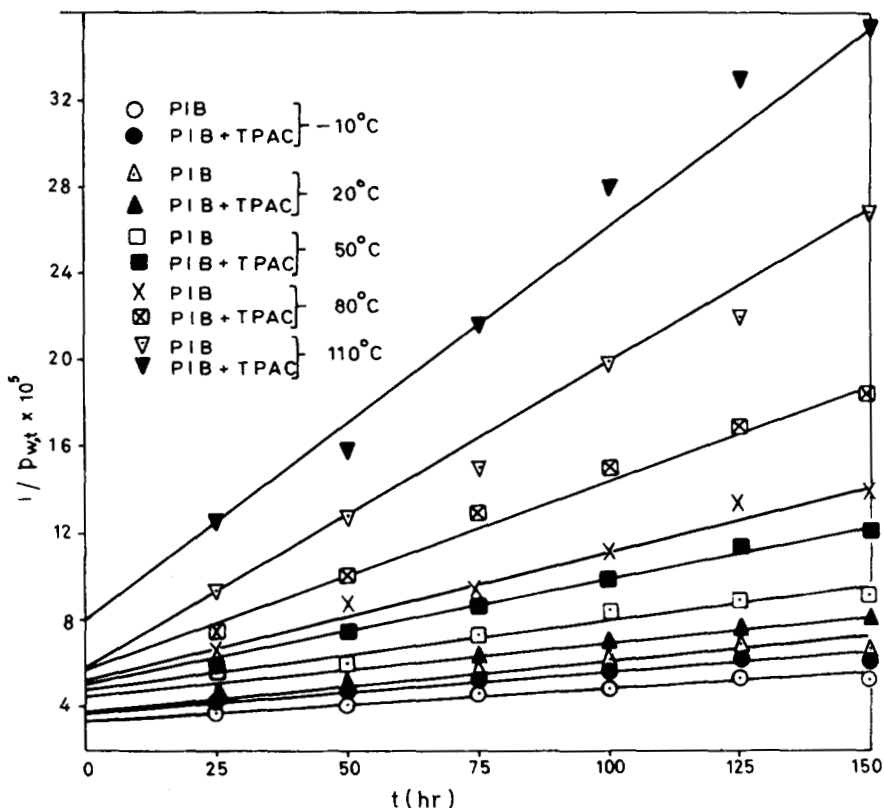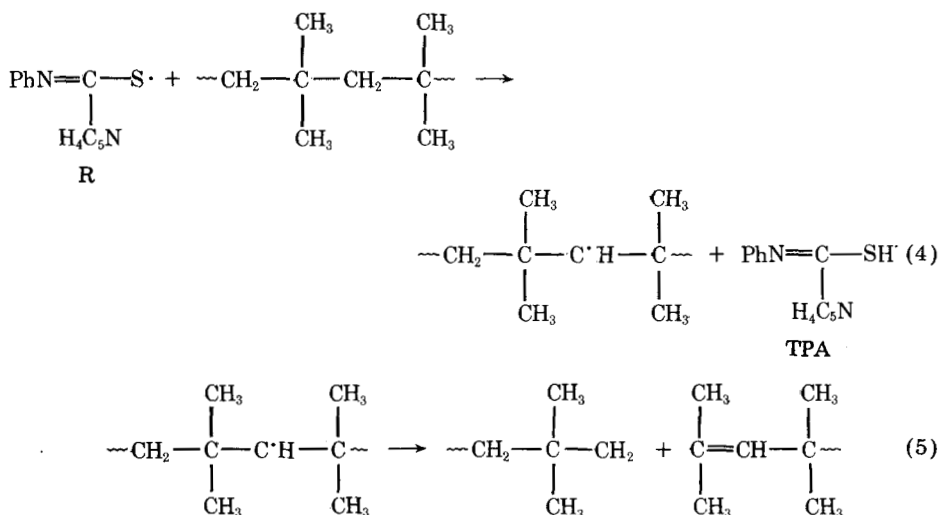
Fig. 7. Change in reciprocal value of weight-average degree of polymerization ($1/p_{w,t}$) during 254-nm irradiation of PIB film with and without 0.01 wt % TPAC at various temperatures.

The radicals (R·) will abstract hydrogen from the PIB chain, and this reaction is leading to degradation in PIB. The probable reaction scheme is

Scheme I.

