A simulation of thermal characteristic parameters with an inverse “S” type curve *

CHANG Mian (常 棉), YU Jiayou (余加佑), WANG Shaojun (王少君),
YANG Liping (杨丽萍), YANG Yi (杨 毅), CAI Shihao (蔡士豪),
SHI Shouheng (石守恒), WANG Yan (王 岩),
(Dalian Institute of Light Industry, Dalian 116001, China)
and P. W. Zhu
(Department of Physical Chemistry, University of Sydney, NSW 2006, Australia)

Received March 20, 1997

Abstract A synthetical equation is proposed to characterize the essential features of the inverse “S” type curve on the basis of summing-up simulation approach of “S” type curve. The two physical variables in the model obtained are discussed and the detailed method used to determine the parameters is given. The model is then presented to describe the crystallization of poly(carylether ether ketone) (PEEK) and thermal decomposition of poly(amide-imide) (PAI) respectively. It is found that some thermal characteristic parameters can be well estimated from the model simulated in computer.

Keywords: polymerization, poly(carylether ether ketone) (PEEK), poly(amide-imide) (PAI), crystallinity.

Although the mechanisms underlying macro- or micro-scopic processes are complicated and vary from one system to another, many physical variables operating in these processes, for example, kinetics of polymerization\cite{1,2} and catalysis mechanism of enzyme\cite{3,4}, appear an universal feature, i.e. an approximate “S” shape curve. A simulation of such a curve can provide useful information on their mechanisms. Despite the fact that some progress has been made toward understanding the mechanisms from simulation of the “S” type curve, the simulation of the physical variables with an inverse “S” type curve, however, has not yet been thoroughly elucidated except for a previous study of the polymer rheology\cite{4}.

In this paper, a synthetical equation is proposed to characterize the essential features of the inverse “S” type curve on the basis of summing-up simulation approach of “S” type curve. The two physical variables in the model obtained are discussed and the method used to determine the parameters is given in detail. The model is then used to describe the crystallization of poly(carylether ether ketone) (PEEK) and thermal decomposition of poly(amide-imide) (PAI) respectively. It is found that some thermal characteristic parameters can be well estimated from the model simulated in computer.

1 Theoretical method

Simulation theory is based on the development of practical knowledge, theoretical research and computing technology. In actual conditions, the influencing factors of a chemical reaction are very complex. Besides factors of thermodynamics and kinetics, various physical changes also
affect the result of a chemical reaction. Therefore, chemical reactions and influencing factors should be studied together to get the best choice of the process.

Physical variables in a lot of chemical relationships are usually known to follow a normal distribution. Such a distribution is usually a Gaussian one. It can be seen, however, that the physical variables in some systems can only be described by a pseudo-normal distribution. In such cases, the simulation based on Guassian distribution will be wrong, and therefore impractical. Accordingly, on the basis of the previous paper\(^{[4]}\), the synthetical equation of polymerization with an inverse “S” type curve is proposed as follows:

\[
D = \{a + b \cdot \exp[- \theta(T) \cdot T^n(T)]\}^m, \tag{1}
\]

where \(a, b \) and \(m \) are constants; \(\theta(T)\) and \(n(T)\) are correlating functions. In eq. (1), variables \(D\) and \(T\) are assumed to follow a pseudo-normal distribution in a process. If some parameters of functions in eq. (1) are fixed, all kinds of correlation equations can be obtained.

(i) If \(a = 1, b = -1, \theta(T) = k = \) constant of kinetical rate, \(m = 1, n(T) = n = \) Avrami exponent; and let \(D = X_c(t)/X_c(\infty) = \) relative crystallinity, \(T = t = \) time, then eq. (1) becomes Avrami’s equation\(^{[5]}\), i.e.,

\[
D = X_c(t)/X_c(\infty) = 1 - \exp(k \cdot t^n). \tag{2}
\]

(ii) If \(a, b = \) constant, \(\theta(T) = \theta = \) constant, \(n(T) = 1, m = -1, \) we have

\[
D = \frac{X_c(t)}{X_c(\infty)} = \frac{1}{(a + b \cdot e^{-\theta t})}, \quad \begin{cases} b > 0, \text{approximately “S” type}^{[1,2]}, \\ b < 0, \text{inverse “S” type}^{[3,4]} \end{cases} \tag{3}
\]

(iii) If \(\theta(T) = 1, n(T) = n = \) constant, others are the same as mentioned above in (ii), we have

\[
D = \frac{1}{[a + b \exp(- T^n)]}. \tag{5}
\]

(iv) If \(a, b = \) constant, \(\theta(T) = \theta = \) constant, \(n(T) = a_1 T + b_1, \) where \(a_1\) and \(b_1\) are constants, \(m = 1,\) then we have

\[
D = a + b \exp[- \theta T^{(a_1 T + b_1)}]. \tag{6}
\]

Equation (6) characterizes the inverse “S” type distribution.

2 Determination of characteristic parameters

Let objective function be as follows:

\[
\Gamma(X) = \| D_k(X) \|^2, \tag{7}
\]

where \(X = (x_1, x_2, x_3)^T, k = 1, 2, \ldots, m; m = \) experimental point number.

The application of the secondary Taylor’s expansion to the objective function gives

\[
\Gamma(x) = \Gamma(X_0) + (\Delta X)^T \cdot \nabla \Gamma(X_0) + \frac{1}{2} (\Delta X)^T \cdot \nabla^2 \Gamma(X_0) \cdot \Delta X, \tag{8}
\]

where \(X_0\) is an initial value, \(\nabla \Gamma(X_0) = A^T D(X),\)

\[
A = [a_{kj}] = \frac{\partial D_k(X)}{\partial X_j}, \quad j = 1, 2, 3;
\]