

Thermal Degradation of Polystyrene

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Synopsis

The importance of the study of thermal degradation of polymeric fuels arises from their role in the combustion of solid propellants. Estimation of the condensed-phase heat release during combustion can be facilitated by the knowledge of the enthalpy change associated with the polymer degradation process. Differential scanning calorimetry has been used to obtain enthalpy data. Kinetic studies on the polymeric degradation process have been carried out with the following objectives. The literature values of activation energies are quite diverse and differ from author to author. The present study has tried to locate possible reasons for the divergence in the reported activation energy values. A value of 30 kcal has been obtained and found to be independent of the technique employed. The present data on the kinetics support to chain-end initiation and unzipping process. The activation energies are further found to be independent of the atmosphere in which the degradation of polymer fuel is carried out. The degradation in air, N₂, and O₂ all yield a value of 30 kcal/mole for the activation energies.

INTRODUCTION

Thermal degradation of polymeric fuels plays an important role during the combustion of solid propellants. The study of the kinetics of the degradation process is useful for a deeper insight into the combustion process. On the other hand, the knowledge about the enthalpy change associated with the degradation process can be used for the estimation of condensed-phase heat release¹ during combustion. Although a lot of work on polymer degradation has been done, data on enthalpy changes are scarce. Thus, the first objective of the present investigation is to estimate the enthalpy change during polystyrene degradation. The same was obtained from differential scanning calorimetric (DSC) thermograms.

Many papers related to the kinetic study of the polystyrene degradation process are available, but the important point in them to note is the fact that activation energy E values differ quite significantly from author to author. This may be due to the difference in (a) experimental technique used in the study, (b) kinetic equations employed, and (c) method of preparation of polymer. The second objective in the present investigation was, therefore, to check the constancy of E by employing different techniques such as DSC, thermogravimetric analysis (TGA), and mass spectrometry. Additional information regarding the role of different atmospheres (in which polystyrene decomposes) on E values has also been accomplished.

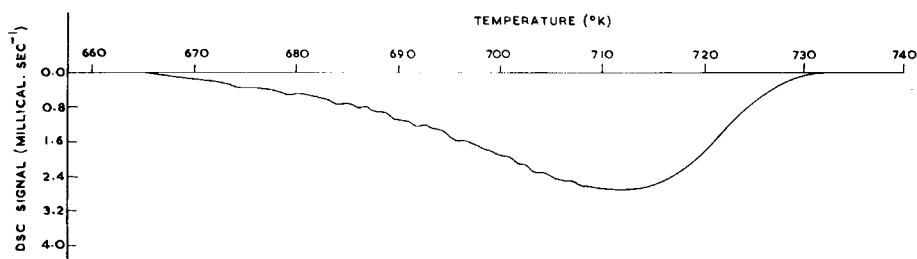


Fig. 1. Scanning DSC thermogram of PS at scan speed of 32°C/min (wt of PS = 2.89 mg).

EXPERIMENTAL

Procedure and Presentation of Experimental Results

Polystyrene (PS) was prepared by polymerizing inhibitor-free and fractionally distilled styrene monomer using 1% benzoyl peroxide. The viscous prepolymer was cured at about 40°C for about 15 days to get a hard, tough mass. PS in the form of chips, obtained by careful machining, was used in the thermal degradation studies. The molecular weight, as determined from viscosity measurements in benzene, was found to be 1.02×10^5 .

DSC thermograms at atmospheric pressure and in N₂ atmosphere were obtained (at a speed of 16°C, 32°C, and 64°C/min) as described in detail in a recent publication.² The experiments were done on a Perkin-Elmer DSC-1B instrument during one of the authors' (K.K.) stay at the University of Leeds, U.K. The amount of PS in each run was taken between 2.5 to 3.0 mg. A typical DSC thermogram of PS is displayed in Figure 1. The E calculations were done by the procedure described earlier.² The results are presented in Table I.

The mass-spectrometric experiments were done on a Dempster-type MS-10 mass spectrometer supplied by A.E.I. (U.K.). The sample was decomposed in a Corning glass tube having a spoon arrangement for dropping the sample at the base of the tube. The tube was heated in a cylindrical furnace. The temperature control of the furnace was about $\pm 1^\circ\text{C}$ of the required temperature. The amount of sample in each run was around 10 mg.

