Journal of Thermal Analysis, Vol. 52 (1998) 765–772

A MODIFIED METHOD FOR T-CR-T DIAGRAM CONSTRUCTION
Application to polyethylene glycol

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Abstract

The analysis of DSC experimental data from solidification is improved, thanks to a modified isoconversional method. The validity of the proposed method is tested for a polyethylene glycol with a mean molecular weight of 6000. The temperature-cooling rate-transformation diagrams reveal good agreement between the experimental and calculated data.

Keywords: DSC, isoconversional method, polyethylene glycol, T-CR-T diagrams

Introduction

Several techniques have been utilized to investigate the kinetics of crystallization processes. The literature [1–5] demonstrates that thermoanalytical techniques (TA), such as differential thermal analysis (DTA) and differential scanning calorimetry (DSC), are the most often applied. As a general rule, experiments are performed under isothermal or continuous heating rate conditions. For this reason, several models [6–12] have been developed to reproduce experimental data under such conditions, and several kinetic analysis methods have been proposed to correlate the experimental data with the mathematical models and to test their validity and applicability [13–19]. Once a reliable model has been determined, one can construct time-temperature transformation (T-T-T) and temperature-heating rate-transformation (T-HR-T) diagrams. Such diagrams provide a global description of the crystallization kinetics.

Quite surprisingly, the number of publications devoted to the kinetic analysis of solidification from the melt is relatively low. This situation may be attributed to the lack of theoretical models describing the solidification kinetics under continuous cooling conditions.

This has led us to work in this direction. In the present report, we present a modified isoconversional method [15–19] to analyse TA experimental data ob-

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1418–2874/98/ $ 5.00

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Kluwer Academic Publishers, Dordrecht

tained under continuous cooling conditions. The method was applied to the study of the solidification process of a polyethylene glycol with a mean molecular weight of 6000 (PEG 6000). The experimental and theoretical results are summarized in a temperature-cooling rate-transformation (T-CR-T) diagram.

Kinetic study

The transformations of processes studied by TA techniques are often governed by the following differential equation:

$$\frac{d\alpha}{dt}=k(T)f(\alpha) \tag{1}$$

where α is the degree of conversion, $d\alpha/dt$ is the rate of conversion, $k(T)$ is the rate constant and $f(\alpha)$ is the function describing the kinetic model. Within the temperature range where crystallization can be investigated by TA, it may be assumed that crystallization is promoted by the pre-existing nuclei. The rate constant can therefore be described by the Arrhenius equation.

This approach cannot be applied to solidification from the isotropic melt. The Arrhenius equation expresses a transformation rate increase as a function of temperature, while in solidification processes the rate behaves reversibly. The reason is that in this case the process is driven not by nucleus growth, but by nucleation. Since nuclei do not exist, their formation must be described first. Hence, a certain amount of undercooling, $\Delta T=T_f-T$, where T_f is the melting temperature, is necessary to induce solidification [20]. The driving force for nucleation is the Gibbs energy difference (ΔG) between the liquid and the crystal. At low undercooling, ΔG is proportional to ΔT. According to these assumptions, the rate constant can be approximated to [21]

$$k(T)=Ae^{-(B/T\Delta T^2)} \tag{2}$$

where A displays a smooth dependence on temperature with respect to the exponential factor, and B is a constant proportional to $\sigma^3/\Delta S_f^2$, where σ is the interface energy between the liquid and the nucleus and ΔS_f is the melting entropy.

Kinetic analysis

The experiments were carried out in Mettler DSC30 equipment. The instrument was calibrated for enthalpy and temperature by using indium, lead and zinc as standards. Two types of experiments were performed: constant heating rate and constant cooling rate measurements. Constant heating rate experiments were performed at 20 K min^{-1} up to the liquid state. Constant cooling rate experiments were performed from the (assumed) isotropic melt state at rates ranging from 10 to 65 K min^{-1}.

The main objective of kinetic analysis is to find both a reliable kinetic model and the parameters involved in the rate constant. The isoconversional method [15–19] was applied to find the activation energy for a given degree of conversion (α). Here, it is adapted to evaluate the constant B in the case of solidification from an isotropic melt.

