Kinetic study on the first stage during thermal degradation of polystyrene

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The kinetic parameters of the first stage of polystyrene degradation have been investigated to elucidate the reaction mechanisms using the flow reactor system. The decrease in molecular weight of polystyrene was recorded at minute intervals over the temperature range 310°–390°C. Generally, the first and second stages were observed by thermogravimetric analysis (t.g.a.), however in the early stage of the degradation volatile yields of at least 5% occurred. Therefore, using t.g.a. analysis it is difficult to detect this earlier stage. It became evident that the first stage in the earlier part of the reaction could be detected by g.p.c. analysis. We have observed the hidden kinetic parameters of the nature of the first stage of the polystyrene degradation. The results indicate that the main chains were degraded randomly with the small quantitative volatile groups in the first stage and the rates of decrease in molecular weight in the first stage against reaction temperatures were evaluated as $\log k_s = 12.0 - 41300/RT$.

Keywords Thermal degradation; molecular weight; polystyrene degradation; kinetic parameters; polymers

INTRODUCTION

It has been observed that a characteristic initial drop in molecular weight followed by a more gradual decrease in the latter stages, occurs during the thermal degradation of polystyrene[1,2]. The mechanism of the initial drop in molecular weight was explained in terms of ruptures of weak links which are randomly distributed in the polymer chain[3,4]. The kinetic investigation of the first stage, involving the initial drop in molecular weight, has been carried out mainly by t.g. analysis, but these investigations used hourly interval measurements on the reaction. However, since the rate of decrease in molecular weight is very fast, and also, at a relatively high temperature, a large amount of volatile groups were formed[5,6] and it was very difficult to separate the degraded polystyrene from volatile products. Thus, we have developed a special flow reactor system, with which the kinetic parameters in the earlier part of the reaction were recorded at minute intervals (20 minutes and below). In this report, the initial drop in molecular weight for the first stage of polystyrene degradation is discussed.

EXPERIMENTAL

Materials

A pure polystyrene containing no additives was used. The number average molecular weight of the polystyrene sample was 2.05×10^4, this sample was prepared by radical polymerization, from Mitsubishi–Monsanto Chemical Co. Ltd.

Apparatus and procedure

The thermal degradation reactor is a fixed bed flow reactor system developed for the thermal degradation of vinylic polymers, consisting of 3 components: a sample melting section (feeding nozzle involved), a reaction section and a product recovery section. The reactor tube, 23 mm in diameter and 370 mm in length, was made of stainless steel. To recover the degraded polymer from the early part of the reaction, an inner cell had been placed within the reactor tube. The rashigring was crushed and subsequently placed within the cell. The flow diagram is shown in *Figure 1*, and the flow reactor and the inner cell are shown diagrammatically in *Figures 2* and *3* respectively. Just before carrying out the reactions, approximately a few grams of the polystyrene sample was placed in the sample melting section and allowed to melt at about 170°C. From a position on top of the reactor tube, the melted sample was fed into the reactor. The melted sample was then fed into the inner cell situated within the reactor tube and allowed to settle on the surface of the crushed rashigring. After a given time, the inner cell

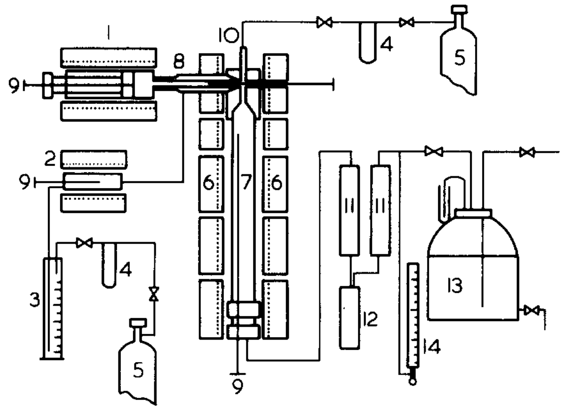

Figure 1 Flow diagram of experimental apparatus: 1, melter; 2, steam generator; 3, mess cylinder; 4, manometer; 5, He bomb; 6, electric furnace; 7, reactor tube; 8, feeding nozzle; 9, thermocouple; 10, carrier gas inlet; 11, cooler; 12, trap; 13, gas holder; 14, soap film flow meter

