Photodegradation of poly(2,6-dimethyl-1,4-phenylene oxide) film with metal isopropylxanthates

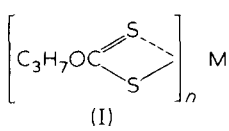
R. Chandra, B. P. Singh, S. Singh and S. P. Handa
Department of Applied Sciences and Humanities, Kurukshetra University, and Department of Applied Chemistry, Regional Engineering College, Kurukshetra 132119, *India*
(*Received* 28 *April* 1980; *revised* 14 *August* 1980)

The effect of metal (Co and Zn) isopropylxanthates over the range of 0.3 to 2.5% (w/w) on the photodegradation of poly(2,6-dimethyl-1,4-phenylene oxide) film was examined, by changes in the carbonyl i.r. absorption, hydroperoxide, weight average molecular weight and quantum yield of the polymer samples. The data have been processed to yield the heats of activation of the system. The photodegradation of the polymer was affected by the kind of metal, concentration of the xanthates, wavelength of irradiated light, and by the temperature. Zinc isopropylxanthate was found as a photostabilizer whereas cobalt isopropylxanthate merely enhanced the degradation. The presence of metal xanthates changed the u.v. spectra of the polymer.

INTRODUCTION

Poly(2,6-dimethyl-1,4-phenylene oxide) (PDMPO) was specifically chosen for these investigations because it is primarily a commercial moulding material whose applications are limited by the deterioration of some of its useful properties by solar radiation. Therefore, the photostabilization and degradation of PDMPO is a problem of considerable technological importance and scientific interest. Little has been published[1-3] on the photodegradation of polymeric materials in connection with the elucidation of the photodegradation mechanism and the preparation of self-disposal packing materials with controlled degradation during weathering. It is well known that trace amounts of metallic impurities or additives present in polymers play an important role in the photodegradation of the substrates. Some such additives act as photosensitizers while others act as quenchers. Nevertheless, in the lower temperature range at least, the same hydroperoxidation process as occurs in polymers plays a major role.

In the present investigation therefore, we set out to study the effect of the metal (Co and Zn) isopropylxanthates (I) on the photodegradation of PDMPO film and in the presence of air at low temperature range 253–353 K where thermal degradation is not significant.



(I)

The photodegradation was followed by light scattering and potassium ferri-oxalate actinometry, and the data have been processed to calculate the values of wt average *MW*, degree of degradation, specific rate constant, the enthalpy, free energy and quantum yield of the activation processes. The changes in carbonyl and hydroperoxide contents of the irradiated PDMPC films have also been determined. It was found that the effect depended on the kind of metal, concentration of the xanthates and the wavelengths of irradiated light. The results and the mechanism are supported by comparing u.v. and i.r. spectra of photodegradation of PDMPO films, both in the presence and absence of xanthates.

EXPERIMENTAL

Sample preparation

The sample of poly(2,6-dimethyl-1,4-phenylene oxide) (PDMPO) has been prepared by following the Hay polymerization[4]. Prior to use the polymer was purified by three reprecipitations from benzene solution in methanol and dried overnight under vacuum at 60°C. The polymer obtained had a wt average *MW* of 64 500 g mol^{-1} determined by light scattering photometer. The continuous film of even thickness (0.12 mm) was prepared by casting the solution of PDMPO in benzene containing metal xanthates on quartz plate which was sealed with a pyrex plate having a 5 cm diameter bore. The film was dried to a constant weight under high vacuum for 24–30 h. The purified metal (Zn and Co) isopropylxanthate[5] samples were supplied through the courtesy of Mr E. V. Thomas, Rubber Research Institute of India, Kottayam.

Photodegradation

Films were placed at right angles to, and 7.5 cm distant from the light source, a Hanovia chromatolite low pressure mercury lamp, and irradiated with monochromatic light of 253.7 and 365.0 nm wavelengths at 253, 273, 293, 313, 333 and 353 K temperatures for various periods. The temperature of the system was controlled to within ±0.1°C.

