Thermal behaviour of polyethylene-block-poly(methyl methacrylate) block copolymer: effect of multiple heating and cooling rates versus mathematical artefact

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Abstract

The melting and crystallization behaviours of a polyethylene-block-poly(methyl methacrylate) (PE-b-PMMA) diblock copolymer and a PE homopolymer were investigated using multiple heating and cooling rate differential scanning calorimetry (DSC) experiments, and modelling of the crystallization kinetics and lamellar thickness distribution. This new model was first validated applying literature and experimental data. The model-predicted morphology \(n = 3.2\) closely matched the spherulitic morphology \(n = 3\), which was determined using polarized optical microscopy. For each experimental cooling rate, the model predicted diblock copolymer crystallinity that well matched the entire DSC crystallinity curve, notably for an Avrami–Erofeev index of \(n = 2\); and apparent crystallization activation energy that hardly varied with the cooling rates used, relative crystallinity \(u\), and crystallization temperature or time. This disfavours the concept of variable activation energy. The use of the right crystallization model and parameter estimation algorithm is important for addressing the mathematical artefact. Under non-isothermal cooling, the PE-b-PMMA diblock copolymer, as per the model prediction, crystallized without confinement \(n \neq 1\), preserving the cylindrical structure. From the characteristic shapes of the crystallization function \(f(\alpha(T))\) versus \(1/T\) and crystallization rate versus \(\alpha\) plots, the resulting \(T_{\text{c,max}}\) and narrow \(\alpha_{\text{max}}\) range can guide the search for an appropriate crystallization model. The overall treatment illustrated in this study is not restricted to a PE homopolymer and a PE-b-isotactic PMMA block copolymer. It can be generally applied to crystalline homopolymers and copolymers (alternating, random and block), as well as their blends. The block copolymers and blends can be crystalline–amorphous as well as crystalline–crystalline. © 2014 Society of Chemical Industry

Keywords: PE-b-PMMA diblock copolymer; Avrami–Erofeev non-isothermal crystallization model; multiple heating and cooling rates; invariable activation energy; SSA; DSC

INTRODUCTION

The diblock copolymer of ethylene and methyl methacrylate (PE-b-PMMA), a polar ester, is an important compatibilizer,1 and an effective dyability enhancer.2–4 During processing, it melts and crystallizes under heating and cooling, respectively. Therefore, it is worthwhile investigating its crystallization and melting behaviours, with reference to a PE homopolymer. Of particular significance is the crystallization within the block copolymer microdomains that can introduce intriguing morphologies on the micro- and nanoscale. Such morphologies originate from the capability of the copolymer blocks to self-organize and separate into microphases. Consequently, block copolymers that combine the characteristics of multiple homopolymers show interesting properties. Several excellent reviews on block copolymer crystallization are available in the literature.5–7 The practical importance arises from the significant effect of the resulting crystallinity and morphology on the physical and chemical properties of PEs.

The PE-b-PMMA diblock copolymer consists of a semi-crystalline PE hard block and an amorphous PMMA soft block. The crystallization temperatures of linear PEs vary from 118 to 125 °C.8–10 In contrast, the glass transition temperature of isotactic PMMA ranges from 53 to 58 °C.11,12 Therefore, the diblock copolymer of the two components has the features that only the PE block is crystallizable.
and the corresponding PE crystallization temperature is greater than the PMMA glass transition temperature (soft confinement case). Hence, to study the influence of the PMMA functional soft block on crystallization kinetics (through model and experiment) is both interesting and important.

The crystallization kinetics of PEs, in general, have been studied using (i) constant cooling rate DSC non-isothermal crystallization experiments and (ii) isothermal crystallization experiments. However, the non-isothermal mode has distinctive advantages over the isothermal mode which have been recently reviewed. Crystal behaviour is customarily investigated by evaluating crystallization kinetics, which are expressed in terms of crystal growth dimension $n$, activation energy $E_a$ and frequency factor $k_o$. These parameters are called the crystallization kinetics triplet. $E_a$ is important because it is related to the rate of crystallization. Therefore, it should be determined as correctly as possible without any influence of mathematical artefacts. On this particular subject, the findings published in the literature are divided. Several authors report that $E_a$ of a transformation process varies with cooling/heating rates, extent of fractional phase transformation or temperature. On the contrary, others strongly oppose this view. Galwey has published excellent reviews on this theme. One may consult these reviews and the references cited therein. These reports conclude that the concept of variable/instantaneous activation energy, which has been applied to handle non-isothermal kinetic data, is unacceptable because it is not mechanistically sound. This arises due to inadequacies in the assumptions underlying the computational methods.

