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# Analysis of the nonisothermal crystallization kinetics in three linear aromatic polyester systems

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## Abstract

Melt or cold crystallization kinetics has a strong bearing on morphology and the extent of crystallization, which significantly affects the physical properties of polymeric materials. Nonisothermal crystallization kinetics are often analyzed by the classical Johnson–Mehl–Avrami–Kolmogorov (JMAK) model or one of its variants, even though they are based on an isothermal assumption. As a result, during the nonisothermal (e.g. constant heating or cooling rate) crystallization of polymeric material, different sets of model parameters are required to describe crystallization at different rates, thereby increasing the total number of model parameters. In addition, due to the uncorrelated nature of these model parameters with the cooling or heating rate, accurate modeling at any intermediate condition is not possible. In the present work, these two limitations of the conventional approach have been eliminated by exhibiting the existence of a functional relationship between cooling or heating rate and effective activation energy during nonisothermal melt or cold crystallization in three linear aromatic polyesters. Furthermore, it has been shown that when the JMAK model is used in conjunction with this functional relationship, it is possible to precisely predict the experimental nonisothermal melt or cold crystallization kinetics at any linear cooling or heating rate with a single set of model parameters.

*Keywords:* Linear aromatic polyesters; Differential scanning calorimetry (DSC); Crystallization kinetics; Modeling; Cooling rate; Heating rate

## 1. Introduction

Crystallization kinetics has a strong bearing on morphology of polymeric materials and the extent of crystallization, which significantly affects the physical properties. In a recent work, Supaphol et al. [1] have meticulously studied the nonisothermal (constant cooling rate) crystallization kinetics from melt during cooling in three different types of linear aromatic polyesters, namely, polyethylene terephthalate (PET), polytrimethylene terephthalate (PTT), and polybutylene terephthalate (PBT) by differential scanning calorimetry (DSC). In a subsequent work [2], Supaphol et al. have also studied the nonisothermal (constant heating rate) cold-crystallization kinetics during heating of PTT from the glass state. The experimental crystallization data obtained at seven different cooling or heating rates were subsequently analyzed by a number of available models, including the Avrami, Tobin, Ozawa and Ziabicki analyses. In their work, Supaphol et al. [1,2] observed that the Johnson–Mehl–Avrami–Kolmogorov (JMAK) model provides a very good fit to their experimental data. However, it is important to note that in their work, for each of the seven cooling or heating rates, different JMAK model parameters were required to describe the crystallization kinetics. In addition, as these large numbers of model parameters were uncorrelated with the cooling rate, it is not possible to make predictions at any intermediate cooling or heating rates. This defies two basic objectives of any modeling exercise, i.e. to minimize the number of model parameters and to have prediction capability for any intermediate condition.

In the present work, the above experimental data of the three polyesters are re-analyzed. The difficulties and limitations of using the classical JMAK approach to model

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crystallization kinetics under nonisothermal transformation are illustrated. Furthermore, a modification to the JMAK model is proposed for accurate prediction of nonisothermal (constant cooling or heating rate) crystallization kinetics from polymeric melts with a single set of model parameters. Subsequently, it is shown that the same methodology can also describe the nonisothermal cold crystallization kinetics under a constant heating rate.

## 2. Theoretical background

The Johnson–Mehl–Avrami–Kolmogorov (JMAK) model [3–5] or its variants [6–8] are widely used to phenomenologically describe crystallization kinetics of polymers from melt [1,9–11], glasses [2,12,13] and amorphous alloys [14,15]. The classical JMAK model – which captures the overall transformation kinetics, incorporating both the constituent nucleation and growth processes – provides a very convenient way of describing the overall transformation kinetics, and therefore is commonly used for describing crystallization as well as other phase transformations (e.g. recrystallization of cold worked materials). This is in spite of the several limitations of the JMAK model, for which modifications are often proposed [16] to extend the validity of this model beyond its limits of applicability. The classical JMAK model is given by [17]:

$$X(t) = 1 - \exp(-(Kt)^n) \tag{1}$$

where $X(t)$ is the fraction crystallized after the time $t$, and $n$ the Avrami exponent, which varies from 1.0 to 4.0, depending on the growth dimensionality and nucleation conditions (e.g. constant nucleation rate, and site saturation) [17]. The Avrami exponent is expected to remain constant during a phase transformation, unless the mechanism changes. The temperature ($T$) dependent rate constant is given by the Arrhenius equation:

$$K = K_0 \exp\left(-\frac{Q}{RT}\right) \tag{2}$$

where $K_0$ is the pre-exponent coefficient, $R$ the gas constant, and $Q$ the overall activation energy for phase transformation.