TABLE I
Activation Energy Values for Thermal Degradation of Polystyrene

Technique	Temperature range, °C	E , kcal/mole
DSC	370–380	32 ± 3
TGA		
(i) in air	320–390	29 ± 2
(ii) in N ₂	290–390	32 ± 2
(iii) in O ₂	340–375	28 ± 2
Mass spectrometry		
(i) formation of styrene	360–430	31 ± 4
(ii) formation of ethylene	360–430	30 ± 2
(iii) formation of benzene	360–430	44 ± 2

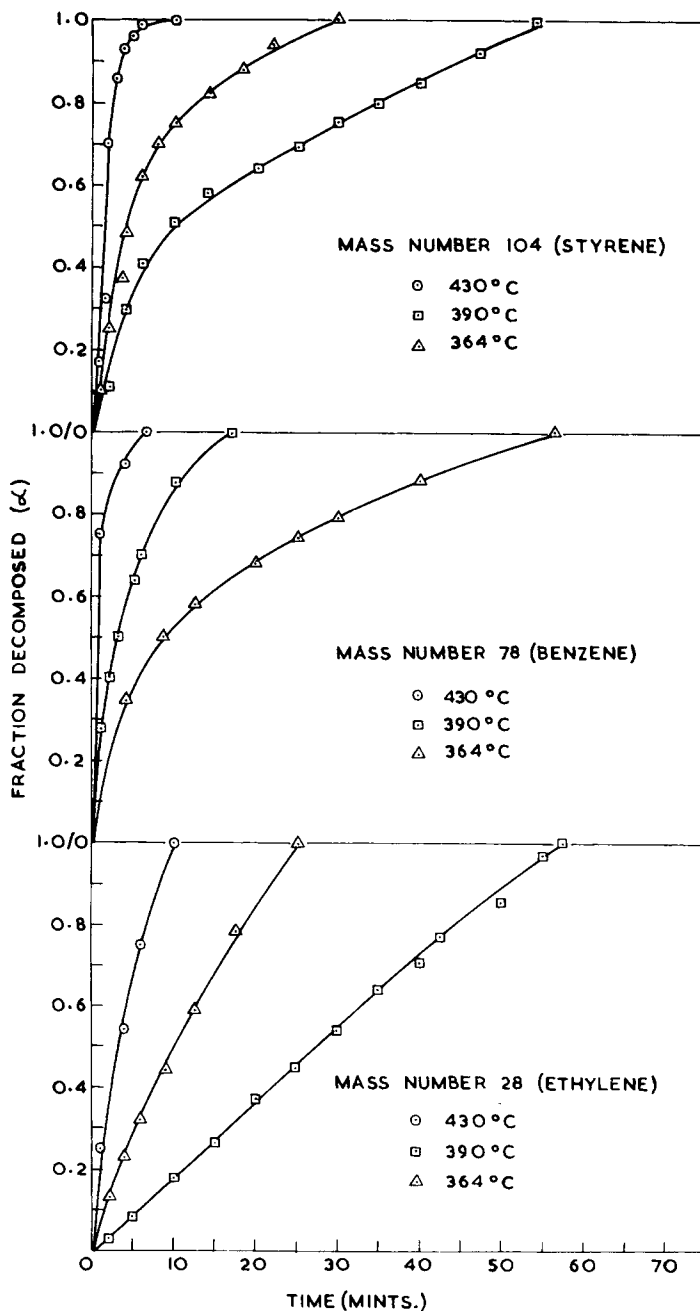


Fig. 2. Plot of fraction α vs. time for the evolution of ethylene, benzene, and styrene at different temperatures, in mass-spectrometric analysis.

The pressure inside the sample tube during the experiment was of the order of 10^{-1} to 10^{-3} mm, whereas inside the mass spectrometer it was around 10^{-7} to 10^{-8} mm.