In the context of the present study, the following relevant studies are reviewed. Supaphol et al. determined the effective crystallization energy of three linear aromatic polyesters – poly(ethylene terephthalate) (PET), poly(trimethylene terephthalate) (PTT) and poly(butylene terephthalate) (PBT) – using the Friedman method and the Vyazovkin method, and non-isothermal DSC experiments. The Friedman method showed that the crystallization energy of PET and PBT, unlike that of PTT, monotonically increased with relative crystallinity. Also, for this case, the coefficient of determination $R^2$ decreased with an increase in relative crystallinity. Supaphol et al. defended this finding by arguing that the nucleation energy decreased with increasing melt conversion or decreasing temperature. The Vyazovkin method applied to PET showed an opposite trend. Sahay and Krishnan modelled the crystallization energy of the three polymers using the isothermal version of the Avrami–Erofeev equation where the activation energy was assumed to decrease with the logarithmic increase of cooling rate. The model prediction consistently conformed to this assumption for each polyester. However, the analysis of Sahay and Krishnan has the limitation that the semi-logarithmic relationship between activation energy and cooling rate is mechanically unsound. Therefore, this work practically reduces to a relationship between activation energy and cooling rate is mechanically unsound. Therefore, this work practically reduces to a relationship between activation energy and cooling rate.

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![Image](wileyonlinelibrary.com/journal/pi)

**EXPERIMENTAL**

**Synthesis of polymers**

We used the PE-b-isotactic PMMA diblock copolymer and the PE homopolymer that we synthesized in our earlier study, applying Me₃Si(Ind)₂ZrMe₂ and methylaluminoxane (MAO; 10 wt% in toluene). For the diblock copolymer, a sequential polymerization of ethylene and methyl methacrylate was used. All the synthesis procedures are detailed elsewhere.

**Characterization of synthesized polymers**

The synthesized PE-b-isotactic PMMA diblock copolymer and the PE homopolymer were characterized using several analytical techniques: gel permeation chromatography, Crystaf, $^1H$ NMR spectroscopy and DSC. Table 1 summarizes the objectives of
We assume that \( k \) follows the typical Arrhenius relation: 
\[
k(T) = k_0 \exp(-E_a/RT),
\]
where \( k_0 \) is the overall crystallization frequency factor, \( E_a \) is the crystallization activation energy and \( R \) is the universal gas constant. Then, Eqn (1) can be written as follows:
\[
\frac{da}{dt} = k_0 \exp\left(-\frac{E_a}{RT}\right) \times f(\alpha(t))
\]
(2)

For a given mass of polymer, being crystallized with a cooling rate \( dT/dt = \beta \), using a differential scanning calorimeter, Eqn (2) can be expressed as
\[
\frac{da(T)}{dt} = \frac{k_0}{\beta} \exp\left(-\frac{E_a}{RT}\right) \times f(\alpha(t))
\]
(3)

Several authors have used the original form of the Kissinger equation, published in 1957, in polymer crystallization studies.\(^{35,46,47}\) However, this misses the intercept part. Lately, this has been revisited in the literature.\(^{37-39}\) Starting with Eqns (1)–(3), those studies independently derived the Kissinger equation that includes an intercept. The detailed mathematical derivations are available in the references cited. This version of Kissinger equation is written as
\[
\ln \left( \frac{\beta}{T_{pc}^2} \right) = \frac{E_a}{RT_{pc}} - \ln \left( \frac{k_0 R}{E_a} \times \left( \frac{d\alpha}{dt} \right)_{\alpha=0} \right)
\]
(4)

where \( T_{pc} \) is the peak crystallization temperature (also called crystallization exothermic peak) corresponding to a given cooling rate. The subscript \( \alpha=0 \) denotes the values related to rate maximum. Therefore, \( E_a \) can be calculated by plotting \( \beta/T_{pc}^2 \) as a function of \( 1/T_{pc} \), provided a linear relation is obtained.

Equation (4) shows that the validity of the Kissinger method depends on the fact that the intercept \( \ln[(k_0 R/E_a) \times (d\alpha/dt)_{\alpha=0}] \) does not depend on \( \beta \) or \( k_0 \). Otherwise, the intercept will not be constant. The plot mentioned above will deviate systematically from a straight line, producing a systematic error in \( E_a \).\(^{37,38}\) Also, \( T_{pc} \) should vary with \( \beta \).

### The OFW method

This method results from the following rearrangement of Eqn (3):\(^{22,32,48,49}\)
\[
\ln(\beta) = \frac{E_a}{RT_{pc}} + \ln \left( \frac{k_0 f(\alpha)}{d\alpha/dT} \right)
\]
(5)

Equation (5) shows that, for the same value of \( \alpha \), plotting \( \ln(\beta) \) as a function of \( 1/T \) gives a straight line if the crystallization function \( f(\alpha) \) and \( d\alpha/dT \) or their ratio do not change with the change of cooling rates for all values of \( \alpha \). From the slope, we can calculate \( E_a \).

### Friedman method

Equation (3) can also be written as follows: \(^{22,31,32}\)
\[
\ln \left( \frac{d\alpha}{dT} \right) = -\frac{E_a}{RT} + \ln \left( \frac{k_0 f(\alpha)}{\beta} \right)
\]
(6)

Therefore, for the same value of \( \alpha \), \( \ln(d\alpha/dT) \) plotted against \( 1/T \) will result in a straight line provided \( f(\alpha) \) does not depend on \( \beta \), or their ratio remains constant. From the slope, we can calculate \( E_a \).