Although the JMAK equation was originally formulated to describe phase transformation under isothermal conditions, using the additivity principle (where nonisothermal profiles are discretized into small isotherms), they are often used to model phase transformations under nonisothermal conditions as well [18,19]. The rule of additivity was first established by Avrami [20] for isokinetic phase transformations, where the nucleation and growth rates are proportional over the temperature range of interest. Although, Cahn [21] had postulated that the rule of additivity can be applied to all the rate independent reactions, in a recent work, Lusk and Jou [22] has shown that the additivity rule can be applied only to reactions which are general isokinetic. The JMAK equation with a constant $n$ is one such general isokinetic relation. Ruitenberg et al. have analyzed the isothermal and nonisothermal transformation kinetics and have correlated the JMAK parameters under these two conditions [23]. Furthermore, they have shown that Kissinger, Ozawa and Marseglia plots are equivalent models in the JMAK framework. In a recent work, Kempen et al. have described and shown the equivalence of the isothermal and nonisothermal transformations via the path variable function [24]. They have inferred that though the JMAK equation in principle holds true for specific and extreme cases of pure site nucleation or pure continuous nucleation, it can also be used for reasonable description of the kinetics, even if a mixture of these mechanisms simultaneously occurs during the reaction. It was also mentioned that using the JMAK equation to study the kinetics of phase transformations, as above, may yield only a phenomenological description, and the kinetic parameters may not necessarily have a physical meaning. Vyazovkin has proposed a model-free isoconversional method, with variable activation energy, to analyze nonisothermal reaction kinetics [25]. In his work, the concept of variable activation energy was justified by the multi-step nature of complex solid-state reactions. Although the concept of variable activation energy and erroneous usage of the “activation energy” term is a debatable topic in the thermo-analytical literature [26,27], it is often used to interpret experimental data [28,29] under nonisothermal conditions.

The basic assumption in the isothermal kinetics-based JMAK model and its variants to model nonisothermal processes is that there is no difference in phase transformation kinetics under isothermal and nonisothermal conditions. Evidently, this quasi-isothermal methodology of evaluating nonisothermal kinetics will result in erroneous predictions if the nonisothermal effects (e.g. heating rate or change in heating rate effects) are present. Recently, it was shown [30,31] that the heating rate and change in heating rate could indeed affect the nonisothermal transformation kinetics, rendering the quasi-isothermal JMAK model ineffective under these conditions. Therefore, it is necessary to modify the widely used JMAK model, so that its applicability is extended for accurate prediction of nonisothermal transformations, while retaining the simplicity of this approach.

## 3. Methodology

The experimental melt crystallization kinetics data for the three linear aromatic polyesters polyethylene terephthalate (PET), polytrimethylene terephthalate (PTT), and polybutylene terephthalate (PBT), as well as cold crystallization kinetics data for PTT were obtained from the original works in the form of a fraction crystallized as a function of temperature at different cooling or heating rates. In all these original works, nonisothermal (constant cooling or heating rate) kinetics data were analyzed using the available quasi-isothermal JMAK model. The limitations of these analyses are illustrated. In the present work, these experimental data are modeled with the classical JMAK approach, by discretizing the nonisothermal profile into small isothermal profiles. The prediction from the classical JMAK approach is also compared with the proposed approach, where an additional functional relationship (derived from experimental data) between effective activation energy and cooling or heating rate is used in the JMAK framework.

## 4. Results

### 4.1. Melt crystallization behavior during nonisothermal cooling

In their work, Supaphol et al. [1] have carefully studied the nonisothermal kinetics of three linear aromatic polyesters, from a fusion temperature of 280 °C for PTT and PBT and 300 °C for PET. The nonisothermal cooling of the melt from fusion temperature to room temperature (30 °C) was carried out at seven different cooling rates between 5 and 50 °C/min. These experimental data were analyzed by the Avrami, Tobin, Ozawa and Friedman methods and very good fits were reported for Avrami model. The model parameters, i.e. Avrami exponents and rate constants from the original work [1] are given in Table 1. Although the coefficient of determination ($R^2$) values are very high, suggesting good model predictions, different Avrami exponents and rate parameters ($K$) were used for different cooling rates, i.e. these parameters were determined by individually fitting the experimental data corresponding to different cooling rates. The two major problems of this procedure are that (a) a large number of model parameters (two per cooling rate) are required to model the crystallization kinetics, (b) as these parameters are un-correlated (Table 1) to the cooling rates, from these available model parameters, predictions cannot be made for any intermediate cooling rates. This defies two basic objectives of any modeling exercise, i.e. to minimize the number of model parameters and to have prediction capability at any intermediate condition.