The evolution of various species, having mass numbers 28 (ethylene), 78

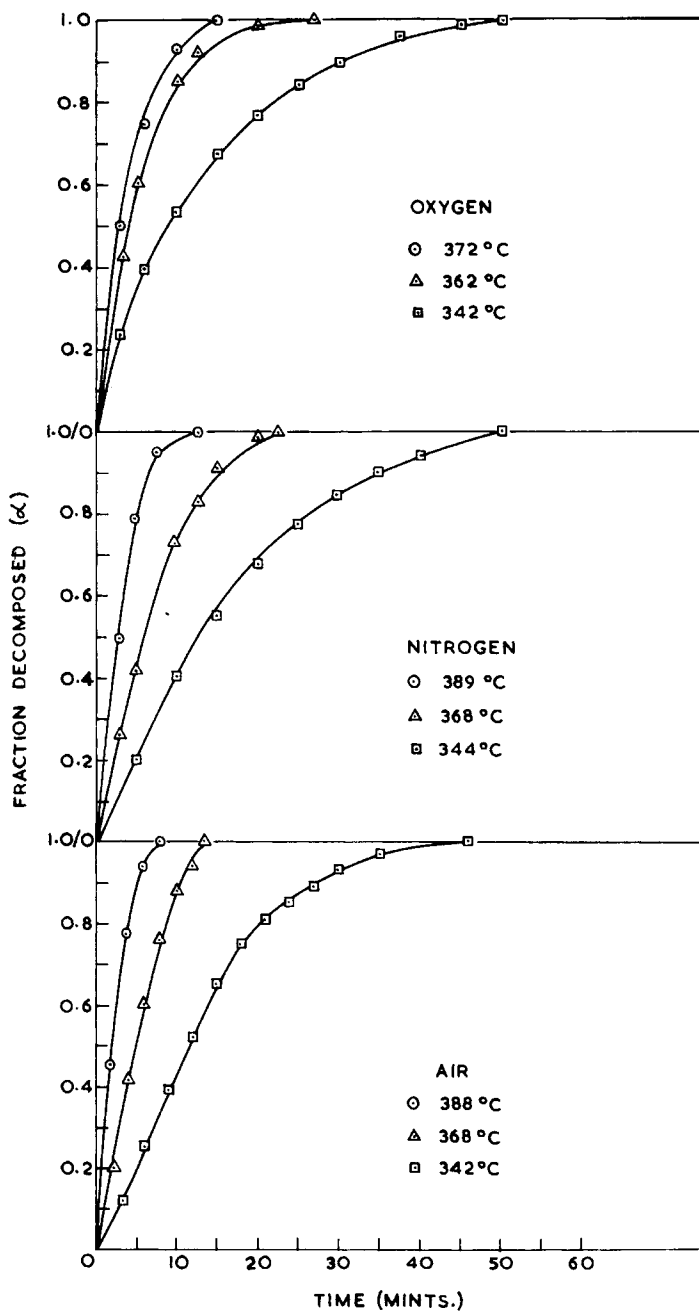


Fig. 3. Plot of fraction α vs. time in TGA runs in atmosphere of air, nitrogen, and oxygen.

(benzene), and 104 (styrene), in terms of ion current (μa) was isothermally followed with time. The experiments were carried out at temperatures of 364°C, 390°C, and 430°C. Fraction decomposed (α)-versus-time curves were deduced from the above experiments to calculate E from the Jacobs and Kureishy⁴ method. The results are presented in Table I and Figure 2.

TGA experiments were carried out on a conventional McBain-Baer-type³

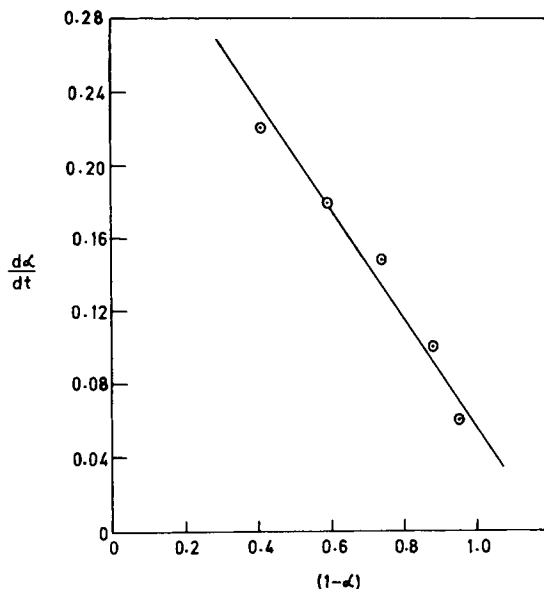


Fig. 4. Plot of $d\alpha/dt$ vs. $(1 - \alpha)$ (TGA studies) in a typical run in N_2 .

