

# Thermal Degradation of Polystyrene. I. Chain Scission at Low Temperature in Air

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## Synopsis

The thermal degradation of polystyrene was studied in air at temperature where volatile formation is negligible. Plots of degree of degradation  $\alpha$  vs.  $t$  are linear and confirm the random nature of chain scission, but the intercepts are temperature dependent and the rate constant decreases with temperature, showing that oxygen plays a role in the chain-end initiation and deactivation of the free-radical centers. IR spectra indicate the formation of an acetophenone-type structure during degradation. The kinetic analysis using various methods yield an activation energy value of 30–35 kcal/mole.

## INTRODUCTION

The thermal and oxidative degradation of polystyrene has been investigated by many workers.<sup>1–4</sup> Cameron and MacCallum<sup>2</sup> have emphasized in their review the points of agreement and disagreement by various workers. Further, the main problem seems to be the presence of weak links and their role in changing the molecular weight during the degradation process. Jellinek,<sup>3</sup> and Grassie and co-workers<sup>5,6</sup> have contended that the initial change in molecular weight is due to the scission of weak links. Wall and co-workers,<sup>7</sup> on the basis of the theoretical models, assert that the changes in molecular weight are due predominantly to intermolecular transfer followed by chain-end initiation. Cameron and Kerr<sup>8</sup> carried out experiments under vacuum and under conditions where no volatile is produced. They used the expression

$$\frac{1}{X_t} - \frac{1}{X_0} = kt \quad (1)$$

$X_0$  and  $X_t$  are the number-average degrees of polymerization at zero and time  $t$ , respectively; and  $k$  is the first-order rate constant for bond scission. The degree of degradation  $\alpha$  was defined as

$$\alpha = \frac{1}{X_t} - \frac{1}{X_0} \quad (2)$$

If the polymer molecule contains randomly distributed weak links which break rapidly on degradation, the degree of degradation is related to time as

$$\alpha = \beta + kt \quad (3)$$

where  $\beta$  is the fraction of the thermolabile weak links that are ruptured during degradation. During their studies they concluded<sup>8</sup> that  $\beta$  is independent of

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temperature, and for anionically polymerized polystyrene  $\beta$  is zero. The weak links were suggested to be randomly distributed within the polymer chains.

In the studies by these workers oxygen or air was eliminated. The purpose of this work is to investigate the role of oxygen present in air during the low-temperature degradation when no or very few volatiles are formed. On prolonged heating, degradation at low temperatures also leads to weight loss under isothermal conditions. Hence, kinetic parameters such as temperature coefficient or activation energy, frequency factor, and order of reaction are also reported here.

## EXPERIMENTAL

### Materials

Commercial molding-grade polystyrene [Poly Chem. (India) Ltd., Bombay] was purified by repeated solution in benzene and precipitation in methanol and dried and used for the study of molecular weight change. Unpurified sample of PS was used in the study of mass loss by TG.

### Isothermal Experiments

Isothermal experiments were recorded in terms of mass loss versus time. The commercial sample as received was powdered and heated in a platinum crucible. Polymer samples (50 mg) were degraded in air at constant temperature. The isothermal weight change and molecular weight determination were conducted at temperatures from 205 to 250°C in air.

### Molecular Weight

The limiting viscosities were measured in benzene at  $30 \pm 0.1^\circ\text{C}$  using a Tuan Fuoss viscometer. Molecular weight of the degraded polymer was measured by viscometry. The single-point viscosities were measured and were converted to limiting viscosity  $[\eta]$  through the modified Huggins equation<sup>9</sup>

$$[\eta] = \frac{2^{1/2} (\eta_{sp} - \ln \eta_{rel})^{1/2}}{C} \quad (4)$$

where  $C$  is the polymer concentration in benzene in g/dl. The values of the Mark-Houwink constants  $K$  and  $a$  were  $0.97 \times 10^{-4}$  and 0.74, respectively, to calculate the viscosity-average molecular weight.<sup>10</sup>