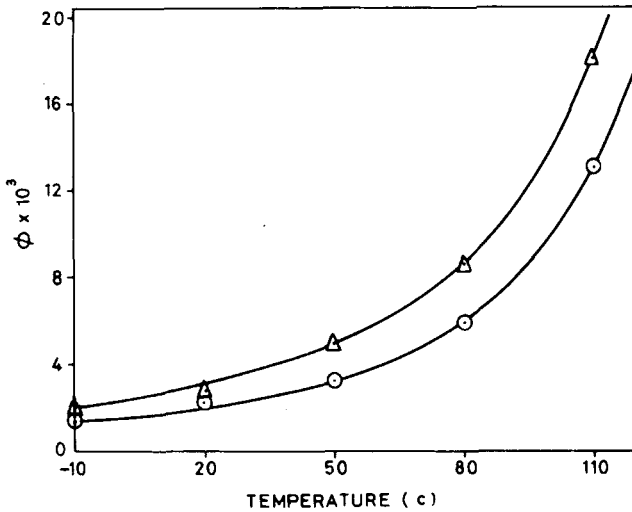The consequences of this mechanism are (1) α-thiopicolinanilide (TPA) must

Fig. 8. Variation of quantum yield (ϕ_{cs}) during 254-nm irradiation of PIB film with and without 0.01 wt % TPAC as function of temperature: (⊙) PIB; (△) PIB + TPAC.

be formed; (2) termination may occur as a result of combination between PIB radicals, one mode of which would lead to an increase in the degree of branching of the polymer; (3) the R· radicals might enter the polymer as the result of a combination reaction.

Figure 12 shows the IR absorption spectra of irradiated film of PIB containing 0.01 wt % of TPAC. The overall acceleration behavior of TPAC with increasing
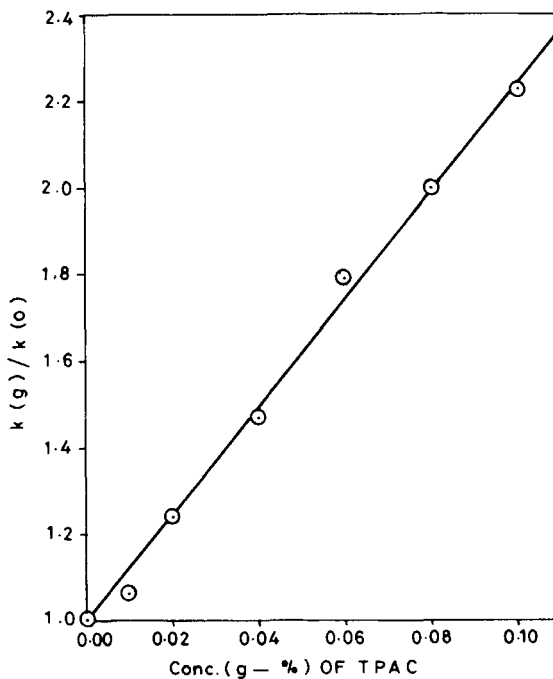
Fig. 9. Effect of concentration of TPAC on the rate of sensitization of degradation of PIB film during 254-nm irradiation at 20°C.
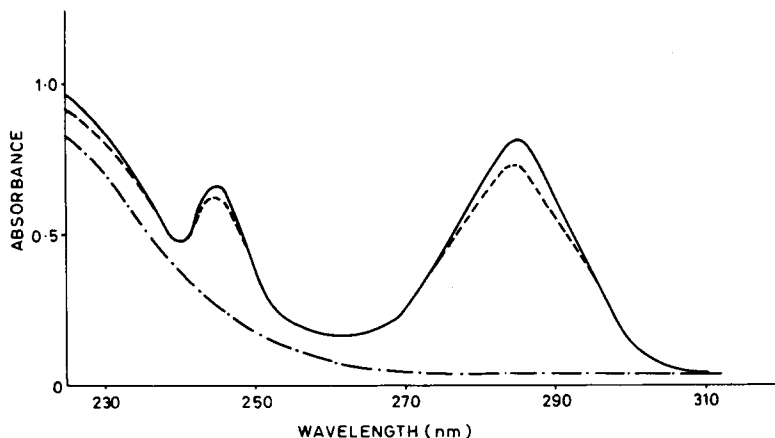
Fig. 10. Changes of UV spectra of TPAC in isooctane ($10^{-4}\,M$) during 50 min of 254-nm light irradiation: (—) before irradiation; (- - -) in oxygen-free solution; (-·-) in oxygen-saturated solution in a cell of 1-cm path.