Analysis of the experimental crystallization data for PTT, PBT and PET with the classical JMAK model and additivity principle showed that experimental data of a single cooling rate can be accurately modeled, which is consistent with the original work. However, when the same model parameters are used for other cooling rates, it does not result in accurate predictions. For example, when crystallization kinetics data for the cooling rate of 15 K min$^{-1}$ were modeled using the classical JMAK approach, reasonably good fits were obtained between experimental data (symbols) and the JMAK model prediction (broken lines) for crystallization of PBT systems (Fig. 1a). The model parameters for this dataset were n as 3.0, $K_0$ as $1.69 \times 10^{-9}$ s$^{-1}$, $Q$ as $-61.6$ kJ mol$^{-1}$. However, as is evident from this figure, with these model parameters, the prediction for other cooling rates becomes poor. Similar observations were made for the PET and PTT systems given in Figs. 2a and 3a, respectively. Hence, it can be concluded that the classical JMAK model cannot be used to get global fits – to describe crystallization kinetics for all the cooling rates with a single set of model parameters – in these three systems, even though good individual fits for each cooling rate can be obtained from different sets of model parameters.

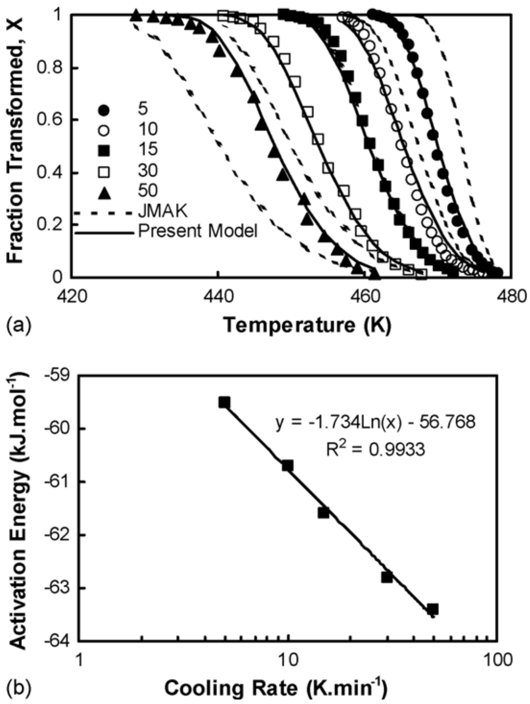

Fig. 1. (a) Comparison of experimental data (symbols) with the classical JMAK model (broken line) using a unique set of model parameters and proposed model (solid line) for melt crystallization in the PBT system. (b) Variation in activation energy with cooling rate for the PBT system.

Table 1
Nonisothermal crystallization kinetic parameters taken from original work [1] for PET, PTT and PBT systems based on Avrami analysis

| $\Phi$ (°C min$^{-1}$) | PET | | PTT | | PBT | |
|---|---|---|---|---|---|---|
| | $n$ | $K$ (min$^{-1}$) | $n$ | $K$ (min$^{-1}$) | $n$ | $K$ (min$^{-1}$) |
| 5 | 3.98 | 0.18 | 3.78 | 0.42 | 3.98 | 0.37 |
| 10 | 2.97 | 0.37 | 4.05 | 0.64 | 6.17 | 0.45 |
| 15 | 3.29 | 0.43 | 3.92 | 0.86 | 4.56 | 0.73 |
| 20 | 2.26 | 0.43 | 3.86 | 1.17 | 3.97 | 1.03 |
| 30 | 2.56 | 0.65 | 3.62 | 1.35 | 4.71 | 1.18 |
| 40 | 2.54 | 0.75 | 3.20 | 1.26 | 3.73 | 1.73 |
| 50 | 2.86 | 0.88 | 3.73 | 1.18 | 3.62 | 2.11 |

