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A Mathematical Model for the Kinetics of Crystallization in Crystaf

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Summary: A series of ethylene homopolymers and ethylene/1-hexene copolymers with different molecular weight distributions (MWD) and chemical composition distributions (CCD) was analyzed by crystallization analysis fractionation (Crystaf) at several cooling rates to investigate the effect of MWD, CCD, and cooling rate on their Crystaf profiles. Using these results, we developed a mathematical model for Crystaf that considers crystallization kinetic effects ignored in all previous Crystaf models and can fit our experimental profiles very well.

Keywords: chemical composition distribution; crystallization analysis fractionation (Crystaf); modeling; molecular weight distribution; polyethylene

Introduction

Consisting of simple monomeric units, polyethylene and its analog, hydrogenated polybutadiene, have been viewed as simple model polymers. This is partly true for some specially synthesized samples having chain microstructures that allow us to draw several conclusions on the effect of chain microstructure and topology on physical properties. However, the notion that we have thoroughly understood this polymer is far from the true. In fact, the chain microstructure and topology of commercial polyethylene are far from simple, but rather extremely complex.

Average microstructural properties such as number average molecular weight and average comonomer content are insufficient to describe the physical properties of such complex polymers. Details on both intra- and intermolecular heterogeneity (e.g., molecular weight distribution, chemical composition distribution, sequence length distribution, and long chain branching level) are often required to fully describe commercial polyethylene. Despite the fact that understanding chain microstructure and structure-property relationships is crucial for developing new generations of polymers, establishing reliable structure-property relationships remain a challenging task for polymer engineers.

Crystallization analysis fractionation (Crystaf) is an important polyolefin characterization technique because it can analyze crystallizability distribution of semicrystalline polymers and this distribution can be used to infer the molecular weight distribution (MWD) of homopolymers, the chemical composition distribution (CCD) of binary copolymers, and the tacticity distribution (TD) of stereoregular polymers.[1–3] Quantitative distributions can be obtained using a calibration curve, a relationship between chain crystallizability and chain microstructure for each case.

Crystaf involves the non-isothermal crystallization of polymer chains from a dilute solution. During crystallization, the concentration of polymer remaining in solution is monitored as a function of crystallization temperature (integral Crystaf distribution). The first derivative of the integral Crystaf distribution (differential Crystaf distribution) represents the weight fraction of polymer that crystallizes at each temperature.

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Table 1.
Properties of polyethylene and poly(ethylene-*co*-hexene) samples.

Sample (Trade Name)	Polymer Type	Number average molecular weight (M_N)	Polydispersity Index (PDI)	Mol percent of 1-hexene
PE8	Ethylene homopolymer	7,900	3.20	0
PE16 (SRM1475)	Ethylene homopolymer	15,400	3.51	0
PE32 (SRM1483)	Ethylene homopolymer	31,600	1.31	0
PE48	Ethylene homopolymer	47,900	2.15	0
EH06	Ethylene/1-hexene copolymers	36,100	2.5	0.68
EH15	Ethylene/1-hexene copolymers	35,200	2.35	1.51
EH31	Ethylene/1-hexene copolymers	34,300	2.18	3.14

Several attempts have been made to model Crystaf profiles. The models proposed in the literature can be divided into two groups: models based on Stockmayer's bivariate distribution,[4–6] and models based on Monte Carlo simulation.[7–9] Although these models can describe Crystaf profiles for a certain set of samples and fractionation conditions, they suffer from a major conceptual flaw because they assume that the fractionation occurs at, or near to, thermodynamic equilibrium. We have recently shown that this is not the case and that crystallization kinetic effects influence Crystaf analysis.[10] For a typical operation condition (a cooling rate of 0.1 °C/min), Crystaf is far from thermodynamic equilibrium, because using slower cooling rates broaden Crystaf peaks and shift them to higher crystallization temperatures.

In this paper, we propose a new semi-empirical mathematical model that accounts for the effect of crystallization kinetics during Crystaf analysis. The model was validated by fitting experimental Crystaf profiles measured at several cooling rates for a series of ethylene homopolymers and ethylene/1-hexene copolymers. Good agreement between the experimental data and the model was obtained for all the samples investigated.