Isoconversional method adaptation

A basic assumption in the DSC technique is that the heat flow, Φ, is proportional to the conversion rate:

$$\Phi = \frac{\mathrm{d}\alpha}{\mathrm{d}t}\Delta H \tag{3}$$

where ΔH is the enthalpy of the crystallization process. On substitution into Eq. (3) of Eqs (2) and (1), the following kinetic equation is obtained:

$$\Phi = \Delta Hk(T)f(\alpha) = \Delta HAe^{-(B/T\Delta T^2)}f(\alpha) \tag{4}$$

Calculation of the constant B is based on a multiple-scan method that requires several measurements at different cooling rates. Taking logarithms from Eq. (4) yields

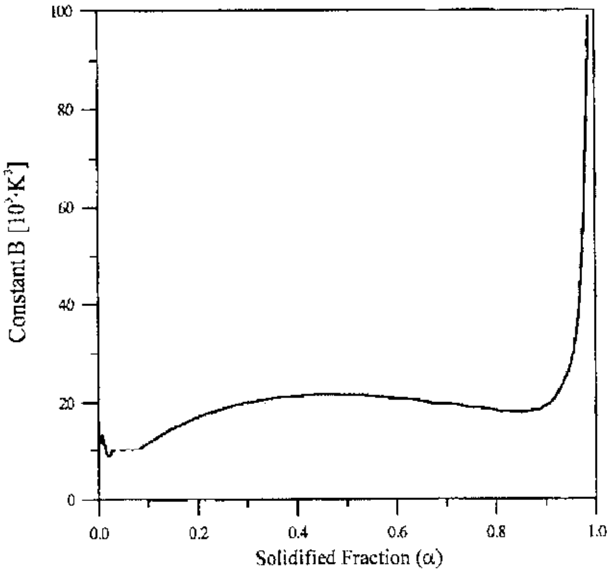

Fig. 1 Constant B evaluated by the isoconversional method *vs.* transformed fraction α for PEG 6000. The values of B were obtained from experiments at cooling rates of 10, 20, 40, 50, 55, 60 and 65 K min^{-1}

$$\ln\frac{\Phi}{\Delta H} = \ln[Af(\alpha)] - \frac{B}{T\Delta T^2} \qquad (5)$$

The slope of $\ln(\Phi/\Delta H)$ *vs.* $(1/T\Delta T^2)$ provides the constant B for a given α. If we repeat the procedure for different values of α, the invariance of B with respect to α (which is a basic assumption for the validity of the model) is checked in a simple and reliable manner. This operation allows testing of the T_f accuracy at same time. A first estimation of T_f results from previous heating, where samples are completely melted.

Figure 1 depicts constant B evaluated by the isoconversional method for different values of α in the PEG 6000 sample. The dependence of B on α within the range of α 0.2–0.9 is observed to be slight. This confirms the validity of the rate constant model. As usual for low and high α values, Φ tends to zero, which explains the divergence of the results. The values of the melting temperature T_f and the constant B were obtained from the best fitting to the experimental data under a constant cooling rate regime. The values retained are T_f=45.4°C and B=20256 K^3.

Kinetic model determination

The kinetic model and the coefficient A can readily be determined from a knowledge of functions $y(\alpha)$ and $z(\alpha)$, defined by [15–19]:

$$y(\alpha) = \Delta HAf(\alpha) \qquad (6)$$

$$z(\alpha) = \Delta Hf(\alpha)g(\alpha) \qquad (7)$$

where $g(\alpha)$ is defined by

$$g(\alpha) = \int_0^{\alpha}\frac{1}{f(\alpha')}\mathrm{d}\alpha' \qquad (8)$$

Once B and T_f are known, it is possible to evaluate the functions $y(\alpha)$ and $z(\alpha)$ directly from the experimental data:

$$y(\alpha) = \Phi e^{x} \qquad (9)$$

$$z(\alpha) = -\frac{\Phi e^{x}}{\beta}\int_{T_f}^{T} e^{-x'}\mathrm{d}T' \qquad (10)$$

where $x=B/T\Delta T^2$ and β is the cooling rate. Equation (9) was obtained directly from Eq. (4). Equation (10) was obtained by use of Eq. (8) and multiplying by Eq. (9).

