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THESIS

SIMULATION OF TEMPERATURE RISING ELUTION FRACTIONATION (TREF) USING POPULATION BALANCE AND KINETIC MODELS

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A Thesis Submitted in Partial Fulfillment of
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Temperature rising elution fractionation (Tref) is a characterization technique widely used for estimating chemical composition distribution (CCD) of semi-crystalline copolymers. To elucidate the quantitative fractionation mechanism and accurately interpret Tref profiles, several Tref models have been proposed. However, all previous Tref models are based on the equilibrium fractionation and, therefore, cannot describe the important kinetics roles in Tref analysis observed in experiments.

In this investigation, a new mathematical model of Tref was developed based on the population balance concept with the incorporation of kinetic models describing crystallization and dissolution during the fractionation process, which are ignored in all previous Tref models. The results showed that the proposed Tref model can describe the effects of molecular weight, comonomer content, and operating conditions (i.e., cooling rate, heating rate, and solvent flow rate) on Tref profiles of ethylene homopolymers and ethylene/1-olefin copolymers observed from experiments very well. The simulated Tref calibration curves based on the proposed model were also investigated as an efficient alternative to the experimental Tref calibration curves, which is often, required the tedious process.

Moreover, Monte Carlo simulation and the modified Tref model are used to predict Tref profiles of polymers with more complex microstructures (i.e., polymer blend and linear olefin block copolymers). The modified Tref model was found to be useful to help identify the link between Tref profiles and chain microstructures of polymers.

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Student's signature Thesis Advisor's signature

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Ekaphol Siriwongsarn
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LIST OF ABBREVIATIONS

α = Proportionality constant for Crystaf model

α_c = Proportionality constant during crystallization step for Tref model

α_d = Proportionality constant during elution step for Tref model

BI = Block index

$C(T_{e,x})$ = Concentration of eluted polymer at the exit of Tref column at $T_{e,x}$

cc = Average α-olefin molar fraction of population group

$cc(LES)$ = Average α-olefin molar fraction of population group with LES

CCD = Chemical composition distribution

C_d = Concentration of polymer dissolved

Cef = Crystallization elution fractionation

$C_{exp}(T_{e,x})$ = Concentration of eluted polymer at the exit of Tref column obtained from experiment

$C_{\mathrm{model}}(T_{e,x})$ = Concentration of eluted polymer at the exit of Tref column obtained from simulation

cp = Ethylene/1-olefin choice probability

cpp = 1-olefin propagation probability

CR = Cooling rate

Crystaf = Crystallization analysis fractionation

CSA = Chain shuttling agent

χ = Flory-Huggins interaction parameter

DCL = Distribution of crystallizable lengths

ΔH_{F_i} = Molar melting enthalpy for pure crystal with crystallizable blocks L_i

ΔT_c = Crystallization temperature increment

ΔT_e = Elution temperature increment

LIST OF ABBREVIATIONS (Continued)

$\overline{F_1}$ = Average mole fraction of monomer type 1 of copolymer

ϕ_0 = Volume fraction for solvent in the liquid solution

ϕ_i = Volume fraction for x_i-size species in the liquid solution

HR = Heating rate

k = Avrami prefactor for Crystaf model

k_c = Avrami prefactor describing crystallization kinetics for Tref model

k_d = Avrami prefactor describing dissolution kinetics for Tref model

LES = Longest ethylene sequence

L_i = Length of crystallizable blocks

$m(LES)$ = Mass fraction of population group with LES

$M(LES)$ = Total mass of population group with LES

$m(r)$ = Mass fraction of population group with chain length of r

$M(r)$ = Total mass of population group with chain length of r

M_1 and M_2 = Molecular weights of monomers type 1 and 2

m_c = Crystalline mass fraction

M_c = Total crystalline mass fraction

M_{CO} = Molecular weight of 1-olefin

M_{MO} = Molecular weight of ethylene

M_N = Number average molecular weight

mw = Molecular weight of the structural unit

MWD = Molecular weight distribution

n = Avrami component for Crystaf model

N = Number of interconnecting control volumes

n_c = Avrami component describing crystallization kinetics for Tref model

n_d = Avrami component describing dissolution kinetics for Tref model

LIST OF ABBREVIATIONS (Continued)