0032 3861/81/040523-04$02.00

Molecular weight determination

The stock solutions of PDMPO were prepared by dissolving the films in a known volume of distilled Analar benzene. In order to remove suspended impurities, solutions were centrifuged (15 000 rpm) for about an hour. The supernatant solutions from the tubes were withdrawn by means of a pipette and transferred into a filtering G_5 sintered glass funnel directly. Solutions of various concentrations were obtained by adding known volumes to the stock solutions to a known volume of the solvent in the light scattering cell. Zimm plots have been employed to estimate the wt average MW, as a function of time. The dissymetry ratios have been utilized to calculate the particle scattering factors for correction of the light scattering data. These light scattering investigations were made with a Brice–Phoenix light scattering photometer (Phoenix Precision Instruments Co. Philadelphia, USA). The refractive index increment for PDMPO (dn/dc) in benzene were determined using a Brice–Phoenix differential refractometer; the values of 298 K are $n_0 = 1.502$ and $dn/dc = 0.114$ at $\lambda = 546.0$ nm.

Spectrophotometric measurements

Absorption measurements were carried out with a Perkin–Elmer Spectracord (Model 4000) recording u.v. spectrometer and a Perkin–Elmer (Model 21) i.r. Spectrophotometer. The u.v. spectra of PDMPO samples were measured in a 1 cm quartz cell.

Determination of carbonyl

The changes in i.r. spectra of the polymer samples due to carbonyl groups, were analysed by a base line method[6], and the effects of metal isopropylxanthates were estimated.

Determination of hydroperoxides

Polymer hydroperoxides produced by u.v. radiation of PDMPO film were determined by a modified iodometric method[7].

Actinometry

If in the polymer chain, each bond is being of equal strength and accessibility, then the following relation[8] holds:

$$\frac{1}{P_{n,t}} - \frac{1}{P_{n,0}} = \frac{m}{wN} \varphi I_a t \qquad (1)$$

where w is weight of irradiated polymer, m is the molecular weight of the monomer, N is the Avogadro number, I_a is the light intensity absorbed in the polymer sample, φ is the quantum yield, and $p_{n,0}$ is the number average degree of polymerization initially and $p_{n,t}$ at any time t during the degradation. If the number average degree of polymerization is equated to the weight average degree of polymerization, and a most probable distribution ($2p_n = p_w$) is assumed before and after degradation, then the quantum yield φ can be determined from equation (1) by plotting $1/p_{w,t}$ vs. irradiation time t. The $p_{w,t}$ can be conveniently determined by light scattering measurements. The values of I_a can be determined by potassium ferri-oxalate actinometry[9]. By using the same technique the light intensity flux of 253.7 and 365.0 nm light from the lamp at the polymer film have been found 2.38×10^{-9} and 1.78×10^{-11} Einstein s^{-1} cm^{-2} respectively.

RESULTS AND DISCUSSION

One can evaluate s, the average number of cuts per single chain, using the equation derived by Montroll and Simha[10], on a purely statistical basis for random degradation of long-chain molecules:

$$p_{w,t} = \alpha^2 p_{w,0} + 2(1-\alpha)[(1-\alpha)^{p_{w,0}} + \alpha p_{w,0} - 1]/\alpha^2 p_{w,0} \qquad (2)$$

where α is the degree of degradation. Here $\alpha = s/p_{w,0} - 1 \simeq s/p_{w,0}$ since $p_{w,0}$ is large. In the early stages of the degradation, when α and s are small, the term $s/p_{w,0}$ is small and, compared with unity, can be ignored. Similarly, $s^2/p_{w,0}$ is small compared with $(e^{-s} + s - 1)$. Under these restrictions this equation reduces to:

$$p_{w,t}/p_{w,0} = (2/s^2)(e^{-s} + s - 1) \qquad (3)$$

which is identical to the equation deduced by Sakurada and Okamara[11]. This equation has also been used successfully to study the kinetics of degradation of natural rubber[12], polyethylene[13], nitrated Egyptian cotton[13] and polystyrene[15].

