

Degradation Mechanism of Styrene–Polyester Copolymer

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Synopsis

The degradation mechanism of styrene–polyester copolymer was studied by various experimental techniques such as TGA, DTA, IR spectroscopy, pyrolysis gas chromatography, and GCMS (gas chromatography–mass spectrometry). It is concluded that, mainly, there are two first-order degradation reactions during thermal degradation in the presence of air. The first step involves the scission of crosslinks/weak links with liberation of free linear chains. The second degradation step involves random scission of the free linear chains into smaller fragments. The various fragments were identified by pyrolysis gas chromatography and by GCMS. In oxygen atmosphere, the polymer was found to obey first-order kinetics with a single rate constant. Apparently, due to presence of oxygen species at the degrading surface, the two rate constants obtained during thermal degradation reaction are altered in such a fashion as to give a single rate constant.

INTRODUCTION

There is a considerable interest in the degradation of polymers because of their widespread use in practically all the major industries. In recent years, their use as rocket fuel in hybrid/solid rocket motors has given additional importance to the degradation mechanism of various crosslinked copolymers. One of such polymers having wide practical utility is styrene–polyester copolymer. During our investigation of heterogeneous combustion^{1–4} of this polymer, we have extensively studied its degradation behavior, and the results are communicated herein.

EXPERIMENTAL

Preparation of Polymers

All the chemical reagents used were analytical grade. The ratios of maleic anhydride and phthalic anhydride during the preparation of linear polyesters were changed systematically to study the effect of molar compositions on the kinetic parameters of degradation. Excess glycol and reaction water were removed by distillation under reduced pressure (10 mm). The product was cooled to room temperature and then dissolved in fractionally distilled styrene. The crosslinking of the linear polyester with styrene in the presence of 0.1% benzoyl peroxide as initiator was carefully controlled in a thermostat. The molar ratio of maleic anhydride:phthalic anhydride:styrene in polymers, represented as M:P:S, is, for polymer 1, 0.4:0.6:0.4; polymer 2, 0.5:0.5:0.5; polymer 3, 0.6:0.4:0.6; polymer 4, 0.5:0.5:1.0.

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Thermal and Oxidative Degradation by TGA Under Isothermal Conditions

Thermal degradation was conducted at 200, 250, 300, 350, 400, and 450°C with all the polymers. For the oxidative degradation, the temperatures were 250, 300, 350, and 400°C. The flow rates of oxygen were 2, 4, 6, and 8 L/min. The flow rates were measured by a gas flowmeter. The experimental details have been discussed earlier.¹

TGA at Different Heating Rates

The analysis was carried out on powdered polymer samples (44–100 and 100–150 BS mesh) at 5, 10, and 15°C/min. The temperature was raised from ambient to 600°C in all cases.

Combined Derivatographic Analysis

The derivatography of the system of Paulic, Paulic, and Erdey, manufactured by M/s. M.O.M. (Hungary Optical Works), was employed for the present study. Traces of different functions such as TGA, DTA, TGA for weight loss data, and temperature T were obtained photographically from this instrument. For DTA, a mixture of ignited alumina and powder sample in the ratio of 1:1 was used as an inert material. Pure polymer sample was used as the test material.

IR Spectroscopic Study

The IR spectra of the original sample and its residues collected at different times and at different temperatures were taken by preparing KBr pellets. The experimental details have been discussed before³.