The experimental functions $z(\alpha)$ and $y(\alpha)$, divided by $A\Delta H$ and ΔH, respectively, are plotted in Fig. 2 for a cooling rate of 40°C min^{-1} (points). Once we know the α values for which $z(\alpha)$ and $y(\alpha)$ are maximal, we can find the kinetic model which best describes the measured data, and its kinetic parameters [17]. In our case, the most suitable $f(\alpha)$ function corresponds to the autocatalytic two-parameter Šesták-Berggen (SB) model [22]. Table 1 shows the kinetic exponents m and n of the SB model and the coefficient A calculated for the kinetic model proposed at different cooling rates. The experimental DSC (points) and calculated

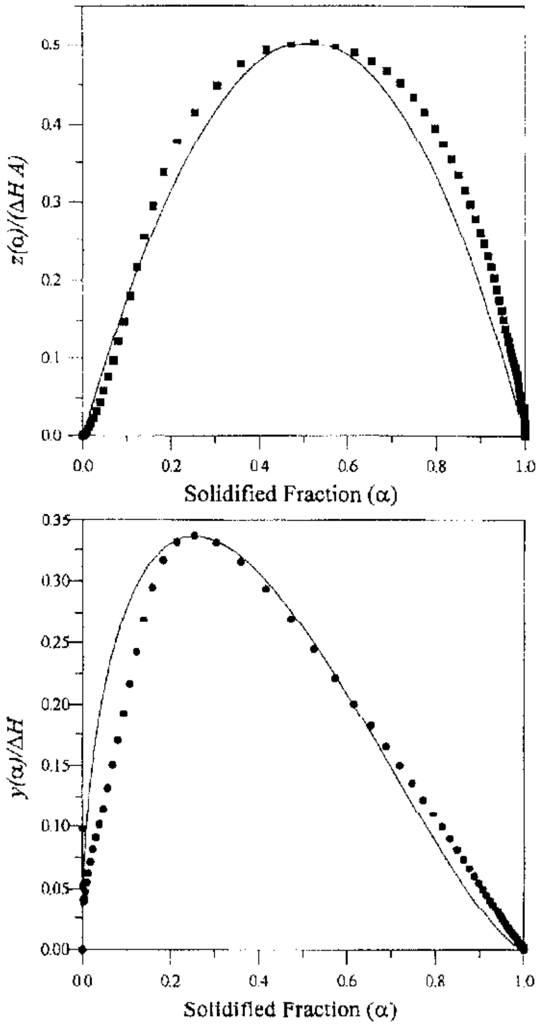

Fig. 2 Dimensionless $z(\alpha)$ and $y(\alpha)$ for a cooling rate of 40 K min^{-1}. Points represen experimental DSC data on PEG 6000. Solid lines are calculated from the SB model with kinetic exponents m=0.49 and n=1.4

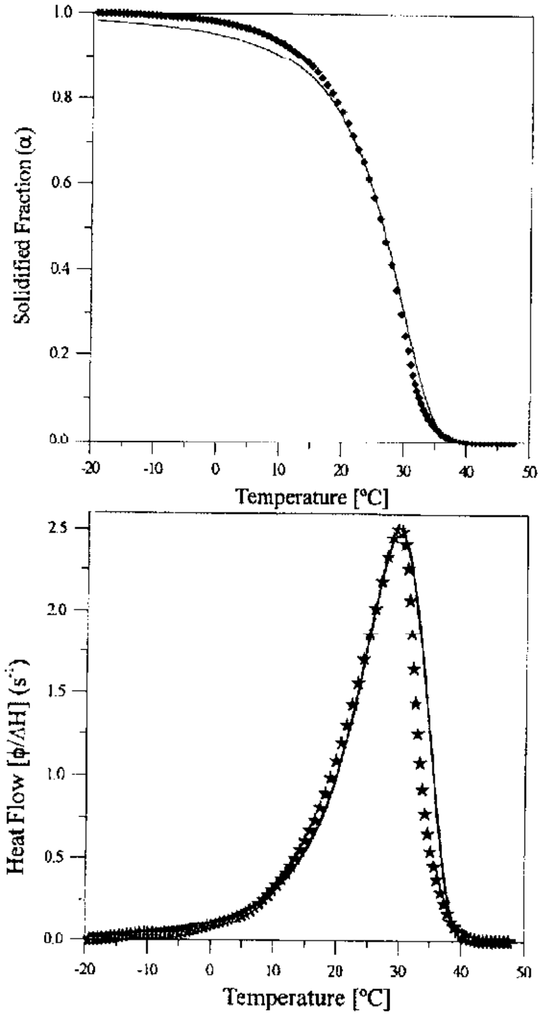

Fig. 3 Solidified fraction *vs.* temperature and heat flow divided by enthalpy *vs.* temperature for a cooling rate of 40 K min^{-1}. Points represent experimental DSC data on PEG 6000. Solid lines are calculated from the SB model with kinetic exponents m=0.49 and n=1.4

