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Effect of molecular weight and average comonomer content on the crystallization analysis fractionation (Crystaf) of ethylene α-olefin copolymers

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Abstract

The effect of molecular weight and average comonomer content on the crystallization analysis fractionation (Crystaf) of ethylene/1-hexene copolymers was investigated experimentally and modeled via stochastic simulations. Molecular weight and comonomer content are the main structural parameters that affect the crystallizability of polymer molecules from dilute solutions. Sets of samples with varying molecular weight and comonomer content were prepared to study each effect separately. Although both structural parameters significantly affect the shape of Crystaf profiles, comonomer content is the main determining factor for Crystaf peak location for most molecular weights of interest. The results of the stochastic simulations show good qualitative agreement with the experimental data, but also indicate some clear limitations that might be related to the kinetics of crystallization effects during Crystaf analysis.

Keywords: Chemical composition distribution (CCD); Crystallization analysis fractionation (Crystaf); Monte Carlo simulation

1. Introduction

The chemical composition distribution (CCD), also referred as short chain branch distribution (SCBD), of ethylene-α-olefin copolymers significantly affects the physical and thermal properties of these materials. It is therefore necessary to have quantitative analytical techniques for measuring CCD. Temperature rising elution fractionation (Tref) has been used for several years [1,2], but is a very tedious technique. Recently, crystallization analysis fractionation (Crystaf) was developed as a good alternative to Tref [3–6]. Requiring shorter analysis time, Crystaf provides results comparable to the ones from Tref. Crystaf involves a single-step solution crystallization process, where polymer molecules precipitate at different temperatures according to their crystallizabilities. The results from Crystaf, which are in the form of amount of polymer remaining in solution at each crystallization temperature, can be converted to CCD using a calibration curve that relates crystallization temperature and comonomer content. Since Crystaf is still a relatively new polymer analysis technique, a more quantitative understanding of the detailed fractionation mechanism and how polymer molecular structure influences fractionation is required. In this work we begin to address these issues.

In the case of ethylene-α-olefin copolymers, the average comonomer content and molecular weight are the main structural characteristics that affect their crystallizability and thus their fractionation by Crystaf. Beigzadeh et al. [7,8] proposed a Monte Carlo model for Crystaf fractionation which was based on certain assumptions about the crystallization mechanism and the relationship between lamella thickness and crystallization temperature. The results from the model showed good agreement with their limited experimental data for ethylene/1-octene copolymers. Later, Costeux et al. [9] derived an analytical solution for

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Nomenclature

AvgES	average ethylene sequence (see Fig. 3)
CC	average comonomer content
CPP	comonomer propagation probability
ES	ethylene sequence (see Fig. 3)
LES	longest ethylene sequence (see Fig. 3)
M_n	number average molecular weight
M_{CO}	molecular weight of comonomer (hexane = 84)
M_{MO}	molecular weight of monomer (ethylene = 28)
r_N	number average chain length
PP	propagation probability
T_S	supercooling temperature
T_S^0	equilibrium dissolution temperature
T_C	crystallization temperature
α	constant in Eq. (4)
ζ	lamella thickness

the numerical approach proposed by Beigzadeh et al. [7,8]. They also thoroughly investigated the model considering a wider range of parameters but without experimental validation. Recently, Sarzotti et al. [10,11] reported experimental results on the effect of comonomer content on Crystaf profiles for ethylene/1-hexene copolymers. Herein, we make use of extensive experimental data to evaluate and to propose an improvement to the original model of Beigzadeh et al. [7,8].

2. Experimental

2.1. Samples

Ethylene/1-hexene copolymers were used in this investigation. The effect of number average molecular weight was studied using fractions of three metallocene-catalyzed copolymers of varying 1-hexene content. These copolymers were fractionated by molecular weight using a preparative fractionation apparatus (PREP) in solvent/non-solvent mode (PolymerChar, Spain). In PREP, polymer samples are fractionated by controlling the interaction parameter using successive additions of non-solvent to the polymer solution. In our case, xylene and diethylene glycol monobuthyl ether was used as the solvent and the non-solvent, respectively. The polymer samples were dissolved at 130 °C, before holding at 120 °C for stabilization and fractionation. The total volume of solution used in each fractionation step was 180 ml. Table 1 shows the summary of the volume fraction of solvent in solution used for fractionating each sample.

The fractions of each sample have the same average 1-hexene content but different average molecular weights, as shown in Table 2. The molecular weight distribution for each fraction of sample A is displayed in Fig. 1.