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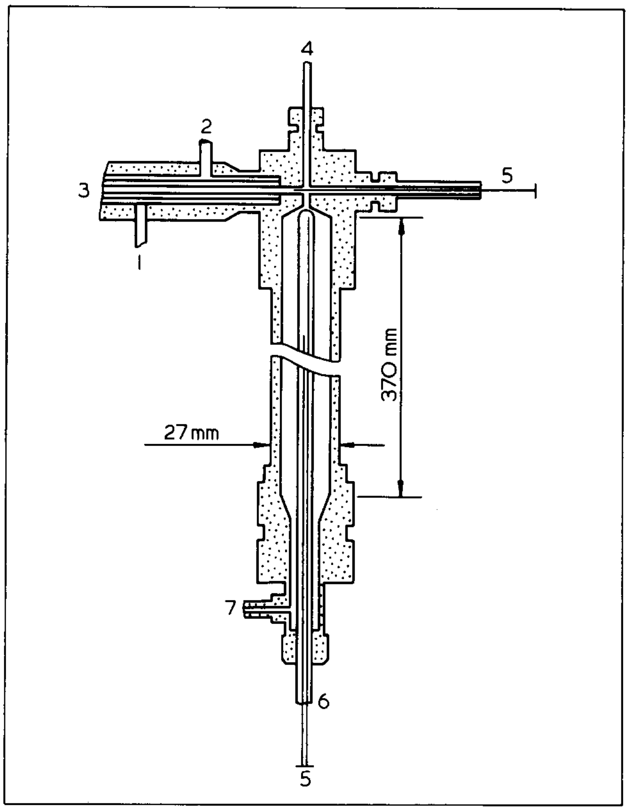

Figure 2 Details of reaction section: 1, coolant in; 2, coolant out; 3, feeding nozzle; 4, carrier gas inlet; 5, thermocouple; 6, thermocouple holder; 7, outlet (products)

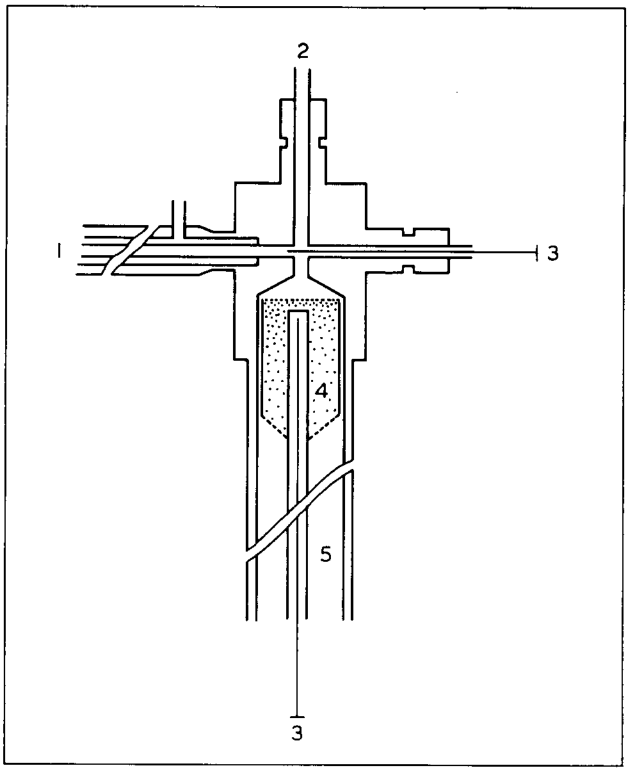

Figure 3 Details of inner cell: 1, feeding nozzle; 2, carrier gas inlet; 3, thermocouple; 4, inner cell; 5, reactor tube

was removed from the reactor tube. The degraded polymer inside the inner cell was treated with benzene–methanol in preparation for the g.p.c. analysis to follow.

When the feeding sample is fed into the reaction section, a decreased temperature in the reaction section was recovered for a few minutes.