The viscosity-average molecular weight  $\bar{M}_v$  is usually different from the number-average molecular weight  $\bar{M}_n$  and is closer to the weight-average molecular weight  $\bar{M}_w$  than is  $\bar{M}_n$ . In the present system, however, where chain scission is a dominant process, though the initial molecular weight distribution may alter during the degradation process, the ratio  $\bar{M}_w/\bar{M}_n$  will remain the same.<sup>11,12</sup> Therefore, in this case the ratio  $(\bar{M}_n)_0/(\bar{M}_n)_t$  has been assumed to be equal to  $(\bar{M}_v)_0/(\bar{M}_v)_t$  where 0 and  $t$  refer to initial molecular weight and molecular weight at time  $t$ .<sup>13</sup>

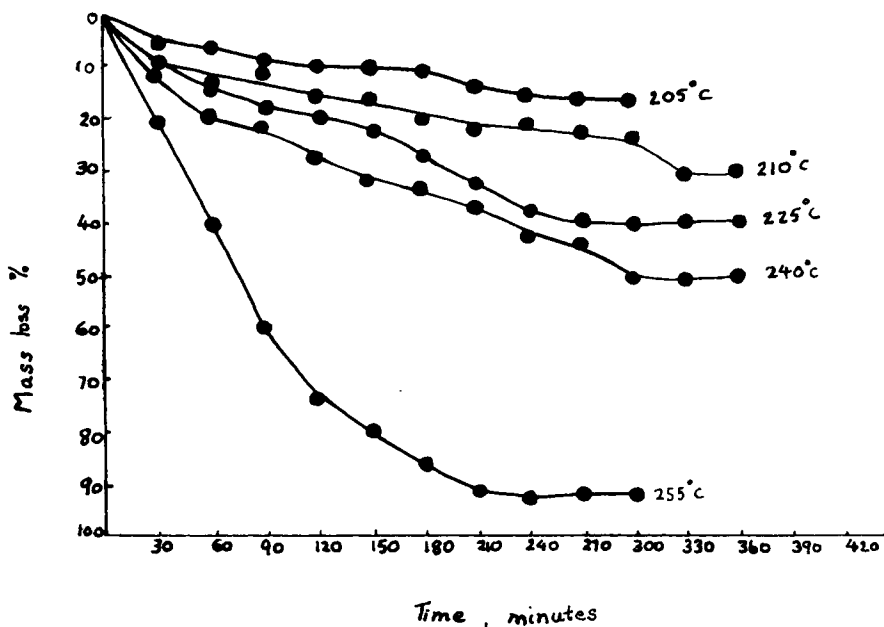


Fig. 1. Mass loss vs. time for thermal decomposition of polystyrene in air.

### IR Spectra

The infrared spectra were obtained by the KBr disc technique using a Perkin-Elmer IR spectrophotometer model 177.

## RESULTS AND DISCUSSION

### Isothermal Thermogravimetry

Plots of mass loss percent versus time are shown in Figure 1 for unpurified polystyrene sample. The rate of mass loss increases as the temperature is raised. Kinetic parameters for degradation were determined using the Madorsky method,<sup>14</sup> the difference equation method,<sup>15,16</sup> and the Avrami-Erofeev equation.<sup>17,18</sup> Avrami-Erofeev plots and Arrhenius plots are shown in Figures 2 and 3, respectively.

### Change in Molecular Weight

Figure 4 shows a plot of molecular weight as a function of time of degradation for polystyrene at various temperatures in air. The plots show a rapid decrease in molecular weight initially which then slows down, suggesting that the initial rapid drop in molecular weight 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 the number-average molecular weight should be proportional to the square of the number-average molecular weight at that time.<sup>4,19</sup> Therefore, in order to clarify the type of bond scission, the rate in the decrease of molecular weight with time,  $dM/dt$ , was calculated using the relation