Figure 1 gives the variation of the degree of degradation with time for PDMPO films irradiated with and without 0.6% zinc isopropylxanthate (ZIPX) and cobalt isopropylxanthate (CIPX) in air at 253, 273, 293, 313, 333 and 353 K with light intensity flux of 2.38×10^{-9} Einstein s^{-1} cm^{-2}. Inspection of the plots reveals that at each temperature the values of α of the irradiated samples are greater in the presence of CIPX and lower with ZIPX as compared to the corresponding values of neat PDMPO. In the initial stages of the photodegradation of PDMPO, the value of α increases rapidly with time and a point of inflexion is reached after which the α starts decreasing. Such a sharp rise in α in the initial stages, of degradation generally indicates a random breaking of bonds in the polymer chain. In fact, after a sufficiently long interval of time visible opalescence occurs, probably due to crosslinking and microgel formation by the fragments of the PDMPO molecules. It may be seen that, as the temperature of degradation increases, the indication of the formation of crosslinked product appears at shorter time intervals. The appropriate periods and temperatures of degradation were chosen on the basis of the above information so that the reaction is predominantly chain scission with negligible crosslinking.

It can be shown that when the rate of scission of links is proportional to the number of links present at any time, in a random process, $\alpha = k_1 t$ where k_1 is the rate constant. If the plot of α or s, as a function of time is linear, only one kind of rate constant is operative; in other words only one kind of bond is being broken[15,16]. From *Figure 1* it can be seen that the plots of α vs. t are linear, proving that the degradation is taking place by the random breaking of one type of bond. The average values of k_1 were evaluated from the initial slope of α vs. t curve. The average k_1 values at the different temperatures are substituted in the conventional Arrhenius equation $k_1 = Ae^{-\Delta E/RT}$ to obtain the energy of activation (ΔE) and frequency factor (A). A linear plot of $\log_e k_1$ vs. $1/T$ was obtained. The values of ΔE

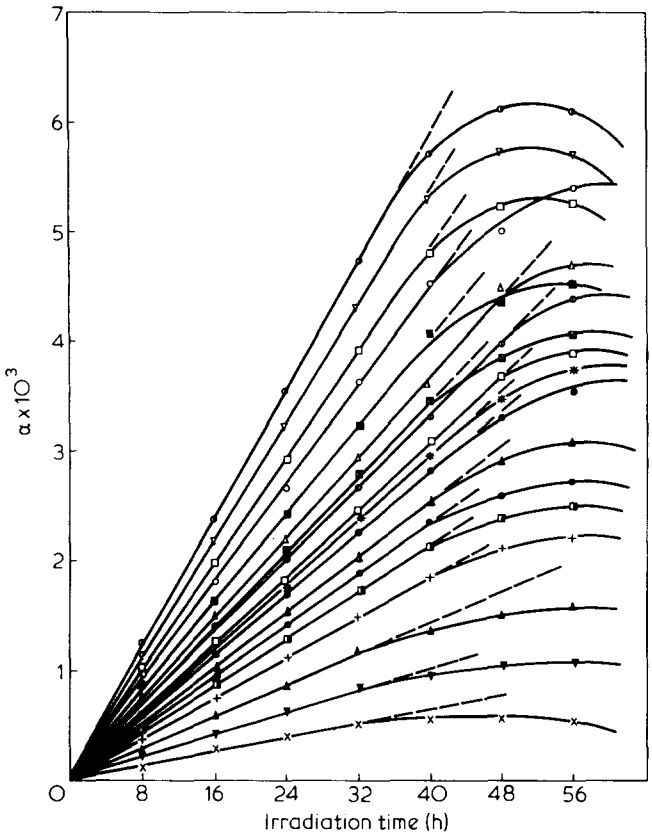


Figure 1 Changes in degree of degradation (α) of PDMPO films irradiated with 253.7 nm light at various temperatures in absence and presence of ZIPX (0.6%) and CIPX (0.6%)

