

A Kinetic Model for Polystyrene (PS) Pyrolysis Reaction

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(Received 4 June 2002 • accepted 11 September 2002)

Abstract—A mathematical model for the pyrolysis reaction of polystyrene (PS) in a semi-batch reactor has been presented. The thermal degradation of PS was flexibly modeled by a combination of random and specific chain-end scissions. Numerical simulation was used to investigate the effect of operating conditions on the PS products spectrum, the results of which were validated by the experimental data. It was found that as the reaction temperature increased (decreased), the monomer fraction in the products became lower (higher) while the trimer higher (lower). No significant variation in the product composition was, however, observed while constant temperature was maintained. These results indicate the reaction temperature is an effective manipulated variable for the control of products composition of PS pyrolysis. The calculation of the optimum temperature trajectories through the optimization study can thus be of interest for achieving productivity enhancement in plastics pyrolysis processes.

Key words: Polystyrene (PS), Pyrolysis, Temperature Effect, Population Balances, Batch Reactor

INTRODUCTION

As the consumption of polymeric materials increases around the world every year, the plastic wastes produced therefrom have created serious environmental problems. To date, most of these plastic wastes have been dumped or incinerated together with other household wastes. These usual disposal options will, however, be forbidden in the near future due to the disadvantages they entail, say, the deficiency of landfill site or the air pollution by toxic gases generated from incineration processes. Under this circumstance, special attention is being paid to pyrolysis as one of the most promising alternatives to the landfill and/or incineration for recycling of plastic wastes. Pyrolysis can convert wasted plastics into valuable raw materials or fuels without generating toxic gaseous emissions from the process itself unlike the incineration [Kaminsky, 1992].

Unfortunately, commercial application of plastics pyrolysis is being hindered not only by the lack of sufficient economic incentives, but also by various operational difficulties such as low heat transfer coefficient and poor mixing [Madras et al., 1997]. Conventional empirical attempts based on the trial-and-error proved to be unsuccessful in finding an effective solution for those problems. The application of the process systems engineering techniques is thus necessitated, considering the immature stage of pyrolysis technology for recycling of polymeric materials. A reliable mathematical model for the pyrolysis reaction of plastics would undoubtedly play a key role in doing so.

This article is concerned with development of a mathematical model for the polystyrene (PS) pyrolysis reaction occurring in a

semi-batch reactor. In our foregoing paper, a simple kinetic model was utilized to find the optimal temperatures minimizing the reaction time of PS pyrolysis where only styrene monomer was taken into account as the pyrolysis products, neglecting the generation of dimer, trimer or possible heavier products [Song and Hyun, 1999]. In general such a postulate cannot stand, except for the special case that a pyrolysis reactor is operated at significantly high pressures [Wang et al., 1995; Madras et al., 1997]. We presented a more general and useful kinetic model capable of describing the products spectrum up to trimer. The truncation after trimer could be justified by the experimental observation that the fraction of heavier oligomers was negligibly small over the operating range conditions considered in the present study. A good agreement between the experimental data and the model simulations has been made, validating the performance of the developed model.

REACTION MODEL

The thermal degradation of PS is different from that of polyethylene (PE) or polypropylene (PP) in that the former preferably produces its monomer as the main product [Kim et al., 1999], while no noticeable preference to a specific product is reported in the pyrolysis of the latter materials. The pyrolysis reaction of styrene-based polymers can be modeled by the chain-end scission only [Madras et al., 1996] or more flexibly by a combination of random and specific degradation in the presence of weak links [Madras et al., 1997; Cha et al., 2002]. Any C-C bond along the polymer backbone can be broken by binary random scission, while the specific positions at the end of polymer with relatively low bond energy are easily attacked by chain-end scission, releasing monomer, dimer, trimer, etc. Combining both reaction paths, we assume the degradation of PS polymer to occur by random scission



and simultaneously by specific degradations

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†This paper is dedicated to Professor Dong Sup Doh on the occasion of his retirement from Korea University.



where $A(x)$ and $A(x')$ are defined as the polymers with molecular weight x and x' , respectively, whereas $A(x_j)$ is a specific product with molecular weight x_j that is detached from a polymer molecule, and k_r and k_j represent the reaction rate constants for the random and the specific degradations, the temperature dependence of which is given as follows:

$$k_r = k_{r0} \exp(-E_r/RT) \quad (3)$$

$$k_j = k_{j0} \exp(-E_j/RT) \quad (4)$$

Our concern is confined to the pyrolysis products up to trimer based on the experimental observations made in our laboratory reactor. Under the operating conditions applied to the reactor in this study, the pyrolysis products are mostly composed of monomer, dimer, and trimer, while a trace of heavier materials over trimer is recovered. Thus, only the light oligomers from monomer to trimer are included in our model as the specific products, which are distinguished by the subscripts 1, 2 and 3, respectively, in Eqs. (2) and (4).