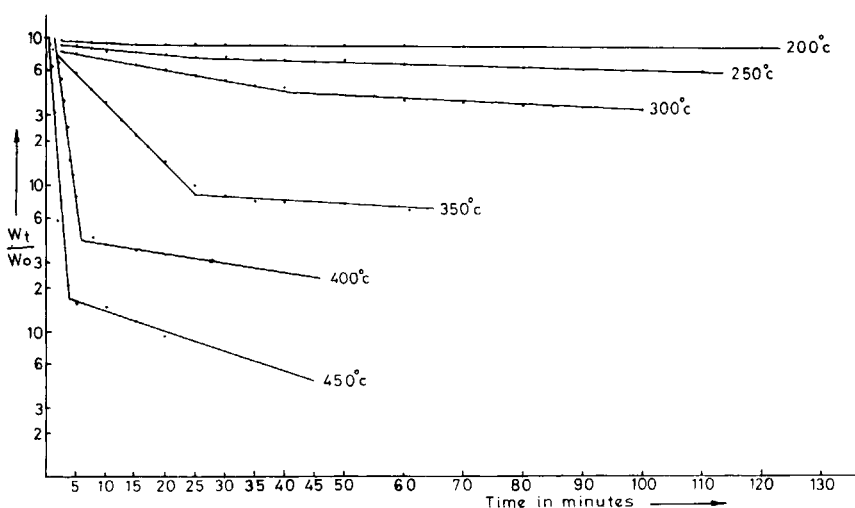


Fig. 1. Typical plots of $\log_{10} W_t/W_0$ versus time of polymer 2 during thermal degradation.

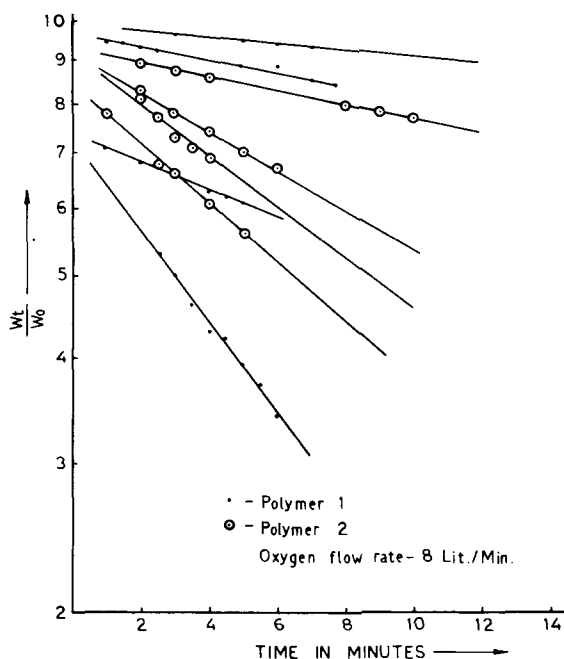


Fig. 2. The typical plots of $\log_{10} W_t/W_0$ versus time of polymer 1 and 2 during oxidative degradation.

GCMS Study

The apparatus used in the study was a double-beam, double-focusing MS-30 DB mass spectrometer (AEI, England). The mass scanning range was varied from m/e 12 onward. The spectra were recorded at a source pressure varying between 2×10^{-5} and 9×10^{-7} torr. The source temperature was always kept

TABLE I
 E and A Values for Rate Constants k_1 and k_2 ($n = 1$ for All Polymers at k_1 and k_2)

Polymer composition M:P:S	E_1 , kcal/mol	$A_1, 10^{-3}$ s^{-1}	E_2 , kcal/mol	$A_2, 10^{-3} s^{-1}$
0.4:0.6:0.4	15.1	0.50	14.2	0.0078
0.5:0.5:0.5	17	0.41	11.9	0.0057
0.6:0.4:0.6	18.2	0.87	11.3	0.0070
0.5:0.5:1.0	14.7	0.37	9.4	0.0033

TABLE II
 E and A Values at Different Flow Rates of Oxygen ($n = 1$ for All Polymers at Different Flow Rates of Oxygen)

Polymer composition M:P:S	2 L/min		4 L/min		6 L/min		8 L/min	
	E , kcal/mol	$A, 10^{-3}$ s^{-1}	E , kcal/mol	$A, 10^{-3}$ s^{-1}	E , kcal/mol	$A, 10^{-3}$ s^{-1}	E , kcal/mol	$A, \times 10^{-3}$ s^{-1}
0.4:0.6:0.4	13.9	0.066	10.1	0.033	9.6	0.006	3.4	0.0005
0.5:0.5:0.5	16.7	0.333	11.4	0.13	5.9	0.001	2.5	0.0011
0.6:0.4:0.6	14.7	0.400	11.1	0.058	7.2	0.006	2.2	0.0013
0.5:0.5:1.0	11.4	0.133	10.2	0.066	9.7	0.054	6.8	0.0173

at 20°C above the sample temperature. For the isolation of double-natured peaks, high resolution and higher recorder speed were used.