+ PDMPO × PDMPO + ZIPX ⋕ PDMPO + CIPX	253K	⊕ PDMPO ▼ PDMPO + ZIPX ⊠ PDMPO + CIPX	273K
● PDMPO ▲ PDMPO + ZIPX ■ PDMPO + CIPX	293K	□ PDMPO ◨ PDMPO X ZIPX ◧ PDMPO + CIPX	313K
△ PDMPO ▲ PDMPO + ZIPX ▽ PDMPO + CIPX	333K	○ PDMPO ⊕ PDMPO + ZIPX ◑ PDMPO + CIPX	353K

and A calculated by the method of least squares are satisfied by the equations:

$$\text{PDMPO} + 0.6\%\ \text{CIPX};\quad k_1 = 7.43 \times 10^{-2} \exp(-2164/RT) \tag{4}$$

$$\text{PDMPO} + 0.6\%\ \text{ZIPX};\quad k_1 = 11.46 \times 10^{-2} \exp 5860/RT) \tag{5}$$

and

$$\text{PDMPO};\quad k_1 = 11.46 \times 10^{-2} \exp 5860/RT) \tag{6}$$

with the activation energies in cal and frequency factor in s^{-1}. The values of k_1 at each temperature for different periods show a good agreement. Even a tenfold variation in the value of k_1 will change the value of the energy of activation by 1.5 kcal.

It is also seen that the photodegradation of the polymer is of zero order with respect to polymer and oxygen concentrations. Simha and Wall[17] have pointed out that the first order law is not applicable for an ordinary random chain scission process. For a zero order reaction ΔE may be equated to the heat of formation of the activated complex ΔH^{+}, without committing any appreciable error. Irrespective of the variations in the values of ΔH^{+} the values of ΔF^{+} remain almost constant around 39.8 kcal mol^{-1} at 400 K in all cases. This concludes that the rate determining step is the same for all the systems.

The quantum yields at 293 K with a light of $\lambda = 253.7$ nm for the photodegradation of neat PDMPO, PDMPO + 0.6% CIPX and PDMPO + 0.6% ZIPX are: 2.62×10^{-4}, 3.98×10^{-4} and 0.52×10^{-4} respectively. The smaller quantum yield is typical of PDMPO in which the initial u.v. absorption occurs at ZIPX incorporated in the matrix of PDMPO films. It indicates that the number of mols of photolytic product tends to be much less than the number of quanta absorbed by the polymer. The smaller quantum yields of the degradation process of PDMPO in the presence of ZIPX 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. Since the reaction is occurring in the condensed phase, it is more likely that the absorbed energy is dissipated by such quenching reactions as recombination and collisional deactivation.

Relative effects of CIPX and ZIPX on the photodegradation of PDMPO were compared by the simultaneous irradiation of the metal xanthates containing films and neat film with the light of 253.7 nm wavelength, i.r. spectra of typical samples are shown in *Figure 2*. The changes in i.r. spectra were observed in the regions; ca. 1740 cm^{-1}, due to carbonyl groups and ca. 3400–3500 cm^{-1}, due to hydroxyl groups. The i.r. spectra of the photooxidized polymer show a gradual increase in carbonyl and hydroxyl absorption. The carbonyl bands of

