European Polymer Journal Vol. 18, pp. 117 to 122, 1982
Printed in Great Britain. All rights reserved

0014-3057/82/020117-06$03.00/0

THERMAL DEGRADATION AND STABILIZATION OF POLY(2,6-DIMETHYL-1,4-PHENYLENE OXIDE)

R. P. SINGH
Polymer Chemistry Division, National Chemical Laboratory, Pune 411008, India

(*Received* 1 *June* 1981)

Abstract—Thermal degradation and stabilization of poly(2,6-dimethyl-1,4-phenylene oxide) have been examined in air in the range 100–400°. Plots of weight-average molecular weight vs time are linear, confirming random chain scission. The breakdown process has also been studied by DTA and TGA. It was concluded that thermal analysis alone was insufficient to characterize the degradation fully so the degradation products were determined qualitatively using i.r. and NMR spectroscopy. The heats of activation for the systems have been calculated and a stabilization mechanism by bis(1-phenyl-3-α-pyridyl triazeno)Cu(II) chelate has been postulated.

INTRODUCTION

The extensive use of plastics for insulation and building materials has created interest in protection against induced and terrestrial environmental conditions. The good thermal stability of poly(phenylene oxide) indicates that it may be useful in practice. Polymers containing aromatic rings have high thermal stability due to the complete conjugation of the chain and the delocalization of the π-electrons. The weight loss method has been used to study the thermal degradation of some halogenated types of poly(phenylene oxide). The degradation depends on many factors and the heating rate is important.

The thermal degradation of poly(2,6-dimethyl-1,4-phenylene oxide) [PDPO] has been reported in vacuum [1] and in nitrogen [2]. Conley *et al.* [3] have studied the degradation above 150° in the presence of oxygen. Recently photostabilization of polymeric materials by metal chelates [4–7] has been reported but little attention has been paid so far to the thermal stabilization. In the present investigation, the effect of bis(1-phenyl-3-α-pyridyl triazeno)Cu(II) chelate on the thermal degradation of PDPO has been studied and the mechanism of stabilization has been discussed. i.r. and NMR spectra have been utilized for qualitative determination of the degradation products.

EXPERIMENTAL

(*i*) *Materials*

Poly(2,6-dimethyl-1,4-phenylene oxide) [PDPO] was synthesized as described previously [8]. The polymer was purified by precipitation from benzene solution in methanol and dried at 60° under vacuum. For the synthesis of bis(1-phenyl-3-α-pyridyl triazeno)Cu(II) [BPTC], 0.372 g (0.002 M) 1-phenyl-3-α-pyridyl triazene [9] ligand was dissolved in 30 ml ethanol and 0.174 g (0.001 M) cupric chloride dihydrate was dissolved in 10 ml ethanol separately. Both systems were heated slowly to ensure solution, then mixed and digested on a water bath for 12 min. A yellowish brown complex separated out; it was filtered off, washed with hot ethanol and dried in an oven at 120°. The chelate is soluble in benzene and pyridine. It is highly stable and does not decompose up to 420°. Analytical data:

Calculated for $C_{20}N_8H_{18}Cu$,

$$N = 12.92\%, \ Cu = 14.66\% \text{ and } H = 4.12\%$$

found

$$N = 12.92\%, \ Cu = 14.75\% \text{ and } H = 4.21\%.$$

(*ii*) *Experimental procedure*

Polymer films [10] on quartz plates were suspended in a forced-air oven at 100, 200, 250, 300, 350 or 400°. The films were degraded for various periods at all the temperatures within ±1°. The molecular weights of the degraded films were determined by light scattering [10].

i.r. and NMR spectra of the treated films of PDPO at 250° were recorded with a Perkin–Elmer (Model-21) i.r. spectrophotometer and WH-90FT NMR spectrometer, respectively. i.r. Spectra were recorded in the absence and presence of 0.1 wt% BPTC.