The gaseous products were initially separated by passing through a gas chromatograph (SE-30) and analyzed by mass spectrometer.

RESULTS

TGA Under Isothermal Conditions

The weight loss data obtained from the experiments during thermal and oxidative degradation were plotted against time. It was found that L. Wilhelmy's equation (a type of first-order rate equation) satisfied the data. The equation is

$$W_t = W_0 e^{-kt}$$

where W_t is weight of the polymer at time t and W_0 is initial weight of the polymer.

Typical plots of $\log_{10} W_t/W_0$ vs. time are shown in Figure 1 and 2 for thermal and oxidative degradation. The values of activation energy and the frequency factor were calculated from the following Arrhenius equation:

$$k = A e^{-E/RT}$$

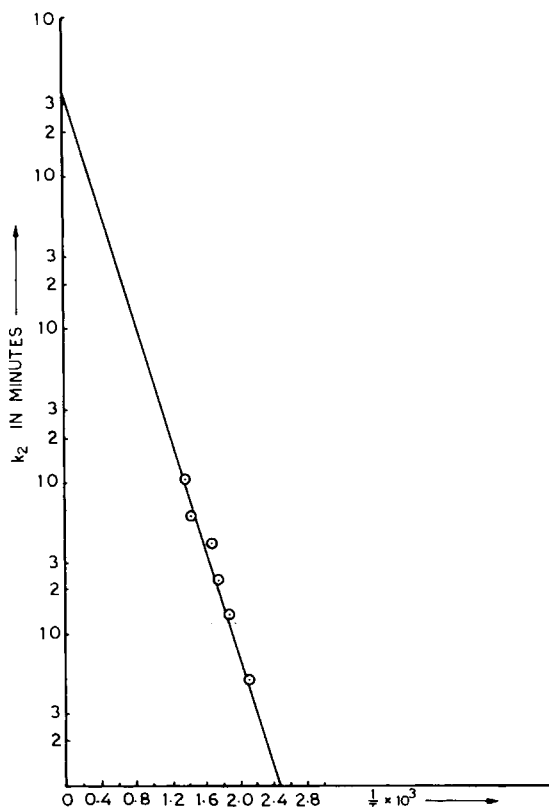


Fig. 3. Typical Arrhenius plot during thermal degradation of polymer 1.

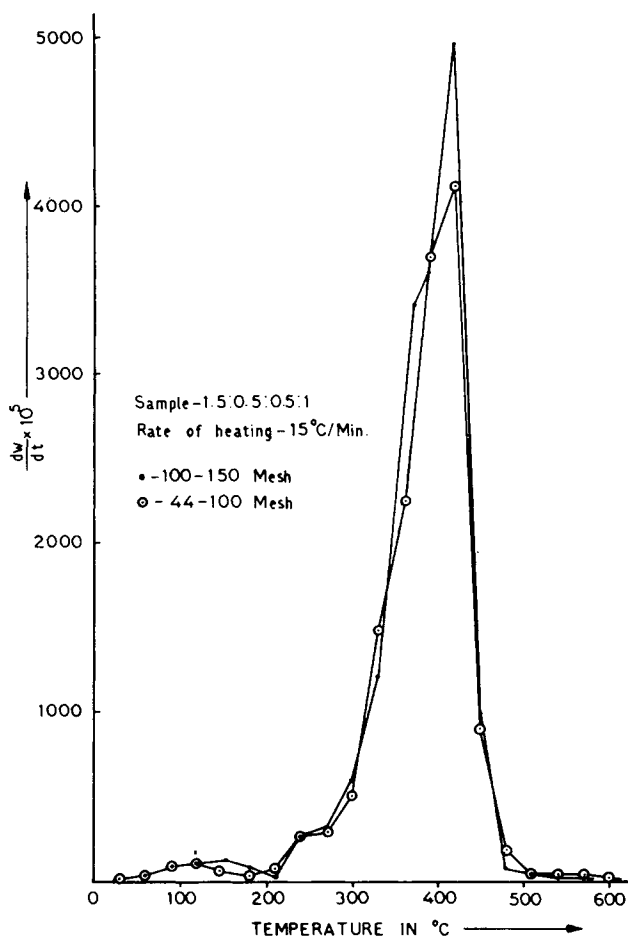


Fig. 4. Typical plot of decomposition rate versus temperature of polymer 4.

where R is the gas constant and T is the absolute temperature. The values are shown in Tables I and II. A typical Arrhenius plot during thermal degradation is shown in Figure 3.