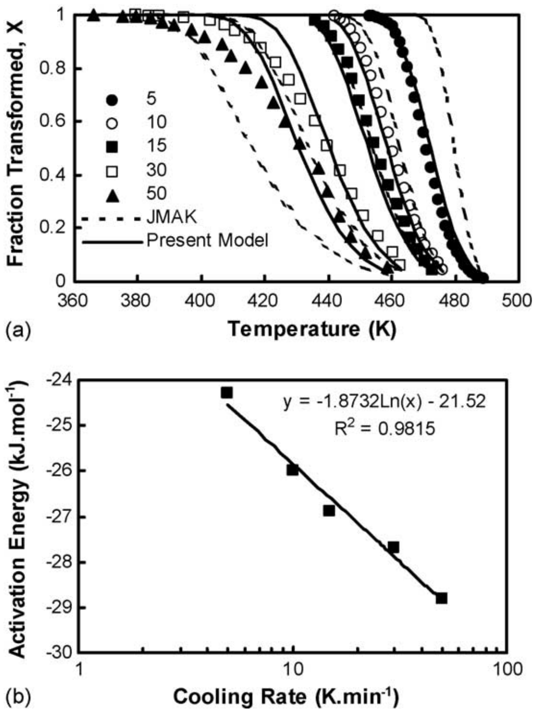

Fig. 2. (a) Comparison of experimental data (symbols) with the classical JMAK model (broken line) using a unique set of model parameters and a proposed model (solid line) for melt crystallization in the PET system. (b) Variation in activation energy with the cooling rate in the PET system.

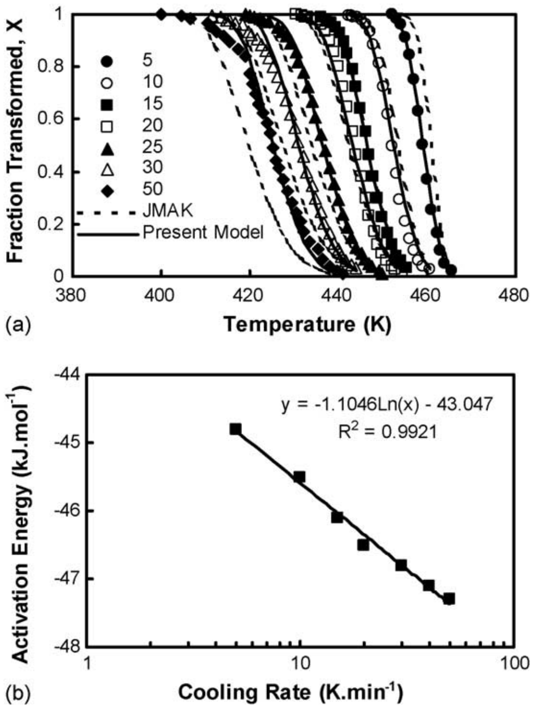

Fig. 3. (a) Comparison of experimental data (symbols) with the classical JMAK model (broken line) using a unique set of model parameters and a proposed model (solid line) for melt crystallization in the PTT system. (b) Variation in activation energy with the cooling rate in the PTT system.

In the present work, in addition to the classical JMAK approach, an alternate methodology was attempted. In the proposed methodology, the effective activation energy was allowed to vary with the cooling rate, so as to find the best fits for each cooling rate, with the same values of other model parameters (pre-exponent constant, $K_0$ and Avrami exponent, $n$). This was done by a global search method, with the objective to obtain a unique exponent and pre-exponent constant, which resulted in minimum error characterized by high value of $R^2$ between model prediction and experimental data. As shown in Figs. 1b, 2b and 3b, in all these three systems, a strong logarithmic relationship (characterized by a high $R^2$) between effective activation energy and cooling rate have emerged from this exercise. This relationship is given as

$$Q = Q_0 + Q_1 \ln(A\phi) \tag{3}$$

where $\phi$ is the rate of change of temperature in K min$^{-1}$ and $Q$ the total effective activation energy having two components, (a) $Q_0$, which is independent of cooling rate and (b) $Q_1 \ln(A\phi)$, which is cooling rate dependent. The constant $A$ in the above equation ($A$ as 1 K$^{-1}$ min) is primarily for the dimensional consistency and as is common practice in Ozawa analysis [1], the negative value for the cooling rate is dropped.