(*iii*) *Carbonyl group*

The carbonyl groups were determined [11] by the intensity of the carbonyl peak in the i.r. spectra.

(*iv*) *Hydroperoxide determination*

To determine the hydroperoxide concentration in the PDPO films, a modified iodometric [12] method was used.

(*v*) *Differential thermal analysis* (*DTA*), *thermogravimetric analysis* (*TGA*) *and differential thermogravimetry* (*DTG*)

These were undertaken in the absence and presence of 0.1 and 0.5 wt% of BPTC with a NETZSCH Thermal Analyser. Samples of 25 mg were employed with a heating rate of 10°/min.

RESULTS AND DISCUSSION

Plots of weight-average molecular weight ($\overline{M}_w$) as a function of time of degradation for PDPO in the absence and presence of 0.1 wt% BPTC at various temperatures in air are shown in Fig. 1. The plots reveal an initial rapid decrease in $\overline{M}_w$ which then slows down but the molecular weight of PDPO is lower in the absence of BPTC than in its presence at each temperature. This indicates that BPTC retards

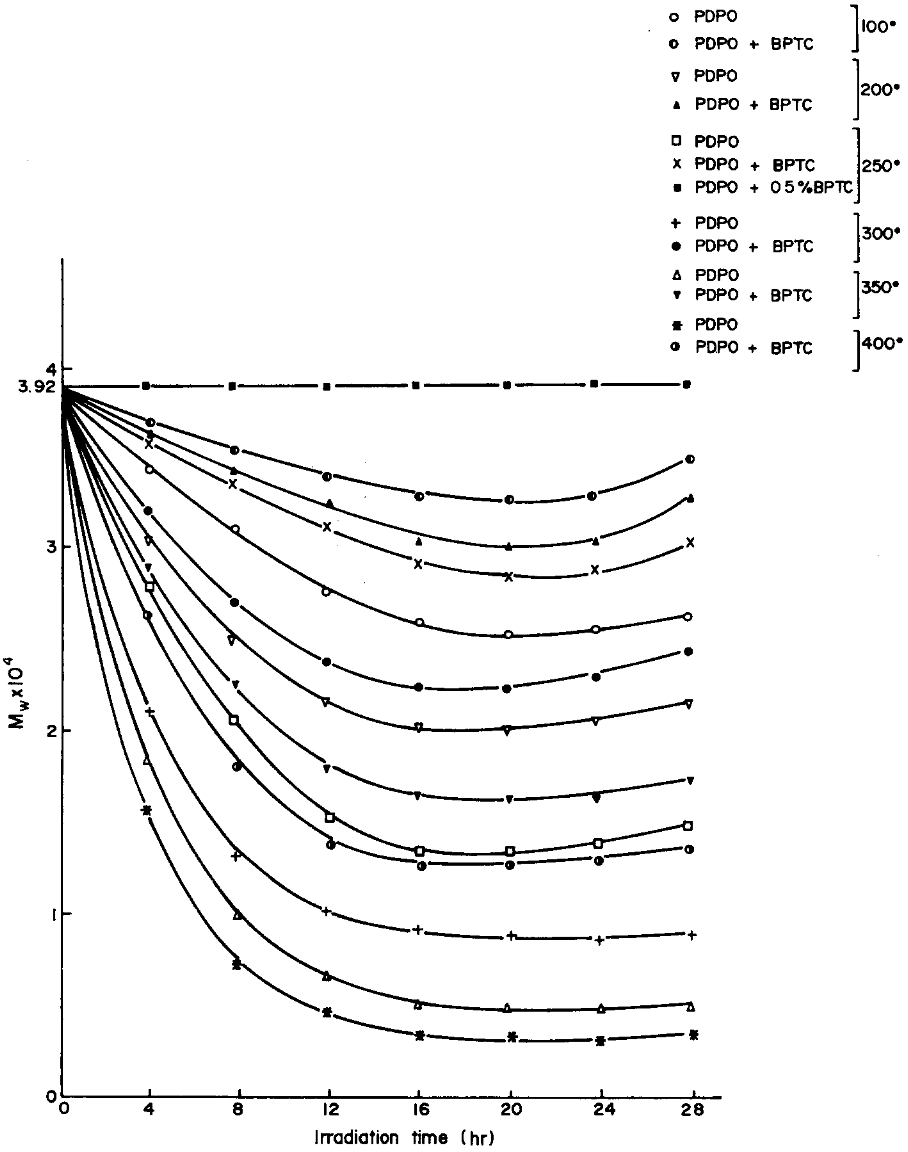


Fig. 1. Variations of weight-average molecular weight of thermally degraded PDPO films in the absence and presence of 0.1 wt% BPTC at various temperatures in air.

the thermal degradation of the polymer. The rapid initial drop in $\bar{M}_w$ is due to random bond scission at various weak links [13, 14] distributed along the polymer chain. The sharp decrease in $\bar{M}_w$ tends to increase on longer periods. This behaviour may be due to detachment of substituents from the aromatic nuclei followed by cross-linking. The figure also shows that 0.5 wt% of BPTC brings a saturation limit to thermal stabilization. The excess of metal ions may induce radical formation by redox reactions and consequent start of degradation.