Continuous population balance for polymer degradation reaction is set up, the PS polymer being considered to be a continuous mixture of different sized molecules with molecular weight x [Wang et al., 1995], i.e.,

$$\frac{df(x, t)}{dt} = 2k_r \int_x^\infty (1/x') f(x', t) dx' - k_r f(x, t) + \sum_{j=1}^3 \{k_j f(x, t) - k_j \int_x^\infty \delta[x - (x' - x_j)] f(x', t) dx'\} \quad (5)$$

For the specific products,

$$\frac{dg_j(x_j, t)}{dt} = k_j \int_x^\infty \delta(x - x_j) f(x', t) dx' \quad (j = 1, 2, 3) \quad (6)$$

Here, $f(x, t)$ and $g_j(x_j, t)$ are the molar density functions for the polymers and the specific products, respectively, and δ is the Dirac delta function. It is implicitly assumed that both random and specific degradations are irreversible, first-order reactions and the reaction rates are independent of the molecular weight. We can conveniently calculate all the key variables of interest such as the product composition, molecular weight distribution of the polymer reactants, etc., by introducing a straightforward moment method instead of directly solving the above cumbersome integro-differential equations. Moment equations can be derived by applying moment operations, i.e., integrating from zero to infinity after multiplying x^n to the Eqs. (5) and (6). The resulting n th moment equations for the polymers and the specific products, i.e., $f^{(n)}(x, t)$ and $g_j^{(n)}(x_j, t)$, are obtained as below:

$$\frac{df^{(n)}(t)}{dt} = (2k_r Z_n - k_r - k_1 - k_2 - k_3) f^{(n)}(t) + \sum_{k=0}^n \binom{n}{k} f^{(n-k)}(t) (-1)^k [k_1 x_1^k + k_2 x_2^k + k_3 x_3^k] \quad (7)$$

$$\frac{dg_j^{(n)}(t)}{dt} = k_j x_j^n f^{(0)}(t) \quad (8)$$

where the superscripts on f and g indicate the order of moments, $\binom{n}{k}$ is the binomial coefficient and Z_n is equal to 1, 1/2 and 1/3 for

$n=0, 1$, and 2, respectively. The moment functions $f^{(n)}(t)$ and $g_j^{(n)}(t)$ are defined as the integrals of the $f(x, t)$ and $g_j(x, t)$ over the molecular weight, x , i.e.,

$$f^{(n)}(t) = \int_0^\infty x^n f(x, t) dx \quad (9)$$

$$g_j^{(n)}(t) = \int_0^\infty x^n g_j(x, t) dx \quad (10)$$

Under the isothermal condition, the Eqs. (7) and (8) become a set of first order linear differential equations with k_r and k_j constant, allowing an analytic solution. However, for the general case where the reaction temperature is varying with time as in the present paper, only a numerical solution is possible.

EXPERIMENT

The experiments for the PS thermal degradation have been carried out in a semi-batch reactor for the validation of the model developed in the foregoing section. The reactor is initially charged with an inert gas (nitrogen, here) to prevent any undesirable combustion reactions from occurring. A schematic of the pyrolysis process set up in our laboratory is shown in Fig. 1, where a monodisperse PS polymer sample (HI425E, Kumho Petrochemical Co., Ltd.) is adopted as the reactants. Under the atmospheric pressure, the PS pyrolysis experiments were undertaken along the three different temperature trajectories. The reaction temperature was increased at the rate of 5 °C/min starting from the room temperature (i.e., 25 °C) until reaching the prescribed temperatures, 360 °C, 375 °C or 390 °C, after which the constant temperature was maintained (Fig. 2). Temperature control was made within the range of ± 1 °C by using a pro-

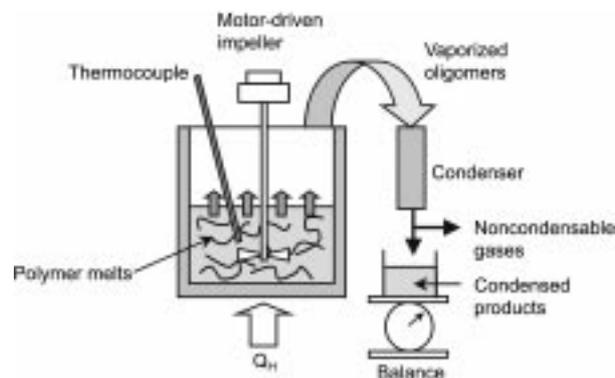


Fig. 1. A schematic diagram of PS pyrolysis processes.