### General linear isoconversional method

To the best of our knowledge, for a polymer crystallizing following a constant cooling rate DSC experiment, a GLIM has not been reported. Hence, we develop this as follows.
After separation of variables and integration, Eqn (3) becomes:

\[
g(\alpha) = \int_a^1 \frac{dx}{f(\alpha)} = \frac{k_0}{\beta} \int_{T_0}^{T} \exp \left(-\frac{E_a}{RT}\right) \, dT \tag{7}
\]

Between 0 and \(T_0\), \(dx/dT = 0\). Therefore, we conclude from Eqn (3) that \(\exp(-E_a/RT)\) will also equal zero. Accordingly, Eqn (7) can be written as follows:

\[
g(\alpha) = \int_a^1 \frac{dx}{f(\alpha)} = -\frac{k_0}{\beta} \int_{T_0}^{T} \exp \left(-\frac{E_a}{RT}\right) \, dT \tag{8}
\]

The integral on the right-hand side of Eqn (8) is called the temperature integral (or Arrhenius integral).\(^\text{50,51}\) This has no analytical solution. However, it can be approximated as follows. Let us define \(x = E_a/RT\). Then, we can write Eqn (8) as

\[
g(\alpha) = \int_a^1 \frac{dx}{f(\alpha)} = -\frac{k_0 E_a}{\beta R} \int_u^\infty \exp \left(-\frac{x}{x^2}\right) \, dx = -\frac{k_0 E_a}{\beta R} \rho_p(u) \tag{9}
\]

Generally, two types of approximations to the temperature integral \(\rho_p(u)\) are available. One is an exponential form and the other is a rational fractional form. The exponential form can be written as\(^\text{50,51}\)

\[
\rho_p(u) = \frac{\exp(-au + b)}{u^c} \tag{10}
\]

\[
\ln(\rho_p(u)) = b - c \ln(u) - au \tag{11}
\]

The rational fractional form can be expressed as

\[
\rho_f(u) = \frac{\exp(-au)}{u^c} \times Q(u) \tag{12}
\]

where \(Q(u)\) represents rational fractions of \(u\), usually ratios between polynomial functions, derived from different series expansions or approximate fitting procedures relative to the values calculated from numerical integration in a certain range of \(u\). Both the above forms have been comprehensively tabulated in the literature.\(^\text{50,51}\)

Combining Eqns (9) and (11), we can write the following general linear model-free isoversional thermo-analytical equation:

\[
\ln \beta = \ln \left(\frac{k_0 E_a}{Rg(\alpha)}\right) + b - \left[\frac{E_a}{RT} + c \ln \left(\frac{E_a}{RT}\right)\right] \tag{13}
\]

For the same value of \(a\) corresponding to different cooling rates, we can assume a value of \(E_a\) and plot \(\ln \beta\) as a function of \(a(E_a/RT) + c\ln(E_a/RT)\). The value of \(E_a\) that gives a straight line with a slope of unity (with a high coefficient of determination \(R^2\)) can be considered as the activation energy of crystallization. Note that Eqn (13) holds as long as \(g(\alpha) = \int_a^1 \frac{dx}{f(\alpha)} \) does not depend on the cooling rate \(\beta\).

The exponential approximation published by Cai and Liu\(^\text{52}\) is rated to be the most accurate one so far reported in the literature, and applies to \(0 < x = E_a/RT < 100\). Here, \(a = 1.00174866236974, b = -0.460120828342246\) and \(c = 1.86847901883656\). Therefore, in this study, we have used these values.

**Non-isothermal Avrami – Erofeev crystallization model**

We have recently published a new non-isothermal crystallization model for crystalline polymers using the Avrami – Erofeev equation that represents the kinetics incorporating the constituent nucleation and growth processes. This model, with detailed assumptions and mathematical derivation, and experimental evidence, is available in our previous paper.\(^\text{18}\) Here, only a summary is provided as follows.

The **non-isothermal Avrami–Erofeev polymer crystallization rate** can be written as

\[
\frac{da}{dT} = \frac{k_0}{\beta} \exp \left[-\frac{E_a^A}{R} \left(\frac{1}{T} - \frac{1}{T_0}\right)\right] \times n (1 - \alpha(T)) \left[-\ln(1 - \alpha(T))\right]^{(n-1)/n} \tag{14}
\]

where we define the following:

\[
f(\alpha(T)) = n (1 - \alpha(T)) \left[-\ln(1 - \alpha(T))\right]^{(n-1)/n} \tag{15}
\]

\[
k'(T) = k_0 \exp \left[-\frac{E_a^A}{R} \left(\frac{1}{T} - \frac{1}{T_0}\right)\right] \tag{16}
\]

\[
E_a^A \text{ (apparent crystallization energy)} = E_{grow} - E_{nucl} \tag{17}
\]

\[
k_0 = \left(\frac{K_N V_0}{V_0}\right) \frac{k_{grow,0}}{k_{nucl,0}} \tag{18}
\]

\[
k_{grow}(T) = k_{grow,0} \exp \left[-\frac{E_{grow}}{R} \left(\frac{1}{T} - \frac{1}{T_0}\right)\right] \tag{19}
\]

\[
k_{nucl}(T) = k_{nucl,0} \exp \left[-\frac{E_{nucl}}{R} \left(\frac{1}{T} - \frac{1}{T_0}\right)\right] \tag{20}
\]

