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THERMAL DEGRADATION OF POLYSTYRENE—4

DECOMPOSITION OF OXYGEN-CONTAINING POLYMERS

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Abstract—The thermal decomposition of two polystyrene samples prepared by radical polymerisation in the presence of oxygen was studied in the temperature range 280–300°C where volatile formation is negligible. The energy of activation for chain scission of the oxygen-containing polymers was lower than that of a reference sample prepared under vacuum. All three polymers contained the same proportion of weak bonds and it was therefore concluded that these structures are not copolymerised peroxide groups.

INTRODUCTION

Despite a voluminous literature stretching back some thirty or more years, the kinetics and mechanisms involved in the pyrolytic decomposition of polystyrene are still not fully understood and papers dealing with various aspects of the subject continue to appear. The main features of the degradation process are now widely accepted and the conversion of polymer to volatile fragments can be accounted for adequately by a mechanism involving chain-end initiation, unzipping to monomer, and inter- and intramolecular chain transfer. Random chain scission (not leading directly to volatile formation) and a first-order termination provide the other important steps in the overall process [1]. Uncertainty, and even controversy, still surround the early stages of the reaction particularly in relation to the part played by structural abnormalities, the so-called "weak links", and various types of chain ends. There is no doubt that the thermal stability of radical polystyrene is influenced by the presence of structural abnormalities. Such polymers are markedly less stable than polystyrenes prepared in anionic polymerisations, probably because the ionic route requires conditions of high purity and is less prone to side reactions, such as transfer and branching. The differences between radical and anionic polystyrenes are most evident in the early stages of the degradation. Indeed, it has been shown that, beyond about 10% conversion to volatiles, the pyrolytic decomposition patterns of the two types of polymer are virtually identical [1].

One of the first studies to reveal important differences between radical and anionic polystyrenes was conducted within the temperature range 280–320°C where volatile formation is negligible, and where degradation is revealed only by a decrease in molecular weight [2]. Plots of the degree of degradation (α) vs time were linear for both types of polymer. For the anionic polystyrenes the lines passed through the origin showing that the reaction was one of simple random scission. The corresponding plots for thermally prepared polymers, however, showed s substantial intercept on the α axis at zero time. This was interpreted as due to a small amount of some very labile structure distributed at random within the polymer chains. It was shown that these structures were not heat-to-head groups, branch points or unsaturated structures, and it was speculated that they were most likely to be peroxide groups incorporated by copolymerisation of traces of oxygen in the monomer [3]. In the present paper we report experiments to test this hypothesis. The degradation behaviour at sub-volatilisation temperatures of three thermally polymerised samples is compared. Two of the samples were prepared in the presence of controlled amounts of oxygen, which is known to copolymerise readily to produce peroxide units [4, 5]; the third, reference sample was prepared under vacuum as before.

EXPERIMENTAL

Styrene monomer (Hopkin & Williams Ltd) was purified as described previously [2] with the additional step that, after washing with water, it was decolourised by passing it through a 7 cm column of chromatography grade alumina. Polymerisations were performed at 60°C to 10% conversion without initiator. The first sample P4 was prepared under high vacuum as before. For samples P3 and P5, 0.5 atm of dried, decarbonated air and 1 atm of pure oxygen respectively, were admitted to the dilatometers before sealing. After sealing, the dilatometers were shaken and inverted several times to dissolve oxygen, but the contents were not disturbed during polymerisation. The rates of polymerisation increased in the order P5 > P3 > P4, i.e. in order of increasing amount of oxygen present. The polymers were purified in the usual manner.

The i.r. spectra of the three polymers were virtually identical and it was not possible to detect peroxide groups even from difference spectra, using a Nicolet Series 7000FT-IR spectrometer, in the 1000–1100 cm^{-1} range where the styrene-peroxide copolymer absorbs strongly [6].