Table 1
Volume fraction of solvent in solvent/non-solvent mixture for each fraction

Sample	Volume fraction of solvent in solvent/non-solvent solution				
	Fraction 1	Fraction 2	Fraction 3	Fraction 4	Fraction 5
A	0.400	0.500	0.556	0.588	1.000
B	0.500	0.526	0.556	0.571	1.000
C	0.500	0.526	0.556	1.000	–

2.2. Crystaf analysis

Fig. 2 is a schematic of Crystaf. In this analysis, the polymer is dissolved in trichlorobenzene (TCB) at a concentration of 0.1 mg/ml. During the dissolution step, the polymer solution is held at a temperature of 160 °C for 60 min to ensure complete dissolution. The temperature is then decreased to 95 °C and kept at this value for for 45 min for stabilization before starting the fractionations. The polymer solution is then cooled at a constant rate of 0.1 °C/min to 30 °C. Polymer chains with low comonomer content crystallize at higher temperatures inside the vessel. Aliquots of the polymer solution are collected via an in-line filter (to avoid sampling the polymer chains that have already precipitated) and transferred to the in-line infrared detector. The infrared detector monitors the change in polymer concentration in solution with temperature, providing the integral Crystaf curve. The differential form of the curve, i.e. the weight fraction change at each crystallization temperature, is then obtained by numerical differentiation of the integral curve. More details on Crystaf operation procedures are presented by Monrabal [3,4].

2.3. Other experimental data

In the second part of this investigation, we make use of the data of Sarzotti et al. [10,11]. They studied the effect of comonomer content on Crystaf analysis using a set of ethylene/1-hexene copolymers synthesized using a single-site catalyst. The samples have, approximately, the same

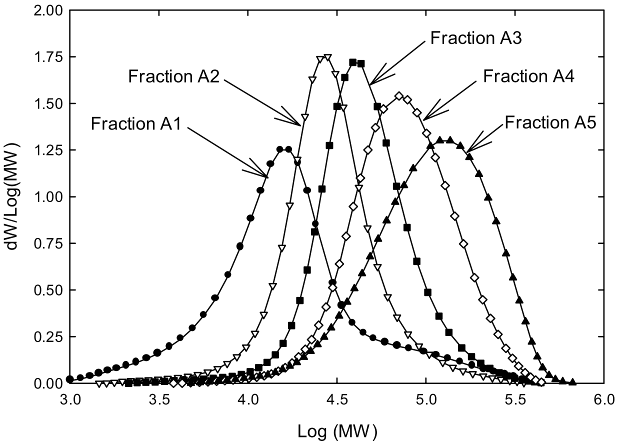

Fig. 1. MWD of each fraction of sample A.

Table 2
Properties of fractionated samples for the study of molecular weight effect

Sample	Number average molecular weight (M_n)	Fractionated sample	Number average molecular weight (M_n)	Number average chain length (r_N)	Mol fraction of 1-hexene (CPP)
A	36,097	A1	16,689	581	0.0127
		A2	28,415	990	0.0127
		A3	44,905	1564	0.0127
		A4	73,195	2549	0.0127
		A5	104,096	3626	0.0127
B	35,153	B1	30,905	1055	0.023
		B2	51,137	1746	0.023
		B3	71,866	2454	0.023
		B4	97,313	3323	0.023
		B5	151,641	5178	0.023
C	34,252	C1	22,944	770	0.032
		C2	32,110	1078	0.032
		C3	39,468	1325	0.032
		C4	67,124	2253	0.032

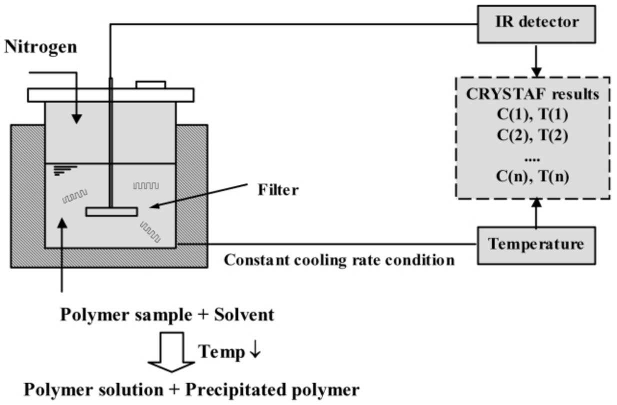

Fig. 2. Schematic diagram of Crystaf.

number average molecular weight (M_n) of 36,300 (well within the range of ± 10% attributed to experimental error in gel permeation chromatography) but different comonomer contents (varying from 0.68 to 4.2 mol% 1-hexene). Table 3 summarizes the information about this set of samples.