In the above equations, \(f(\alpha(T))\) is called the Avrami–Erofeev non-isothermal crystallization function; \(n\) is the dimension of the growing crystal; \(N_0\) is the number of germ nuclei, i.e. the potential nucleus formation sites/defects; \(V_0\) is the initial volume of the molten polymer; and \(K_s\) is the shape factor for the growing nuclei. Equations (19) and (20) have been written according to the particular Arrhenius form reported elsewhere in the literature.\(^\text{53–55}\)

Parameters \(k_{grow,0}\) and \(E_{grow}\) are the frequency factor and activation energy of crystal growth, respectively; \(k_{nucl,0}\) and \(E_{nucl}\) are the corresponding terms for nucleation, respectively. \(T_0\) is the centring temperature. Note that the above type of Arrhenius relation suits the numerical treatment of a typical sigmoidal relative crystallinity versus \(T\) curve.\(^\text{56}\) Additionally, the centring procedure facilitates searching the kinetic parameters by minimizing the statistical correlation between activation energy and pre-exponential factor.\(^\text{55–57}\)

Equation (14) has the following special features:

- It is a kinetic equation and abides by the laws of conservation of mass and energy.
- The kinetic parameters \(k_0, E_a\) and \(n\) can be obtained from a single constant cooling rate DSC trial.
- The interdependence among \(k_0, E_a\) and \(n\) can be determined using the statistical cross-correlation coefficient.
- New insight concerning the effect of polymer microstructure on crystallization can be obtained by plotting \(f(\alpha(T))\) as a function of \(\alpha(T)\) and \(1/T\).
Parameter $\alpha(T)$ is related to the corresponding weight fraction relative crystallinity $\alpha_w(T)$ through the following expression:\textsuperscript{58}

$$
\alpha(T) = \frac{\alpha_w(T)}{\alpha_w(T) + \left[ \rho_c/\rho_s \right] \left[ 1 - \alpha_w(T) \right]}
$$

where $\rho_c$ and $\rho_s$ are the densities of the crystalline and amorphous phases, respectively. For polyethylene, $\rho_c = 1.004 \text{ g mL}^{-1}$ and $\rho_s = 0.853 \text{ g mL}^{-1}$. Parameter $\alpha_w(T)$ can be calculated from a typical constant cooling rate DSC experiment, crystallizing molten polymer non-isothermally, using

$$
\alpha_w(T) = \frac{\Delta H(T)}{\Delta H_{\text{total}}} = \int_{T_0}^{T} \left( \frac{dH}{dT} \right) dT
$$

where $\Delta H_{\text{total}}$ is the maximum enthalpy value reached at the end of the non-isothermal crystallization process and $\Delta H(T)$ is the enthalpy evolved as a function of crystallization temperature $T$. $T_0$ and $T_\infty$ are the start and completion temperatures of crystallization, respectively. $\Delta H_{\text{total}}$ and $\Delta H(T)$ both can be acquired through the software of a standard differential scanning calorimeter.

Equation (21) shows that $T_m$ decreases as $L_{\text{lamella}}$ decreases; the converse is also true. Also, $T_m \rightarrow T^0_m$ as $L_{\text{lamella}} \rightarrow \infty$. Therefore, an asymptotic relation holds between $T_m$ and $L_{\text{lamella}}$. Note that in Eqn (25), $T^0_m$ is the equilibrium melting temperature of a crystalline homopolymer. For a random copolymer, this should be substituted for the corresponding equilibrium melting temperature $T^0_m$, which can be calculated using the Flory model:\textsuperscript{63–67}

$$
\frac{1}{T^0_m} = \frac{1}{T^0_m - \frac{R}{\Delta H_f} \ln X_A}
$$

where $\Delta H_f$ is the heat of fusion of the ethylene repeat unit and $X_A$ is the mole fraction of ethylene in the random copolymer.