Polymer films (0.1 g) were cast from benzene solution (20 ml) on Pyrex glass bulbs 4 cm O.D. The solvent was removed by rotary evaporation at 40°C taking care that a

Table 1. Data on polystyrene samples polymerised thermally at 60°C

Polymer	Polymerisation atmosphere	$\overline{M}_v$ × 10^{-6}	$\overline{M}_n$ × 10^{-6}	No. of weak bonds per 1000 monomer units*	Activation energies (kJ mol^{-1}) for random chain scission at 280–300°C†
P3	0.5 atm air	1.374	0.865	0.0736	190.6 ± 7.7
P4	Vacuum	1.346	0.902	0.0789	203.6 ± 7.8
P5	1 atm oxygen	1.457	—	0.0740	132.8 ± 7.7

* From least squares treatment of data in Figs 1, 2 and 3.

† From least squares treatment of data in Figs 4 and 5. Activation energies calculated from plots of $\overline{M}_v^{-1}$ vs time agreed with these data within experimental error.

uniform film of *ca.* 50 μm was formed. Traces of solvent were removed from the film by heating at 60°C under high vacuum for three days, after which the bulbs were sealed under a vacuum better than 10^{-5} mm Hg. The polymer samples were degraded by immersing the bulbs in a molten salt bath (equimolar mixture of KNO_3 and $NaNO_3$ of m.p. 223°C) maintained at the required temperature ±0.5°C by a F. and M. regulator. Temperatures quoted in this paper refer to polymer film temperatures which were found to be *ca.* 0.5°C below the bath temperature.

After the required degradation time the bulbs were opened and the contents dissolved in toluene for viscosity measurements. Limiting viscosity numbers for degraded and undegraded polymers were measured at 30°C in toluene in a suspended level dilution viscometer equipped with photocells for automatic timing with a Hewlett–Packard Autoviscometer type 5901B. Viscosity average molecular weights $\overline{M}_v$ were calculated from the Mark–Houwink constants K and a, 1.04 × 10^{-4} and 0.733 respectively [7]. For degraded polymers, the degree of degradation α was calculated as previously by a procedure which allows for the changing distribution of chain lengths during random degradation [8]. For this purpose the original computer programs were rewritten in Algol and run on an Elliot-NCR 4120 computer. This treatment has been used successfully by other workers [9] and copies of the program are available from the authors on request.

Number-average molecular weights $\overline{M}_n$ were obtained directly for several degraded and undegraded samples by osmometry at 37°C with a Mechrolab 501 High Speed Osmometer employing cellulose membranes of 0.01 μm pore size with toluene as solvent. Values of $\overline{M}_n$ thus obtained agreed satisfactorily with the values calculated from $\overline{M}_v$ by the computer program.

The viscosity-average molecular weights of the three polymers used in this work are shown in Table 1.

RESULTS AND DISCUSSION

The degree of degradation (α) vs time of heating for polymers P3, P4 and P5 are plotted in Figs 1, 2 and 3 respectively. In all cases the plots are linear and the four lines on any individual graph pass through the same intercept on the α axis within experimental error. This reproduces exactly the behaviour observed previously with thermal polystyrenes [2] and indicates that the scission reaction within the temperature range 280–300°C, follows the relationship.

$$\alpha = \beta + kt \qquad (1)$$

where k is the first-order rate coefficient for random scission of "normal" bonds. The parameter β represents the fraction of highly labile bonds in the polymer. For anionically synthesised polymers β was zero

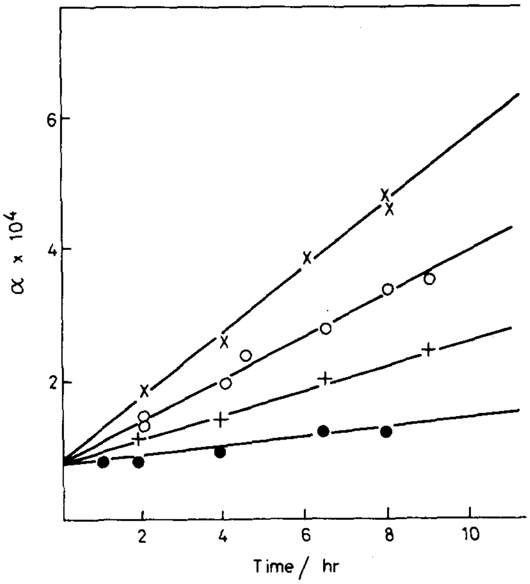

Fig. 1. Degree of degradation (α) vs time of heating for polystyrene P3. Temperatures (°C) ● 280; + 290; ○ 295; × 300.