irradiation time is reflected in the gradual decrease of various bands.   The irradiated sample had a new absorption band at 899 cm^{-1}, which can be assigned to a vinyl double bond.   The total unsaturation was determined previously by addition of iodine monochloride.   The presence of TPA would be indicated by an absorption in the 2550–2600 cm^{-1} region corresponding to the fundamental S—H stretching frequency.   Figure 12 shows that this band is absent; but owing to the fact that TPA absorbs very weakly at the concentration level likely to be encountered (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 the amount of TPA present, recourse must be made to the UV absorption spectrum 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 coefficients for
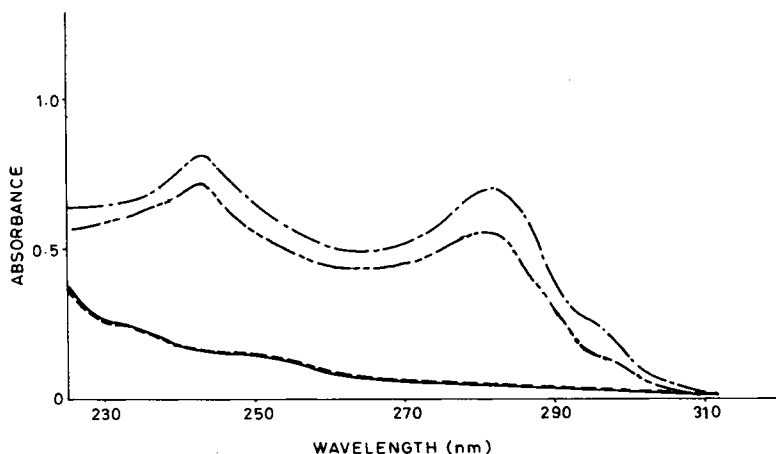

Fig. 11. Change of UV spectra of PIB film (ca. 80 μm) blended with TPAC (0.01 wt %) during 12 h of 254-nm light irradiation: (—) pure PIB film before irradiation; (- - - -) pure PIB film after irradiation; (-·-) blended sample before irradiation; (— ·· —) blended sample after irradiation.
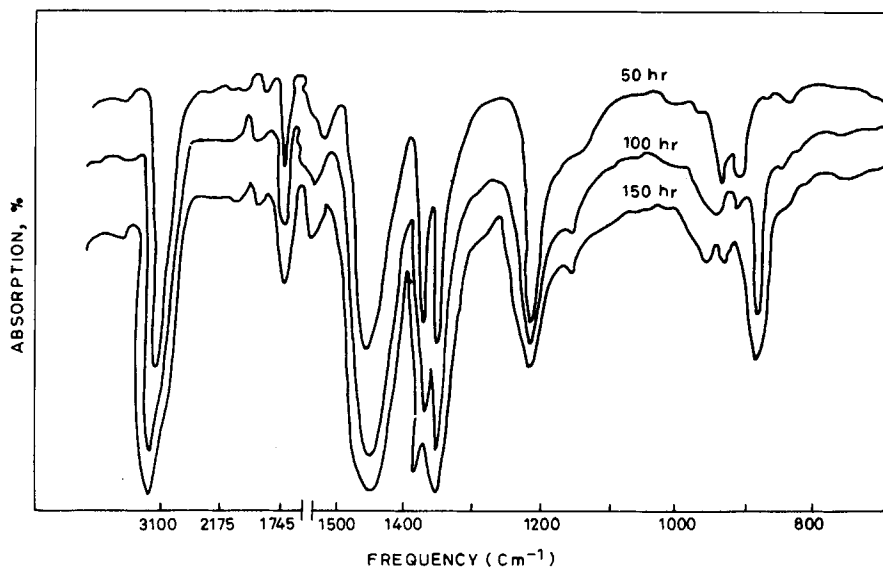
Fig. 12. Change in infrared absorption during 254-nm irradiation of PIB film with 0.01 wt % TPAC.

TPA at 246 and 285 nm are 195 and 145, respectively. The spectra in Figure 13 were obtained from a sample which had undergone the same treatment as that used for the IR analysis. A known weight of the degraded film was dissolved
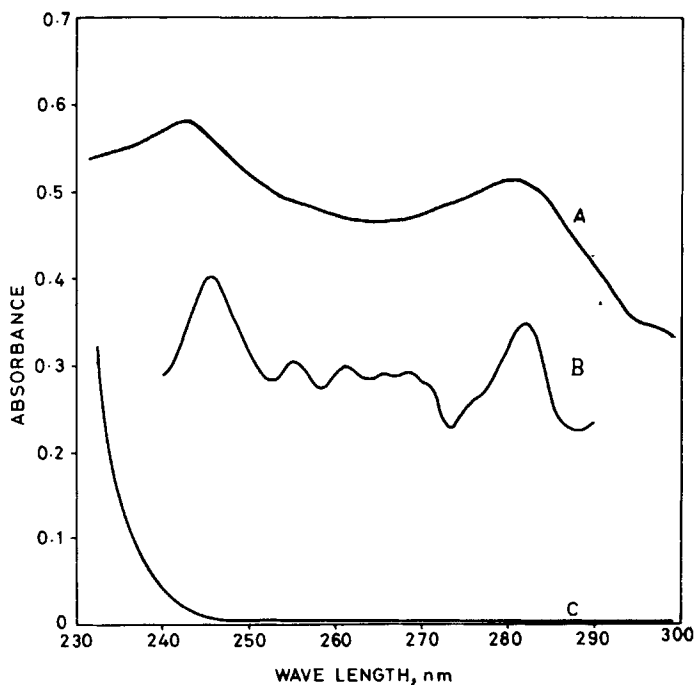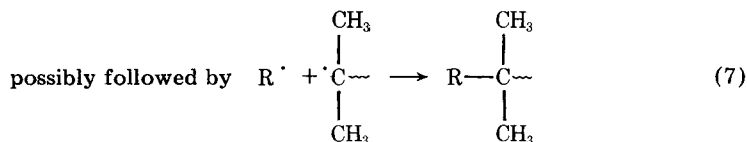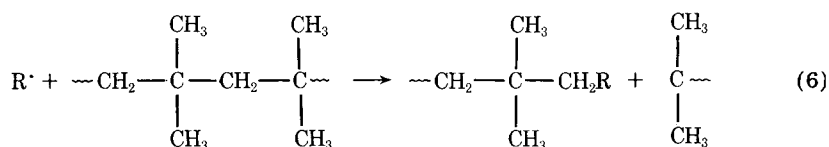