Figure 2 shows the variations of dissymmetry ratio Zd (ratio of scattered intensity at 45° to that at 135°) as a function of time for PDPO degraded in the absence and presence of 0.1, 0.5 and 0.75 wt% of BPTC in air for programmed periods at 250°. Zd decreases monotonously with time but the values of Zd of the degraded films are greater in the presence of 0.1 wt% BPTC than in its absence. This indicates that BPTC retards the thermal degradation of PDPO. The figure also shows that 0.5 wt% of the stabilizer leads to a saturation limit in the thermal stabilization of PDPO.

The activation energies of a chain scission process in PDPO in the absence and presence of 0.1 wt% BPTC were estimated from Arrhenius plots as 12.8 and 15.1 kcal/mol respectively. The rate equations for the early part of the breakdown may therefore be represented as:

$$k = 6.78 \times 10^{-2} \exp[-12800/RT]\ \mathrm{sec}^{-1}\ [\mathrm{PDPO}] \quad (1)$$

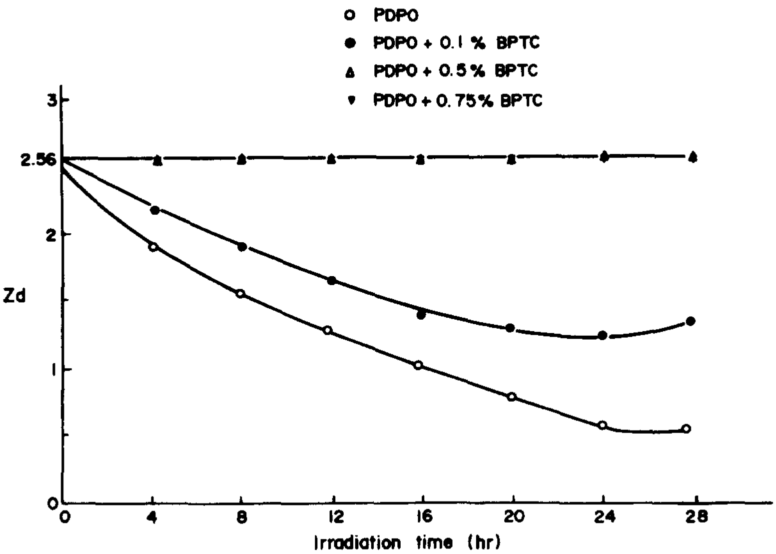


Fig. 2. Variations in dissymmetry ratio of thermally degraded PDPO films with time in the absence and presence of BPTC at 250° in air.

and

$$k = 9.17\,10^{-2}\exp[-15100/RT]\,\mathrm{sec}^{-1}.$$

$$[\mathrm{PDPO} + 0.1\ \mathrm{wt\%}\ \mathrm{BPTC} \quad (2)$$

The values of *k* are nearly constant with time indicating the reactions to be zero order. Simha and Wall [15] have pointed out that the first order law is inapplicable for an ordinary random chain scission process. Chandra and Bhatnagar [16] have confirmed that this type of degradation is zero order with respect to polymer and oxygen concentrations.

