

# Crystallization and Nematic–Isotropic Transition Activation Energies Measured Using the Kissinger Method

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**ABSTRACT:** The activation energies for crystallization in poly(3-hydroxybutyrate) and for nematic–isotropic transition in liquid–crystalline polyesters have been calculated based on data obtained with a dielectric method and differential scanning calorimetry (DSC), respectively. This study explores the feasibility of using a modified Kissinger method to calculate the activation energies of these transitions. It has been found that the activation energy for crystallization in poly(3-hydroxybutyrate) is 109 kJ/mol. The activation energy for nematic–isotropic transition in the liquid crystals is 487 kJ/mol. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 80: 2535–2537, 2001

**Key words:** crystallization; nematic–isotropic transition; activation energy; differential scanning calorimetry; Kissinger method

## INTRODUCTION

There are a number of methods for measuring the activation energy of a transformation. The common methods include Rutherford backscattering spectrometry<sup>1</sup> and electron spin resonance.<sup>2</sup> One other simpler method is based on measured transformation temperatures at varying heating rates, the Kissinger method.<sup>3</sup> Originally developed in conjunction with differential thermal analysis (DTA), this method is suitable for first-order transformations, one exception of which is the melting process. Because in DTA and the later-developed differential scanning calorimetry (DSC), the surface effect of melting<sup>4,5</sup> cannot be entirely eliminated, the melting process there is not first-order in effect. This leads to the absence of overheating in melting, a well-established phenomenon that is useful in the temperature calibration of DTA/DSC. The temperature calibration of DTA/DSC equipment is usually carried out us-

ing the melting of pure metals with known melting points. If the melting point depended on the heating rate, such calibration would be impossible.

The Kissinger method was modified by Mittemeijer et al.,<sup>6–8</sup> a modification that is used more often than the original. In the present work, this modified method was used to calculate the activation energies of crystallization and nematic–isotropic transition in polymers using data in the literature. The equation used to calculate the activation energy is

$$\ln \frac{T_f^2}{Q} = \frac{E}{RT_f} + \ln \frac{E}{Rk_0} + \ln \beta_f$$

where  $T_f$  is the characteristic temperature for the given process (crystallization or nematic–isotropic transition),  $Q$  is the heating rate,  $E$  is the activation energy,  $R$  is the gas constant, and  $k_0$  and  $\beta_f$  are constants.  $k_0$  is the preexponential factor in the equation describing the overall process.  $\beta_f$  is a constant when  $RT/E \ll 1$ . A value for  $k_0$  can be obtained if  $\beta_f$  is known, implying adop-

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tion of a specific kinetic model. For details of the derivation of the equation, see Mittemeijer et al.<sup>9</sup>

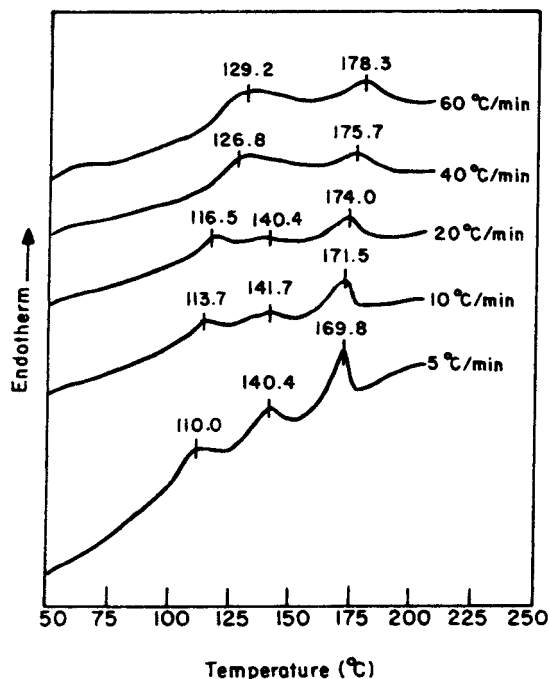
It may be pointed out again that this method is not applicable to melting, which is effectively not a first-order reaction because of the surface phenomenon. Invariably, calorimetry equipment is calibrated using the melting point of standard pure metals, because there is no activation energy (i.e., any overheating). The fact that the melting points of pure metals remain constant at different heating rates should not lead to the conclusion that the activation energy for melting is infinitely large.

## EXPERIMENTAL

Poly(3-hydroxybutyrate) (PHB)<sup>10</sup> and liquid-crystalline polyester (LCPE)<sup>11</sup> were investigated. The PHB was a commercial sample of bacterial origin, supplied by Aldrich (Milwaukee, WI). PHB is a naturally occurring, highly crystalline thermoplastic polymer that is suitable for injection molding and extrusion. In addition, it shows gas barrier properties comparable to those of poly(vinyl chloride) and poly(ethylene terephthalate). The combination of these properties may enable PHB to compete with commodity polymers in the packaging industries, especially in areas where nonbiodegradable plastic items are not allowed because of environmental pollution. A special property of PHB is the formation of large spherulites, which is probably the result of its exceptional purity. For this reason, PHB has been studied as a model of spontaneous polymeric nucleation and crystallization, in that it is free from any catalyst residues that are typically used in the synthesis of polyolefins.