It is interesting to note that with only four model parameters given in Table 2, it is possible to model the crystallization kinetics for the seven different cooling rates in all the three systems. The high value of $R^2$ and close fits between model prediction (solid line) and experimental data (symbols) presented in Figs. 1a, 2a and 3a for the PBT, PET and PTT systems, exhibit the efficacy of this methodology. The drastic reduction in number of parameters in the present work is evident from the comparison between Tables 1 and 2. It must be noted that with the four model parameters derived in the present work, the crystallization kinetics can be accurately described not only for the cooling rates at which experiments were conducted, prediction at any other intermediate cooling rate can also be made.

### 4.2. Cold crystallization behavior during nonisothermal heating

Supaphol et al. have also carried out detailed studies [2] on the nonisothermal cold crystallization kinetics of PTT by melting samples at 275 °C, quenching in liquid nitrogen to get a glassy state and then conducting crystallization kinet-

Table 2
Nonisothermal crystallization kinetic parameters from present work for PET, PTT and PBT systems

| System | $n$ | $K_0$ (s$^{-1}$) | $Q_0$ (kJ mol$^{-1}$) | $Q_1$ (kJ mol$^{-1}$) | $R^2$ |
|---|---|---|---|---|---|
| PET | 3.0 | 6.72E−6 | −21.5 | −1.88 | 0.975 |
| PTT | 3.0 | 7.1E−8 | −43.05 | −1.1 | 0.993 |
| PBT | 3.0 | 1.69E−9 | −56.77 | −1.73 | 0.994 |
| PTT[a] (cold) | 4.0 | 1.02E3 | 34.88 | −2.06 | 0.991 |

[a] Cold crystallization kinetics from the glass state during heating.

Table 3
Nonisothermal cold crystallization kinetic parameters taken from the original work [2] for the PTT system based on Avrami analysis

| $\Phi$ (°C min$^{-1}$) | $n$ | $K$ (min$^{-1}$) |
|---|---|---|
| 5 | 5.21 | 0.720 |
| 7.5 | 5.33 | 1.054 |
| 10 | 5.30 | 1.317 |
| 12.5 | 5.64 | 1.487 |
| 15 | 5.93 | 1.735 |
| 20 | 5.47 | 2.325 |
| 25 | 5.07 | 2.871 |
| 30 | 4.97 | 3.385 |

ics experiments during subsequent nonisothermal heating. The nonisothermal heating kinetics from the glass state was carried out in the temperature range of 25–275 °C at eight different constant heating rates between 5 and 30 °C min$^{-1}$. Similar to the melt crystallization kinetics, here also different models including the Avrami model were used to analyze the experimental data (Table 3) and were found to give very high $R^2$ values between model prediction and experimental data. As was observed earlier, here also, different values of uncorrelated Avrami exponent and rate constants were used to model experimental data corresponding to different heating rates. Therefore, although a large number of model parameters were derived, due to the uncorrelated nature of these parameters to heating rates, prediction at any intermediate heating rate is not possible by using these parameters.

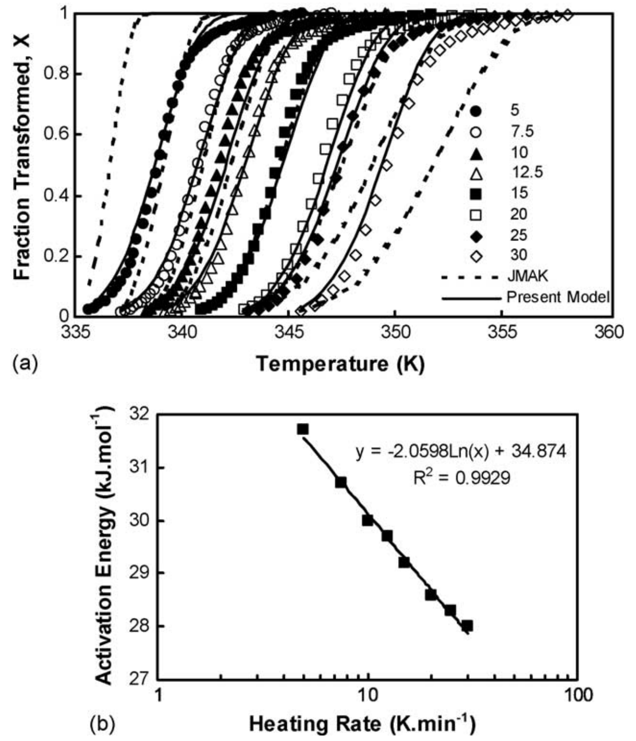

Fig. 4. (a) Comparison of experimental data (symbols) with the classical JMAK model (broken line) using a unique set of model parameters and a proposed model (solid line) for cold crystallization in the PTT system. (b) Variation in activation energy with the heating rate in the PTT system.

