Modeling of Fractionation in CRYSTAF Using Monte Carlo Simulation of Crystallizable Sequence Lengths: Ethylene/1-octene Copolymers Synthesized with Single-Site–Type Catalysts

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ABSTRACT: Monte Carlo simulation was used to model the fractionation process in crystallization analysis fractionation (CRYSTAF). Five poly(ethylene/1-octene) samples synthesized with a single-site–type catalyst were used to verify the simulation results. It was proposed that the fractionation mechanism be controlled by the crystallization of the longest ethylene sequence in each chain. Good agreement between experimental and simulation results verified the validity of the proposed fractionation mechanism. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 80: 2200–2206, 2001

Key words: CRYSTAF; ethylene copolymers; crystallization; Monte Carlo simulation

INTRODUCTION

Crystallization analysis fractionation (CRYS-TAF) is a good alternative technique to TREF (temperature rising elution fractionation) analysis. Whereas TREF requires two fractionation steps (i.e., crystallization and elution), CRYSTAF is done in a single crystallization step that considerably reduces the analysis time. The operation procedure of CRYSTAF has been reported extensively elsewhere.[1–3] In summary, a very dilute solution (0.1–0.2 wt %) of a polymer sample at temperatures higher than its melting point is cooled down very slowly (6–12°C/h) and the solution concentration is recorded at certain temperature intervals, yielding a cumulative concentration curve. The derivative of this curve with respect to temperature represents the weight fraction of precipitated polymer at each temperature (similar to a TREF chromatogram). Although CRYSTAF (or TREF) results are used to estimate the copolymer composition distribution in polyolefins, the true relationship between the two is still to be found. Apparently, precise knowledge of the precipitation mechanism in these methods is required to relate CRYSTAF results to the copolymer composition distribution.

In the present work a mechanism for the fractionation process in CRYSTAF is proposed. Five different ethylene/1-octene random copolymers synthesized with a single-site–type catalyst were used for model verification. Monte Carlo simulation was employed to simulate the chain microstructures of the above-mentioned samples.

FRACTIONATION MECHANISM IN CRYSTAF

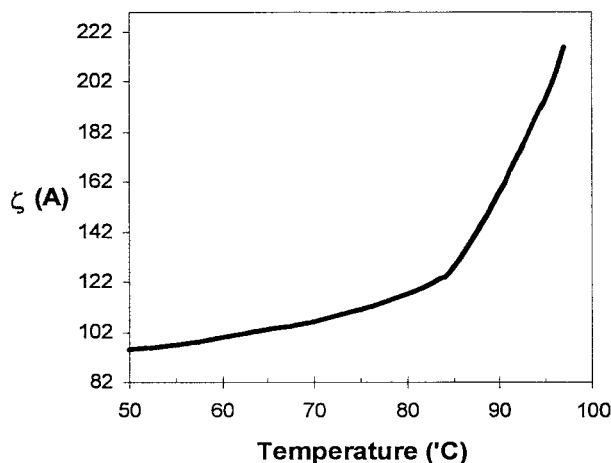Typically, the crystals formed from dilute solutions are several microns in lateral dimensions

Figure 1 Temperature dependency of crystal thickness for polyethylene in xylene.

and are of the order of 100 Å thick. This thickness is fairly uniform among the crystallites but is very sensitive to the crystallization conditions, particularly the crystallization temperature. Figure 1 illustrates a typical dependency of crystal thickness versus temperature[4,5] for polyethylene in xylene. The outward appearance of a polyolefin single crystal, formed from dilute solutions, depends on the chemical structure of the chain and crystallization conditions (temperature, nature of the solvent, cooling rate, etc.). Polyolefin single crystals in their simplest form are monolayer lamella, which are often rhomboid[6] (Fig. 2). The axes a and b of a crystalline cell correspond to the long and short diagonals of a rhombus, whereas axis c, along which macromolecular chains are directed, is perpendicular to the crystal plane. Because the length of macromolecules constitutes thousands of angstroms, whereas the thickness of a single crystal is not more than 200 Å, a chain has to fold several times to fit into the crystal. The reentry requirement clearly demands some type of chain folding[4,7]; however, the exact nature of the chain return is not obvious.
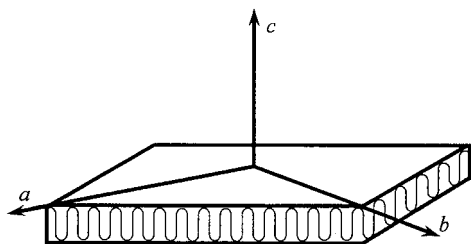

Figure 2 Diagram of the arrangement of crystallographic axes in lamellar crystal of polyethylene.