Experimental Part

Materials

Seven polyethylene samples (four ethylene homopolymers and three ethylene/1-hexene copolymers) were used in this investigation. Table 1 summarizes some average properties of these samples. Two of the samples (PE16 and PE32, with trade names SRM1475 and SRM1483, respectively) were purchased from the National Institute of Standards and Technology (NIST, USA). The other polyethylene samples were synthesized in the olefin polymerization laboratory at University of Waterloo in a 300 mL Parr autoclave reactor operated in semi-batch mode. A detailed description of the polymerization procedure can be found in a previous publication.[11]

Crystaf

Crystaf analysis was performed using a Crystaf model 200 manufactured by PolymerChar S.A. (Valencia, Spain). The polymer was dissolved in 1,2,4 trichlorobenzene (TCB) in a 60 mL, stirred crystallization vessel at a concentration of 0.1 mg/mL. The polymer solution was held at 160 °C for 60 min to ensure the complete dissolution of the polymer. Then, the temperature of the solution was decreased to 110 °C and kept at that temperature for 45 min for stabilization before starting the fractionation. During analysis, the temperature of the crystallization vessel was reduced to 30 °C under constant cooling rates (0.02–1.0 °C/min). The decrease in polymer concentration in TCB solution with temperature was monitored using an in-line infrared detector. The amount of polymer crystallized at each temperature was obtained by numerical differentiation.

Crystaf Model

Model Formulation for Homopolymers

For isothermal polymer crystallization, the relationship between crystallinity, $X(t)$, and

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time, t, can be described using the Avrami equation,

$$X(t) = 1 - \exp(-k \cdot t^n) \qquad (1)$$

where n and k are the Avrami constants. This equation can be used to describe crystallization from polymer melts and from polymer solutions.[12–14] The fractionation in Crystaf is not isothermal; however, for a group of homopolymers with similar chain microstructures, the range of crystallization temperatures during Crystaf analysis is very narrow. Therefore, we first make the assumption that both Avrami parameters can be considered constant for each homopolymer at each condition.

The Avrami exponent, n, is known to be constant over a range of temperatures, so it should be a constant over a range of cooling rates as well. However, the Avrami parameter k depends greatly on the crystallization temperature and, therefore, on cooling rate. The parameter k used in the model for homopolymers should be considered an effective or apparent parameter (i.e., an average value measured over a range of temperatures) at each cooling rate. We will show that, despite of this simplification, we can still use the model to describe the Crystaf profiles very well for the polyethylene samples studied in this investigation.

To use Equation (1), we must establish a relationship between the crystallization temperature, T_C, and the crystallization time, t. Generally, a slow, constant cooling rate, CR, is used during Crystaf analysis. Therefore, the relationship between crystallization temperature and time can be simply written as:

$$\frac{dT_C}{dt} = -CR \qquad (2)$$

At the onset of crystallization ($t = 0$), the crystallization temperature should be equal to the dissolution temperature, T_d. For the case of homopolymers, T_d is a function of kinetic chain length, r. The modified Gibbs-Thomson equation introduced by Beigzadeh et al.[7] was used for this purpose:

$$T_d(r) = T_d^o\left[\frac{r - \alpha}{r}\right] - T_S \qquad (3)$$

In Equation (3), T_d^o is the equilibrium dissolution temperature of a chain with infinite length (this parameter depends on solvent and polymer type), T_S is a supercooling temperature (to account for supercooling during Crystaf analysis), and α is a constant that is inversely proportional to the enthalpy of fusion. To reduce the number of parameters in the model, Equation (3) is rearranged as follows,

$$T_d(r) = A - \frac{B}{r} \qquad (4)$$

where

$$A = T_d^o - T_S \text{ and } B = T_d^o \times \alpha \qquad (5)$$

Since both T_d^o and T_S are essentially constant for a given polymer/solvent combination, we expect the value of the parameter A to remain constant. Similarly, because α is a constant that is inversely proportional to the enthalpy of fusion, the parameter B should also remain constant for all cooling rates.