Analysis

The degraded polystyrene was analysed by g.p.c. using a 2000GH × 2 + 4000GH × 2 column which was supplied by the Toyo Soda Co. Ltd. The details were the same as described previously[6,8].

RESULTS AND DISCUSSION

The relationship between the decrease in molecular weight and reaction time in the temperature range 310°–390°C is shown in *Figure 4*. The decrease in molecular weight of polystyrene at each reaction temperature was clearly observed where the reaction times were less than 20 min. These reaction times in the present work were shorter than those in the preceding works[1–4]. The decrease in molecular weight of polystyrene as reported[1–4] had been recorded at hourly intervals. They have never recorded at minute intervals as we have done. As can be seen from *Figure 1*, the curves are characterized by the fact that the decrease in molecular weight seems to slow down when a certain chain length is reached. These chain lengths seem to be shorter at higher temperatures. These results were the same as that described for thermally prepared polystyrene at lower temperatures, i.e., 248°–340°C[9]. Thus, the decrease in molecular weight of polystyrene showed a similar tendency in the temperature ranges of below ~400°C.

Figure 5 shows the relationship between 's', the average number of breaks per original chain and 't', the reaction time. Although the increase in average number of breaks against the reaction time were shown as a curve, at all reaction temperatures, the curves could be roughly drawn as two straight lines. Consequently, there are two stages, that is the first and the second decreases in the molecular weight of the polystyrene. The rate of molecular weight decrease in the first stage of the thermal degradation is faster than that in the second stage, as can be seen from

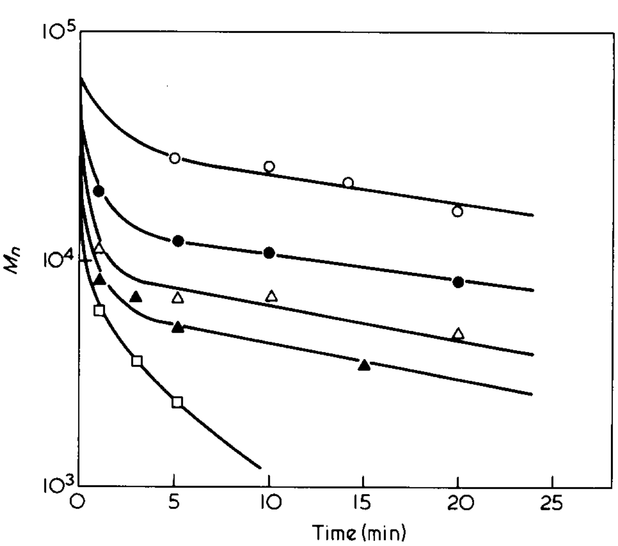

Figure 4 Change in molecular weight of degraded polystyrene with reaction temperatures and time: (○), 310°C; (●), 330°C; (△), 350°C; (▲), 370°C; (□), 390°C

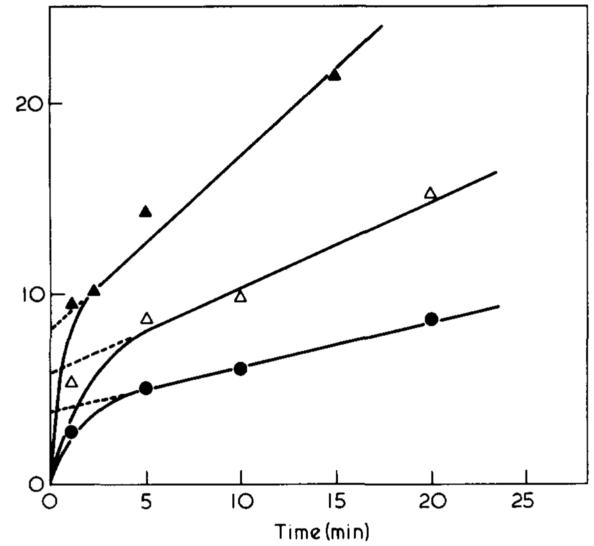

Figure 5 The average number of breaks vs. reaction time: (●), 330°C; (△), 350°C; (▲), 370°C

