Maximum Degradation Rates in Vinyl Polymers

K. KISHORE AND V. A. BHANU, *Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore 560 012, India*

The thermal and thermo-oxidative degradation of thermoplastic vinyl polymers has been studied extensively. However, there are several features which are either controversial or not understood clearly. From dynamic thermogravimetric (TG) studies in our laboratory we have observed that in thermo-oxidative degradation, although it starts at lower temperatures compared to thermal degradation, the rate of main degradation (between 20 and 80%) is always higher in the latter case. Such an observation borne out by a few literature TG curves, but no explanation whatsoever is available for this anomaly. In this letter we attempt to carry out a systematic TG study on few vinyl polymers in N_2 and O_2 to explain this behavior. It may be pointed out that here we deal with an empirical comparison of the overall average degradation data (based on dynamic TG), which do not represent a comparison of the actual degradation rates based on the main chain links of the polymers.

EXPERIMENTAL

The thermogravimetric analysis was carried out using Stanton Redcroft TG 750/770 instrument. The gases (O_2 or N_2) were flushed at a rate of 25 mL/min. A sample weight of 3–7 mg and a heating rate of 3°C/min were maintained in all runs. This low heating rate was used in the present work so that adequate thermal equilibrium would be maintained between the sample and the heating assembly. The polymers studied were polypropylene (PP), poly(1-butene) (PB), and polystyrene (PS).

RESULTS AND DISCUSSION

The overall polymer degradation reaction can be represented as follows:

$$A_{(solid)} \rightarrow B_{(solid)} + C_{(gas)}$$

for which the general rate equation is

$$\frac{dx}{dt} = k(1 - x)^n \tag{1}$$

where k is the rate constant, n is the order of the reaction, and the fraction x of the overall degradation occurring at any time t is expressed as

$$x = \frac{(W_0' - W')}{W_0'} \tag{2}$$

where $W_0' = W_0 - W_r$, W_0 being the initial weight of the sample, W_r the inactive weight of the residue, and $W' = W - W_r$, with W the weight of the sample at temperature $T(K)$ and time t.

Equation (3) is obtained by introducing the heating rate ($\phi = dx/dT$) and the Arrhenius equation ($k = Ae^{-E/RT}$) in eq.(1):

$$\frac{dx}{dT} = \frac{A}{\phi} (1 - x)^n e^{-E/RT} \tag{3}$$

Upon applying the conditions for the maximum rate ($d^2x/dT^2 = 0$), eq.(3) yields

$$\left(\frac{dx}{dT}\right)_m = \frac{E(1 - x_m)}{nRT_m^2} \tag{4}$$

where E is the activation energy of degradation, R is the gas constant, and x_m and T_m represent the fraction of overall average degradation that has occurred and the temperature (in K), respectively, corresponding to the maximum rate $(dx/dT)_m$, of degradation. For convenience, we call eq. (4) the maximum rate equation in the text. The maximum rate of overall degradation can be calculated from eq.(4), provided E and n are known, while x_m and T_m can be obtained from a dynamic TG run.

The literature E and n values for PP, PB, and PS are given in Table I except for thermal degradation of PB owing to the lack of any reported value. It may be pointed out that in the literature the kinetic studies on polymer degradation mostly center around evaluation of activation energy without paying much attention to the frequency factor or order of reaction. In the absence of authentic n values for the polymers used in the present study, the order of reaction was taken as unity. It has been reported that thermoplastic polymer degradation generally follows first-order kinetics.[2] From the literature, the average value of E was derived from the range of similar E values quoted by various authors (see Table I). The E values for PP, PS, and other similar polymers are in the range of 50–70 kcal/mol for thermal degradation. An approximate value of 60 kcal/mol was therefore taken for the thermal degradation of PB.