quartz spring balance. The temperature of the furnace was $\pm 1^\circ C$ of the required temperature. The weight of the sample taken in each run was about 30 mg. The α -versus-time plots were obtained at various temperatures ($290^\circ C$ – $390^\circ C$). The experiments were done at atmospheric pressure and in the presence of O_2 , N_2 , and air separately. The E calculations were done by the Jacobs and Kureishy⁴ method. The results are presented in Table I and Figures 3 and 5.

DISCUSSION

Enthalpy Data

The enthalpy change during the degradation of polystyrene was calculated from the DSC thermograms obtained at various heating rates. The total area under the peak was calculated and compared with that of a standard indium peak of known weight to yield the enthalpy of polystyrene degradation.⁵ This was found to be 65.5 ± 3.3 cal/g, or 6.82 ± 0.34 kcal/mole.

Activation Energies

Calculations of E from DSC thermograms were done by the method outlined earlier.² It may be noted that while determining the E values, (a) the fraction decomposed (α)-versus-reduced time plots showed that the kinetic behavior was the same at different heating rates, and (b) no assumption regarding reaction order was made. The E calculation was done by using the following equation:

$$\frac{S}{\Delta H} = A(1 - \alpha)^n e^{-E/RT}$$

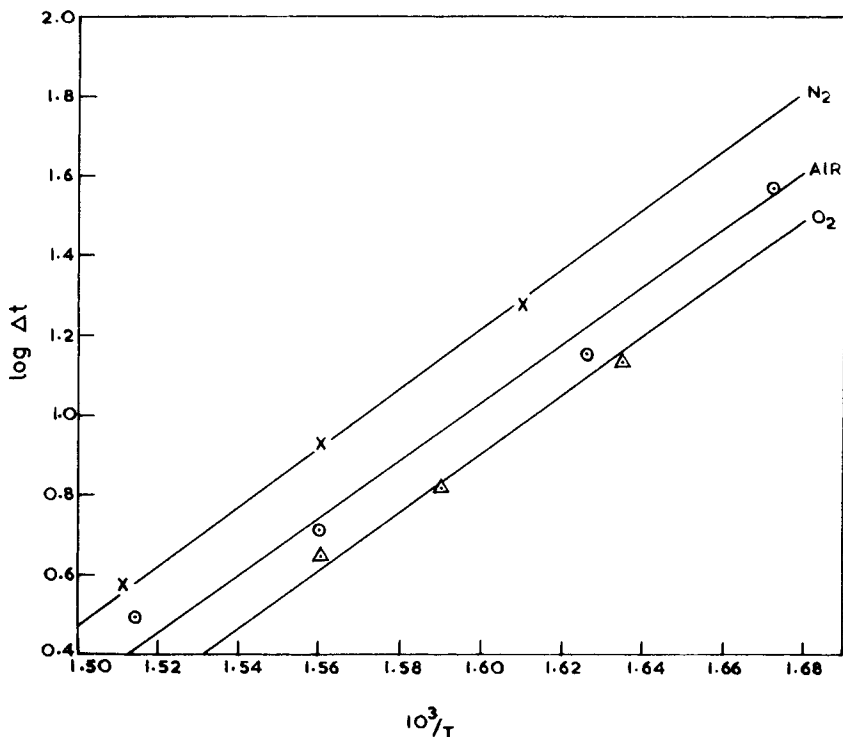


Fig. 5. Plot of $\log \Delta t$ vs. $1/T$ for TGA results in N_2 , air, and O_2 , where Δt represents the time taken by polystyrene to decompose from fraction $\alpha = 0.1$ to fraction $\alpha = 0.8$, and T is absolute temperature.

where S is the DSC signal in cal/sec at a particular fraction α degraded; ΔH is the total heat in cal/g under the endotherm. n is the order of reaction; R is the gas constant; A is the frequency factor; T is the absolute temperature at fraction α degraded in a scanning run; and E is the activation energy. E is calculated from the slope of the plot of $\log S/\Delta H$ versus $1/T$; $(1 - \alpha)^n$ is maintained constant at various scanning operations. The E values are reported in Table I.