Figure 5. Since each rate of molecular weight decreases between these stages was different, we can deduce that the molecular weight decrease in each stage of the degradation was as the result of a different mechanism. These stages cannot be clearly distinguished because of the molecular weight decrease that subsequently takes place. However, the molecular weight decrease in the first stage of the degradation could be evaluated in terms of the intercept on the vertical line of *Figure 2* obtained by extrapolating the second stage of the curves back to zero time, as the intercept on the vertical line may be considered as belonging to a part of the first stage of the degradation. The numerical value of the intercept obtained at each reaction temperature was different and it increased with an increase in the reaction temperature. This is so because the average number of breaks in the first stage of the degradation does not keep at a constant level, and is varied with differing reaction temperatures. These results were different from those reported by Cameron *et al.*[3,4]. In their experiments, the intercept on a vertical line in the plot of the average number of breaks vs. the reaction time was not varied with reaction temperature. The average number of breaks is less than about 0.2 per 1000 monomer units. From the results described above, they concluded that the scissions of the weak links existing randomly in the main chain made an important contribution to the initial rapid drop in molecular weight in the first stage of the degradation. They also estimated that the labile structures which decomposed in the first stage of the degradation were oxygenated groups, probably peroxide links.

The average number of breaks in the first stage of the degradation obtained in the present work is greater by about 10 times than that of weak links reported by Cameron *et al.*[3,4]. It was also observed that the average number of breaks of the first stage was varied with reaction temperature. Consequently, the contribution of the weak links cannot be disregarded at where the average number of breaks is less than 1 per 1000 monomer units, but the rapid initial drop in molecular weight in the first stage of the degradation cannot be explained in terms of only the scission of the weak links. Some other explanation must be applied to account for the rapid initial drop in molecular weidht of the first stage which causes the intercept in *Figure 5*.

Figure 6 shows the relationship between the percentage decrease in molecular weight and volatilization. The volatilization was calculated from the following equations[10].

$$k = 2.1\ \exp(25)\ \exp(-37000/RT)$$

$$-\ln(1-x) = kt \qquad x\text{: volatilization (\%)}$$

Here, when the volatilization was greater than ~20%, it was observed that the decrease in the molecular weight centred at one curve. In the range below about 10% volatilization, the decrease in molecular weight proceeds rather than the formation of volatile groups at higher temperatures. The large proportion of volatile groups formed from the degraded polystyrene were of oligomer size. It was considered that the process of decrease in molecular weight of original polystyrene to this oligomer was the first stage of the degradation. Volatile groups were confined to a small quantity in the first stage, as can be seen from *Figure 6*. Furthermore, the volatilization was less than ~3% of the weight of polystyrene at the intercepts of all the temperatures in *Figure 5*. Therefore, it was considered that the formation of volatile groups is negligible and only the scission of main chains takes place in the first stage of the degradation.

As described above, the main chains were degraded randomly with the small quantitative volatile groups in the first stage of the degradation. We evaluated the decrease in molecular weight in the first stage of the degradation by using the following equation[11].

$$1/D_{pt} - 1/D_{po} = s/D_{po} = k_s t - 2k_{ri} t$$

Here, D_{po} and D_{pt} are the number average degrees of polymerization at zero and time t, respectively. 'k_s' is the first-order rate constant for bond scission and 'k_{ri}' is the