Now we show how to calculate the distributions of lamellar thickness and chain fold length, using a typical DSC endotherm. For this purpose, we assume that the rate of heat flow, at a given temperature, is proportional to the mass of a crystal (having a lamellar thickness between $L_{\text{lamella}}$ and $L_{\text{lamella}} + dL_{\text{lamella}}$ and chain fold $-\text{CH}_2-$ repeat unit between $n$ and $n + dn$ that has melted during $dT$).\textsuperscript{60,61} Accordingly, the melted crystallite mass fraction $\chi_i$ at time $t_i$ and temperature $T_i$ is given by

$$
\chi_i(t) = \int_{t_0}^{t} \left( \frac{dH}{dH/dt} \right)_{t+1} dt - \int_{t_0}^{t} \left( \frac{dH}{dH/dt} \right)_{t} dt
$$

Note that all the integrals in Eqn (27) are automatically generated as a function of time and temperature by the software of a standard computer-assisted DSC instrument.

The weight-average lamellar thickness is given by\textsuperscript{64}

$$
L_{\text{wav}} = \sum_{j=1}^{n} \frac{L_{\text{lamella},j} \chi_i(L_{\text{lamella},j+1} - L_{\text{lamella},j})}{\sum_{j=1}^{n} \chi_i(L_{\text{lamella},j+1} - L_{\text{lamella},j})}
$$

**Crystallization kinetics parameter estimation**

Equation (14), representing the non-isothermal Avrami–Erofeev polymer crystallization rate, was evaluated by a least-squares fitting of the model parameters. For this purpose, the $\alpha_w(T)$ versus $T$ data points, generated by single constant cooling rate DSC experiments, were taken over the entire crystallization profile. All the $\alpha_w(T)$ was converted to the corresponding $\alpha(T)$ using Eqn (21).

The above crystallization rate equation was numerically solved using the fourth-order Runge–Kutta method (MATLAB ODE 45). The centring temperature $T_0$ was taken equal to 370 K. The right-hand side of Eqn (14), containing $-\ln(1 - \alpha(T))$, has a point of discontinuity at $\alpha(T) = 1$. This was overcome by approximating $\alpha(T) \approx 0.99$.

The kinetic parameters were determined at the 95% confidence limit. For each heating rate, 48 experimental data points were taken for parameter estimation. Thus, for a given value of $n$, the degree of freedom for the model was 45 (number of data points minus number of parameters to be estimated: 48 – 3). Therefore, enough experimental data were considered to iterate the model...
parameters. This particular feature makes the model predictions more accurate. The global model parameters were estimated by feeding the selected DSC data points of all the cooling rates into Eqn (14). Convergence was accepted when the model function changed less than the specified tolerance of $10^{-8}$.

The performance of the developed crystallization model (for different values of $n$) was assessed based on the following:

- coefficient of determination ($R^2$);
- lower SSR (sum of the squares of the residuals);
- lower cross-correlation coefficient ($r$); and
- smaller individual confidence intervals for the model parameters.

RESULTS AND DISCUSSION
We discuss the results of the study under the following subsections:

- activation energy estimated using the selected isoconversional methods;
- Avrami–Erofeev model-predicted crystallization parameters: $n$, $E_a$, and $k_0$;
- effect of cooling rate on relative crystallization function $f(\alpha(T))$ and normalized crystallization rate $\varphi$; and
- polymer thermal fractionation, and relation between overall crystallinity and average lamellar thickness.

### Activation energy estimated using selected isoconversional methods
Figures 1 and 2 show three-dimensional plots of activation energy $E_a$, relative crystallinity $\alpha$ and the coefficients of determination $R^2$ for the following isoconversional methods: Kissinger, OFW, Friedman and GLIM. The common general comments are as follows. For each polymer, the $R^2$ values are fairly low. Therefore, the calculated $E_a$ values cannot be accepted. Also, they are not invariant of either the method used or the relative crystallinity $\alpha$. Therefore, the above linear isoconversional methods cannot be recommended to determine crystallization activation energy $E_a$ of the experimental polymers, though the use of these methods has been customarily reported in the literature.$^{21,24,26,35,46,47}$ The consequential poor performance may be attributed to the methodical limitations we have underscored earlier. Hence, we discuss in the next subsection the use of the rigorous Avrami–Erofeev non-isothermal model to calculate the crystallization parameters, including the activation energy, for the experimental polymers applying multiple cooling rate DSC experiments.

### Avrami–Erofeev model-predicted crystallization parameters: $n$, $E_a$, and $k_0$
We first validated our new model using the data published in the literature. We used the data of Chen et al.$^{68}$ Figure 3 illustrates that this model is applicable to poly(trimethyl terephthalate)-block-poly(ethylene glycol) block copolymer that was crystallized using a DSC cooling rate of $20^\circ\text{C} \cdot \text{min}^{-1}$. The model-predicted morphology ($n = 3.2$) closely matches the spherulitic morphology ($n = 3$) which was determined using polarized optical microscopy. This shows the level of consistency between model prediction and experiment. The remaining crystallization parameters for the crystalline–crystalline diblock copolymer mentioned above turn out to be $E_a = 60.92 \text{ kJmol}^{-1}$ and $k_0 = 0.0280 \text{ min}^{-1}$.

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**Figure 1.** Estimation of crystallization activation energy of PE homopolymer using selected isoconversional methods: Kissinger, OFW, Friedman and GLIM.