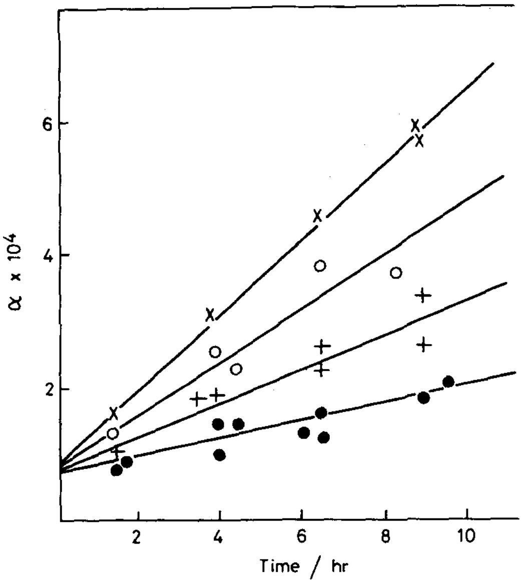

Fig. 2. Degree of degradation (α) vs time of heating for polystyrene P4. Temperatures (°C) ● 280; + 290; ○ 295; × 300.

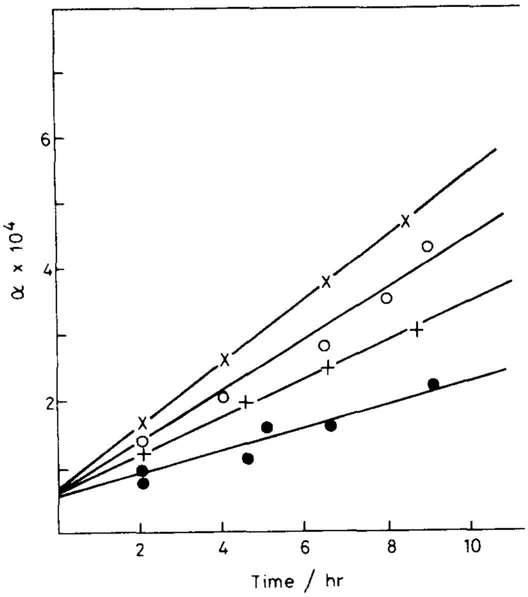

Fig. 3. Degree of degradation (α) vs time of heating for polystyrene P5. Temperatures (°C) ● 280; + 290; ○ 295; × 300.

[2]. From the values of β the number of "weak bonds" per 1000 monomer units for P3, P4 and P5 shown in Table 1 were obtained. The three values are identical within experimental error and are very close to those obtained previously from polystyrene samples prepared thermally in vacuum [2]. The hypothesis that the weak bonds in radical polystyrenes are peroxide groups requires that the proportion of such weak bonds in the samples lie in the order P5 > P3 > P4. Clearly this hypothesis is no longer tenable.

Differences in thermal stabilities among the three polymers become apparent, however, when the "normal" chain scission reactions are examined more closely. Thus, the slopes of the lines in Figs 1, 2 and 3 yield values of the rate coefficients for chain scission and these are plotted in Arrhenius form in Figs 4 and 5 from which the activation energies in Table 1 were calculated. The activation energies for the main phase of the chain scission reaction lie in the order P4 > P3 > P5. For P4, the reference sample prepared under high vacuum, the energy of activation for bond scission is in good agreement with the figure (205 kJ mol^{-1}) obtained in an earlier study [2]. For P5, on the other hand, the energy of activation for chain scission is lower than any the authors have encountered in the literature, and is in the range of bond dissociation energies recorded for dialkyl peroxides and for the alternating copolymer of polystyrene and oxygen, poly(styrene peroxide) [6].

The lower thermal stability of P5 compared with a polystyrene prepared under vacuum is also observable at higher temperatures where volatile fragments are evolved. Thus, thermal volatilisation analysis (heating rate 10°C min^{-1}) revealed that volatiles from the main degradation process were detectable at 347°C from P5 compared with 371°C for the oxygen-free polymer.