3. Simulation

3.1. Chain microstructure

Fig. 3 is a schematic of an ethylene-α-olefin copolymer chain, which includes the necessary definitions of ethylene sequence (ES), longest ethylene sequence (LES), and average ethylene sequence (AvgES). Considering a single molecule, we define ES as the number of ethylene units incorporated in a segment of the polymer chain (each segment is separated by one or more comonomer units). In each copolymer molecule, there is a distribution of ES as there is generally more than one ethylene segment per molecule. Again considering only one molecule, the LES is defined as the largest ES and AvgES is the average ES value. These definitions can naturally be extended to any other polymer chains formed of crystalizable and amorphous segments.

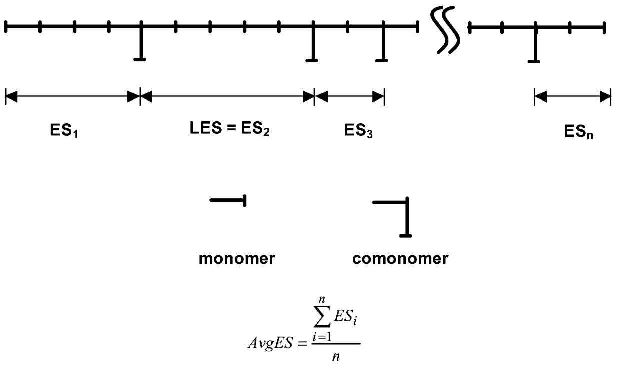

Fig. 3. Illustration of ethylene sequence (ES), longest ethylene sequence (LES), and average ethylene sequence (AvgES) for a LLDPE molecule.

Table 3
Properties of samples for the study of comonomer effect

Sample	Number average molecular weight (M_n)	Number average chain length (r_N)	Mol fraction of 1-hexene (CPP)	PDI
1	34,533	1138	0.0420	2.16
2	34,252	1151	0.0314	2.18
3	34,872	1190	0.0232	2.16
4	36,291	1258	0.0151	2.35
5	36,097	1259	0.0121	2.43
6	37,165	1310	0.0068	2.50

3.2. Monte Carlo simulation

We make use of Monte Carlo simulations to generate a population of copolymer molecules that have the statistical properties of an ethylene-α-olefin copolymer synthesized with a single-site or metallocene catalyst [7,8]. These simulations depend upon two parameters: an overall propagation probability (PP) and a comonomer propagation probability (CPP). The parameter PP is compared to a randomly generated number to decide whether the chain propagates or terminates. If the chain propagates, the parameter CPP is used to choose between the addition of an ethylene or of an α-olefin molecule. For metallocene-catalyzed copolymers, PP can be calculated from the number average chain length (r_N) and average comonomer content (CC) as follows:

$$r_N = \frac{M_n}{M_{CO} \times CC + M_{MO}(1 - CC)} \tag{1}$$

$$PP = \frac{r_N - 1}{r_N} \tag{2}$$

where M_n is the number average molecular weight, M_{CO} is the molecular weight of comonomer (84 for 1-hexene), and M_{MO} is the molecular weight of monomer (28 for ethylene). As such materials are random copolymers CPP and CC are equal. This algorithm was used to generate populations representing unfractionated polymer samples (A, B, C and 1–6).

In order to simulate the molecular weight-fractionated samples (Samples A1–5, B1–5, and C1–4), the preceding algorithm was modified as shown in Fig. 4. Firstly, the experimental MWD of each fractionated sample (e.g. A1) was discretized in n molecular weight classes and the mass fraction (m_i) of each molecular weight class was recorded. Secondly, the LES distribution, $w_i(y)$, was calculated via Monte Carlo simulation for each molecular weight class. Finally, the overall LES distribution for the polymer fraction, $w(y)$, was obtained using the equation:

$$w(y) = \sum_{i=1}^{n} m_i w_i(y) \tag{3}$$

An important assumption made in the second step of the above procedure was that each molecular weight fraction has the same average comonomer content. This hypothesis is valid for polymers made with single-site catalysts under uniform polymerization conditions, such as the ones investigated herein. Analysis of metallocene-catalyzed LLDPEs by GPC–FTIR also confirmed that average comonomer content is independent of molecular weight [12].

For the solvent/non-solvent system, the effect of comonomer content and crystallinity on fractionation is negligible since the fractionation is carried out at a temperature higher than the polymer dissolution temperature. This concept was suggested from the theoretical treatment by Stockmayer and Fixman [13] and later confirmed with experimental work by Tung [14].