TABLE I
Activation Energies for Polymer Degradation from Literature[a]

Polymer	Atmosphere	Activation energy[b,c] (kcal/mol)
PP	O_2	15.7(3), 9.6, 34.4, 32.4(4), 22.6, 24.9(5), 25(6)
	N_2	50.1(7), $\overline{63.8, 54.4}$(5), 68(8), $\overline{58, 55, 62.5}$(9), $\overline{58,54}$(10), 56(11), 68.1(12), $\overline{52.8, 24.7}$(13)
PB	O_2	28(6)
PS	N_2	58(16), 44.7(17), 65(18), 42.5(19), 50(20), 60(21), 45(22), 30(15), 35(23), 78(10), 70(24), 74(11).
	O_2	29(14), 30(15)

[a] The values in parentheses indicate the reference.

[b] Activation energy values for experiments done in vacuum are cumulated with N_2 while those obtained for experiments done in air are cumulated with O_2.

[c] A solid line below the energy value indicates a common reference given next to the last value.

TG thermograms of polymers are shown in Figure 1 in N_2 and O_2. From numerous x and T values the average rates at various temperatures are calculated by using the equation

$$\frac{dx}{dT} = \frac{x_2 - x_1}{T_2 - T_1} \tag{5}$$

The successive values of x and $T(K)$ are chosen from experimental TG curve at the smallest possible intervals, so the above approximation is valid. The maximum rate $(dx/dT)_m$ and corresponding x_m and T_m (the average of the two x's and T's used to calculate $(dx/dT)_m$ by using eq.(5)) are obtained by using a simple FORTRAN program run on a DEC-1090 computer. The maximum rate so obtained is designated as the experimental $(dx/dT)_m$ and is listed in Table II. From these x_m and T_m values and the average E values (Table II), $(dx/dT)_m$ is calculated by using the maximum rate equation for n taken to be unity. These are presented as calculated $(dx/dT)_m$ values in Table II. In the case of oxidative degradation of PP and PS, although the reaction involves two steps, only the first step is considered for evaluating $(dx/dT)_m$ since the second step involves degradation of char.

Table II shows that the calculated $(dx/dT)_m$ is always higher in N_2 compared to O_2. The experimental $(dx/dT)_m$ shows similar behavior. Thus it can be said that for the polymers examined in the present investigation, maximum rate values in N_2
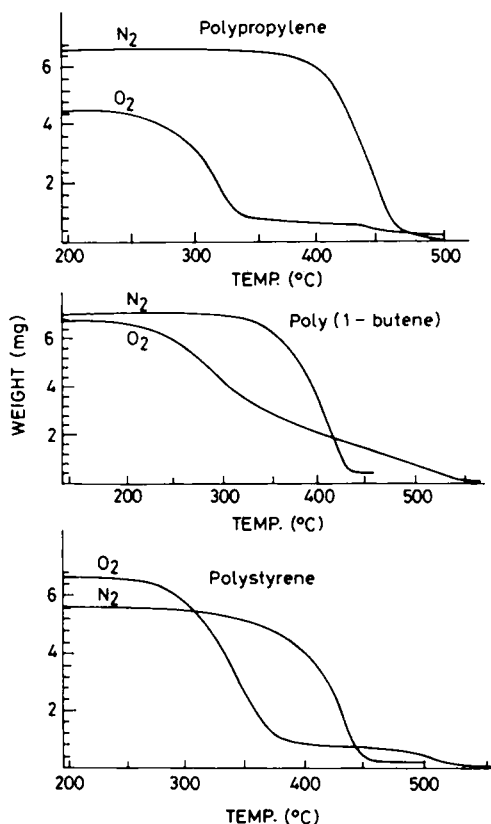

Fig. 1. TG traces of polymers in O_2 and N_2.