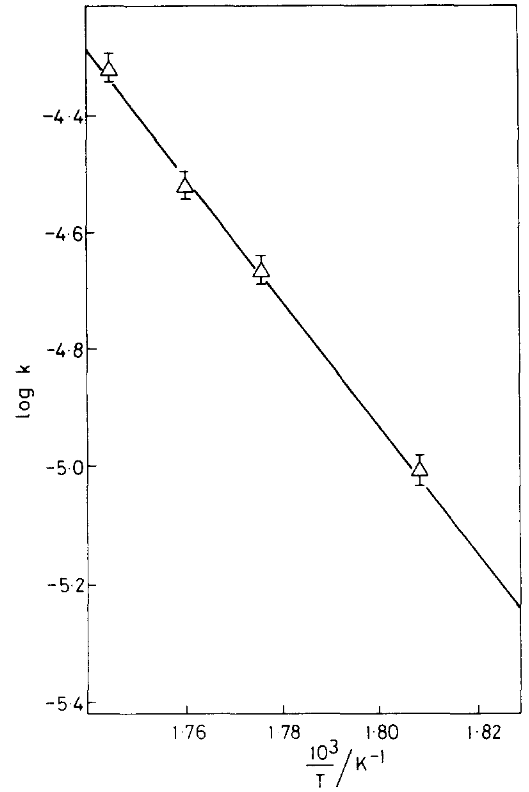

Fig. 4. Arrhenius plot for rate coefficient of bond scission for P3 from Fig. 1.

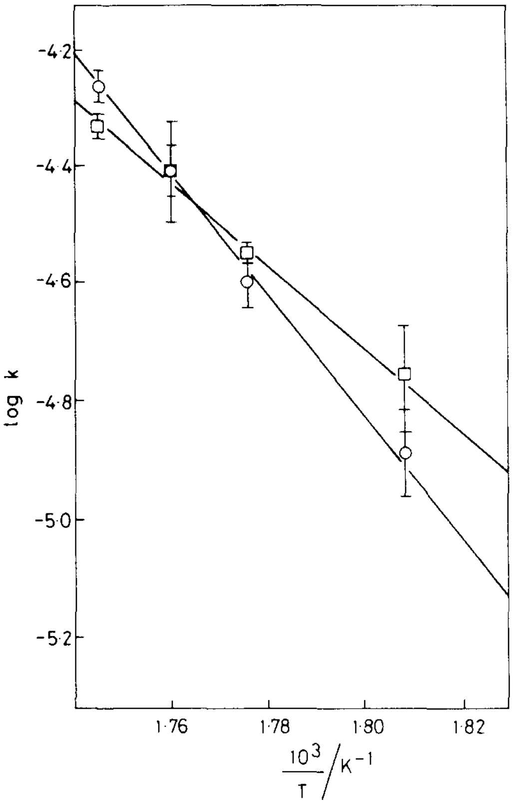

Fig. 5. Arrhenius plots for rate coefficient of bond scission for P4 and P5 from Figs 2 and 3 respectively. ○ P4; □ P5.

In conclusion, the results reported here demonstrate that polystyrenes prepared by radical polymerisation in the presence of oxygen, which is readily incorporated into the polymer as peroxide units, are thermally less stable than oxygen-free polymers prepared under identical conditions. Both types of polystyrenes, however, contain comparable amounts of 'weak links" which we now conclude cannot be peroxides. The precise nature of these structures remains as elusive as ever. It is difficult to conceive of other structures which could fulfill the role. We have also considered the possibility that the ordinate intercept in Figs 1, 2 and 3 is a chain-end effect. The nature of the chain ends in polystyrene, as we shall show in a future publication, has an important influence on thermal stability, but the evidence that weak links originate from labile chain ends is unconvincing at present. It has been suggested that weak links may arise from physical entanglements of chains rather than chemical structures [10]. This idea, however, does not explain why these links exist in radical polystyrenes but not in those prepared by an anionic route.

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