3.3. Crystal thickness and crystallization temperature and their relationship to Crystaf

Polyethylene forms a lamellar crystal structure as it is

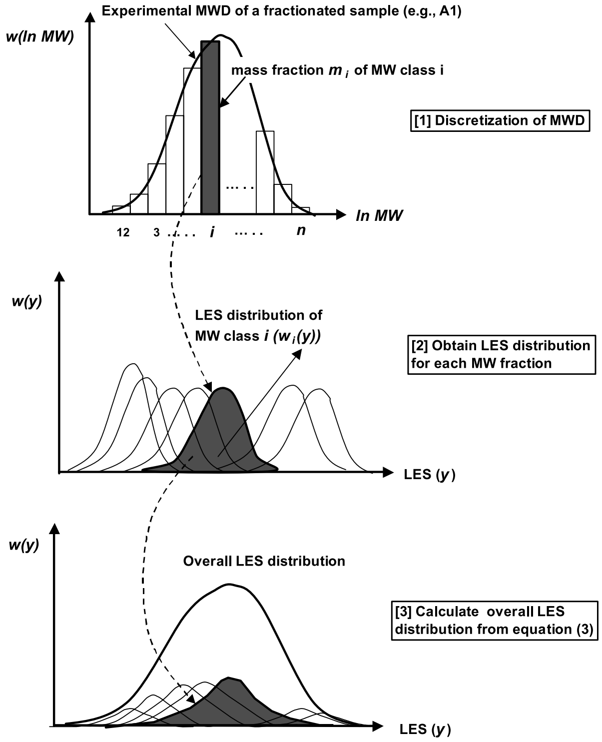

Fig. 4. Illustration of the computational steps for determining LES distribution when the MWD is known.

crystallized from a dilute solution. The lamella thickness (ζ) is a strong function of the crystallization temperature (T_C). This relationship is well described from thermodynamic considerations by the Gibbs–Thompson equation [15]:

$$T_C = \frac{T_S^0(\zeta - \alpha)}{\zeta} - T_S \tag{4}$$

Beigzadeh et al. [7,8] introduced an additional empirical parameter (T_S) to account for supercooling during the crystallization process. In this equation, T_S^0 is the equilibrium dissolution temperature and α is a constant related to the enthalpy of fusion.

In the Crystaf model proposed by Beigzadeh et al., the lamella thickness is assumed to be proportional to the LES. This assumption is based on the hypothesis that comonomer units cannot be part of the lamella lattice. Therefore, the longest ethylene sequence (LES) is the first segment in the chain to crystallize as Crystaf temperature decreases, thus determining the lamella thickness. As soon as the LES crystallizes, the entire molecule precipitates from solution and is no longer detected by the IR detector. Consequently, according to this model, Crystaf profiles are obtained from Eq. (4) by simply substituting ζ by the LES distribution and finding values for the parameters α, T_S^0, and T_S that adequately represent the experimental data.

This is clearly a bold simplification of a rather complex problem, since it ignores chain folding and polymer crystallization kinetic effects. However, it will be shown that this approach can be used as a semi-empirical model to better understand the crystallization phenomena taking place in Crystaf. In the present study, we will also consider the AvgES distribution as an alternative to the LES distribution for modeling Crystaf profiles.

4. Results and discussion

4.1. Effect of number average molecular weight (M_n)

Molecular weight can affect the crystallizability of polymer chains in two subtle ways. Firstly, a molecule with higher molecular weight has more difficulty folding and fitting into the crystal lattice than another with lower molecular weight. Chain movement is certainly more difficult for a molecule with high molecular weight as the hydrodynamic radius and friction coefficient increase with molecular weight. Secondly, molecular weight can affect the crystallization process because it is related to the LES distribution. Costeux et al. [9] showed that LES increases with molecular weight. As the LES can be related to crystallization temperature through the Gibbs–Thomson equation, molecular weight inevitably affects the crystallization process.

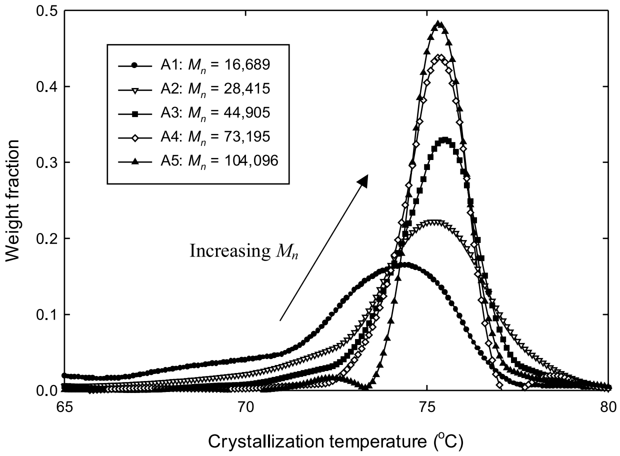

Fig. 5. Effect of molecular weight on Crystaf profile (Experimental results).