Table I   Average Properties of Poly(ethylene/1-octene) Samples

Sample	MFI	Density	1-Octene mol %	M_n	PDI
A	3	0.902	5.64	29600	2.20
B	0.5	0.910	3.85	38000	2.21
C	1	0.910	4.00	34400	2.31
D	3.5	0.910	4.26	29300	2.15
E	6	0.911	4.16	22000	2.54

Adapted from Reference 7.

In ethylene/1-octene random copolymers the ethylene sequences form the crystallizable sections. The 1-octene portions of chains are not crystallizable, because of the bulky branches, and form the amorphous sections. Since the lengths of ethylene sequences are usually much smaller than the main chain, they may not be long enough to fold several times or even once while crystallizing. However, ethylene sequences of different chains can position themselves close to each other and crystallize, if their lengths are equal to or greater than the crystallite thickness being formed. As shown in Figure 1, the crystallite thickness is a strong function of temperature (particularly at high temperatures); therefore, at each temperature ethylene sequences that have lengths equal to or greater than the crystallite thickness at that temperature will crystallize and precipitate. The present work proposes that the length of the longest ethylene sequence in the chain
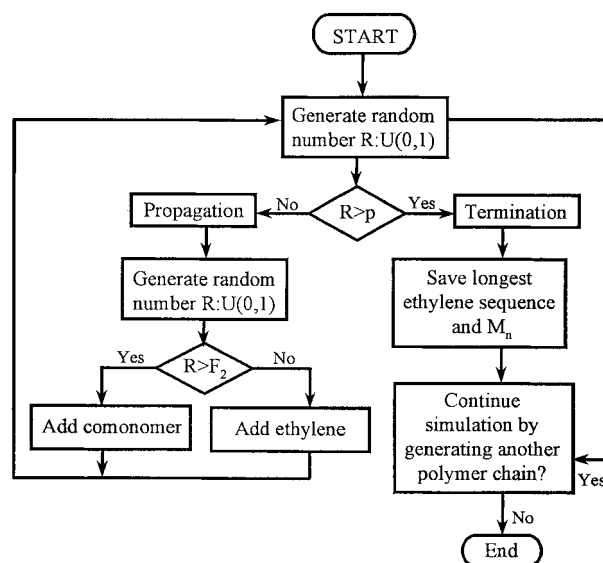

Figure 3 Flow chart for Monte Carlo simulation.

Table II   Values of the Parameter Used in Monte Carlo Simulation

Sample	X_n	Propagation Probability	Comonomer Propagation Probability
A	904.12	0.99889	0.0564
B	1216.68	0.99918	0.0385
C	1096.81	0.99909	0.04
D	927.92	0.99892	0.0426
E	698.50	0.99857	0.0416

is the determining factor in the fractionation process in CRYSTAF.

To verify the validity of the proposed fractionation mechanism, five different poly(ethylene/1-octene) samples synthesized with a single-site–type catalyst were used. The characteristics of the samples are shown in Table I. Synthesis and characterization details were previously reported elsewhere.[8]

SIMULATION

A Monte Carlo model was employed to simulate the microstructure of the polymer samples shown in Table I. Number-average molecular weights (M_n), determined by size-exclusion chromatography[8] and copolymer composition (F_2), determined by carbon-13 nuclear magnetic resonance,[8] were the only values used to determine the simulation parameters. The flowchart of the computer program is shown in Figure 3.

The number-average chain length x_n for each sample can be easily calculated from M_n and F_2 values with the following equation:

$$x_n = \frac{M_n}{112 \times F_2 + 28 \times (1 - F_2)} \tag{1}$$

This parameter is related to the propagation probability by the following equation[9]:

$$x_n = \frac{1}{1 - p} \tag{2}$$

Therefore, the propagation probability can be easily calculated by rearranging eq. (2):

$$p = \frac{x_n - 1}{x_n} \tag{3}$$

The value of the copolymer composition (F_2) was directly used as the probability of 1-octene propagation. Table II shows the employed simulation parameters.

Two hundred thousand chains were simulated for each sample. At the termination of each chain, the number-average molecular weight (M_n) and the length of the longest ethylene sequence were recorded.