The crystallization kinetics was monitored dielectrically using thin amorphous PHB films, which were obtained by pressing the PHB powder between two copper electrodes at 185°C for 5 min to obtain a condenser, which was also quenched in liquid nitrogen.<sup>10</sup> Dielectric measurement details were given in a previous publication, from which the data were taken for the present analysis.<sup>10</sup>

The LCPE polymer was poly[(phenylsulfonyl)-*p*-phenylene 1,10-decamethylenebis-(4-oxybenzoate)] (PSHQ10), which was synthesized, via polymerization, at the University of Akron.<sup>11</sup> The PSHQ10 was found via gel permeation chromatography to have a weight-average molecular weight of 48,000 relative to polystyrene standards



**Figure 1** Differential scanning calorimeter plots of an as-cast PSHQ10 liquid crystal dried at 80°C for 3 days (courtesy of Han et al.<sup>11</sup>). The first temperature in each curve is the melting temperature and the last is the nematic–isotropic transition temperature.

and a polydispersity of about 2 after several fractionations.

The film preparation procedure for PSHQ10 can be found in a previous publication.<sup>11</sup>

## RESULTS AND DISCUSSION

Two processes were studied: crystallization in PHB and nematic–isotropic transition in LCPE. Calculations were based on transition peak temperatures measured by the dielectric method (for PHB) and DSC (for LCPE), respectively. Figure 1 gives examples of DSC plots. At the heating rate of 5°C/min, three peaks appear:

1. at 110°C, representing the melting point of low-temperature melting crystals;
2. at 140°C, representing the melting point of high-temperature melting crystals; and
3. at 170°C, representing the nematic–isotropic transition temperature.

At higher heating rates (40 and 60°C/min), the intermediate peak does not appear and the low-tem-

**Table I Onset Cold Crystallization Temperature as a Function of Heating Rate and the Activation Energy in Poly(3-hydroxybutyrate)**

Heating Rate (°C/min)	Onset Crystallization Temperature (°C)
0.2	24.0
0.5	30.0
1	31.5
2	38.0
5	46.1
Activation energy (kJ/mol)	109 ± 11
$r^2$	0.97

perature peak becomes much broader. This seems to indicate that a small amount of high-temperature melting crystals is present in the low-temperature melting crystals. This observation suggests that the intermediate peak that appeared at low heating rates originated from recrystallization taking place during the DSC run.<sup>11</sup>

In the case of poly(3-hydroxybutyrate), the temperatures were read from a graphical diagram (Fig. 6 in Saad et al.<sup>10</sup>). In the case of polyesters, numerical data given in the literature<sup>11</sup> were used. Table I gives the result of activation energy of crystallization for the poly(3-hydroxybutyrate) samples, where the error is estimated using the method given in Mendenhall and Beaver.<sup>12</sup> In the Kissinger method, peak temperature instead of onset temperature should strictly be used for a transition process. The use of onset temperature here effectively assumed that the two temperatures follow the same trend of variation with heating rate. The value obtained here compares favorably with the activation energy for cold crystallization of poly( $\beta$ -hydroxybutyrate) by An et al.,<sup>13</sup> using DSC data and the Kissinger model (93 kJ/mol). The similarity is significant, given that the present value is calculated from dielectric data.

For the two PSHQ10 polymers, the nematic-isotropic transition occurs at about 175°C. The activation energy is  $487 \pm 41$  kJ/mol ( $r^2 = 0.98$ ), for the sample dried at 80°C for 3 days.

In a previous study, the activation energy of crystallization for a  $\text{Li}_2\text{O}-\text{Fe}_2\text{O}_3-\text{MnO}_2-\text{CaO}-\text{P}_2\text{O}_5-\text{SiO}_2$  glass was measured to be 312 kJ/mol.<sup>14</sup> In another study, the activation energies of 74–122 kJ/mol were obtained for the clustering and ordering processes in Fe–C martensite.<sup>15</sup> The

method adopted in the present study has also been used to calculate the activation energy for various transformations in other types of materials. In the decomposition of kaolinite and halloysite, this is measured to be about 155 kJ/mol.<sup>3</sup> In intermetallics, the activation energies associated with the metastable-to-stable transformation range from 170 to 737 kJ/mol.<sup>16</sup>

This work demonstrated the suitability of using dielectric measurement and DSC data for measuring activation energy for transitions in polymers, a result that can then be used in theoretical modeling and design of materials-processing parameters.

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