TGA at Different Heating Rates

A typical plot of decomposition rate dw/dt vs. temperature is shown in the Figure 4.

Combined Derivatographic Study

A typical plot of TGA, DTA, and weight loss data is shown in Figure 5. It can be noted that there are three peaks for the DTA curves. The first is exothermic, whereas the second and third are endothermic in nature.

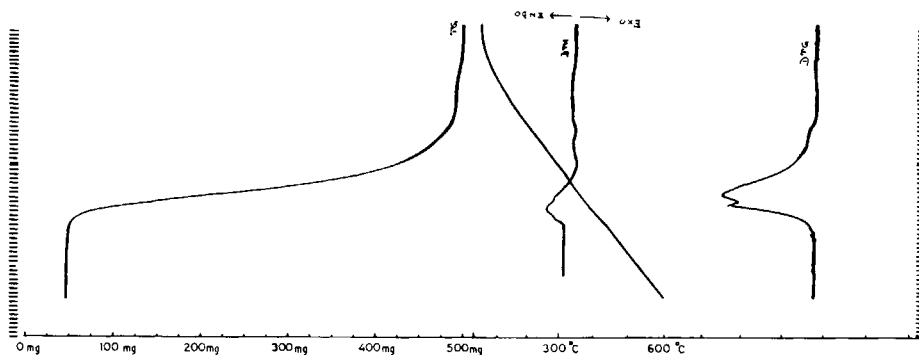


Fig. 5. Typical plot of TGA, DTA, and weight loss data of polymer 2.

Pyrolysis Gas-Chromatographic Study

Typical pyrolysis chromatograms of a polymer and of a standard polystyrene polymer are shown in Figures 6 and 7. By comparing the two chromatograms with the reference compounds, the following compounds were identified in the vaporized phase of the polymer: (1) carbon dioxide, (2) propylene, (3) methane, (4) styrene, (5) benzaldehyde, (6) propylene glycol, (7) phthalic anhydride, (8) phthalic acid, (9) long-chain ester molecule.

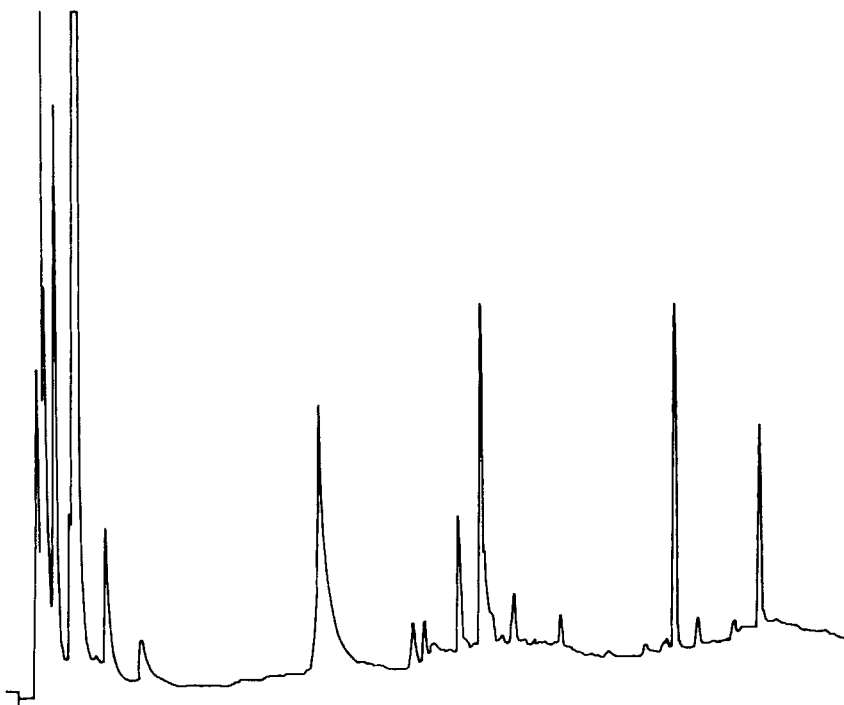


Fig. 6. Typical pyrolysis chromatogram of polymer 2.