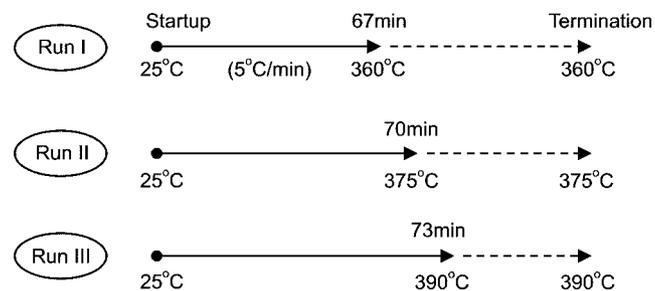


Fig. 2. Three different temperature trajectories imposed on the PS pyrolysis reactor.

grammable PID controller. As the degradation reactions begin, low molecular weight materials evaporate, emitting at the top of the reactor. The vaporized materials are liquefied through the condenser to be collected in the holder on the balance. The fraction of noncondensable volatiles was assumed to be negligibly small under the present operating temperatures below 400 °C. The weight of the condensed products was being monitored reading the balance, while the composition of the products was analyzed by using gas chromatography (M600D, YoungLin Instrument Co., Ltd.) based on the ASTM D2887.

RESULTS AND DISCUSSION

Fig. 3 shows the increasing yield of the PS pyrolysis products with time following the three different temperature trajectories explained earlier. These results indicate that the thermal degradation of PS is triggered when the reaction temperature arrives at around 360 °C. The yield curves become more sharpened as the higher temperature is imposed. The products yield achieved in our pyrolysis reactor is 0.97 at best as shown Fig. 3. The undesirable coking reaction explains this incomplete conversion.

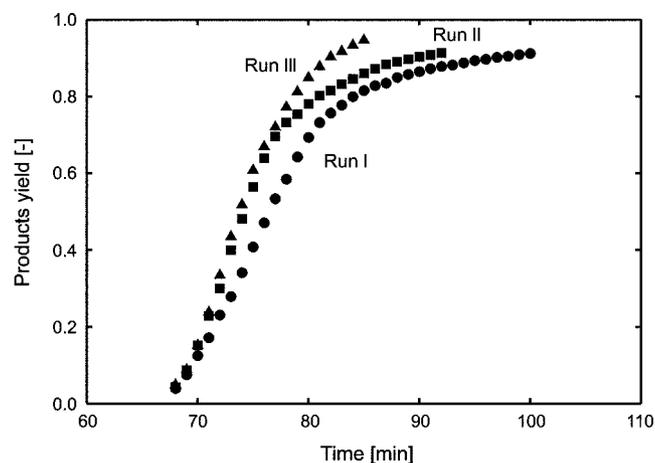


Fig. 3. The yield of PS pyrolysis products with time along the three different temperature trajectories set in Fig. 2.

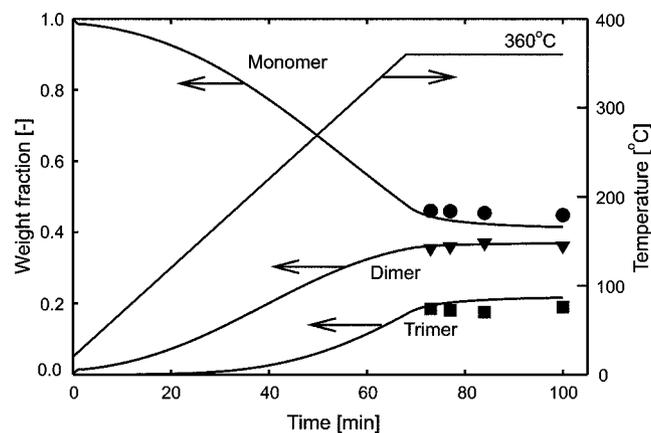


Fig. 4. The composition change of the PS pyrolysis products with time.