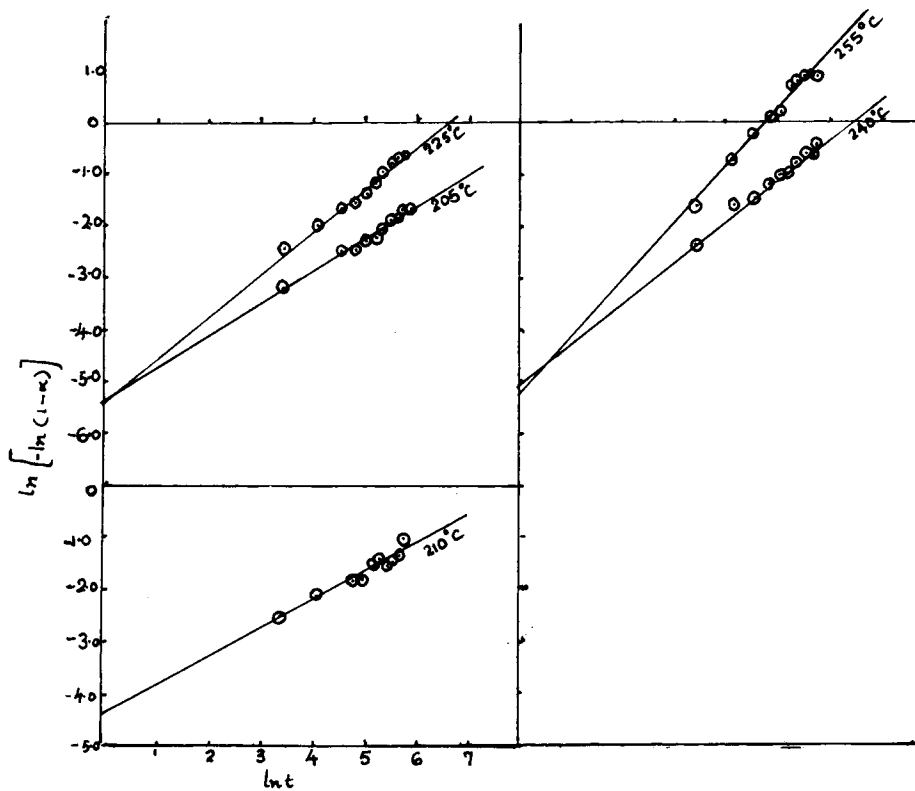


Fig. 2. Avrami-Erofeev plot.

$$\frac{dM}{dt} = \frac{\bar{M}_0 - \bar{M}_t}{t} \tag{5}$$

where  $\bar{M}_t$  and  $\bar{M}_0$  are the viscosity-average molecular weight at time  $t$  and zero, respectively. The plot of  $dM/dt$  vs.  $M_t^2$  is shown in Figure 5. The plots were found to be linear. The plots suggest that the chain scission is random and that

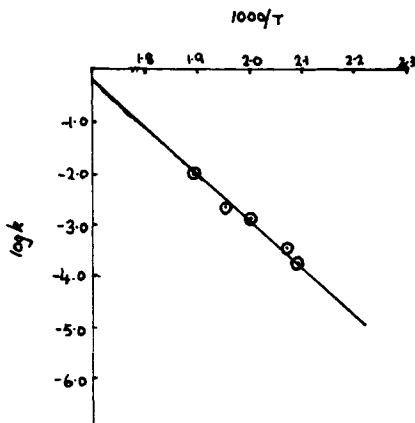


Fig. 3. Arrhenius plot for Avrami-Erofeev graphs ( $\log k$  vs.  $1000/T$ ).

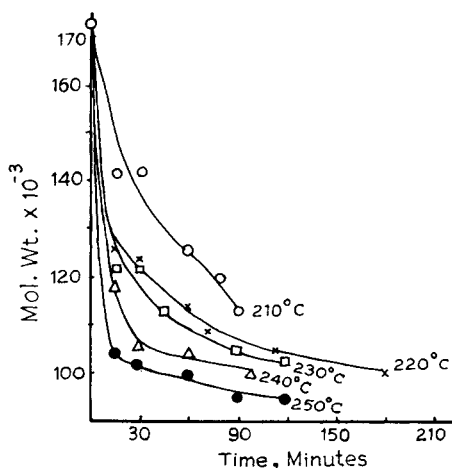


Fig. 4. Variation of average molecular weight of polystyrene as a function of time of heating.

two kinetically independent units are taking part in the scission of bonds in a polymer. The activation energy of slow chain scission in polystyrene was estimated from Arrhenius plots (Fig. 6) and yielded a value of  $30 \pm 5$  kcal/mole. The value is compared with the experimental values in Table I.