**Figure 2.** Estimation of crystallization activation energy of PE-$b$-isotactic PMMA diblock copolymer using selected isoconversional methods: Kissinger, OFW, Friedman and GLIM.

**Figure 3.** Estimation of crystallization activation energy of PE homopolymer and PE-$b$-isotactic PMMA diblock copolymer, respectively, with the experimental profiles as a function of temperature for various cooling rates. To improve clarity, we exclude the plots for $\beta = 10$ and $17.5^\circ\text{C} \cdot \text{min}^{-1}$. We observe that for either polymer, the rigorous non-isothermal Avrami–Erofeev model (developed using a set of phenomenological assumptions) predicts very well the entire experimental relative crystallinity profiles with coefficients of determination $R^2 = 0.960–0.997$. These values are much higher than those estimated using the isoconversional methods discussed above.

The main finding as regards Figures 4 and 5 is that a single value of $n = 2$ represents the whole crystallization regime – primary as well as secondary – for all the experimental cooling rates. This result is physically significant. This means that the mechanism of nucleation and crystal growth used in the development of the constitutive model equation holds, irrespective of cooling rate, throughout the whole crystallization process. This evidences how the present model overcomes the drawbacks and limitations of the existing non-isothermal crystallization models. Therefore, the assumption of a change in crystallization mechanism, as reported in the literature,$^{24,69–72}$ does not appear to be necessary.
Figure 3. Validation of the new crystallization model using the data of Chen et al. Model-predicted morphology matches that determined using polarized optical microscopy.

Figure 4. Comparison of non-isothermal Avrami–Erofeev model-predicted relative crystallinity profiles with the corresponding DSC-determined profiles under various cooling rates for PE homopolymer. Plots for 10 and 17.5 °C min⁻¹ have been excluded to improve clarity.

Figure 5. Comparison of non-isothermal Avrami–Erofeev model-predicted relative crystallinity profiles with the corresponding DSC-determined profiles under various cooling rates for PE-b-isotactic PMMA diblock copolymer. Plots for 10 and 17.5 °C min⁻¹ have been excluded to improve clarity.

Figure 6. Effect of cooling rate on the model-predicted apparent activation energy $E_A = E_{\text{grow}} - E_{\text{nucl}}$ for both polymers.

diblock copolymer. Values of $E_A$ are 34.45 and 44.75 kJ mol⁻¹, respectively, for these two polymers. The corresponding frequency factors $k_0$ are 0.886 and 0.685 s⁻¹, respectively.

The expression $E_A = E_{\text{grow}} - E_{\text{nucl}}$ (Eqn (17)) includes the energy needed to activate the two parallel events of nucleation as well as crystal growth, each of which has its own energy barrier. As per the model prediction, $(E_{\text{grow}} - E_{\text{nucl}})_{PE-b-PMMA} > (E_{\text{grow}} - E_{\text{nucl}})_{PE-homopolymer}$. This means the following: (i) $E_{\text{grow}}_{PE-b-PMMA} > E_{\text{grow}}_{PE-homopolymer}$; (ii) $E_{\text{nucl}}_{PE-b-PMMA} < E_{\text{nucl}}_{PE-homopolymer}$; and/or a combination of (i) and (ii).

The proposed explanation can be ascribed to the particular chemical structure and composition of the PE-b-isotactic PMMA diblock copolymer, which is, by definition, a functional PE. The end-capping PMMA block is the functional component that consists of the pendant –CH₃ and bulky –COOCH₃ (ester) groups (Figure 7). This offers steric hindrance to crystallization, which in turn decreases the overall rate of crystallization. The work of Pracella et al. also supports this view.

The Avrami–Erofeev index $n$ is determined to be 2 for the PE homopolymer and the PE (semi-crystalline)-b-isotactic PMMA (glassy amorphous) diblock copolymer, which is supported by literature-reported transmission electron microscopy (TEM). This model prediction signifies that the non-isothermal crystallization
in the diblock copolymer takes place without confinement \( (n \neq 1) \), producing sigmoidal kinetics and preserving the cylindrical structure. Benchmarked with the typical three-dimensional spherical crystal growth \( (n=3) \), we note that the crystal growth is relatively impinged in either case. Based on the above value of \( n \), the crystal growth (with respect to PE) in both polymers may be approximated as mostly cylindrical under all experimental cooling rates. The post-crystallization morphology of a \( [\text{PE (semi-crystalline)}]_{2} - [\text{polystyrene (glassy amorphous)}]_{24} \) diblock copolymer, determined using TEM, supports our model-predicted morphology.\(^{44,58}\) However, it should be noted that variation in degree of cooling and volume fraction of PE affects the post-crystallization morphology.