The i.r. spectra of the degraded PDPO, recorded after various periods at 250°, are shown in Fig. 3. The broad absorption band at 3465 cm^{-1} which develops upon degradation of PDPO is due to the OH group. There is gradual intensification of hydroxyl, aldehyde and carbonyl bands and they continue to grow with the time of degradation. The carbonyl bands are found at 1726 and 1692 cm^{-1} after heating in air. The 1692 cm^{-1} peak was assigned to carboxylic acid and 1726 cm^{-1} to the ester carbonyl. These peaks are the oxidation products of the methyl group which gives alcohol (3360 cm^{-1}), aldehyde and carboxylic acid, which in turn, can decarboxylate under drastic con-

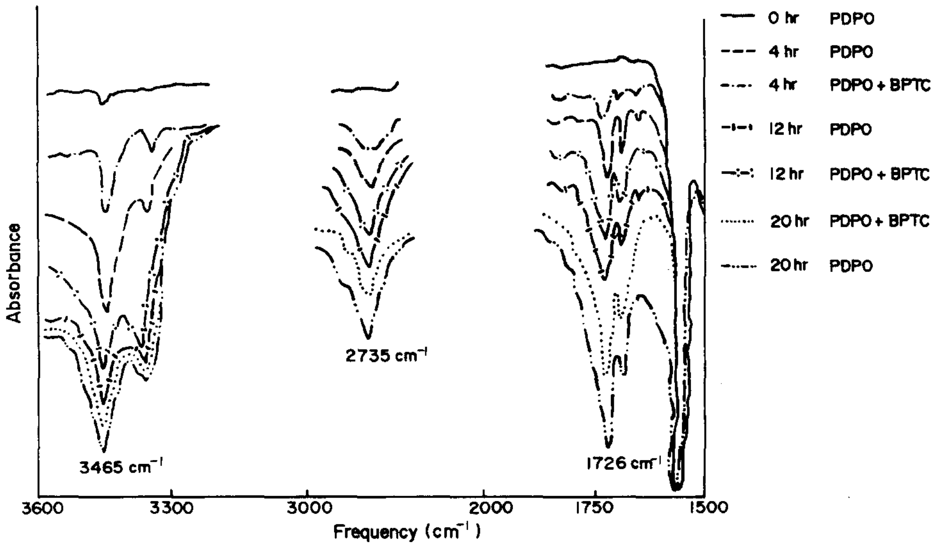
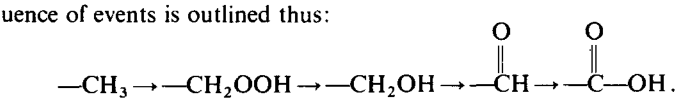


Fig. 3. Variations in i.r. spectra of thermally degraded PDPO films in the absence and presence of 0.1 wt% BPTC at 250° in air.

ditions. The sequence of events is outlined thus:



$$-CH_3 \rightarrow -CH_2OOH \rightarrow -CH_2OH \rightarrow -\overset{\overset{O}{\|}}{C}H \rightarrow -\overset{\overset{O}{\|}}{C}-OH. \qquad (3)$$