(full lines) heat flow and degree of transformation are compared in Fig. 3 for a cooling rate of 40°C min^{-1}. Figures 2 and 3 demonstrate that the two-parameter SB model gives a good description of the solidification process.

Temperature-cooling rate-transformation diagrams

T-CR-T diagrams can be obtained from the kinetic model by use of Eq. (8):

$$g(\alpha) = -\frac{1}{\beta}\int_{T_f}^{T} k(T')\mathrm{d}T' \qquad (11)$$

Figure 4 shows calculated T-CR-T curves (full lines) and experimental DSC data for α=0.1, 0.3, 0.5, 0.7 and 0.9. The chosen kinetic exponents and coeffi-

Table 1 SB kinetic exponents and pre-exponential factor logarithm calculated from experimental data

Cooling rate/K min^{-1}	n	m	$\ln A/1\ \mathrm{min}^{-1}$
10	1.9	0.33	2.3
20	0.9	0.26	2.2
40	1.4	0.49	2.3
50	1.6	0.50	2.3
55	1.4	0.52	2.4
60	1.6	0.54	2.4
65	1.6	0.44	2.2

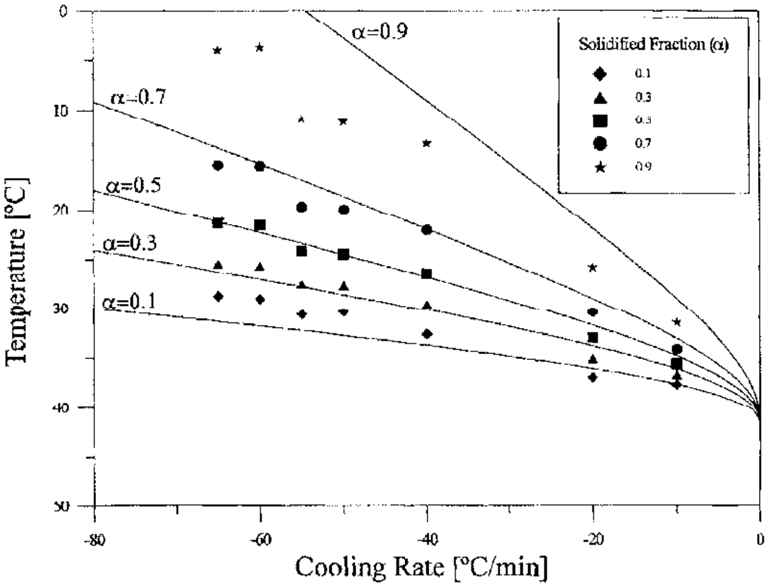

Fig. 4 Calculated T-CR-T curves (solid lines) for the SB model and experimental DSC data (points) for α=0.1, 0.3, 0.5, 0.7 and 0.9. The chosen kinetic exponents and the preexponential term are the averages of the values introduced in Table 1 (m=0.48, n=1.5 and $\ln A$=2.3 min^{-1}). SB kinetic exponents and pre-exponential factor logarithm calculated from experimental data

cient A are the averages of the values introduced in Table 1. As expected for any solidification process, the solidification onset shifts to higher temperatures when the cooling rate decreases. There is good agreement between the experimental data and the calculated T-CR-T curves for the range of α between 0.3 and 0.7 according to the results obtained in the determination of constant B.

Conclusions

The thermodynamics and kinetics of the solidification process of a PEG 6000 were analysed by means of DSC. The kinetic analysis was performed with a modified isoconversional method. Several measurements at different cooling rates were used in the determination of the constant rate parameters.

It has been established that the two-parameter SB model gives a good description of the solidification process.

A T-CR-T diagram was constructed for a wide range of conditions and showed good agreement between the experimental data and the T-CR-T curves obtained by calculation. This verifies the reliability of the method utilized and the validity of the rate constant model description.

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