The cocrystallization of the chains was then mimicked by classifying the chains according to their longest ethylene sequence. This procedure will generate a weight distribution of longest crystallizable sequences, as shown in Figure 4 for sample A. To convert this distribution to CRYSTAF profile, it is necessary to relate the length of
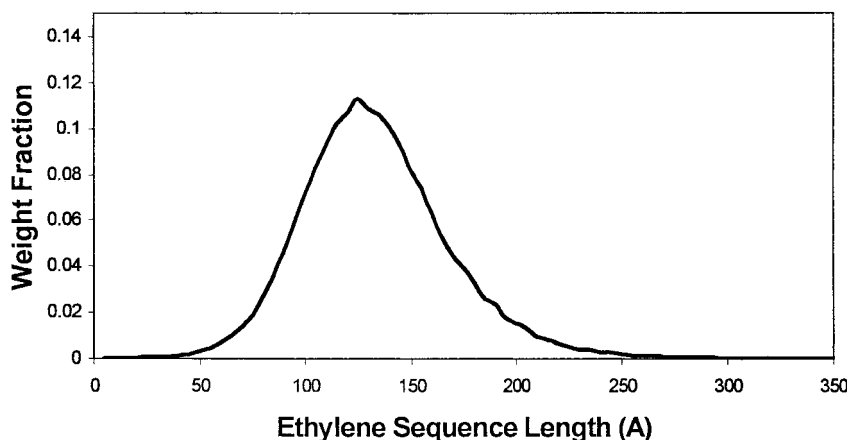

Figure 4   Weight fraction of polymer chains versus their longest ethylene sequence.
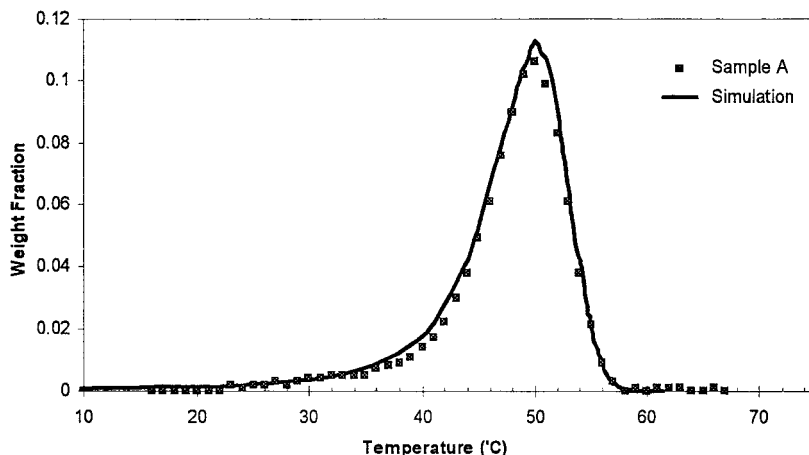
Figure 5 CRYSTAF and simulated chromatograms for sample A.

the longest ethylene sequence to the corresponding crystallization temperature. The next section explains how this can be accomplished.

CRYSTALLITE THICKNESS–TEMPERATURE RELATIONSHIP

As shown in Figure 1, crystallite thickness is a strong function of temperature. Although crystallization in solution is highly dependent on the employed solvent, the shape of the crystallite thickness–temperature curve for almost all solvents is the same.[4,5]

As proposed by Jackson and Mandelkern,[5] the critical size of the nucleus in the chain direction, ζ^*, is inversely proportional to the free energy of

fusion at the crystallization temperature. Therefore,

$$\zeta^* \sim \frac{1}{\Delta f_u(v_2, \, T_c)} = \frac{kT_s^0}{\Delta H_u(T_s^0 - T_c)} \qquad (4)$$

Rearranging eq. (4), and identifying ζ^* with ζ (the length of the longest ethylene sequence that is equal to the crystallite thickness at each temperature) yields