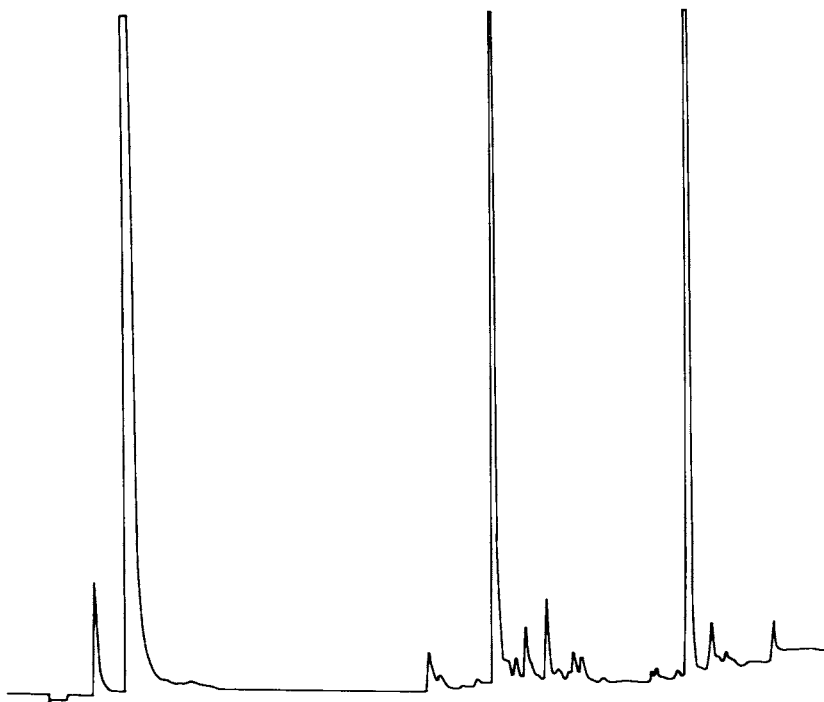


Fig. 7. Typical pyrolysis chromatogram of a standard polystyrene polymer.

GCMS Study

The above products were also identified by GCMS. Typical mass spectra of the gaseous products are shown in Figure 8.

DISCUSSION

From Figure 1, it is quite evident that there are two first-order reactions during thermal degradation of the polymers under isothermal conditions. It can be assumed that up to a certain point, the polymer degrades with a first-order rate constant, say, k_1 and then with another first-order rate constant, k_2 . However, there is only one first-order rate constant at which the degradation is taking place at all flow rates of oxygen gas (Fig. 2). It seems that the rate constants k_1 and k_2 of the thermal degradation reaction are altered in such a fashion as to give a single first-order rate constant during oxidative degradation.

Grassie and co-workers⁵⁻⁷ have invoked the concept of scission of weak links first, followed by end initiation and unzipping to explain the degradation of various polymers. This basic concept is introduced to suit the structure of this