Cameron and Kerr<sup>8</sup> have also shown that chain scission occurs at low temperatures under vacuum, when no volatile is formed. In order to further strengthen the view, the degree of degradation  $\alpha$  defined as in eq. (2) is related to the first-order rate constant for bond scission. For randomly distributed weak links which break rapidly in the initial stages, the degree of degradation is given as

$$\alpha = \beta + kt \quad (3)$$

where  $\beta$  is the fraction of weak bonds present in a polymer chain and  $k$  is the first-order rate constant for bond scission. A plot of  $\alpha$  as a function of time of

TABLE I  
Values of Activation Energy of Degradation of PS

Technique	Method used	Temperature range, °C	Activation energy, <sup>a</sup> kcal/mole
TG	Madorsky method <sup>b</sup>	205–255	34
TG	difference equation method <sup>b</sup>	205–255	30
TG	Avrami-Erofeev <sup>c</sup>	205–255	35
Viscosity measurements	molecular weight change <sup>c</sup>	210–250	30
Literature value	TG in air <sup>d</sup>	320–390	$29 \pm 2$
	TG (vacuum) <sup>d</sup>	318–348	58
	melt viscosity measurements <sup>d</sup>	248–340	24.5
	low temperature (vacuum) <sup>e</sup>	280–300	49

<sup>a</sup> Most probably error is  $\sim 5$  kcal.

<sup>b</sup> M. C. Gupta and J. Dwarakanath, *J. Thermal. Anal.*, **17**, 109 (1980).

<sup>c</sup> This work.

<sup>d</sup> K. Kishore, V. R. Pai Verneker, and M. N. R. Nair, *J. Appl. Polym. Sci.*, **20**, 2355 (1976).

<sup>e</sup> G. G. Cameron and G. P. Kerr, *Eur. Polym. J.*, **4**, 709 (1968); **6**, 423 (1970).

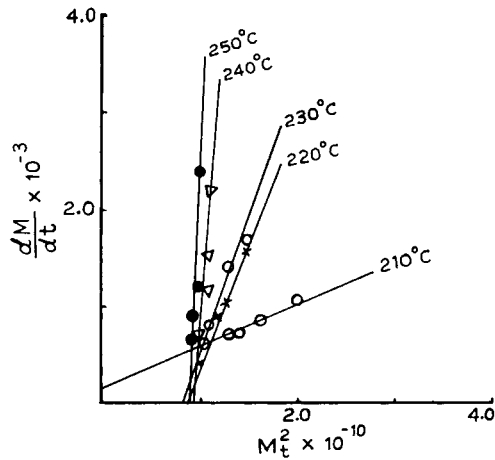


Fig. 5. Rate of change of molecular weight as function of  $M_t^2$  ( $dM/dt$  vs.  $M_t^2$ ).

sample heating at various temperatures is shown in Figure 7. The set of curves are linear and have an ordinate intercept which depends on the temperature of the heating. The presence and the magnitude of the ordinate intercept in the graph indicate the existence and the fraction of weak links ( $\beta$ ) in a chain. The values of  $k$  and  $\beta$  are given in Table II. It is clear from the table that (1)  $\beta$  depends on temperature and (2)  $k$  decreases with temperature in the presence of air.

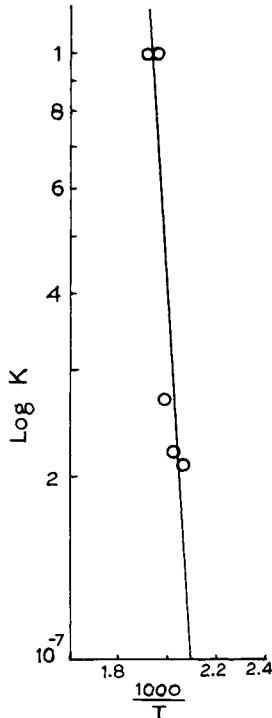


Fig. 6. Arrhenius plot. (Values of  $k$  from Fig. 5.)