Fig. 13. Ultraviolet absorption spectra of: (A) photodegraded PIB precipitated from isooctane; (B) α-thiopicolinanilide; (C) isooctane layer after precipitation of PIB and washing with water.

in 100 mL isooctane and after precipitation and washing, the volume of the filtrate was 20 mL. A study of the partition of TPA between the two layers in a mixture of exactly the same composition showed that, for a concentration of 2.5 $\times 10^{-5}$ mol TPA in 10 mL isooctane, the final distribution of TPA was isooctane layer 60% and water + acetone layer 40%. If the TPA radicals R· 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 account of the distribution, would then be 0.281 and 0.202, respectively. Figure 13 shows that no TPA-type absorption occurs in the 240–290 nm region by the isooctane layer. The optical density at 246 is 0.004, and that at 285 is 0.002; and if this were due to TPA, the amount present would correspond to about 1.5% of the TPA radicals R· produced in the system. This is in good agreement with the figure obtained from the IR analysis.

It must be concluded (Fig. 13) that the majority of the TPA radicals R· (at least 95%) become attached to the degraded polymer. Figure 13 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 R· to the degraded PIB chains. The exact position of the maximum would appear to depend to some extent upon the irradiation time. This suggests that the absorbing group is itself further changed by further irradiation. The optical density of PIB film is approximately proportional to the irradiation time. Comparison with the spectrum for TPA reveals that a wavelength shift has occurred, the absorption maxima at 241 and 280 nm appearing to correspond to the maxima at 246 and 285 nm in the free TPA. It is interesting to note that if a calculation is made assuming the extinction coefficients to be unchanged, all the radicals of TPAC in the system appear to have become attached to the polymer.

These absorption spectra show conclusively that degradation results mainly from attack upon the polymer chain by the R· radicals. They also show that the first stage in the reaction is not hydrogen abstraction from the polymer, and that the R· radicals responsible for degradation combine with the degraded material.

It is apparent that these results are inconsistent with the simple degradation mechanism already[17] outlined. An alternative scheme, involving direct scission of the polymer by the radicals R· rather than hydrogen abstraction followed by scission is:

$$R\cdot + \ \sim CH_2-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}\sim \ \longrightarrow \ \sim CH_2-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2R \ + \ \underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}\sim \qquad (6)$$

$$\text{possibly followed by} \quad R\cdot + \cdot\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}\sim \ \longrightarrow \ R-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}\sim \qquad (7)$$

Scheme II.

The requirements of this scheme are (1) no α-thiopicolinanilide is produced, (2)

all the radicals produced from TPAC enter the degraded material; (3) there should be no increase in the degree of branching on degradation.

The experimental results are in accord with these requirements. An explanation why R· radicals do not abstract hydrogen from PIB probably involves the enhanced resonance energy of the *tert*-butyl radicals which may be detected in PIB by absorption at 1240 cm^{-1} in the IR spectrum.

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

The PIB itself possesses a very low amount of light-absorbing groups such as those present as chain-attached groups or in impurities. The 254-nm exposure of PIB alone causes only a small change in UV spectra in comparison with UV spectra obtained in the presence of TPAC. Hence, the photosensitization begins with absorption of light by the TPAC. The maximum UV absorption occurs at the surface of the polymeric film containing a uniform distribution of TPAC. The excess energy of the excited TPAC may be lost in any of several ways: reemission of radiation, radiationless conversion to the ground state, a energy transfer, or it can lead to the formation of free radicals which are responsible for further free radical generation and sensitization of the photodegradation of PIB.

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