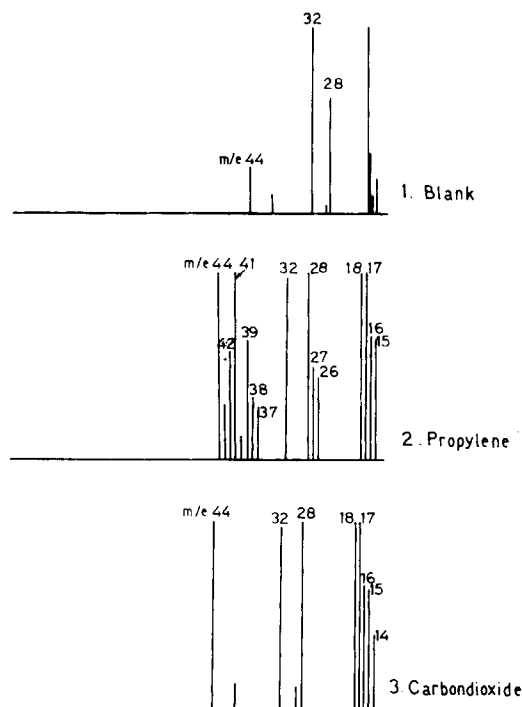
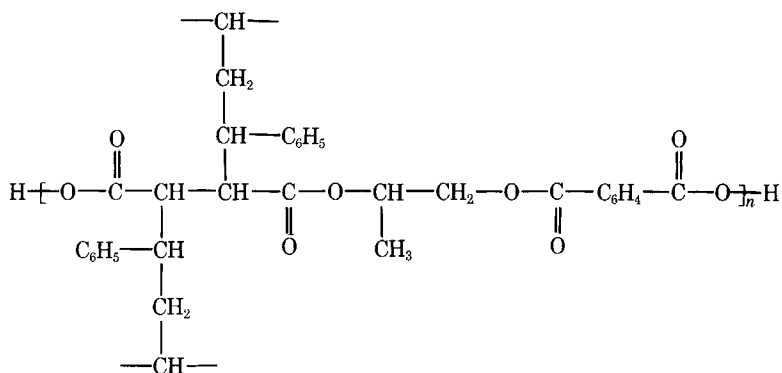


Fig. 8. Typical mass spectra of the gaseous products.

polymer. By examining the structure of the polymer which is given below,



one can expect first the scission of highly strained crosslinks as well as weak links in the polymer chains. Then, the random scission of linear chains will continue till a critical size of vaporizing is formed. This is defined as fragment size vaporizing (FSV) by Kumar and Stickler.⁸

Now, if we examine the E values from Tables II and III, it can be observed that there is a considerable difference between the values obtained from thermal and oxidative data. This was checked by repeated experiments to ensure the trend. In fact, there is no definite trend in E and k values when the degree of crosslinking is increased; but, as expected, the polymer degrades faster at higher concentrations of oxygen.

TABLE III
 Average E , A , and n Values from Direct Solution Methods

Polymer composition M:P:S	First step of degradation reaction			Second step of degradation reaction			Third step of degradation reaction		
	E , kcal/mol	A , s ⁻¹	n	E , kcal/mol	A , s ⁻¹	n	E , kcal/mol	A , s ⁻¹	n
0.4:0.6:0.4	10 ± 2	500 ± 10	0.8	20 ± 2	1500 ± 100	1	16 ± 2	100 ± 10	1
0.5:0.5:0.5	12 ± 2	800 ± 10	0.8	24 ± 2	1700 ± 100	1	14 ± 2	150 ± 10	1
0.6:0.4:0.6	8 ± 2	400 ± 10	0.8	26 ± 2	2000 ± 100	1	13 ± 2	140 ± 10	1
0.5:0.5:1.0	9 ± 2	450 ± 10	0.8	18 ± 2	1300 ± 100	1	12 ± 2	100 ± 10	1