Experimental Crystaf profiles for the molecular weight fractions of sample A (recall that each fraction has the same 1-hexene content of 1.27 mol%) are shown in Fig. 5. Fractions of samples B and C show the same trends. The results show that as the molecular weight increases, the Crystaf profiles become narrower. This change on the shape of Crystaf profiles is especially pronounced for the low molecular weight fractions, with the appearance of a low crystallinity tail. Nieto et al. [16] performed Crystaf analysis of a series of ethylene homopolymers of varying molecular weights. They found that the Crystaf profiles of homopolymers changed with molecular weight in a similar way as shown in Fig. 5.

Although a trend of increasing peak temperature with molecular weight is also visible, it is well within the experimental error of ± 1 °C. Thus, this effect is practically negligible for this variable. This allows the construction of calibration curves relating comonomer content and peak position that are independent of molecular weight for most polymers of commercial interest.

However, it is interesting to notice that the onset of crystallization takes place at lower temperatures as molecular weight increases for samples A2–A5. This is probably related to crystallization kinetics effects, since shorter chains can crystallize faster than longer ones and therefore are likely to be closer to the assumed thermodynamic equilibrium. Evidently, if the molecular weight is too small (fraction A1), the LES becomes too short to crystallize at a high temperature and a decrease in the onset of crystallization temperature is observed.

Fig. 6 compares experimental and simulation results (based on LES distribution) for these fractions. The computation was done using two parameters reported by Beigzadeh et al. [7,8] ($\alpha = 10$, $T_S^0 = 89$ °C) while the supercooling temperature was chosen to match the present experimental data. The simulations qualitatively agree with the experimental results. Especially important is the fact that the model can properly describe the low temperature tails for the lower molecular weight fractions. One can, however, observe increasing discrepancies between model and experiments as molecular weight increases.

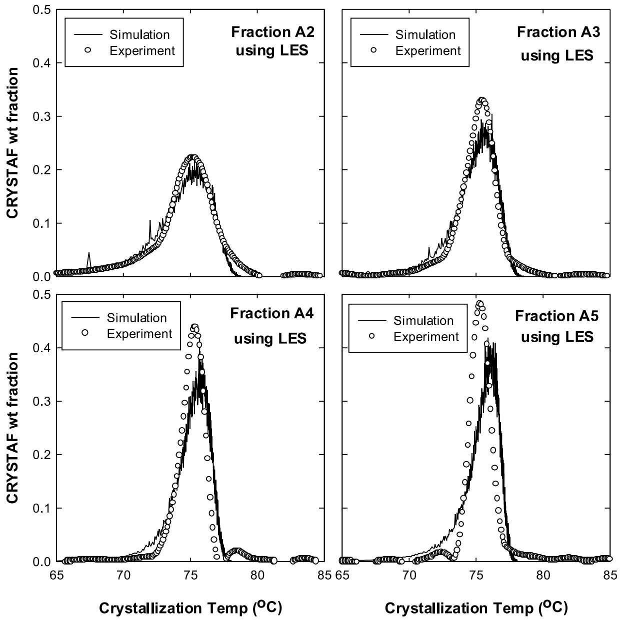

Fig. 6. Comparison between experimental data and simulation results using LES distribution for various M_n (fractions of sample A, $\alpha = 10$, $T_S^0 = 89$ °C).

Using the LES distribution, the best-fit supercooling temperature (T_S) in Eq. (4) was found to be a function of the number average chain length and comonomer content. Fig. 7 shows the relationship for each set of fractionated samples (sample A, B, and C). Interestingly, molecular weight and comonomer content (up to a limiting comonomer fraction when the comonomer effect overtakes the influence of molecular weight) synergistically affects the supercooling temperature, as indicated by the steeper slope of the curve for sample C.

4.2. Effect of comonomer content

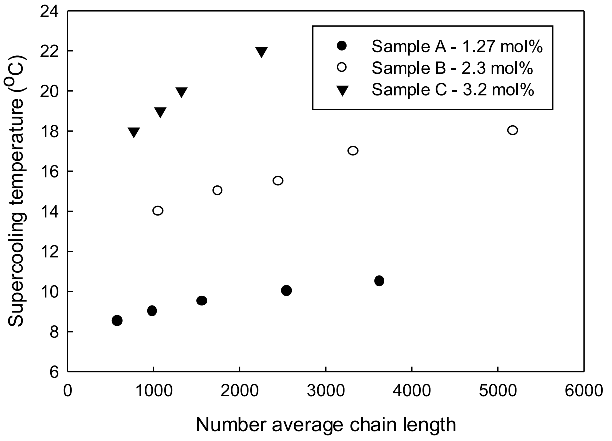

Fig. 7. Effect of number average chain length on supercooling temperature for various comonomer content levels.