The E calculation for TGA and mass spectral results (in N_2 , O_2 , and air) were obtained by using the Jacobs-Kuraieshy⁴ method. The advantage of this method is that it is independent of the assumption made according to the topochemical model. In essence, this method deals with the time taken (Δt) for the thermal decomposition to proceed from one α value to another α value, where α represents the fraction of material decomposed; Δt , therefore, is equal to the inverse of the rate of reaction. Mathematically, it can be represented by following equation:

$$k = \frac{F_{(\alpha_{n+1}-\alpha_n)} - F_{\alpha_n}}{t'_{n+1} - t'_n}$$

where F is a function of α ; α_n and α_{n+1} are the values of the fractional decomposition α at times t_n and t_{n+1} , respectively.

If the experiment is carried out at different temperatures, then, for the same value of α , the above equation at a particular temperature is given by

$$k = \frac{\text{const}}{t'_{n+1} - t'_n} = \frac{\text{const}}{\Delta t_{(\alpha_{n+1} \text{ to } \alpha_n)}}$$

The plot of $\log \Delta t$ or $\log (1/\Delta t)$ versus T^{-1} is linear with a slope of $E/2.303R$.

Whereas the E calculations of all TGA in an atmosphere of O_2 , N_2 , and air and mass-spectrometric data were done by the Jacobs-Kurieshy method, the TGA data in air were also found to fit the Avarami-Erofeev equation

$$[-\ln(1-\alpha)]^{1/2} = kt$$

where α is the fraction decomposed at time t and k is the rate constant; and the activation energy calculation was done by plotting the corresponding $\log k$ values versus $1/T$. This equation gives a better idea about the calculation which essentially deals with nucleation. It shows that nuclei are growing in two dimensions. This calculation also gives an idea about the topochemical model. It is interesting to point out that (i) the E value from this calculation is in agreement with the E value from the Jacobs and Karieshy method (Table I) (air), and that (ii) the E values in N_2 , O_2 , and air are the same (Fig. 5 and Table I). The implication of this will be discussed at some later stage.

Mass-spectrometric results showed that the E values for the formation of styrene and ethylene were the same (around 30 kcal/mole), while that for benzene was different (44 kcal/mole). This indicates that styrene and ethylene are primary products and benzene is a secondary product.

The reported E values in the literature (Table II) for polystyrene degradation differ significantly from author to author, while our values using three different techniques (Table I) are around 30 kcal/mole. Our values have been derived mostly without assuming any reaction order. Thus, 30 kcal/mole may be taken as an authentic value for the thermal degradation of PS. The divergence in the earlier values does not seem to arise from the technique, because we obtained a consistent value irrespective of various tech-

TABLE II
Reported Values of Activation Energy for Polystyrene Degradation

Technique	Temperature range, °C	Order of reaction	Equation used ^a	E , kcal/mole	Reference
Melt viscosity measurements	248–340	—	1	24.5	15
TGA using tungsten spring balance	348–398	0	2	44.7	16
Micro-TGA (dynamic)	—	—	—	76, 83	17
Gas chromatography	320–360	—	—	52	18
Melt viscosity measurements	265–320	0	—	20, 39	19
TGA (vacuum)	318–348	0 to 1	—	58	20
DTA (17°C/min) in N_2					21
3–22% decomposition	—	0	3	64	
22–90% decomposition	—	1.1	3	70	
Dynamic TGA (5°C/min) (vacuum)	246–430°C				22
up to 10% decomposition		0	4	46	
15–95% decomposition		1	4	60	
Dynamic TGA in N_2 (2°C/min)		0	5	35	23
TGA	—	—	6	65	7
Melt viscosity measurements	—	—	—	48	24

^a Details of eqs. (1) to (6) are given in Appendix.

niques used. Our E calculations do not assume any order of reaction, whereas other workers have assumed mostly zero or first order in their calculations. The reason for the divergence may, therefore, be the erroneous use of the equation or the method of the preparation of the polymer.