We also have to consider the difference between the temperature measured in the Crystaf oven and the temperature inside the crystallization vessel (temperature lag, T_l). For our Crystaf instrument, the empirical relation between the temperature lag and cooling rate was reported in our previous publication:[10]

$$T_l = 5.02 \times CR - 0.05 \qquad (6)$$

This empirical equation was established for a cooling rate range of 0.02–1 °C/min, which covers the experimental conditions studied in the present investigation.

Considering the temperature lag in the system, the initial condition for Equation (2) is $T_C(0) = T_d(r) - T_l$. We must integrate Equation (2) with this initial condition to obtain the relationship between crystallization temperature and time:

$$t = \frac{(T_d(r) - T_l) - T_C}{CR} \qquad (7)$$

We obtain our final equation relating the degree of crystallinity as a function of chain length, cooling rate, and crystallization

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temperature for homopolymers by combining Equation (1), (4), and (7):

$$X(r,T_C)=\begin{cases}0 & ,\ T_C \geq T_d(r)-T_l\\ 1-\exp\left\{-k\left[\frac{(A-B/r-T_l)-T_C}{CR}\right]^n\right\} & ,\ T_C < T_d(r)-T_l\end{cases} \tag{8}$$

Since crystallization takes place only when the temperature is lower than $T_d - T_l$, the crystallinity is set to 0 when the temperature is higher than $T_d - T_l$. Because crystallization takes place from a dilute solution, an increase in crystallinity is related to a decrease in the weight fraction of polymer remaining in solution, $C(T_C)$. We propose a very simple equation to describe this relationship (the integral Crystaf profile):

$$C_{\mathrm{model}}(T_C) = \sum_{r=1}^{\infty} m(r)\cdot(1-X(r,T_C)) \tag{9}$$

where $m(r)$ is the weight fraction of chains with kinetic chain length of r. The differential Crystaf profile can be obtained by differentiation of Equation (9) with respect to the crystallization temperature, i.e. by calculating $\mathrm{d}C_{model}(T_C)/\mathrm{d}T_C$.

The model parameters (n, k, A, and B) were determined by minimizing the sum of the squares of differences between the simulated and experimental Crystaf profiles (Φ):

$$\Phi = \sum_{T_C=T_{initial}}^{T_{final}} \left(C_{\mathrm{model}}(T_C) - C_{\exp}(T_C)\right)^2 \tag{10}$$

Model Formulation for Binary Copolymers

The Crystaf model for homopolymers can be extended to binary copolymers such as ethylene/1-olefin copolymers. In the case of homopolymers, molecular weight is considered as the key factor influencing the chain crystallizabilities. However, in the case of binary copolymers, the longest ethylene sequence (LES),[7] which depends on both molecular weight and comonomer content, is considered to be the key factor determining chain crystallizability.[7] The theoretical expression describing the weight distribution function of LES for random copolymer, $W(LES)$, was reported in our previous publication:[8]

$$W(LES) = \frac{(1-P_a)(1-pp)}{P_a}\begin{bmatrix}F(1-pm^{LES})\\ -F(1-pm^{LES-1})\end{bmatrix} \tag{11}$$

The function $F(K)$ and parameter P_a in Equation (11) are defined as,

$$F(K) = \frac{P_a.K}{(1-P_a.K)^2}\left[LES(1-\frac{P_a.K}{1-pm^{LES}}) + \frac{P_a.K}{1-pm}\right] \tag{12}$$

$$P_a = \frac{pp(1-cp)}{1-(cp.pp)} \tag{13}$$

where pm is the monomer addition probability ($pm = pp.cp$), cp is the monomer/comonomer choice probability ($cp = 1\text{-}cpp$), cpp is the comonomer propagation probability, and pp is the propagation probability. Note that the comonomer propagation probability (cpp) is equal to the average comonomer mole fraction in the copolymer for random copolymers. The chain propagation probability (pp) can be calculated from the number average chain length (r_N) and average comonomer content with the expressions,

$$pp = \frac{r_N - 1}{r_N} \tag{14}$$

$$r_N = \frac{M_N}{M_{CO}\times cpp + M_{MO}(1-cpp)} \tag{15}$$

where M_N is the number average molecular weight, M_{CO} is the molecular weight of the comonomer (84 g/mol for 1-hexene), and