The results of modeling the cold crystallization kinetics in the PTT system by the classical JMAK model (broken lines are for the JMAK model prediction, symbols are for experimental data) is similar to our earlier observations on the PTT, PET and PBT systems during melt crystallization, i.e. even though the kinetics for a particular heating rate (15 K min$^{-1}$) can be well described, the same model parameters fail to describe crystallization behavior at other heating rates (Fig. 4a) with good accuracy. However, when the methodology proposed in the current work is used to model the cold crystallization kinetics in the PTT system, as shown in Fig. 4b, exactly the same functional relationship (Eq. (3), similar to PTT, PET and PBT systems during melt crystallization) evolved from the global search method. Here also, with a single set of model parameters (given in Table 2) it was possible to precisely predict (with high $R^2$ value) the crystallization kinetics for all the heating rates (solid lines in Fig. 4a).

In addition to the accurate prediction of experimental data, is interesting to note that the present work (Table 2) uses integer values of the Avrami exponent ($n$) whereas “real numbers” were used in earlier work (Tables 1 and 3).

## 5. Discussion

It is shown that the description of nonisothermal crystallization kinetics by the quasi-isothermal approach requires a large number of model parameters, yet it does not have the prediction capability at any intermediate condition. In the present work, the existence of a functional relationship between the cooling or heating rate and effective activation energy has been shown for three different linear aromatic polymers. Although this functional relationship has been semi-empirically derived, it enables accurate prediction of crystallization kinetics with a single set of model parameters. The significance of this functional relationship has been discussed below.

The classical theory of an activated complex suggest that for reactions or transformations under near equilibrium condition, the free energy of the reactant phase and product phases are considered to be at the two minimum free energy positions, separated by a maximum at the metastable state (activation complex). A lower activation energy barrier in effect enhances the transformation or reaction kinetics. The functional relationship between the cooling rate and the effective activation energy derived in the present work indicate that with an increase in the cooling rate, the effective activation energy decreases.

Before examining the heating or cooling rate dependence of effective activation energy, let us compare isothermal transformation kinetics (which could be considered as nonisothermal kinetics with an extremely low heating or cooling rate) with nonisothermal kinetics. A number of other phase transformation studies on diverse material systems indicate accelerated kinetics as well as reduced effective activation energy under nonisothermal condition. Li et al.

have reported [11] that activation energy for nonisothermal crystallization (154 kJ mol$^{-1}$) of the ePP system is lower than that for the isothermal condition (163 kJ mol$^{-1}$). In another case, the activation energy for crystallization of the amorphous $Pd_{40}Cu_{30}P_{20}Ni_{10}$ was found to decrease from 336 kJ mol$^{-1}$ under isothermal condition to 258 kJ mol$^{-1}$ under nonisothermal condition [14]. Decrease in effective activation energy has been also observed during reduction of $Fe_2MoO_4$ by hydrogen gas, from 173.5 kJ mol$^{-1}$ under isothermal condition to 158.3 kJ mol$^{-1}$ under nonisothermal condition [32]. Acceleration in transformation kinetics, which can be indirectly attributed to reduction in activation energy, has also been reported during densification of zinc powders [33], age hardening kinetics in Ti–6Al–4V [34], and grain growth kinetics in steel [30], all under nonisothermal cyclic condition, where the heating rate as well as the change in heating rate effects prevail. These results from very diverse material systems as well as different types of transformations suggest that nonisothermal transformation kinetics are indeed higher than the isothermal condition and nonisothermal processing provides an opportunity to significantly improve the productivity of industrial operations.