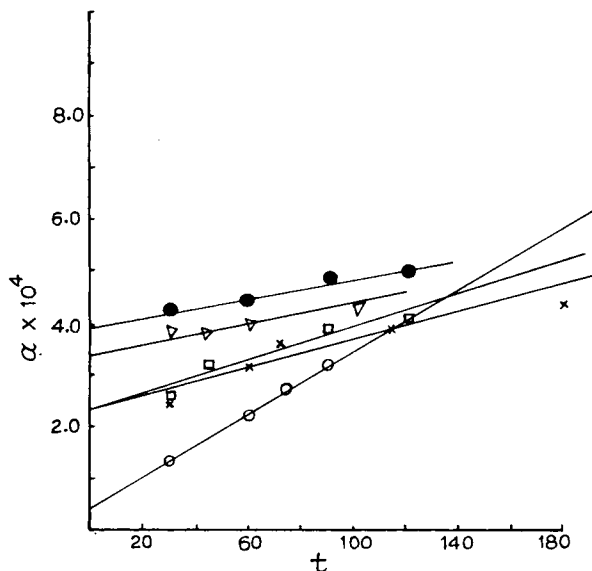


Fig. 7. Degree of degradation  $\alpha$ ,  $1/X_t - 1/X_0$ , as function of time. Temperature, °C:  $\circ$  210,  $\times$  220,  $\square$  230,  $\Delta$  240,  $\bullet$  250.

It has been suggested by Cameron and Kerr<sup>8</sup> that the preferential rupture of weak links might be at chain ends and might have formed by the oxygen from air or elsewhere. These groups break down rapidly initially and give free radicals which abstract a hydrogen atom at random from within the same or another polymer chain. This clearly is indicated by the temperature dependence of  $\beta$  and  $dM/dt$  vs.  $M_t^2$  plots. When  $\beta$  is plotted as a function of temperature of degradation (Fig. 8), 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.

However, the rate constant is found to decrease with temperature. The studies of Cameron and Kerr<sup>8</sup> on the effect of radical catchers on the thermal degradation of polystyrene under vacuum suggests that oxygen of the air is a radical catcher and initially formed radicals are deactivated by oxygen, thereby reducing the overall rate of degradation at higher temperatures. Thus, oxygen reduces the frequency of transfer of thermolabile chain ends and scission decreases.

Thus, oxygen from air plays a dual role of initiating the rupture of chain ends by combining and as a free-radical catcher, thus decreasing the frequency of the transfer reaction. Under these conditions the degradation comprises the two

TABLE II  
 $\beta$  and the Chain Scission Rate Constant at Various Temperatures

Rate constant, $10^6 \times \text{min}^{-1}$	Temperature, °C	$\beta \times 10^4$
3.13	210	0.40
1.4	220	2.34
1.6	230	2.30
0.1	240	3.5
0.1	250	3.9

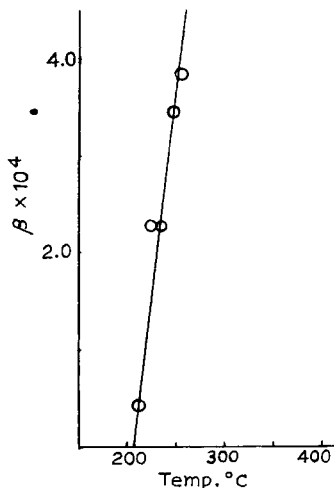


Fig. 8. Plot of  $\beta$  vs.  $T$ .

following stages: (1) Chain-end initiation and rapid scission of weak links present randomly which give rise to intercept  $\beta$ , and (2) the deactivation of radicals to give a permanent chain break, which is indicated by the decrease of  $k$ .

Grassie<sup>4</sup> has suggested that the decrease in  $k$  could also be due to the effect of platinum. The platinum surface in the presence of oxygen catalyzes the nonchain scission of weak links. Hence,  $k$  would decrease with temperature.

It was suggested by previous workers<sup>8</sup> that the chain-end initiation could also be due to the presence of traces of oxygen during polymerization which may give rise to styrene polyperoxide. The IR spectra (Fig. 9) of the undegraded polystyrene do not show the presence of such a polyperoxide in the sample used. However, the IR spectra of the degraded polystyrene recorded at various temperatures (as shown in Fig. 10) showed changes in the carbonyl region of the spectrum. An intense sharp band developed at  $1685\text{ cm}^{-1}$  and continued to grow with the duration of degradation.