### Cooling rate versus relative crystallization function \( f(\alpha(T)) \) and normalized crystallization rate \( \varphi \)

Figures 8 and 9 show how the non-isothermal relative crystallization function \( f(\alpha(T)) \) varies as a function of inverse DSC cooling temperature \( 1/T \) for the homopolymer and diblock copolymer, respectively, for various cooling rates. The match between experiment and Avrami–Erofeev model prediction is excellent. Note that \( f(\alpha(T)) \) can be physically interpreted as the temperature-dependent crystallization rate constant \( k'(T) \), i.e. (see Eqn (14))

\[
f(\alpha(T)) = \frac{d\alpha(T)/dT}{k'(T)}
\]

Each polymer shows similar variation pattern – a sharp rise in \( f(\alpha(T)) \) followed by a gradual decline – as the crystallization temperature decreases. \( f(\alpha(T)) \) shows a maximum corresponding to a particular cooling temperature \( T_{\text{cmax}} \). The effect of cooling rate on \( f(\alpha(T)) \) and \( T_{\text{cmax}} \) is marginal. \( T_{\text{cmax, homopolymer}} = 113.2^\circ \text{C} \) and \( T_{\text{cmax, copolymer}} = 112.5^\circ \text{C} \). These findings (typical shape of the curve and fairly constant \( T_{\text{cmax}} \)) additionally imply that the Avrami–Erofeev crystallization mechanism prevails for both polymers, irrespective of cooling rate variation, throughout the crystallization process for a fairly constant value of crystal growth dimension \( n = 2 \). Therefore, the PMMA block does not practically interfere with the crystal growth dimension. (See also the discussion of Figure 12 below.) These \( T_{\text{cmax}} \) values are close to the corresponding cooling rate-average peak crystallization temperatures \( T_{pc} \) \((113.8 \text{ and } 113.5^\circ \text{C})\). The closeness of these crystallization temperatures reflects minimal dilution effect by the PMMA block, which is associated with the poor miscibility of the amorphous block with the crystalline one.\(^{44,58}\)

Figures 10 and 11 illustrate how the normalized crystallization rate \( \varphi \) varies as a function of relative crystallinity \( \alpha \), where

\[
\varphi = \frac{d\alpha/dT}{(d\alpha/dT)_{\text{max}}}
\]

Values of \( \varphi \) range from 0 to 1. The common observation is that, for each polymer, the shape of \( \varphi \) is convex upward and skewed to the right. The influence of cooling rate on the shape of \( \varphi \) is not significantly pronounced. The \( \alpha_{\text{max}} \) range for the homopolymer and diblock copolymer turn out to be the same \( (0.25 \text{ to } 0.36) \), showing that it is a weak function of cooling rate \( \beta \). These findings reaffirm the earlier conclusion that the same crystallization mechanism holds for both polymers, irrespective of cooling rate variation, throughout the crystallization process for a fairly constant value of \( n = 2 \). The observed convex shape and \( \alpha_{\text{max}} \) range appear to typically represent the Avrami–Erofeev crystallization mechanism. Note that the \( \alpha_{\text{max}} \) range mentioned above differs from what has been reported in the literature \( (\alpha_{\text{max}} = 0.62 \text{ to } 0.64) \).\(^{74}\) In that case, the temperature integral \( \int \exp(-E_a/RT) \, dT \) was approximated. However, we integrated this numerically, which is more accurate. Consequently, the effect of the present mathematical treatment on \( \alpha_{\text{max}} \) turns out to be quite significant.
Thermal behavior of PE-b-PMMA

Figure 10. Variation of normalized crystallization rate $\varphi$ as a function of relative crystallinity $\alpha(T)$ under different cooling rates for the PE homopolymer.

Figure 11. Variation of normalized crystallization rate $\varphi$ as a function of relative crystallinity $\alpha(T)$ under different cooling rates for the PE-b-isotactic PMMA diblock copolymer.

Polymer thermal fractionation, crystallinity and average lamellar thickness

Figure 12 compares the SSA fractionation results for the two experimental polymers – PE-b-isotactic PMMA diblock copolymer and PE homopolymer – and an additional ethylene–1-hexene random copolymer (1-hexene = 2.5 mol%). We synthesized this random copolymer in our laboratory using a silica-supported metallocene catalyst: SiO$_2$/MAO/(BuCp)ZrCl$_2$. We included this in the SSA experiments to (i) ensure that the SSA DSC experimental conditions used were suitable and (ii) differentiate among the microstructures of the three subject polymers.

The ethylene–1-hexene random copolymer shows five distinct melting peaks (105.4, 109.7, 114.0, 117.7, and 123.2°C). Each SSA peak signifies a population of backbones that have the same branch content (side-chain branching), crystallinity (crystallizable sequence length) and lamellar thickness. The branch content is inversely related to crystallinity and lamellar thickness; however, the latter two are usually directly proportional. Therefore, the branch content decreases, and the crystallinity and lamellar thickness increase with an increase in these peak melting temperatures.