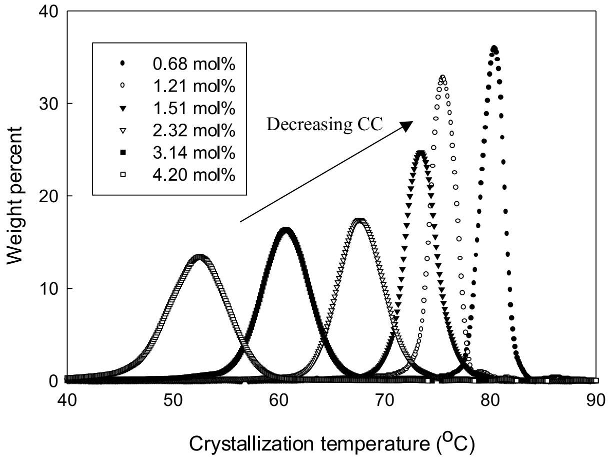

Fig. 8. Effect of comonomer content on Crystaf profile (Experimental results from Sarzotti et al. [10,11]).

The crystallizability of ethylene-α-olefin copolymers is primarily determined by comonomer content. As the amount of comonomer incorporated into the polymer chains increases, the crystallizability of the chain decreases and the crystallization temperature is lowered.

Crystaf experimental results of Sarzotti et al. [10,11] are shown in Fig. 8. Their results show the significant decrease in Crystaf peak temperature as comonomer content increases. The results also display another significant effect of comonomer: a broadening of the Crystaf distribution as comonomer content increases.

The same features can also be observed in the simulation results (Fig. 9). The model overestimates the severity of the low temperature tail and underestimates the temperature for the onset of crystallization. The discrepancies increase as comonomer content decreases. This indicates a systematic lack of fit between the LES-based Crystaf model and the experimental data.

The supercooling temperature, T_S, was found to increase linearly with comonomer content as shown in Fig. 10. Since it was previously demonstrated that T_S increased linearly with kinetic chain length, least squares regression was used to obtain Eq. (5) relating the supercooling temperature to comonomer content and molecular weight:

$$T_S = 1.387 + 6.818 \times 10^{-4} \times r_N + 5.689 \times 10^2 \times CPP \quad (5)$$

All our experimental data and those of Sarzotti et al. [10,11] were used to obtain Eq. (5). Fig. 11 compares the results predicted with Eq. (5) and the experimental data. We recall that Eq. (5) applies to the LES-based model described previously.

4.3. Comparison between Crystaf simulations based the LES and AvgES distributions

As demonstrated previously (Fig. 9), the LES-based model over predicts the tailing of the distributions and under predicts the temperature for the onset of crystallization. An

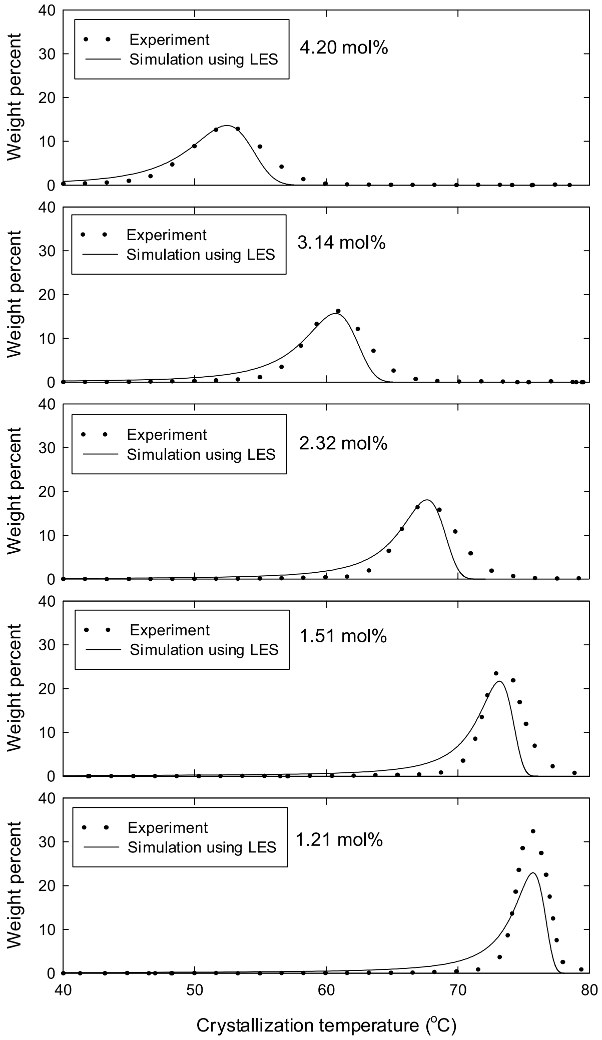

Fig. 9. Comparison between experimental and simulation results using LES distribution for various levels of comonomer content ($\alpha = 10$, $T_S^0 = 89$ °C).