Mechanism of Degradation

Interpretation of E can help in understanding the mechanism of the degradation process. The exact mechanism of polymer degradation depends upon the nature of the polymer. However, general classifications of mechanism can be established; those according to Rabinovitch are given below⁶:

(a) Scission of bonds; (i) random scission; (ii) scission of weak links.

(b) Reverse polymerization: (i) end initiation and unzipping; (ii) random initiation unzipping.

Following various possible mechanisms⁷ have been put forth for the pyrolysis of polystyrene although controversy still exists concerning its proper mechanism.

I. Based on the belief that degradation products are mainly monomer, dimer, trimer, and tetramer (up to 500°C) and that the molecular weight of residue drops sharply at the initial stages followed by a slower process, Jellinek⁸ says that degradation occurs owing to the rapid breaking of a finite number of weak links distributed randomly over the polymer backbone. The weight loss rate of the polymer is given by following zero-order rate law:

$$\frac{dm}{dt} = - \left(\frac{P_k}{P_f} \right) k_i m_0$$

where (experimentally) $P_k k_i = 3.54 \times 10^{13} \exp(-44,700/R^\circ T) \text{ sec}^{-1}$, m_0 and m are the polymer masses taken initially and at time t , P_f is the effective degree of polymerization after the weak links are broken, P_k is the kinetic chain length, and k_i is the initiation step rate constant.

II. Based on the experimental fact that the rate of production of gaseous products is maximum at 30–40% volatilization, Simha and Wall⁹ argue against the idea of weak links and propose that degradation occurs by random initiation followed by unzipping to yield polymer of shorter kinetic chain length. The degradation rate is given by

$$\frac{dm}{dt} = - k_r m_0 (1 + P_c) P_c e^{P_c k_r t} (1 - e^{-k_r t})$$

where P_c is the size of the initial chain below which evaporation rather than further degradation in the condensed phase would be favored, and k_r is the rate constant for random splitting of any bond. If $P_c = 7$, then experimental value of k_r is given as follows:

$$k_r = 1.54 \times 10^{14} \exp(-55,000/R^\circ T) \text{ sec}^{-1}.$$

III. Grassie and co-workers^{10–12} present a sort of unified approach of the above two views and say that initial decrease in molecular weight is due to the breaking of weak links followed by the end-initiation and unzipping process to control the volatile production. The breaking of the weak links is given by the following first-order rate law:

$$\frac{dw}{dt} = k_w W$$

where W is the number of weak links per original chain, and k_w is the rate constant for breaking the links, where k_w (experimental) is given by

$$k_w = 1.8 \times 10^{19} \exp(-65,000/R \text{ } ^\circ T) \text{ sec}^{-1}.$$

The rate of volatile (monomer) production is given by

$$\frac{dm}{dt} = -K_m/\sqrt{P}$$

where P is the degree of polymerization of the residue. Experimental value of K (a combination of various rate constants) is given as follows:

$$K = 4.6 \times 10^{17} \exp(-58,000/R \text{ } ^\circ T) \text{ sec}^{-1}.$$

IV. A fourth possible view^{13,14} adopts Grassie and co-worker's idea about the rate of volatiles but considers that initial decrease in molecular weight may be due to random scission instead of weak-link fission. Accordingly;

$$\frac{d\left(\frac{1}{P}\right)}{dt} = k_s \left(1 - \frac{1}{P}\right)$$

where $k_s = 7.8 \times 10^{15} \exp(-65,00/R \text{ } ^\circ T) \text{ sec}^{-1}$.

It is difficult to argue in favor of any particular mechanism as stated above, and it may so happen that more than one mechanism is consistent with the observed rate laws. The result of E , i.e., 30 kcal/mole for styrene and ethylene and 44 kcal/mole for benzene, in fact, point in this direction. In his discussion on the mechanism of polymer degradation, Rabinovitch⁶ states that for chain-end initiation and unzipping, the following equation holds good:

$$\frac{dn}{dt} = k'n$$

where n is the number of breakable bonds in unvolatilized polymer backbone at time t , and k' is the rate constant. This equation with proper modification could be put to the test with the TGA data (in N_2) from the present investigation. The assumption we make is that the total number of breakable bonds in unvolatilized polymer, n , is proportional to its fraction of weight undecomposed, $1 - \alpha$. The above equation then can be written as

$$-\frac{d\alpha}{dt} = k'(1 - \alpha).$$

In Figure 4 it is evident that the above equation holds good, i.e., the polymer degradation follows end initiation and unzipping.