In contrast to numerous comparisons between the isothermal and nonisothermal transformation kinetics presented above, relatively few attempts have been made to examine the effect of heating or cooling rates on activation energy or phase transformation kinetics. Xu et al. have mentioned that the crystallization rate increases with increasing cooling rates [9] during nonisothermal melt crystallization in PP and PP/Mont nanocomposites. In another study, the effective activation energy during nonisothermal recrystallization of cold rolled low carbon steel was found to decrease from 522 to 259 kJ mol$^{-1}$ when the heating rate was increased [35]. In a recent work [31], the present authors have also shown that during the nonisothermal crystallization kinetics from the amorphous state in $Se_{71}Te_{20}Sb_9$ as well as $Ge_{20}Te_{80}$ glass systems, the activation energy not only decreases with an increase in the heating rate, there exists a log-linear functional relationship (identical to Eq. (3) in present work) between the heating rate and activation energy. Also, the present authors have shown the validity of the above relationship during nonisothermal crystallization from melt in four other polymeric systems, namely, polypropylene (PP), PP organic-montomorillonite nanocomposite, metallocene polyethylene and elastomeric PP systems [36]. Therefore, at least for ten different systems (four in the current work and six in earlier work) and two different types of transformations (crystallization from melt during cooling as well crystallization from the amorphous state during heating), the same functional relationship between effective activation energy and the heating or cooling rate, have been found, which accurately describes the nonisothermal transformation kinetics in conjunction with the JMAK model.

In spite of good model predictions and these independent observations, the present work does not provide a mechanistic significance to the proposed variation in effective activation energy. This is, in fact, an actively debated topic in the recent thermo-analytical literature [26,27]. Although Eq. (2) with constant $Q$ is frequently used as an overall rate equation incorporating the nucleation and growth phenomenon [1,9–11,17], a more accurate phenomenological description of polymer crystallization is accomplished by using a variable effective activation energy [38,39]. A temperature dependence of $Q$ is obtained by using an isoconversional method and is further parameterized in terms of the Hoffman–Lauritzen theory [39]. In the present work, the observed cooling or heating rate dependence of the effective activation energy is likely to reflect the difference in temperature regions associated with the difference in cooling or heating rates [37]. In effect, this dependence incorporates the temperature dependence of the activation energy as determined by isoconversional methods [38,39]. It is also important to note that in the present work, at very high crystallization fractions (e.g. >0.9 in Figs. 3a and 4a), the model predictions are slightly inaccurate, which is expected in modeling crystallization kinetics with a single Arrhenious equation [38]. The two distinct regimes exhibiting Arrheniusian and anti-Arrheniusian behaviors during polymer crystallization have been shown earlier [38]. In addition, the common term “effective activation energy” used in this article and earlier work [1,9–11] is not phenomenological “activation energy” but the temperature coefficient of the rate [37,38]. Also, as Eq. (3) has been semi-empirically derived from the experimental data, it cannot be treated as a general equation until it is derived from the non-equilibrium thermodynamics principles. Further work is needed in this direction.

The main contribution of this work is to provide a simple methodology for describing the nonisothermal kinetics in the JMAK framework with very few model parameters. This is in contrast to the original work [1,2], where different uncorrelated Avrami model parameters were used at different cooling or heating rates. As has been discussed in the previous section, the present work does not address some of the inherent limitations of the JMAK model in describing the nonisothermal polymer crystallization kinetics.

## 6. Conclusions

Important findings from the present work based on the analysis of nonisothermal crystallization kinetics in three different linear aromatic polyesters are summarized below:

i. Quasi-isothermal models enable prediction of nonisothermal melt or cold crystallization kinetics for individual cooling or heating rates but fail to describe all the cooling or heating rates with a single set of model parameters.
ii. In addition to the large number of model parameters, due to the uncorrelated nature of cooling or heating rates and model parameters, the quasi-isothermal approach cannot be used to predict crystallization kinetics at any intermediate condition.

iii. In the global search technique used in the present work, the same log–linear relationship between effective activation energy and the cooling or heating rate has emerged in three different polymeric systems, confirming the general nature of this functional relationship.
iv. Due to the semi-empirical derivation of the functional relationship, further work is required to provide a mechanistic significance as well as prove it from first principles. The inherent limitation of using the JMAK model with a single overall Arrhenious relationship, instead of two separate rates corresponding to nucleation and growth processes, is not addressed in this work.
v. Nevertheless, this function relationship in conjunction with the classical JMAK model, enables accurate prediction of nonisothermal melt or cold crystallization kinetics at any cooling or heating rate with a single set of model parameters.
vi. In the present approach, accurate predictions were made with integer Avrami exponents as opposed to real numbers used in prior work.

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