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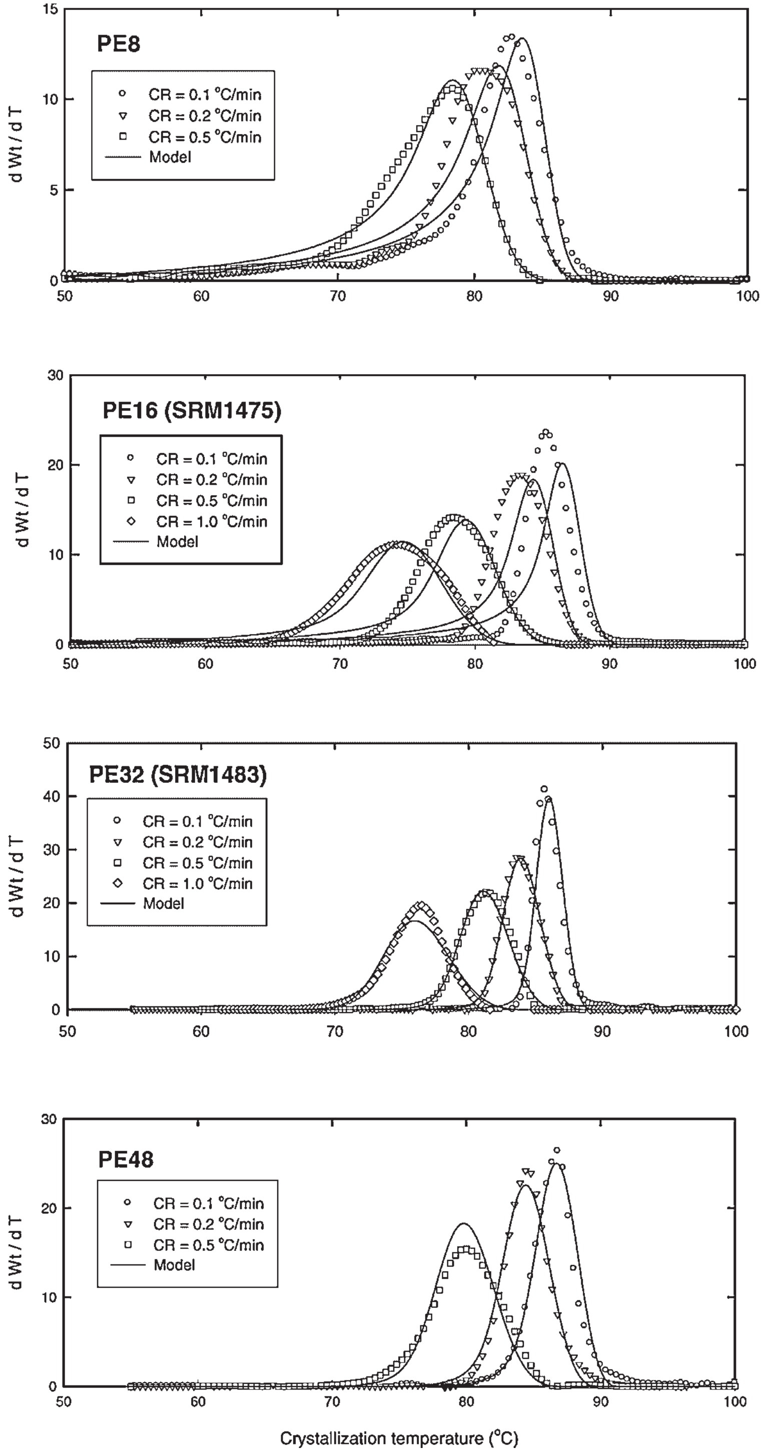

Figure 1.
Comparison between experimental and modeled Crystaf profiles for polyethylene measured at several cooling rates.