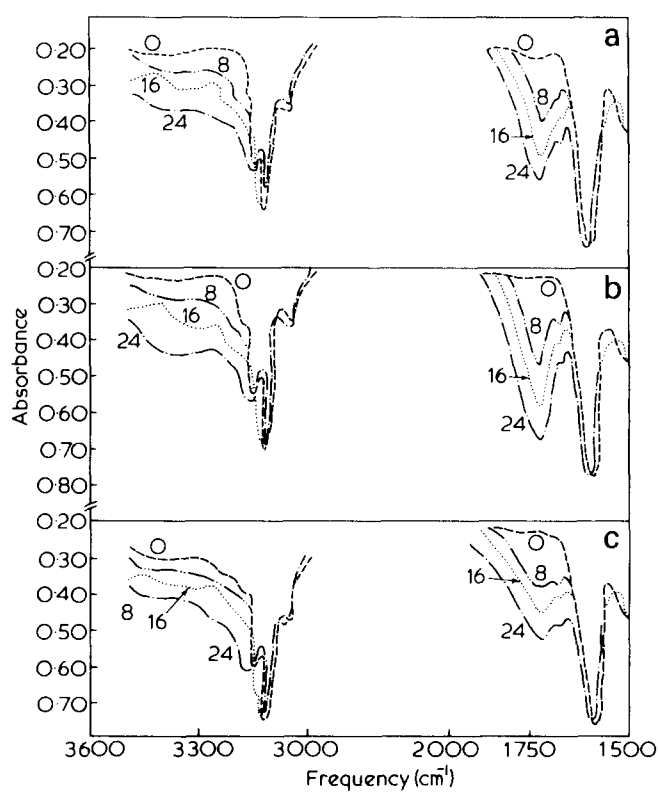


Figure 2 Changes in i.r. spectra of PDMPO films irradiated with 253.7 nm light at 293 K. (a), PDMPO; (b), PDMPO + CIPX (0.6%); (c), PDMPO + ZIPX (0.6%)

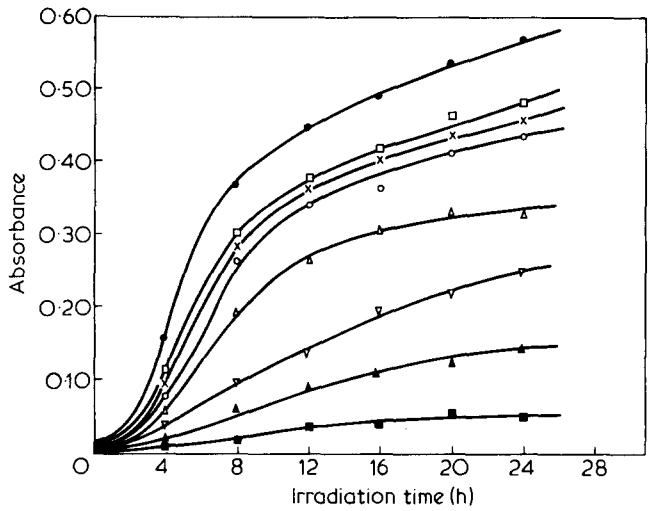


Figure 3 Changes in carbonyl i.r. absorption of 253.7 nm irradiated PDMPO film (□) containing: (●), 0.6% CIPX (X), 0.3; (○), 0.6; (△), 1.0; (▽), 1.5; (▲), 2.0; (■), 2.5% ZIPX

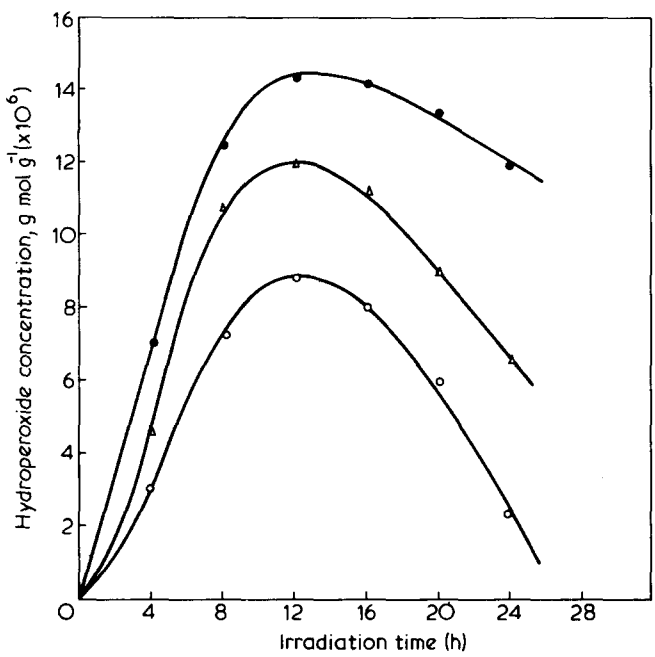


Figure 4 Changes in concentration of hydroperoxide groups in PDMPO films (△) irradiated with 253.7 nm light at 293 K in the presence of 0.6% CIPX (●) and 0.6% ZIPX (⊙)

the oxidized plastic film with and without CIPX appear sharper throughout their term of exposure. This may indicate that even in the early stages, photooxidation gives rise to a greater variety of carbonyl-containing degradation products, which can be a consequence of a faster reaction rate or a less discriminate attack by reacting species.