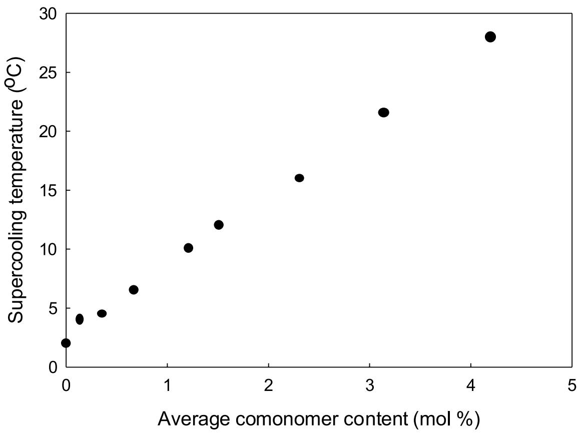

Fig. 10. Effect of comonomer content on the supercooling temperature for constant M_n ($M_n \approx 35{,}000$).

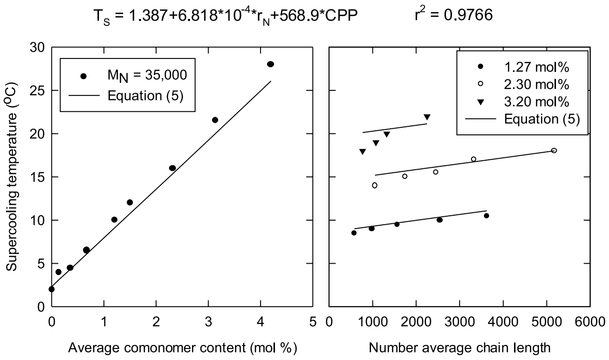

Fig. 11. Effect of comonomer content and molecular weight on the supercooling temperature (model using LES distribution).

alternative model can be proposed using the AvgES distribution to replace the LES distribution in Eq. (4). This method involves the same numerical procedure as described by Costeux et al. with the exception that the lamella thickness is now assumed to be determined by the AvgES instead of the LES.

After refitting the parameters α and T_S in Eq. (4) ($\alpha = 6$, $T_S^0 = 89$ °C), the AvgES-based model performs better than the LES-based model. Figs. 12 and 13 compare the AvgES-based simulations of the Crystaf profiles with experimental data for the fractions of sample A and for samples 1 through 5. As compared to the LES-based model, the AvgES-based model slightly improves the fit of the experimental data for the fractionated samples (compare Figs. 6 and 12), but this improvement becomes significant for the samples with different level of comonomer content (compare Figs. 9 and 13). The improved prediction of the onset of crystallization temperature and low temperature tail are strong evidences in

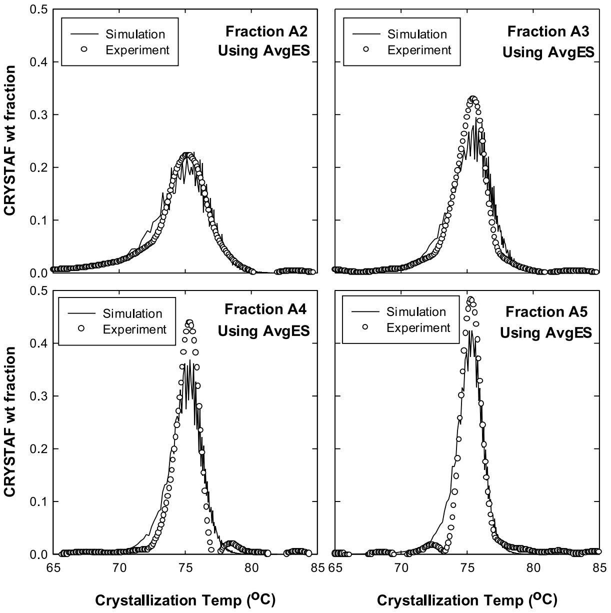

Fig. 12. Comparison between experimental data and simulation results using AvgES distribution for various M_n (fractions of sample A, $\alpha = 6$, $T_S^0 = 89$ °C).