It has been suggested by the study of NMR, IR, and UV<sup>1</sup> that a structure similar to an aromatic carbonyl structure like acetophenone might be a primary degradation product. The carbonyl frequency of acetophenone has been reported to be  $1689\text{ cm}^{-1}$ . The carbonyl frequency of degraded polystyrene is found to be  $1685\text{ cm}^{-1}$ , thus indicating that an aromatic carbonyl structure is present when polystyrene is heated in presence of air.

On the basis of our observation and the study of previous workers on the oxidative degradation<sup>1,17</sup> of polystyrene, the thermal degradation of polystyrene might be explained on the basis of the oxygen preferentially attacking hydrogens found on the backbone of the polystyrene chain, and the initial product may be hydroperoxide. The carbonyl structure of the final product results from the decomposition of this hydroperoxide via free-radical center formation.

## SUMMARY AND CONCLUSIONS

The results reported in this present communication can be summarized as follows:

- (1) Polystyrene decomposes by chain-end initiation and random chain scission



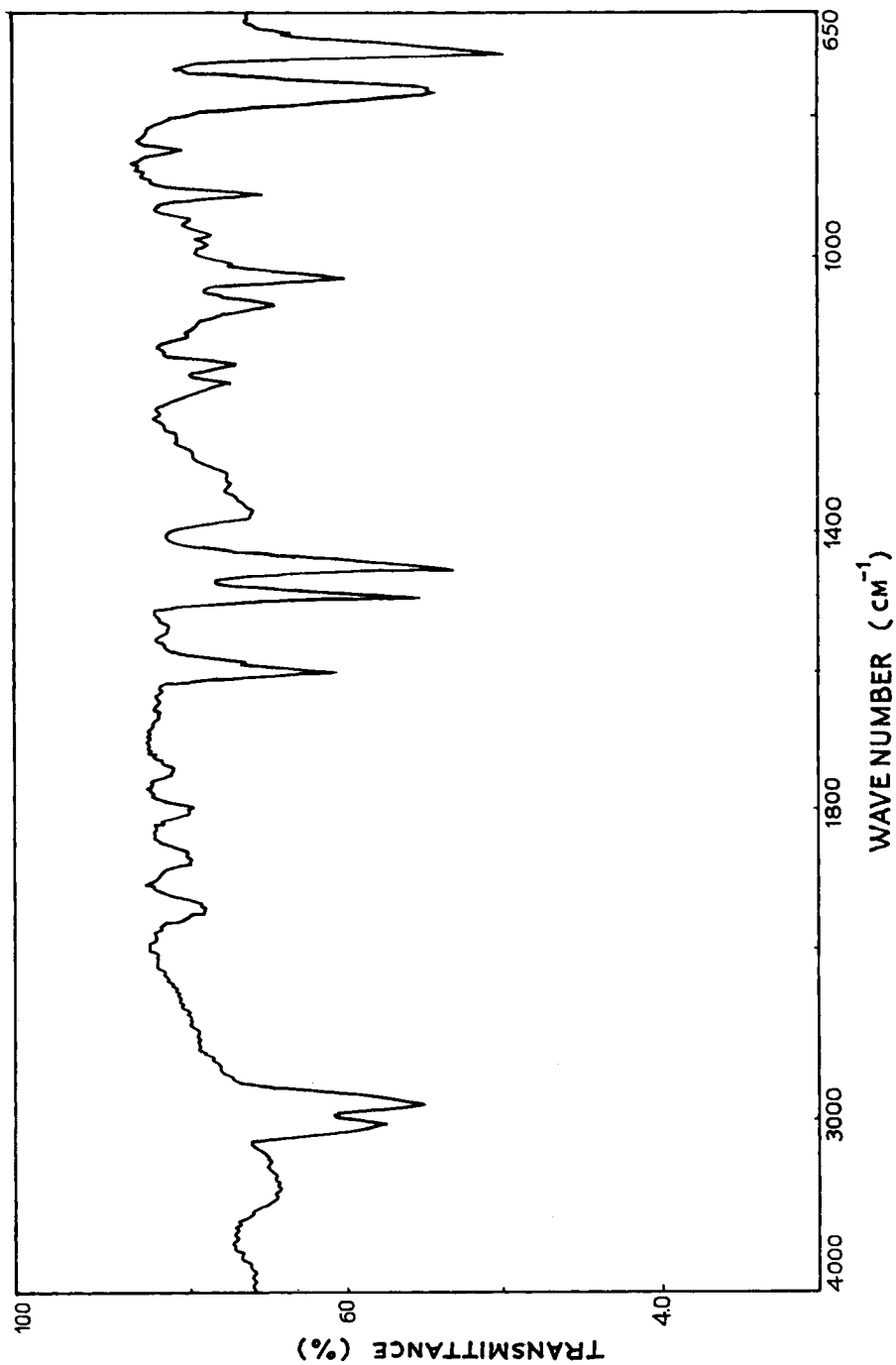


Fig. 9. IR of polystyrene.