The changes in carbonyl i.r. absorption of xanthate-containing samples and neat samples are shown in *Figure 3*. Under similar conditions of irradiation — time, temperature, wavelength etc. — the contents of carbonyl groups of polymer film with CIPX are higher whereas with ZIPX are lower than that of the neat PDMPO films. Specifically, CIPX accelerates the photodegradation, whereas ZIPX retards it.

The effect of the concentration of metal isopropylxanthates on the photodegradation of PDMPO was also examined (*Figure 3*). The changes in carbonyl i.r. absorption (1740 cm^{-1}) of PDMPO must be temperature dependent to some extent, but the constancy of the data indicates the swamping action of the ZIPX. CIPX, which accelerated the photodegradation of PDMPO at all concentrations, enhanced the rate of degradation and the effect increased with increasing concentration of the CIPX.

The hydroperoxide contents of oxidized polymer were measured by iodometry, and plotted against the time of irradiation at 293 K in *Figure 4*. The hydroperoxide was rising to a maximum concentration at 12 h. The results suggest that ZIPX destroys hyperperoxides formed during the oxidation of the polymer to stable products such as alcohols and carbonyl compounds.

In the photodegradation of polymeric materials the wavelength of light irradiated is extremely important. As shown in *Figure 5*, when PDMPO film is exposed to light filtered through a monochromatic filter of the wavelength 365.0 nm, the change in carbonyl region in i.r. spectra of the irradiated samples was much less than that of samples irradiated with 253.7 nm filter. Plots of carbonyl content in sample films against irradiation time indicate that the extent of photodegradation of neat PDMPO film, irradiated with 365.0 nm light, is much lower than that of the polymer irradiated with 253.7 nm light. Also, the photodegradation of the polymers is much less with 365.0 nm light than with 253.7 nm light during 56 h irradiation in the presence of both metal isopropylxanthates tested (at 0.6%).

To clarify the degradation mechanism, the u.v. spectra of irradiated PDMPO film at 293 K in the presence and absence of 0.6% ZIPX and CIPX have been investigated. The wavelength primarily responsible for the photodegradation of PDMPO is supposed to be ca. 280 nm. This is probably due to carbonyl groups which attach to the macromolecular chains. The u.v. spectrum of irradiated PDMPO film at ca. 280 nm gradually increases with the time of irradiation. However, PDMPO film containing CIPX, which accelerated the photodegradation of the polymer, the increase of the u.v. spectrum at ca. 280 nm is faster than that of neat PDMPO. However, with PDMPO film containing ZIPX which retarded the photodegradation, the increase of the u.v. spectrum at ca. 280 nm is slower than the increase of neat PDMPO film. The u.v. spectrum of neat ZIPX has also an absorption

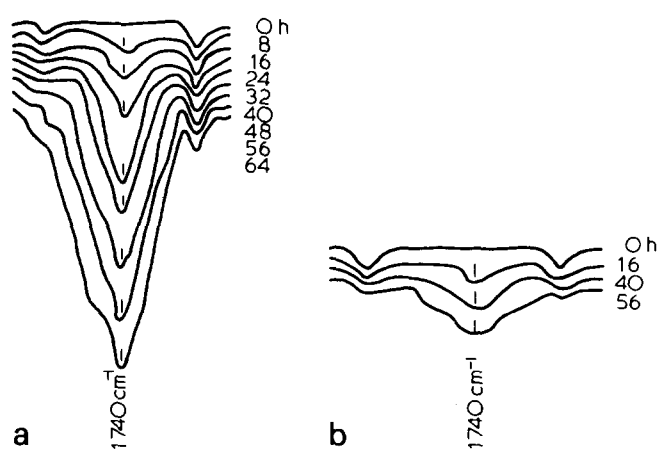


Figure 5 Carbonyl absorptions of irradiated PDMPO films. (a) With 253.7 nm filter; (b) with 365.0 nm filter

peak at ca. 280 nm. It may, therefore, behave as a u.v. absorber. CIPX, which enhances the degradation of the polymer, shows no absorption peak at ca. 280 nm.