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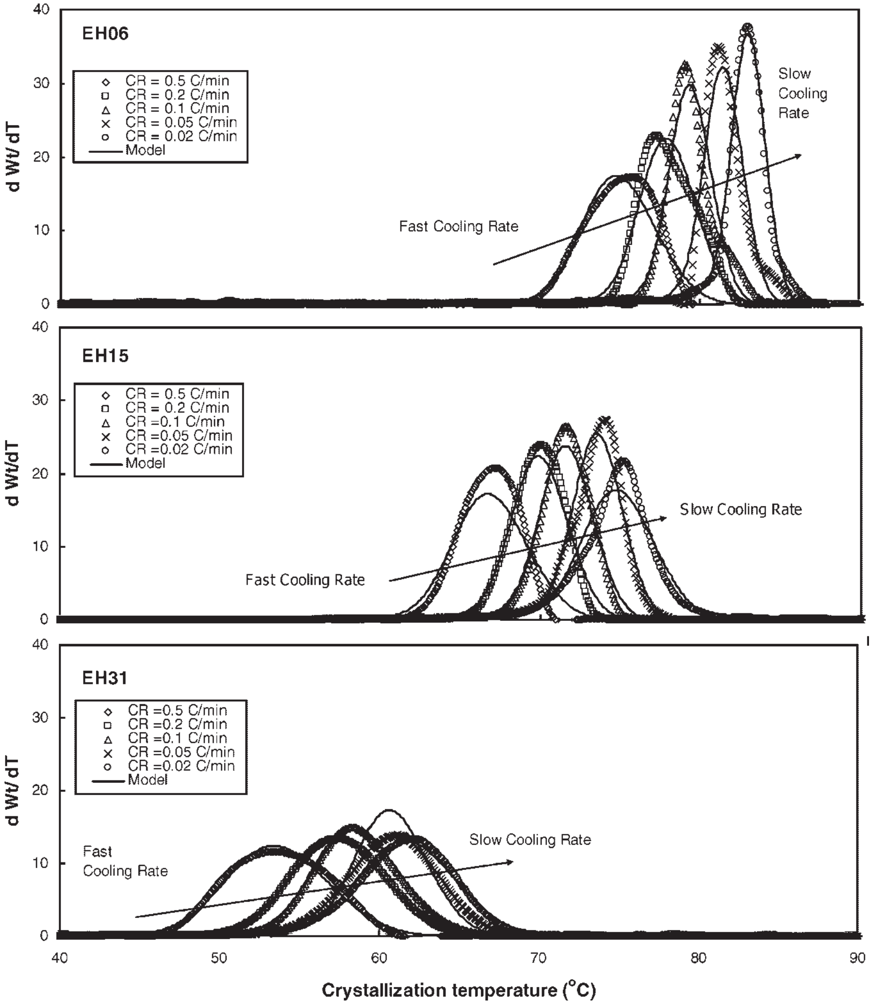

Figure 2.
Comparison between experimental and modeled Crystaf profiles for ethylene/1-hexene copolymers measured at several cooling rates.

M_{MO} is the molecular weight of the monomer (28 g/mol for ethylene).

Following the assumption that the longest ethylene sequence (LES) is the key factor governing chain crystallizability, instead of molecular weight as for homopolymers, we can rewrite Equation (3) to (8) substituting r by LES. Note that the parameters A and B for binary copolymers in Equation (5) are no longer constant as the equilibrium dissolution temperature is a function of comonomer content.

Taking the information from the weight distribution function of LES, W(LES), calculated from Equation (11) into account, the simulated Crystaf profile of copolymers can be calculated as:

$$C_{\text{mod}el}(T_C) = \sum_{r=1}^{\infty} (W(LES) \cdot (1 - X(LES, T_C))) \tag{16}$$

Using the same approach, the model parameters $(n, k, A, \text{and}\, B)$ were determined by minimizing the sum of the squares of the differences between the simulated and

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experimental Crystaf profiles (Φ), Equation (10).

Results and Discussion

Figure 1 and 2 compare experimental and modeled Crystaf profiles polyethylene and ethylene/1-hexene copolymers measured at several cooling rates. The proposed model adequately describes the effect of cooling rate on Crystaf profiles for all samples and correctly follows the broadening of the distributions due to crystallization kinetic effects. The model also captures well the comonomer content effect by predicting the shift of Crystaf profiles to lower crystallization temperatures and the broadening of the distributions as the comonomer content increases.