Fig. 4 shows the change of the products composition along the temperature trajectory chosen in the “Run I” of Fig. 2. A good agreement was obtained between the numerical simulations (solid lines) and the experimental data (symbols), proving a satisfactory performance of the developed model as shown in Figs. 4 and 5. The simulation results were obtained by solving the moment equations derived in the foregoing section. Much valuable information on the reactants and the products of PS pyrolysis such as the number-average molecular weight, polydispersity (PD) can be readily obtained from their first three moments from zeroth to second. As seen in

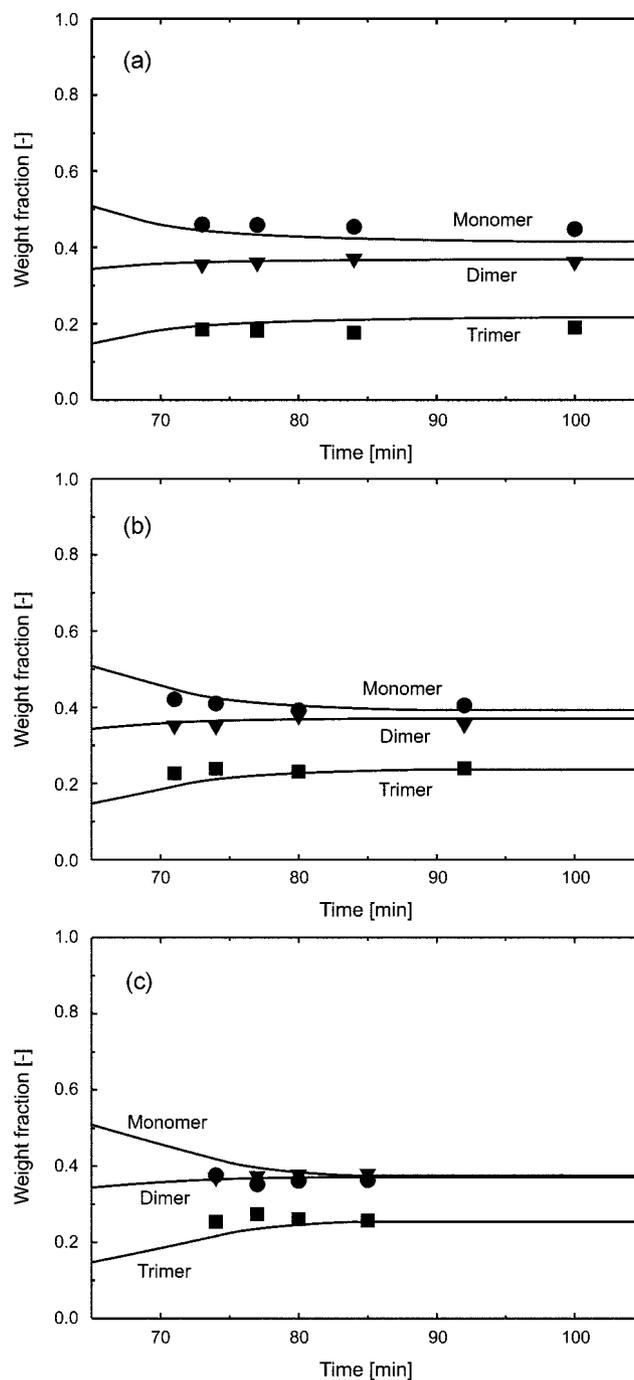


Fig. 5. Comparison of the simulation results with the experimental data: (a) Run I, (b) Run II, and (c) Run III.

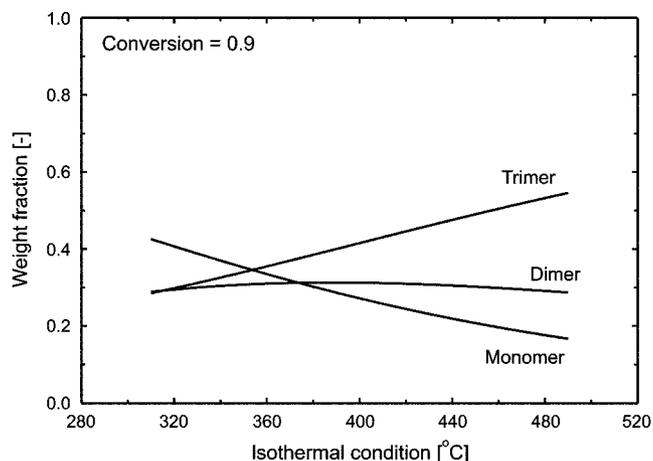


Fig. 6. The change of the products composition at the conversion of 0.9 with temperature.

Fig. 4, the products exhibit a dramatic variation in their composition during the period the temperature is increasing at the constant rate 5 °C/min. The monomer fraction, which is initially around 1.0, is substantially reduced as the temperature becomes higher, whereas the weight fraction of the dimer or trimer, which is negligibly small at the start-up, gradually grows with time. Interestingly, the change of the product spectrum is not considerable after the reaction temperature becomes constant, i.e., after 67 min in Fig. 4. Such observations give an important indication that the product composition in PS pyrolysis reaction is not affected significantly by the time elapse itself, but a strong function of the reaction temperature. Qualitatively the same results can be obtained for other temperature trajectories.