Mechanism of photodegradation and stabilization of PDMPO

The polymer is prepared by oxidative coupling. During preparation the methyl groups[18] of the polymer chain are oxidized into hydroperoxide groups and the polymer might initially have finite concentration of hydroperoxides and their acidic, aldehydic, and alcoholic degradation products. Such hydroperoxides may be involved in the initiation reactions of oxidative processes. On the basis of the experimental results, initiation of the oxidative process can arise by photolysis of the hydroperoxides initially present, or induced as shown in equation (7).

$$RO{-}OH \xrightarrow{h\nu} RO^{\cdot} + {}^{\cdot}OH \qquad (7)$$

The value of $\Delta F^{+} \simeq 39.7$ kcal mol^{-1} obtained is quite close to the 40 kcal mol^{-1} required for the decomposition of O–O bond in the polymer hydroperoxide. It is possible that the Q O–O may be reduced due to various structural factors. The observed data, therefore, can be explained satisfactorily on the basis of this mechanism. One might suspect that oxygen induced formation of hydroperoxides and carried the bulk of the initiation process. However, no induction period was found in the oxidations of PDMPO, even at the lowest temperature. This strengthens the premise that hydroperoxides are initially present in the polymer to catalyse the degradative process.

Propagation by initiator radicals can then proceed to the rest of the polymer (equations 8 and 9).

$$RH \xrightarrow[IH]{I^{\cdot}} R^{\cdot} \xrightarrow{O_2} ROO^{\cdot} \qquad (8)$$

$$ROO^{\cdot} + RH \longrightarrow R^{\cdot} + RO{-}OH \qquad (9)$$

The newly formed hydroperoxide and polymeric radicals can continue the chain process or termination by crosslinking (equations 10 and 11) or by disproportionation to inert degradation products (equation 12).

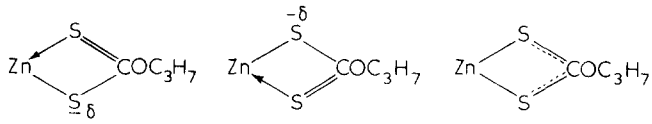
$$2\,R^{\cdot} \longrightarrow R{-}R \qquad (10)$$

$$R^{\cdot} + RO^{\cdot} \longrightarrow R{-}O{-}R \qquad (11)$$

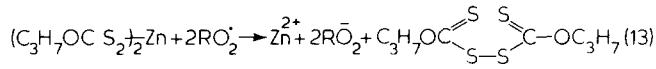
$$2\,RO^{\cdot} \longrightarrow R'{-}\overset{\overset{O}{\|}}{C}{-}H + ROH \qquad (12)$$

On exposure to oxygen-containing atmospheres, the polymer rapidly builds up large amounts of peroxidic species which decompose concurrently with chain scission[18] rather than crosslinking. Further oxidation of the alcohol and aldehyde leads to acidic products which, in turn, can decarboxylate under drastic exposure conditions. The formation of these products is substantiated by the observed increases in the hydroxyl and carbonyl regions of the i.r. spectra.

The mechanism of photostabilization of PDMPO by ZIPX involves both interference with the propagation of the oxidative chain reaction and decomposition of the polymer hydroperoxide. The structure of ZIPX, is represented by a hybrid of the following canonical forms[19].

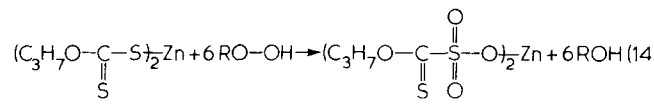


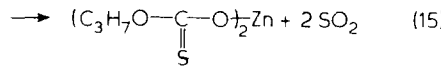
With all these structures the peroxy-radical can be converted into a peroxy-anion by the abstraction of an electron from the electron-rich sulphur atom:



It is suggested that this type of electron transfer process accounts for the stopping of the oxidative chain reaction by the ZIPX.