$$T_c = \frac{T_s^0(\zeta - \alpha)}{\zeta} \qquad (5)$$

where f_u is the free energy of fusion, H_u is the enthalpy of fusion, v_2 is the volume fraction of
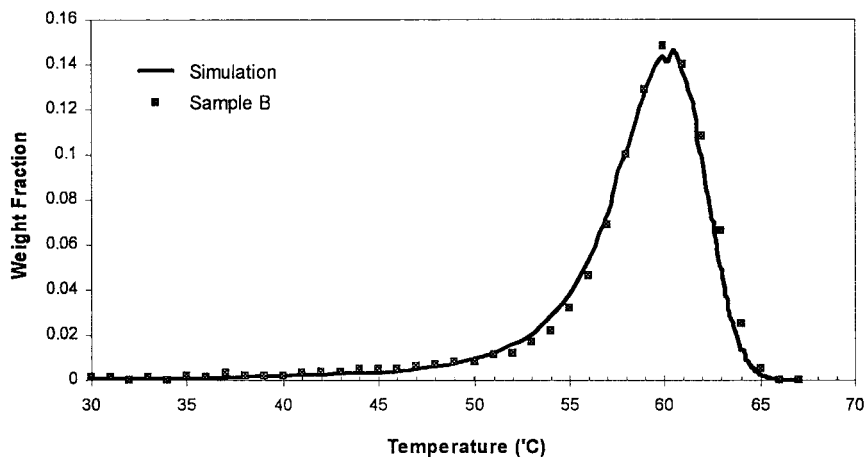

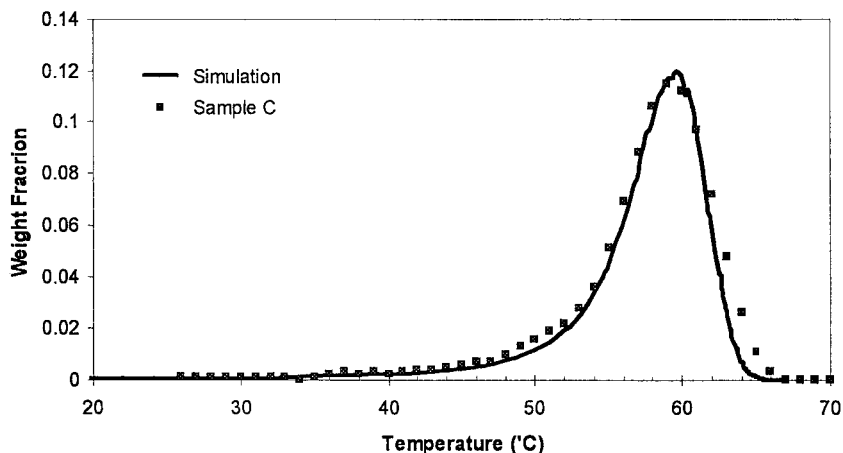**Figure 6** CRYSTAF and simulated chromatograms for sample B.

Figure 7 CRYSTAF and simulated chromatograms for sample C.

polymer, T_c is the crystallization temperature, T_s^0 is the crystallization temperature for a polyethylene chain with infinite chain length, ζ is the length of the longest ethylene sequence in each chain (which is assumed to be equal to the crystallite thickness at $T = T_c$), k is a proportionality constant, and $\alpha = k/\Delta H_u$.

A semiempirical parameter, β, was added to eq. (5) to account for supercooling during crystallization. It should be mentioned that CRYSTAF and TREF chromatograms of a polymer sample are almost identical, except for a shift in CRYSTAF profiles to lower temperatures that result from the supercooling effect.[10] Therefore, eq. (5) was modified to the following equation:

$$T_c = \frac{T_s^0(\zeta - \alpha)}{\zeta} - \beta \qquad (6)$$

The crystallization temperature of a polyethylene chain with infinite chain length in solution (infinite dilution), T_s^0, is a solvent property and is different from solvent to solvent. The values for T_s^0 were found to be[4,5]: 113.0 ± 1.5 for decalin; 118.6 ± 2.0 for xylene, toluene, and tetralin; 127.7 ± 2.0 for n-octane; and 133.1 ± 2.0 for n-hexadecane. The most commonly employed solvent in TREF and CRYSTAF is trichlorobenzene (TCB). Unfortunately, to our knowledge, there are no data in the literature reporting the value of T_s^0 for TCB. However, because TCB is a better solvent for polyethylene
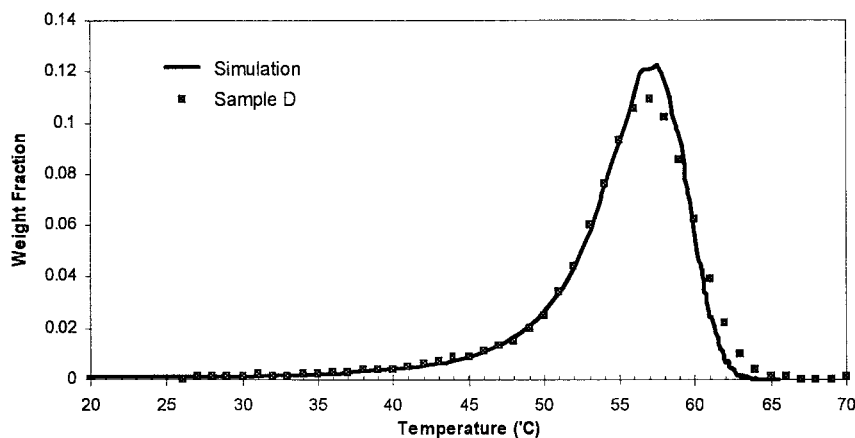