Early in the oxidation, a peak at 1663 cm^{-1} could be seen. A strong aryl-oxygen stretching vibration at 1235 cm^{-1} and the C-H stretching vibration of an aldehyde [17] at 2735 cm^{-1} are also clear. These spectral changes were accompanied by formation of large amounts of gel , indicating cross-linking. Under similar conditions of degradation, the contents of the hydroperoxide, carbonyl and aldehyde groups of base PDPO exceed those of PDPO containing 0.1 wt% BPTC. This is an indication that the stabilizer decomposes unstable reaction intermediates to relatively stable products, such as alcohols, and retards thermal degradation. The NMR of the degraded film at 250° indicated the presence of two $-CH_3$ groups at δ 2.12 and δ 2.23 ppm, one at 6.21 ppm due to aryl hydrogen, possibly an aldehydic unit at 10.18 ppm and a broad peak at δ 10.38 ppm due to the hydrogen atom of the carboxylic group [18]. Mass spectrometric analysis and gas chromatographic data also qualitatively confirm these results [19].

The thermal degradation rate of the polymer was measured by means of the carbonyl contents at 1726 cm^{-1} using an i.r. spectrophotometer. Figure 4 shows the changes in the carbonyl concentration with time at 250° in the absence and presence of 0.1 wt% BPTC. The area of the absorption band is a direct measure of the concentration of carbonyl species. The contents of carbonyl group of the polymer are lower in the presence of BPTC than in base PDPO. This indicates that BPTC retards thermal degradation.

The thermal degradation was also studied by the determination of hydroperoxide groups. The hydroperoxide concentration in the degraded polymer was measured iodometrically and plotted as a function of time at 250° in the absence and presence of 0.1 wt% BPTC (Fig. 5). These plots indicate that BPTC destroys hydroperoxides formed during the thermal oxidation of PDPO to stable products such as alcohol and carbonyl compounds and that it acts as a thermal stabilizer.

From i.r. data it is possible to derive the kinetics of the degradation by measuring the rate of growth of carbonyl and hydroperoxide as a function of time but the mechanism of thermal degradation can be postulated fully by the study of DTA and TGA. Figure 6 illustrates the record of DTA. Programmed heating was used from 0 to 665° at a heating rate of 10°/min in air. Twenty-five mg samples of PDPO in the absence and presence of 0.1 wt% and 0.5 wt% BPTC were used. Full scale sensitivity, ΔT is 0.2 mV upto 665°. In DTA, heat absorbed (endothermic) or liberated (exothermic) as ΔT is plotted vs temperature of the sample. Analysis of DTA curves shows that thermal decomposition of PDPO is a rapid exothermic process at 366.5, 404.0 and 424.5° in the absence and presence of 0.1 and 0.5 wt% of BPTC respectively.

Because of the limited information derived from DTA curves, this technique was not as useful as TGA where a recording of weight loss with increasing temperature is obtained. TGA is basically a means for studying behaviour, and not an absolute identification tool. Figure 7 shows the TGA record for PDPO heated at 10°/min in air. A small weight loss is observed at 135° to 204° due to the glass transition state (T_g = 204°). Rapid weight loss is observed at the start of the corresponding exothermic peak at 366.5° and continued to 665°, where the PDPO sample is completely combusted. In the presence of 0.1 and 0.5 wt% BPTC, a small weight loss starts from 154.5, 182.5° and rapid weight loss from 404 and 424.5° respectively. Derivative thermogravimetry (DTG) shows im-