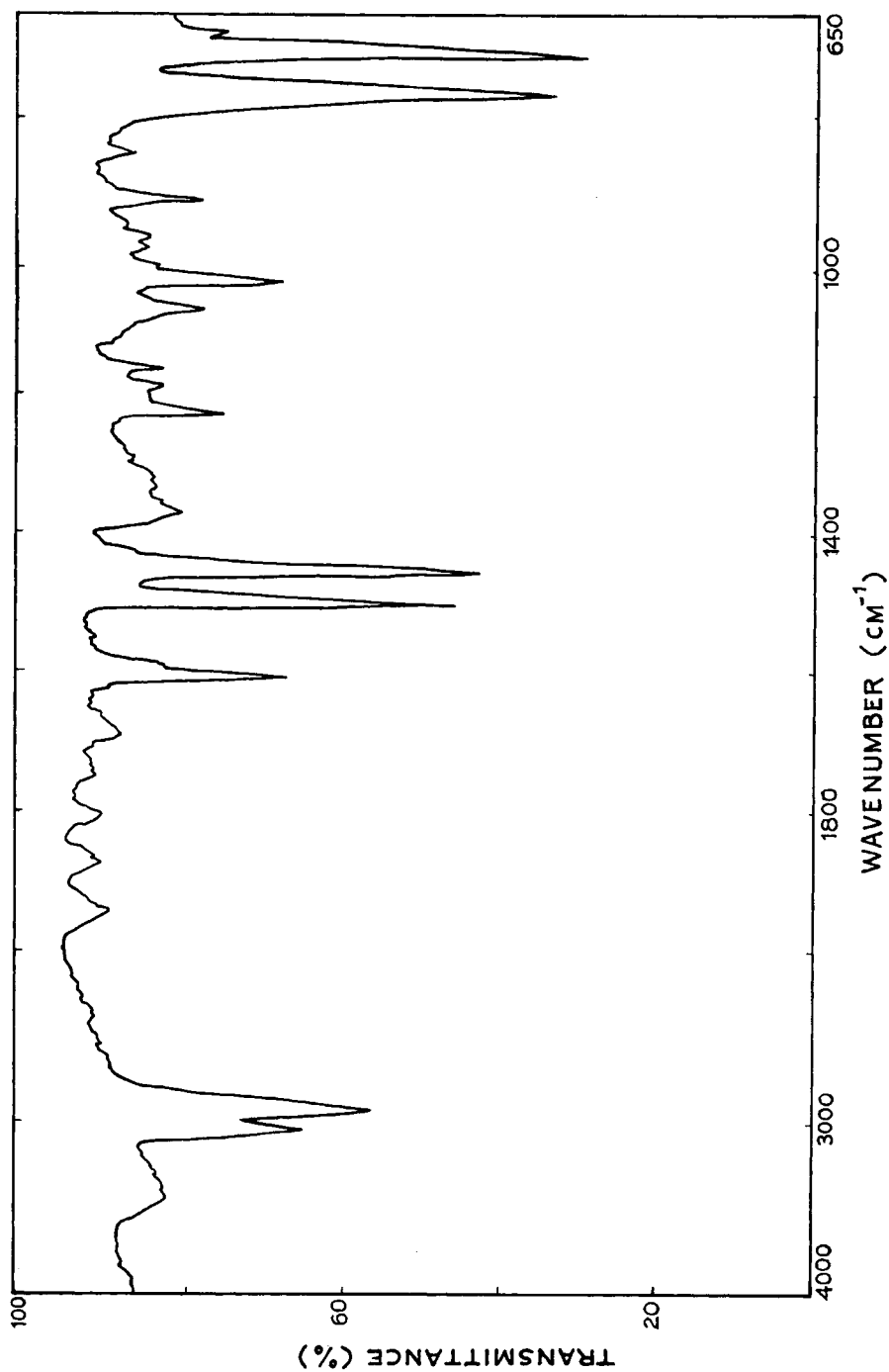


Fig. 10. IR of polystyrene heated at 250°C for 65 min.

in the presence of oxygen in air. This is indicated by a positive intercept  $\beta$ , which is an indicating function of temperature from the plot of  $\alpha$  vs.  $t$ .

(2) There is an initial time of initiation of degradation and then a rapid decrease, which suggests that there are weak links present randomly in the chain and after some time the chain-end initiation starts.

(3) The chain-end initiation may be peroxidic in nature as evidenced by the presence of a carbonyl frequency in IR spectra of the degraded polystyrene.

(4) The rate of chain scission decreased with time (from  $\alpha$ -vs.  $t$ -plot) which may be because of (1) the radical-catching ability of oxygen thus decreasing the frequency of the transfer of the thermolabile chain ends, or (2) the catalytic effect of the platinum surface in the presence of oxygen for the nonchain scission.

(5) The overall activation energy of the degradation is 30–35 kcal/mole as determined by various methods.

(6) The order of the reaction is 1.

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## References

1. H. C. Beachell and L. H. Smiley, *J. Polym. Sci. Part A-1*, **5**, 1635 (1967).
2. G. G. Cameron and J. R. MacCallum, *J. Macromol. Sci., C-A*, 327 (1967).
3. H. H. G. Jellinek, *J. Polym. Sci.*, **3**, 850 (1948).
4. N. Grassie, *Chemistry of High Polymer Degradation Processes*, Interscience, New York, 1956.