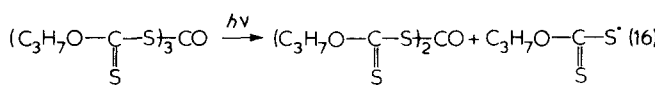
A minor amount of hydroperoxide in the substrate plays an important role in the degradation of polymers and that the hydroperoxide decomposer ZIPX inhibits this degradation as follows:





Gaseous SO_2 can act as a catalyst for ionic decomposition of hydroperoxide groups[20,21].

The acceleration behaviour of CIPX can be explained by the photochemical decomposition of the isopropylxanthate absorbing relatively short wavelength light (260 nm) and the isopropylxanthyl radicals[22,23] generated effectively initiating the photodegradation of the polymer (equation 16):



Therefore, the roles of the metal isopropylxanthates on photodegradation are greatly dependent on the kind of metal, concentration of the xanthates, wavelength of the irradiated light, etc., and, based on these factors, the metal xanthates may show various effect on the photodegradation of the polymers.

ACKNOWLEDGEMENTS

The authors wish to thank the Ministry of Education, Government of India, New Delhi for the award of research fellowships to (B.P.S., S.S., and S.P.H.) and the authorities of the Rubber Research Institute of India, Kottayam, for the laboratory facilities.

REFERENCES

1 Partridge, R. H. *J. Chem. Phys.* 1966, **45**, 1679
2 Ashby, G. E. *J. Polym. Sci.* 1961, **50**, 99
3 Kato, Y., Carlsson, D. J. and Wiles, D. M. *J. Appl. Polym. Sci.* 1969, **13**, 1447
4 Hay, A. S. *J. Polym. Sci.* 1962, **58**, 581
5 Dunn, J. R. *J. Appl. Polym. Sci.* 1960, **4**, 151
6 Luongo, J. P. *J. Polym. Sci.* 1960, **42**, 139

7 Wagner, C. D., Smith, R. H. and Peters, E. D. *Anal. Chem.* 1947, **19**, 976
8 Ranby, B. and Rabek, J. F. 'Photodegradation, Photo-oxidation and Photostabilization of Polymers' Wiley, New York, 1973, 81
9 Calvert, J. G. and Pittz, N. R. Jr. 'Photochemistry', Wiley, New York, 1966
10 Montroll, I. and Simha, R. *J. Chem. Phys.* 1940, **8**, 721
11 Sakurada, I. and Okamara, S. *Z. Physik, Chem.* 1940, **187**, 389
12 Sarfare, P. S., Bhatnagar, H. L. and Biswas, A. B. *J. Appl. Polym. Sci.* 1963, **7**, 2199
13 Lal, K. and Bhatnagar, H. L. *Ind. J. Chem.* 1968, **6**, 149
14 Schulz, G. V. *Z. Physik. Chem.* 1942, **B52**, 50
15 Jellinek, H. H. G. *J. Polym. Sci.* 1949, **4**, 1
16 Jellinek, H. H. G. *Trans. Faraday Soc.* 1948, **44**, 345
17 Simha, R. and Wall, L. A. *J. Phys. Chem.* 1952, **56**, 707
18 Alvino, W. N. *MSc. Thesis*, Seton Hall Univ., South Orange N.J., 1966
19 Chatt, J., Duncanson, L. A. and Venanzi, L. M. *Nature* 1956, **177**, 1042
20 Holdsworth, J. D., Scott, G. and Williams, D. *J. Chem. Soc.* 1964, 4692
21 Scott, G. *Eur. Polym. J. Suppl.* 1969, 189
22 Reich, L. and Stivala, S. S. 'Elements of Polymer Degradation', McGraw-Hill, New York, 1971, 16
23 Neiman, M. B. 'Aging and Stabilization of Polymers', Consultants Bureau Enterprises Inc., New York, 1965, 123