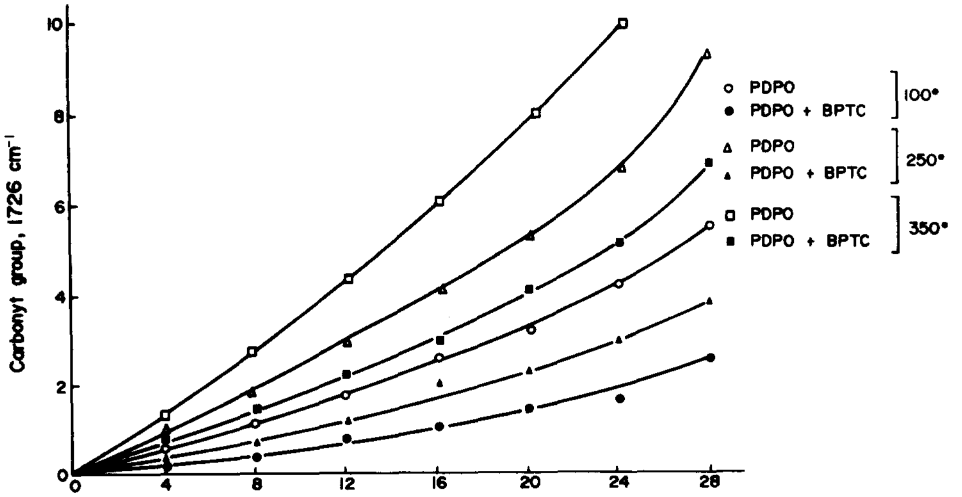


Fig. 4. Variations in carbonyl contents of thermally degraded PDPO films in the absence and presence of 0.1 wt% BPTC in air.

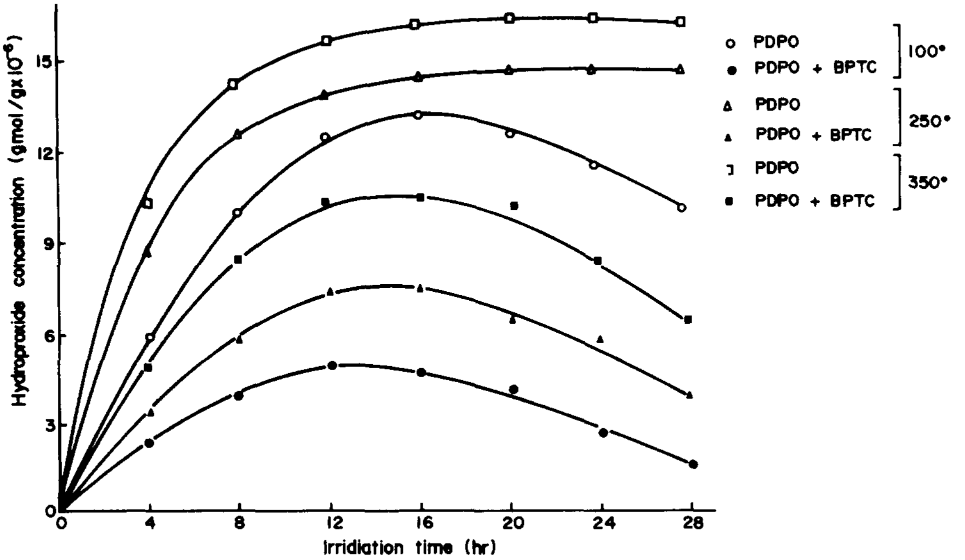


Fig. 5. Variations in hydroperoxide concentration of thermally degraded PDPO films in the absence and presence of 0.1 wt% BPTC in air.

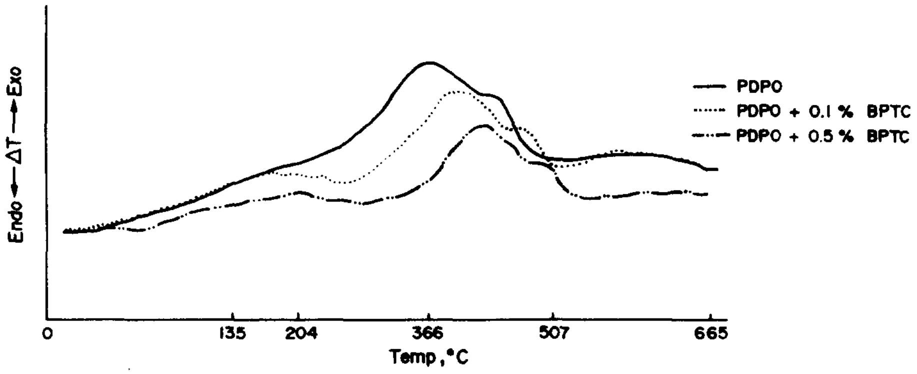


Fig. 6. Differential thermal analysis of PDPO films in the absence and presence of BPTC in air.