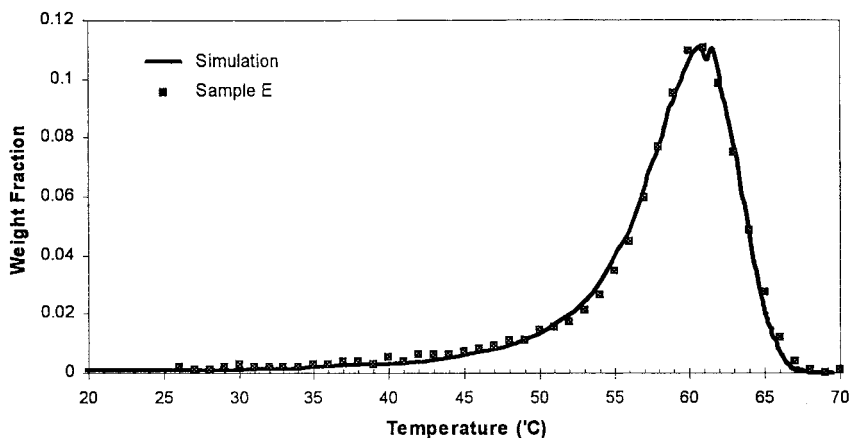**Figure 8** CRYSTAF and simulated chromatograms for sample D.

Figure 9   CRYSTAF and simulated chromatograms for sample E.

than are the above-mentioned solvents, it is expected to have a lower T_s^0 value.

RESULTS AND DISCUSSION

The CRYSTAF chromatograms and simulated chromatograms for the five different poly(ethylene/1-octene) samples, presented in Table I, are shown in Figures 5–9. As can be seen in these figures the simulation results, which are based on the proposed fractionation mechanism, can perfectly predict the tailing observed in the low-temperature region of the CRYSTAF chromatogram. Very good agreement between experimental and simulation results verifies the validity of the proposed fractionation mechanism.

The values of T_s^0 and α were estimated using the linear regression method for the CRYSTAF chromatogram of sample A and the obtained values were used for all samples. These parameters were estimated to be $T_s^0 = 89°C$ and $\alpha = 10$, which is in accordance with the data obtained by Jackson and Mandelkern.[5] The values of β, the semiempirical intercept, for different samples

were chosen by trial and error. This parameter shifts back the simulated curve to lower temperature to account for the supercooling effect. The values of this parameter vary between 18 and 25°C for different samples. The values of these parameters for all poly(ethylene/1-octene) samples are summarized in Table III.

CONCLUSIONS

A mechanism for the fractionation of polyolefin copolymers in CRYSTAF was proposed. According to this mechanism the length of the longest crystallizable sequence in the copolymer chain is the determining parameter in fractionation. Monte Carlo simulation was employed to simulate chains of five different poly(ethylene/1-octene) samples synthesized by a single-site–type catalyst. Very good agreement between experimental and simulation results was observed.

This is the first of a series of studies on fractionation mechanism in CRYSTAF. Polyolefin copolymers synthesized by multiple-site–type catalysts will be analyzed in future reports.

Table III   Values of Parameters in Equation (4) for Different Samples

Sample	T_s^0 (°C)	α	β (°C)
A	89	10	25
B	89	10	20.3
C	89	10	21
D	89	10	22.5
E	89	10	18

NOMENCLATURE

F_2	copolymer composition
f_u	free energy of fusion
H_u	enthalpy of fusion
k	proportionality constant
MFI	melt flow index
M_n	number-average molecular weight
p	propagation probability
PDI	polydispersity index

T_c crystallization temperature

T_s^0 crystallization temperature for a polyethylene chain with infinite chain length

v_2 volume fraction of polymer

α proportionality constant

β intercept

ζ length of ethylene sequence that is equal to the crystallite thickness

ζ^* critical size of the nucleus in the chain direction

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