Optimum model parameters (n, k, A, and B) were obtained by minimizing the function Φ in Equation (10). Figure 3 and 4 shows the Avrami and modified Gibb-Thomson parameters estimated for the polyethylene samples at several cooling rates. As expected, the values of n, A, and B are practically independent of cooling rate (or crystallization temperature). For polyethylene, the average values for these three parameters are $n = 3.96$, $A = 90.45\,^{\circ}\mathrm{C}$, and $B = 654.75\,^{\circ}\mathrm{C} \cdot$ (number of repeating unit). Previous investigations on polymer crystallization from solution by Devoy et al.[12]

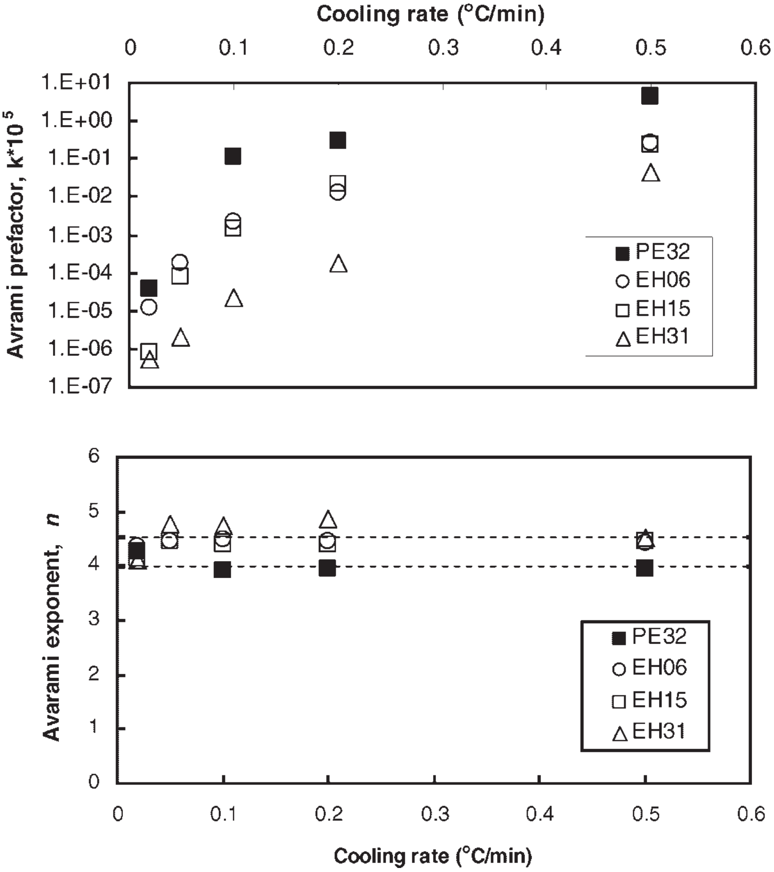

Figure 3.
Estimated Avrami parameters for the Crystaf model. The parameter *k* is an apparent or average value. (The dashed line is the average value for the estimated parameters).