It is worth mentioning that the TGA data (in N_2) in the present investigation were tested for random initiation (also presented by Rabinovitch⁶) as given by following equation:

$$\ln W = -(p_0 - 1) kt$$

where W is the weight fraction decomposed at time t , p_0 is the initial degree

of polymerization, and k is a rate constant. It may be noted that $(p_0 - 1)k$ is constant for a particular polymer but will vary from polymer to polymer. It was observed that the data could not be fitted to the above equation, thus ruling out the possibility of random initiation and unzipping.

Oxidation Degradation

It is well known that degradation is enhanced in the presence of oxygen (oxidative degradation).¹⁴ This is quite evident in our results (see Fig. 5). Our results further show that the same mechanism of degradation, i.e., end initiation and unzipping, holds good in the presence of N_2 , air, and O_2 . This implies that E values should remain the same both in oxidative as well as in nonoxidative degradation. The results listed in Table I are in accordance with this view, giving support to the earlier belief that "the enhancement of rate in oxidative degradation is viewed as oxidative chain-end initiation and unzipping."

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Appendix

$$\frac{dS_1}{dt} = -k_R S \quad (1)$$

where dS_1/dt = rate at which weak points decompose; S = average number of weak points left in an original chain at time t ; and k_R = rate constant. Slope of $\log k_R$ -versus- $1/T$ plot yields activation energy E .

$$n = kt \quad (2)$$

where n = amount of monomer produced in g at time t ; and k is a rate constant. Slope of $\log k$ -versus- $1/T$ plot yields E .

$$V = \log \Delta T - n \log a = -\frac{E}{2.3RT} + \log \left\{ \left[\frac{Z}{(R+1)} \right] \left(\frac{W_{0,c}}{A} \right)^{n-1} \right\} \quad (3)$$

where $a = A - \int_{T_0}^T \Delta T dT$; A = total area under the DTA curve; ΔT = peak height; $W_{0,c}$ = weight fraction of polymer initially present; Z = frequency factor; R = gas constant; and n = order of reaction. \dot{V} versus $1/T$ gives a straight line with slope $E/2.3R$.

$$\Delta \log \left(\frac{dW}{dt} \right) = x \Delta \log W_R - \left(\frac{E}{2.3R} \right) \Delta \left(\frac{1}{T} \right) \quad (4)$$

where dW/dt = rate of reaction; x = order of reaction; T = absolute temperature; $W_R = \Delta_c - \Delta W$; ΔW_c = total weight loss associated with a given reaction; and ΔW = weight loss at a point where dW/dt is taken. Plot of $\Delta \log (dW/dt)$ versus $\Delta \log W_R$ at constant $1/T$ gives x from the slope and E from the intercept.

$$\ln \frac{\alpha}{T^2} = \ln \left(\frac{ZR}{aE} \right) \left[1 - \left(\frac{2RT}{E} \right) \right] - \left(\frac{E}{RT} \right) \quad (5)$$

where $\ln (ZR/aE) [1 - (2RT/E)]$ is taken to be constant; α = fraction decomposed at time t ; and $a = dT/dt$ (heating rate). Therefore, the plot of $\log (\alpha/T^2)$ versus $1/T$ at low values of α yields a straight line with slope of $E/2.3R$.

$$\frac{d\left(\frac{m}{p}\right)}{dt} = k_w m_0 \left(\frac{1}{p_0} + N_w - \frac{m}{p m_0} \right) \quad (6)$$

where p = degree of polymerization; p_0 = initial degree of polymerization; k_w = weak-link scission rate constant; m = mass of the sample at time t ; m_0 = initial mass of the sample; and N_w = number of weak links per monomer unit. Plot of $\log k_w$ versus $1/T$ plot yields a slope equal to $E/2.3R$.

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