TABLE II
Comparative Values of Maximum Degradation Rate of Different Polymers

Polymer	Average value of activation energy (kcal/mol, from Table I)		$(dx/dT)_m \times 10^{-2}$ in O_2 atmosphere		$(dx/dT)_m \times 10^{-2}$ in N_2 atmosphere	
	O_2 atmosphere	N_2 atmosphere	Calculated	Experimental	Calculated	Experimental
PP	23.50	55.57	0.65	2.37	3.35	2.93
PB	28.00	60.00	2.82	0.70	3.38	1.85
PS	29.50	54.35	1.94	1.86	2.05	2.24

are always higher than in O_2. Thermograms reported by Brauman[1] show a similar trend. A close look at the calculated and experimental values of $(dx/dT)_m$ (Table II) shows that they are comparable in a few cases, but deviations occur in others. The exact reasons for this mismatch are difficult to pinpoint at this stage. However, it is likely that it might be due to the assumption that n is unity in all cases. Accurate calculation of n is therefore needed to throw light on this aspect.

The present results have obvious implications for the study of thermal and thermo-oxidative degradation of vinyl polymers. That the initiation in oxidative degradation is much easier compared to thermal degradation is obvious. This leads to the conclusion that faster $(dx/dT)_m$ in N_2 is related to the propagation step. Investigations of the propagation step of thermal and thermo-oxidative degradation may perhaps yield fruitful information and increase our understanding of the degradation mechanism of vinyl polymers.

References

1. S. K. Brauman, *J. Fire Retard. Chem.*, **3**, 138 (1976).

2. B. Rabinovitch, in *Tenth Symposium (International) on Combustion*, The Combustion Institute, Pittsburgh, 1965, pp. 1395–1404.

3. A. A. Ivanov, A. P. Firsov, V. D. Grigoryan, and A. A. Berlin, *Chem. Abstr.*, **71**:61836q (1969).

4. K. Y. Gel and C. C. Rim, *Chem. Abstr.*, **88**:121872m (1978).

5. Z. Osawa, *Chem. Abstr.*,**68**:30350K (1968).

6. L. Reich and S. Stivala, *Autooxidation of Hydrocarbons and Polyolefins*, Dekker, New York, 1969, Chap. 8.

7. N. Grassie and W. B. H. Leeming, *Eur. Polym. J.*, **11**, 809 (1975).

8. T. E. Davies, R. L. Tobias, and E. B. Peterli, *J. Polym. Sci.*, **56**, 485 (1962).

9. L. Reich, *J. Appl. Polym. Sci.*, **10**, 465 (1966).

10. L. Reich, *J. Appl. Polym. Sci.*, **10**, 813 (1966).

11. L. Reich, *J. Appl. Polym. Sci.*, **11**, 161 (1967).

12. S. Kiyoshi and H. Nishizaki, *Chem. Abstr.*, **89**:164248a (1978).

13. O. Yoshiro and M. Kazuo, *Chem. Abstr.*, **69**:97330t (1968).

14. V. N. Esenin, I. A. Krasotkina, and V. M. Gol'dberg, *Chem. Abstr.*, **93**:72440m (1980).

15. K. Kishore and V. R. Pai Verneker, *J. Polym. Sci. Polym. Chem. Ed.*, **14**, 761 (1976).

16. S. L. Madorsky, *J. Polym. Sci.*, **11**, 491 (1953).

17. H. H. G. Jellinek, *J. Polym. Sci.*, **10**, 506 (1953).

18. P. D. Zemany, *Nature*, **171**, 391 (1953).

19. D. R. Bain, *Chem. Abstr.*, **77**:35179g (1972).

20. E. Atherton, *J. Polym. Sci.*, **5**, 378 (1950).

21. D. A. Anderson and E. S. Freeman, *J. Polym. Sci.*, **54**, 253 (1961).
22. H. H. G. Jellinek, *J. Polym. Sci.*, **4**, 13 (1949).
23. A. W. Coats and J. P. Redfern, *J. Polym. Sci. B*, **3**, 917 (1965).
24. L. Reich, *J. Appl. Polym. Sci.*, **10**, 1033 (1966).