5. G. G. Cameron and N. Grassie, *Makromol. Chem.*, **53**, 72 (1962).
6. G. G. Cameron, *Makromol. Chem.*, **100**, 255 (1967).
7. L. A. Wall, S. Strauss, J. H. Flynn, D. McIntyre, and R. Simha, *J. Phys. Chem.*, **70**, 53 (1966).
8. G. G. Cameron and G. P. Kerr, *Eur. Polym. J.*, **4**, 709 (1968).
9. R. M. Shroff, *J. Appl. Polym. Sci.*, **9**, 1547 (1965).
10. J. Brandrup and E. H. Immergut, Eds., *Polymer Handbook*, Interscience, New York, 1967, p. VI-77.
11. C. David, D. Baeyens-Volant, G. Delounois, Q. LuVinh, W. Piret, and G. Geuskens, *Eur. Polym. J.*, **14**, 501 (1978).
12. C. David and D. Baeyens-Volant, *Eur. Polym. J.*, **14**, 29 (1978).
13. T. Ikeda, S. Okamura, and H. Yamaoka, *J. Appl. Polym. Sci.*, **15**, 2971 (1977).
14. S. L. Madorsky, *Thermal Degradation of Organic Polymers*, Interscience, New York, 1969.
15. R. P. Rastogi, M. C. Gupta, and I. A. Khan, *Ind. J. Chem. Educ.*, **5**(3), 15 (1978).
16. M. C. Gupta and J. Dwaraka Nath, *J. Thermal Anal.*, **17**, 109 (1980).
17. M. Avrami, *J. Chem. Phys.*, **9**, 177 (1941).
18. B. V. Erofeev, *C. R. Dokl. Acad. Sci.*, **11**(6) 511 (1946).
19. R. H. Boyd, in *Thermal Stability of Polymers*, Vol. I, R. T. Conley, Ed., Marcel Dekker, New York, 1970, p. 75.
20. A. Strepikheyev, Y. Derevitskaya, and G. Slonimsky, *A First Course in Polymer Chemistry*, Mir Publishers, Moscow, 1971.

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