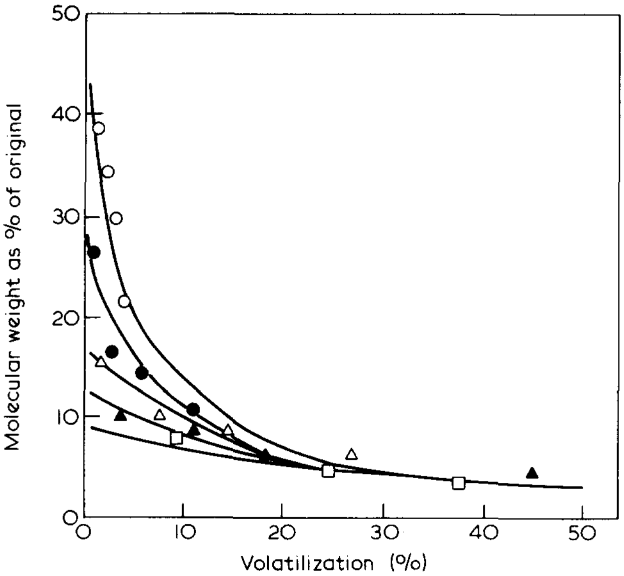

Figure 6 Relationship between decrease in molecular weight and volatilization: (○), 310°C; (●), 330°C; (△), 350°C; (▲), 370°C; (□), 390°C

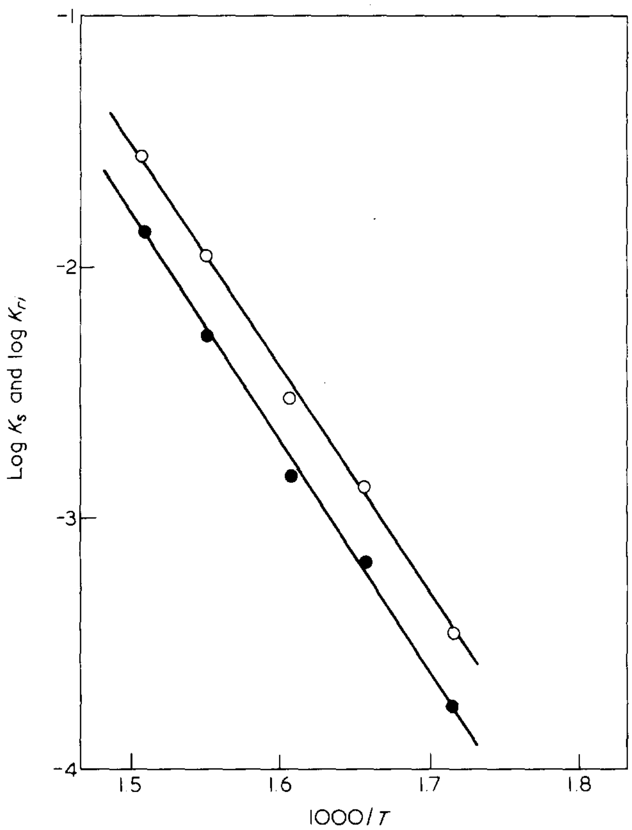

Figure 7 Plots of log k_s and log k_{ri} against $1/T$ for the decrease in molecular weight of the first stage of the degradation: (○), k_s; (●), k_{ri}

rate constant for random initiation. 't' was the reaction time which was required to decrease the molecular weight of the original polystyrene to that of the degraded polystyrene value at the intercept in *Figure 5*. The plots of log k_s and log k_{ri} against $1/T$ are shown in *Figure 7*. Consequently, the following results were obtained respectively.

$$\log k_s = 12.0 - 41300/RT$$
$$\log k_{ri} = 11.7 - 41300/RT$$

In these results, the energies of activation obtained were identical to each other, but those frequency factors were different. It is considered that the energy of activation for bond scission obtained in the present work is roughly equal to that for the random initiation reaction. Thus, rupture of the main chains takes place randomly and its energy of activation is 41.3 kcal mol^{-1} in the first stage of the degradation.

Scission of the main chains in the first stage

The bond dissociation energy of normal C–C bonds in the main chains of polystyrene was about 60 kcal mol^{-1}.[9] The energy of activation obtained in the present work for the first stage of the degradation was 41.3 kcal mol^{-1}. About 20 kcal mol^{-1} difference in the energy of activation between these results was observed. Thus, it was concluded that the direct scission of normal C–C bonds in the main chains did not take place in the first stage of the degradation. However, since the intercept value in *Figure 5* was not the same reaction temperature value, it is necessary to consider not only the scission of weak links, but also the main chain scission with other factors excepting weak links in the first stage of the degradation. It is suggested that the other factors may be more important than the scission of weak links in the main chain.

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