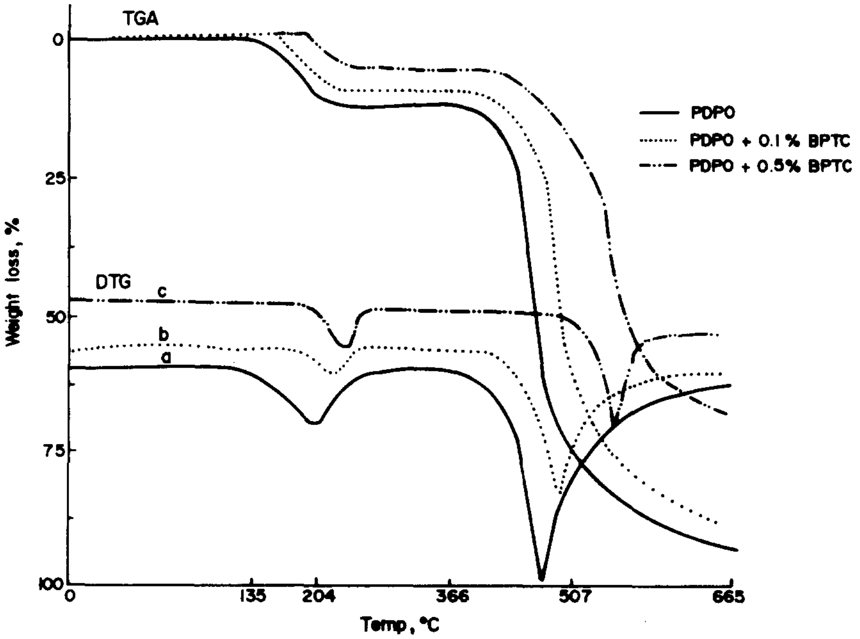
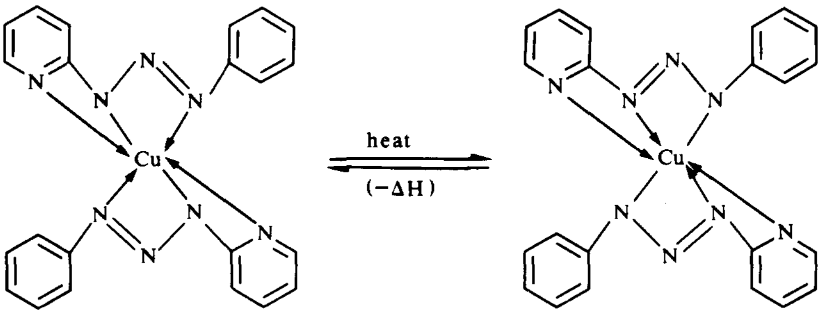


Fig. 7. Thermogravimetric analysis of PDPO films in the absence and presence of BPTC in air.

proved resolution of thermal events and precise comparison of thermal stability (Fig. 7a, b and c).

Mechanism of thermal degradation and stabilization of PDPO

The thermal oxidative degradation of PDPO is a random chain scission process consisting of initiation, propagation, termination and disproportionation reactions [20]. Since the polymer is prepared by oxidative coupling, it seems reasonable that the original PDPO might initially contain finite concentrations of hydroperoxides. Both the newly formed and originally present hydroperoxides initiate the oxidative chain process. The subsequent free radical reactions lead to the formation of various functional groups which can continue the chain or terminate by cross-linking or by disproportionation to inert products. Phenoxy radicals [21] are also formed in the degraded PDPO films confirming that chain cleavage occurs. Thermal energy is quite sufficient to decompose the oxygen—oxygen bond in polymer—hydroperoxide and the point of initial attack is the methyl group. BPTC is represented by the following resonating structures:



The chelate operates by interfering with the initiation process by absorption of heat energy due to the energy difference of d-orbitals. By minimizing the amount of heat energy absorbed by the polymer, the initiation processes are prevented. The metal chelate (BPTC) involves quenching of an excited chromophore of a macromolecule which has absorbed thermal energy. The stabilizer dissipates most of the accepted energy harmlessly as i.r. radiation or heat through its resonating structures, without destroying polymer bonds or its own structure. Thus the chelate acts as a heat screen for the polymer. At the chain branching stage, the chelate decomposes the hydroperoxides into inert products. Carlsson *et al.* [22] have confirmed that the stabilizer slowly migrates through the solid polymer and destroys —OOH groups. BPTC may also introduce additional termination steps by acting as free radical scavenger. In addition BPTC inhibits the process by electron transfer and formation of inert complexes.

It can be concluded that BPTC is an effective thermal stabilizer due to its peculiar characteristics and produces a minimum number of hydroperoxide, carbonyl and hydroxyl groups.

Acknowledgements—The author thanks the C.S.I.R. New Delhi for financial support and the authorities of R. E. College Kurukshetra for laboratory facilities. The assistance of Dr N. D. Ghatge and N. C. L. Pune in providing facilities for recording DTA, TGA and NMR spectra is gratefully acknowledged.

REFERENCES

1. J. H. Golden, *Soc. Chem. Ind. Monograph* No. 13, p. 231. Society of Chemical Industry, London, (1961).
2. H. E. Hoyt, B. D. Halpern and K. C. Tsou, *J. appl. Polym. Sci.* **8**, 1633 (1964).
3. R. T. Conley and W. M. Alvino, *Preprints* **25**, 149 (1965).
4. R. Chandra and R. P. Singh, *Ind. J. Technol.* **18**, 250 (1980).
5. R. Chandra and R. P. Singh, *Makromolek. Chem.* **181**, 1637 (1980).
6. W. A. Miller, *J. chem. Soc.* **18**, 273 (1965).
7. Y. Kato, D. J. Carlsson and D. M. Wiles, *J. appl. Polym. Sci.* **13**, 1447 (1969).
8. R. P. Singh, *Ind. Chem. J.* In press.
9. A. E. Chichibabin and R. L. Persitz, *J. Russ. Phys. Chem. Soc.* **57**, 301 (1925).
10. R. P. Singh, *Eur. Polym. J.* In press.
11. J. P. Luongo, *J. Polym. Sci.* **42**, 139 (1960).
12. C. D. Wagner, R. H. Smith and E. D. Peters, *Analyt. Chem.* **19**, 976 (1947).
13. H. H. G. Jellinek, *J. Polym. Sci.* **3**, 850 (1948).
14. G. G. Cameron and N. Grassie, *Makromolek. Chem.* **53**, 72 (1962).
15. R. Simha and L. A. Wall, *J. phys. Chem.* **56**, 707 (1952).
16. R. Chandra dn H. L. Bhatnagar, *Ind. J. Chem.* **14A**, 469 (1976).
17. A. D. Cross, *Introduction to Practical Infrared Spectroscopy*. Buttersworths, London (1960).
18. R. A. Jerussi, *J. Polym. Sci., A*-1 **9**, 2009 (1971).
19. P. G. Kelleher, L. B. Jassie and B. D. Gesner, *J. appl. Polym. Sci.* **11**, 137 (1967).
20. J. Jachowicz, M. Kryszewski and P. Kowalski, *J. appl. Polym. Sci.* **22**, 2891 (1978).
21. B. Ranby and J. F. Rabek, *ESR Spectroscopy in Polymer Research*, p. 225. Springer Verlag, Berlin (1977).
22. D. J. Carlsson and D. M. Wiles, *J. Polym. Sci. Polym. Chem. Ed.* **12**, 2217 (1974).