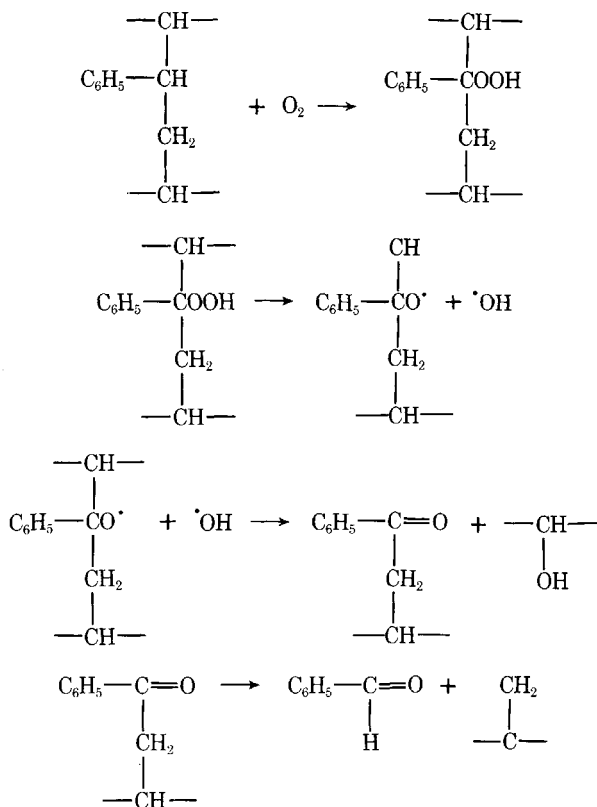
It can be observed from the TGA traces (Fig. 4) that there are four decomposition stages around 120, 240, 360, and 380°C for the overall degradation of the polymers during thermal degradation. The first stage, around 120°C, is due to water losses from the polymer. The second stage, i.e., the first degradation reaction which is taking place in the temperature range of about 160–240°C, is a very minor one. The third and fourth stages, i.e., the second and third degradation reactions that are major in nature, are taking place around 260–360 and 360–480°C, respectively. It can also be noticed that there is a poor demarcation between these last two steps of the TGA traces. This is due to the fact that there is a very little energy difference between these two steps (Table III).

The discrepancy between TGA and the isothermal method regarding the number of degradation stages can be explained as follows. The first water elimination stage around 120°C of the TGA traces was not recorded in the isothermal condition. Due to very minor energy differences between the last two stages of TGA traces, only a single degradation reaction was recorded during the isothermal degradation reaction in the presence of air due to lower sensitivity of the equipment. Hence, k_1 and k_2 of the isothermal method represents the overall degradation rate up to 240°C and the average rate of the last two stages of the TGA traces, respectively.

From the data of the TGA traces (Fig. 4), the kinetic parameters (E , A , and n) of all the three degradation steps of the polymers were evaluated by applying known techniques, i.e., direct solution method,^{9–11} integral method,^{12–15} maximum decomposition method,^{16–18} multiple heating rate method,^{16,19–21} and the difference method.^{10–12,19–21} Only the kinetic parameters obtained from the direct solution method satisfied the weight loss data. The values of E , A , and n for the three degradation steps of polymers 1–4 obtained from the direct solution method are tabulated in Table III. The results indicate that overall degradation satisfies first-order kinetics and that there is no definite trend in the E values with the degree of crosslinking. The large difference in A values between TGA and the isothermal method is due to a difference in physical conditions of the polymers. During TGA, powder polymers were used, whereas during the isothermal method, small rectangular slices of polymers were used.

Now from the Figure 4, it is clear that first step of degradation is an exothermic reaction, while the second and third steps are endothermic in nature. Therefore, it is fair to assume that the first step is due to unstable hydroperoxide formation at the tertiary hydrogen atom (β to the C–C double bond) by the attack of oxygen present in the air. This is in agreement with Bolland's²² hydroperoxide theory.

The scheme of the reaction is as follows:



It is quite probable that hydroperoxide formation may initiate the breaking of highly strained crosslinking bonds. So the second step of degradation, which is endothermic in nature, is mainly due to scission of crosslinks as well as weak links present in the linear chains.

The scission of weak links was confirmed by IR spectroscopy.³ It has been observed that aliphatic portions,

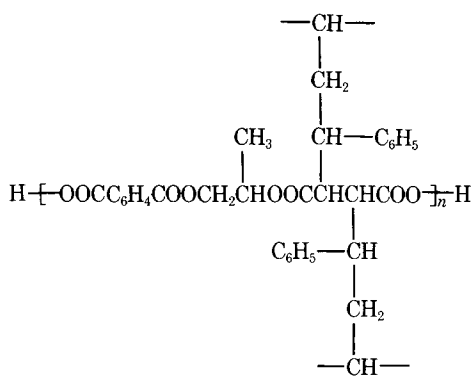


groups, ---CH_3 groups, and the ether groups (both aliphatic and aromatic) are decreasing with heating.