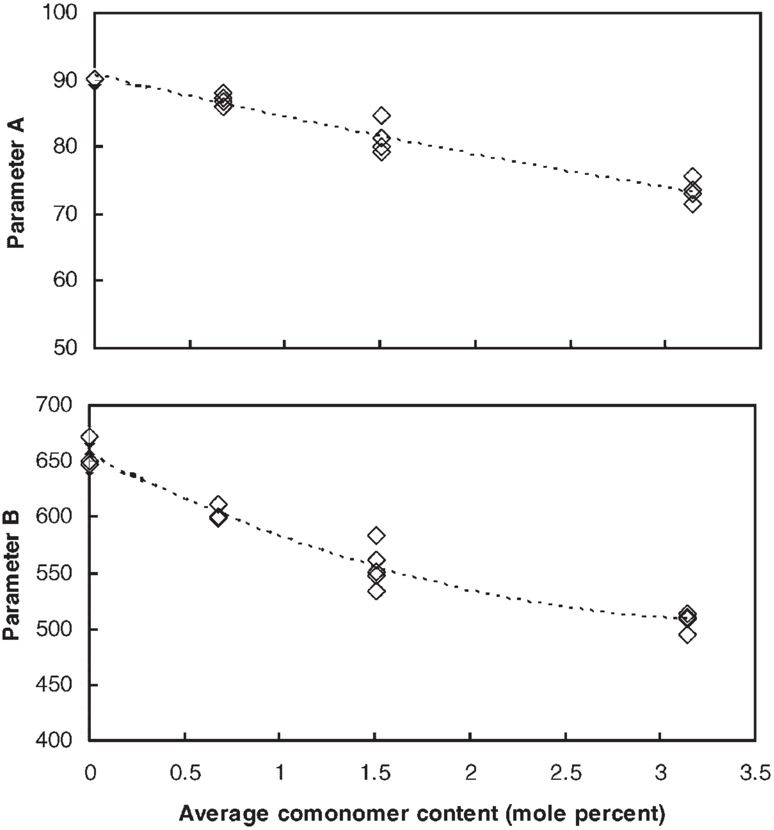

Figure 4.
Estimated Gibbs-Thomson parameters for the Crystaf model as a function of average comonomer content (The dashed lines are to aid the eye only).

and Raiande and Fatou[13–14] showed that the closest integer for parameter *n* for polyethylene in several solvents was 4. This agrees very well with an average *n* value of 3.96 obtained from our parameter estimation. Our average value of parameter *A* (90.45 °C) is also close to the values for the crystallization temperature of ethylene homopolymers in several solvents (85–90 °C) reported earlier by Jackson and Mandelkern.[15]

Our estimated value for the parameter *k* is in the range of 2×10^{-8} to 16×10^{-5} min^{-n}. To the best of our knowledge, no values have been reported for the parameter *k* for polyethylene in TCB, but *k* values for polyethylene crystallized in several other solvents are in the range of 10^{-5} to 10^{-15} min^{-n}.[12–14] It has also been reported that the parameter *k* increases as crystallization temperature decreases. This observation agrees well with our results since we show that *k* increases with increasing Crystaf cooling rates (the faster the cooling rate, the lower the crystallization temperature.)

For ethylene/1-hexene copolymers, the estimated values of the parameter *n* are relatively constant, as expected; however, the average value of the parameter *n* of ethylene/1-hexene copolymers ($n = 4.49$) is slightly higher than the one for polyethylene ($n = 3.96$). The value of parameter *k* was found to increase with a cooling rate as we had also observed for the polyethylene samples. Moreover, the *k* value of ethylene/

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1-hexene copolymers decreases as comonomer fraction increases. This might be because the comonomer unit disrupts the regularity of the chain, thus lowering the chain crystallizability and rate of crystallization; similar observations have been reported in the literature.[16]

Parameters *A* and *B* were found to be relatively independent of the cooling rate used, but strongly dependent on comonomer content. The trends show that both parameters *A* and *B* decrease as comonomer content increases. This is expected and can be explained from Equation (5) because the equilibrium dissolution temperature decreases as the comonomer fraction in the copolymer increases.

In summary, we believe that our model performed quite well considering that the only input for predicting the Crystaf profile of homopolymers is molecular weight and for predicting the Crystaf profile of copolymers is molecular weight and comonomer content.

The model certainly captures the effect of cooling rate on Crystaf profiles peak positions and width. In the case of polyethylene, the model parameters were shown to be within the range of earlier reported values. In the case of ethylene/1-hexene copolymers, these parameters deviate from those found for the homopolymer, but do follow the expected trends.

Applications of this model include construction of the generic Crystaf calibration curves for data interpretation. These calibration curves based on a theoretically sound model could lead to a more efficient use of Crystaf. For example, one may perform an analysis at fast cooling rate (shorter analysis time) and use the calibration curve to help predict the Crystaf profile that would be measured at a slower cooling rate. Demonstration of this approach will be the subject of a future publication.

Conclusions

We developed a new model for Crystaf analysis of homopolymers and binary copolymers that considers the kinetics of crystallization based on the Avrami equation. The model could fit the experimental Crystaf profiles of polyethylene resins measured at a broad range of cooling rates. In addition, the model parameters are theoretically sound and agree with values previously reported in the literature for similar systems. The model also describes well how molecular weight and comonomer content affects the Crystaf profiles of polyethylene and ethylene/1-olefin copolymer samples.

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