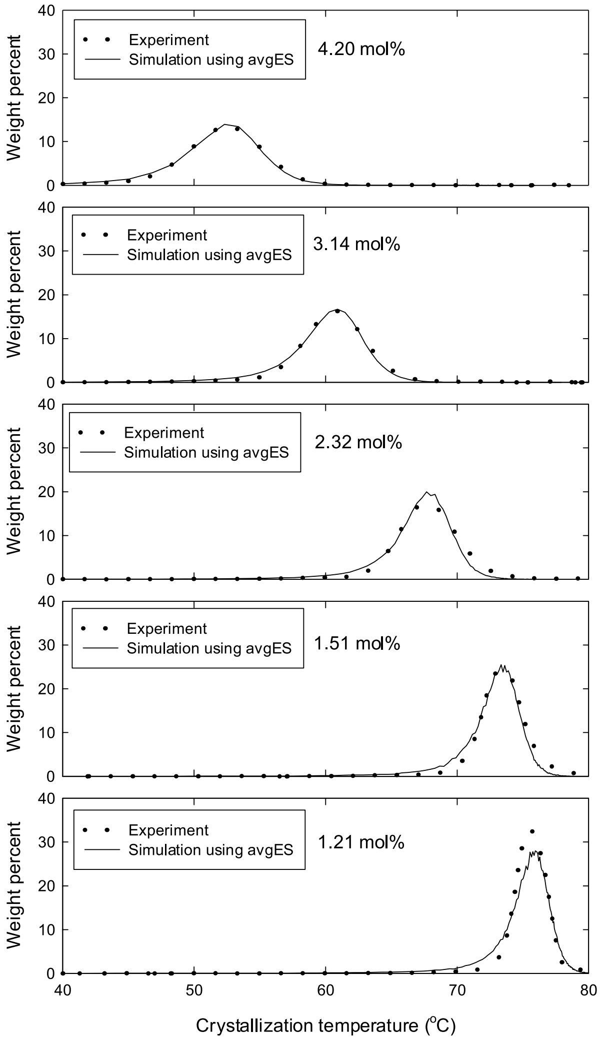

Fig. 13. Comparison between experimental and simulation results using avgES distribution for various levels of comonomer content ($\alpha = 6$, $T_S^0 = 89$ °C).

favor of using the AvgES distribution instead of the LES distribution for modeling Crystaf fractionation.

The reason for the better fit when the AvgES distribution is used can only be speculated in face of these experimental results. Using the LES distribution implies that the fractionation process in Crystaf occurs as close as possible to thermodynamic equilibrium, thus leading to crystals of maximum achievable size under the experimental conditions used during crystallization. This might not be the case, since it is very likely that kinetic effects interfere with the crystallization process in Crystaf, producing smaller crystallites [17]. This might be the reason for the systematic lack of fit when the LES distribution is used to simulate Crystaf profiles. The use of AvgES may indirectly take into account these effects by predicting smaller lamellae than the ones simulated with LES. The AvgEs-based model can then be considered a less fundamental, but perhaps more useful route to model Crystaf fractionation.

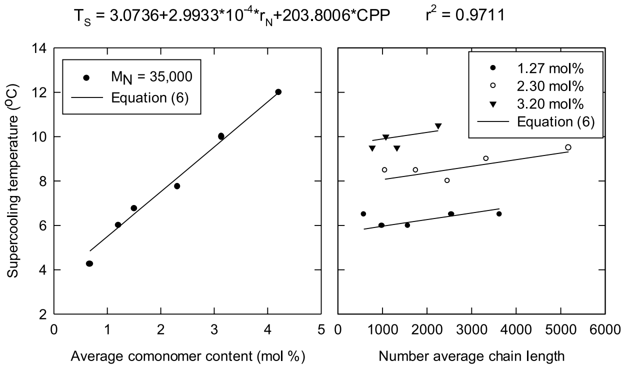

Fig. 14. Effect of comonomer content and molecular weight on the supercooling temperature (model using avgES distribution).

The supercooling temperature was again found to be a function of molecular weight and comonomer content. Eq. (6) is an empirical equation obtained by least squares fit that relates T_S to r_N and CPP for the AvgES-based model:

$$T_S = 3.0736 + 2.9933 \times 10^{-4} \times r_N + 2.038 \times 10^2 \times \text{CPP} \tag{6}$$

Fig. 14 compares the results from the above equation and the experimental data. This model permits the accurate simulation of Crystaf profiles for ethylene/1-hexene copolymers as a function of molecular weight and comonomer content.

5. Conclusions

Both molecular weight and comonomer content significantly affect Crystaf profiles. Although Crystaf peak temperatures are practically independent of molecular weight, an increased tailing of the Crystaf profile in the low temperature region with decreasing molecular weight is observed. The comonomer content is the most important parameter affecting the Crystaf peak temperature location for a given set of operating conditions. Therefore, comonomer content can be quickly estimated using a calibration curve relating peak location and comonomer content.

The model proposed by Beigzadeh et al. [7,8] has good qualitative agreement with the experimental data, but systematic lack-of-fit can be observed. Using the AvgES distribution, instead of the LES distribution, is a better modeling approach for Crystaf profiles.

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