The SSA DSC traces of the PE-b-isotactic PMMA diblock copolymer and PE homopolymer are very similar (Figure 12). This finding signifies that the PE homopolymer and the PE segment of the diblock copolymer, unlike the ethylene–1-hexene random copolymer, are linear; and that PMMA is excluded from chain folding of the PE segment. We next discuss the implication of this conclusion from the perspective of overall crystallinity and weight-average lamellar thickness.

Figure 13 shows that the experimental range of cooling rates practically do not affect the crystallinity of either polymer. The report by Papadimitriou et al. supports this finding. This trend also holds for the weight-average lamellar thickness $L_{\text{wav}}$ which we calculated from the corresponding lamellar thickness distributions using Eqn (28) (Figure 14). That $L_{\text{wav}}$ is not influenced by cooling rate complements the finding of Figure 13. The mathematical relations reported in the literature support these results. The percentage crystallinity of PE-b-isotactic PMMA diblock copolymer was normalized using the mass of the crystallizing PE block. To calculate the lamellar thickness distribution, we used $T_m^0 = 145.5^\circ\text{C}$, $\Delta H_f^0 = 290\ \text{J cm}^{-3}$ and $\sigma_{\text{ssfe}} = 90\ \text{mJ m}^{-2}$, which have been reported to be the best values to use. PMMA is excluded from chain folding. Therefore, these parameters, including $\sigma_{\text{ssfe}}$ (crystallite specific surface free energy), are assumed to be the same for both polymers.

CONCLUSIONS AND FUTURE STUDY

The melting and crystallization behaviours of PE-b-PMMA block copolymer significantly influence its morphology, thermal properties and interfacial applications. Hence, in this study we
investigated these aspects, as a function of multiple heating and cooling rates, using an as-synthesized PE-b-isotactic PMMA diblock copolymer and a PE homopolymer. We summarize the major findings as follows.

We modelled the crystallization kinetics by applying a new non-isothermal Avrami–Erofeev crystallization model and the parameter estimation algorithm (that we recently published) to multiple cooling rate DSC data. We first validated this model using the DSC data of Chen et al. The model-predicted morphology \((n = 3.2)\) closely matched the spherulitic morphology \((n = 2)\), which was determined using polarized optical microscopy. For each experimental cooling rate, the model predicted, for both polymers, relative crystallinity profile that well matched the entire DSC crystallinity profile, notably for a single Avrami–Erofeev index of \(n = 2\). This indicates cylindrical PE crystal growth which is supported by literature-reported TEM. Under non-isothermal cooling, the PE-b-PMMA diblock copolymer, as per the model prediction, crystallized without confinement \((n \neq 1)\), preserving the cylindrical structure.

For both polymers, the model-predicted apparent crystallization activation energy \(E_a^A\) was not found to practically vary with the cooling rates used, relative crystallinity and crystallization time or temperature. This ratifies the invariance of activation energy articulated by Galwey and others, and rejects the concept of *variable/instantaneous activation energy*, which is used in analysing non-isothermal kinetic data. This is a major contribution of this study. This achievement originates from the application of the crystallization model and the appropriate parameter estimation algorithm. This is how we addressed the subject of mathematical artefact. The combined heating rate-based activation energies \(E_a^A\) for the PE homopolymer and diblock copolymer were estimated to be 34.45 and 44.75 kJ mol\(^{-1}\), respectively. The higher \(E_a^A\) of the block copolymer was attributed to steric hindrance imparted by the PMMA block (having pendant \(-\text{CH}_3\) and bulky \(-\text{COOCH}_3\) groups) to crystallization, which in turn decreased the overall rate of crystallization. The model-free isokinetic methods of Kissinger, OFW and Friedman and the GLIM failed to calculate the crystallization activation energy.

The model-predicted relative crystallization function \(f(\alpha(T))\) versus \(1/T\) and normalized crystallization rate \(\varphi\) versus \(\alpha\) plots matched fairly well the corresponding experimental curves. The former plot showed a maximum for \(T_{cmax} \approx 113.0^\circ\text{C}\); the latter (a convex upward curve with left skewedness) showed a narrow \(\alpha_{cmax}\) range \((0.25\) to \(0.36)\) for each polymer. Also, the cooling rates did not significantly affect the shapes, \(T_{cmax}\) and \(\alpha_{cmax}\) range. Therefore, these findings can be instructive in the search for an appropriate crystallization mechanism/model. The closeness of \(T_{cmax}\) to the corresponding peak crystallization temperatures reflects minimal dilution effect by the PMMA block, and hence poor miscibility of the amorphous PMMA block with the crystalline PE block.

The crystallization and lamellar thickness model predictions, and the SSA DSC experiments substantiate that the PMMA block is excluded from chain folding. Consequently, the multiple cooling rates did not appreciably influence \(n\), \(T_{cmax}\), \(\alpha_{cmax}\) range and peak crystallization temperature \(T_{pc}\). A similar remark applies to the influence of multiple heating rates on percentage crystallinity, peak melting temperature \(T_{pm}\), and weight-average lamellar thickness \(L_{wav}\).

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