The dependence of the product composition on the reaction temperature is more clearly represented in Fig. 6. This figure shows the change of the product spectrum in PS pyrolysis reaction at the conversion of 0.9 when different isothermal conditions are imposed. As expected, the weight fraction of monomer is decreased as the reaction temperature becomes higher, but trimer exhibits the reverse trend. For the dimer, unlike the monomer and trimer, the change of its weight fraction with temperature is found to be relatively small over the temperature range between 300 °C and 500 °C considered here. It should be noted that the results in Fig. 6 cannot be compared with those in Fig. 5 because the temperature trajectories followed in the two figures are not identical each other. It has been assumed in Fig. 6 that the constant temperature is realized immediately from the start-up, while there exists a time delay before the reactor arrives at the isothermal line in Fig. 5 because it starts from the room temperature. This fact reasonably gives an answer to the question why, for example, the trimer fraction is the highest among the products at 390 °C in Fig. 6, but not in Fig. 5(c).

The above results indicate that the allowable lowest temperature is favorable to increase the economic value of the PS pyrolysis products by maximizing the monomer fraction. However, that is hindered by the fact that reaction time is exponentially prolonged as the operating temperature drops as shown in Fig. 7, resulting in a severe productivity reduction. Thus, optimal temperature trajectories meeting both conflicting demands should be sought through a systematic optimization study based on a nonlinear programming.

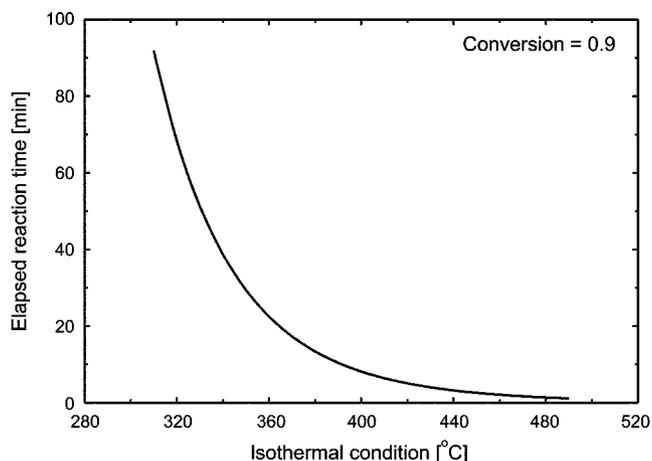


Fig. 7. The change of the elapsed reaction time at the conversion of 0.9 with temperature.

As already emphasized, the development of a reliable mathematical model is essential for obtaining meaningful results applicable to the real process.

CONCLUDING REMARKS

The PS thermal degradation reaction in a semi-batch reactor at the atmospheric pressure has been modeled by a combination of random and specific scissions based on population balances. From the comparison with the experimental data, we could validate the performance of the developed model capable of estimating the composition variation of the pyrolysis products with operating conditions. Further efforts are being made to incorporate the physical changes (e.g., evaporation of pyrolysis products during the reaction) into the reactor model in order to enhance its simulation capability. A more advanced modeling concept of PS pyrolysis including both key physical and chemical aspects will be reported elsewhere in the future.

ACKNOWLEDGEMENT

The authors are grateful for being supported by the research grants from the Korea Energy Management Corporation (KEMCO). This research has also been supported in part by the Korea Science and Engineering Foundation (KOSEF) through the Applied Rheology Center (ARC), an official KOSEF-created engineering research center (ERC) at Korea University, Seoul, Korea.

NOMENCLATURE

- $A(x)$: polymers with molecular weight x
- E_j : activation energy for the j th specific degradation ($j=1, 2, 3$) [kcal/g-mol]
- E_r : activation energy for the random degradation [kcal/g-mol]
- $f^{(n)}(t)$: n th order molecular weight moment of f
- $f(x, t)$: molar density function for polymers [mol/L]
- $g_j^{(n)}(t)$: n th order molecular weight moment of g_j ($j=1, 2, 3$)
- $g_j(x, t)$: molar density function for specific products [mol/L] ($j=1, 2, 3$)

- k_j : reaction rate constant for the j th specific degradation ($j=1, 2, 3$) [hr^{-1}]
 k_r : reaction rate constant for the random degradation [hr^{-1}]
 t : reaction time [hr]
 x : molecular weight of polymers [g/g-mol]
 x_j : molecular weight of the j th specific product ($j=1, 2, 3$) [g/g-mol]
 Z_n : constant in Eq. (7)

Greek Letter

- δ : Dirac delta function

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