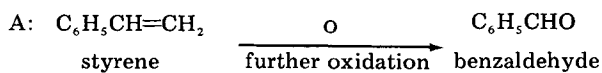
The third degradation step is also endothermic in nature. This step may represent the random scission of the free linear chains formed during the second degradation step into still smaller fragments.

Now, the following scheme for the thermal degradation of this polymer is given from the above observations and from the identification of the vaporized products

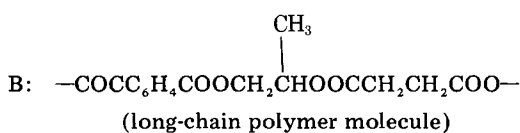
by pyrolysis gas chromatography and by GCMS:



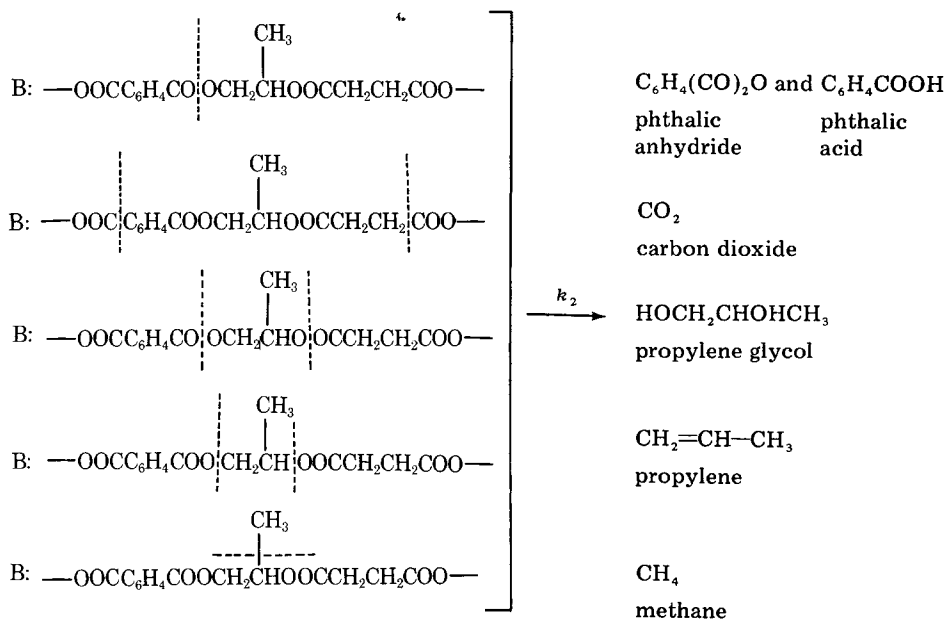
\downarrow k_1 (scission at the crosslinks and weaklinks)



+



B may be broken randomly at different sites shown below by the dotted lines, forming various products in the following fashion:



As the trend of IR traces of the residues obtained at various time interval of oxidative degradation remained almost identical with that of the thermal degradation, we assumed that there is not much difference in the proposed mechanism of thermal degradation with the oxidative degradation of this polymer.

It is proposed that during oxidative degradation, the concentration of oxygen species at the surfaces increases, which modifies the rate of scission of crosslinks/weak links and random scission of linear chain in such a fashion that only a single rate constant is obtained.

CONCLUSIONS

The following conclusions were derived:

(1) There is no appreciable effect of minor variation in molar composition or of particle size on the thermo-oxidative behavior of this polymer.

(2) During isothermal degradation, there are two first-order rates representing the two stages of decomposition. The first step of degradation represents the breaking of highly strained crosslink bonds as well as weak links present in the polymer chain. The second stage of decomposition represents random scission of linear chains formed from the first stage of decomposition into smaller fragments.

(3) During degradation at different heating rates, three steps of degradation were observed. The first step, a minor one, is due to the formation of unstable hydroperoxide which acts as an initiator for the subsequent decomposition steps. The second step, a major one, is due to the bond scission of crosslinks/weak links forming linear chains. The third step is due to the random scission of the linear chain into smaller fragments.

(4) During oxidative degradation, only one first-order reaction is present. This is due to the fact that the bond scission of crosslinks/weak links and the random scission of linear chains are changed in such a way as to give a single reaction.

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