OBC = Linear olefin block copolymer

P_c = Comonomer incorporation probability

P_{cat} = Probability of catalyst mole fraction

P_{cat1} = Probability of mole fraction of catalyst 1

P_{cat2} = Probability of mole fraction of catalyst 2

PDI = Polydispersity index

pm = Ethylene propagation probability

P_m = Monomer incorporation probability

pp = Propagation probability

P_s = Shuttling probability

P_t = Chain transfer probability

$\sum \phi_i$ = Total polymer volume fraction in the liquid solution

R = Gas constant

r = Kinetic chain length

R = Random number

r_1 and r_2 = Reactivity ratios in copolymerization

r_N = Number average chain length

SCBD = Short chain branching distribution

SFR = Solvent flow rate

t = Crystallization time for Crystaf model

T = Temperature

T_A = The elution temperature of ethylene homopolymers

T_{AB} = Analytical Tref elution temperature of a random copolymer with the same average composition as that of the whole OBC

T_c = Crystallization temperature

t_c = Crystallization time for Tref model

$T_c(LES)$ = Crystallization temperature of polymer chain with *LES*

$T_c(r)$ = The equilibrium crystallization temperature of chain length r

LIST OF ABBREVIATIONS (Continued)

$T_{c,0}$ = The initial crystallization temperature

$T_{c,final}$ = The final crystallization temperature

TCB = 1, 2, 4 Trichlorobenzene

T_d = Dissolution temperature

t_d = Dissolution time for Tref model

$T_d(LES)$ = Dissolution temperature of polymer chain with LES

$T_d(r)$ = Dissolution temperature of kinetic chain length r

T_d^0 = The equilibrium dissolution temperature of a chain with infinite length

T_e = Elution temperature

$T_{e,0}$ = The initial elution temperature

$T_{e,final}$ = The final elution temperature

$T_{e,x}$ = Elution temperature at a time step x

T_{Fi} = Melting temperature for pure crystal with crystallizable blocks L_i

T_l = Temperature lag in Crystaf

Tref = Temperature rising elution fractionation

T_s = Supercooling temperature for Crystaf analysis

T_{sc} = Supercooling temperature for Tref analysis

T_{sh} = Superheating temperature for Tref analysis

T_{shift} = Shift temperature of each population group

T_x = The elution temperature of an OBC fraction with narrow CCD

T_{x0} = The elution temperature of random copolymer with the equivalent CCD

τ = Ratio of all chain transfer rates to the propagation rate

V_c = Volume of Tref column

v_i = i^{th} control volume

$W(LES)$ = Weight distribution of LES

$w(r)$ = Weight fraction of chain length

LIST OF ABBREVIATIONS (Continued)

X = Crystallinity for Crystaf model

x = Time step x

X_c = Crystallinity for Tref model

X_d = Dissolved fraction for Tref model

$\bar{x}_n$ = Number average size for the species in the liquid phase

y = Deviation from average copolymer composition

Y_0 = Molar volume ratio for solvent/monomer.

SIMULATION OF TEMPERATURE RISING ELUTION FRACTIONATION (TREF) USING POPULATION BALANCE AND KINETIC MODELS

INTRODUCTION

Polymer characterization provides the information of polymer microstructures that can help us understand polymerization process (e.g., polymerization conditions, catalysts) and structure-property relationships. It is important to determine not only average microstructural information (e.g., average molecular weight, and average comonomer content) but also the details of microstructural distributions (e.g., molecular weight distribution (MWD), chemical composition distribution (CCD)) because such distributions can also significantly influence polymer properties and its applications (Wild, 1991; Soares and Hamielec, 1995a).

The CCD, which describes the distribution of comonomer content among copolymer chains, can be obtained by fractionation of polymer molecules according to chain crystallizabilities. Temperature rising elution fractionation (Tref) is the first technique specifically developed to estimate CCD. Recently, other characterization techniques (i.e., crystallization analysis fractionation (Crystaf), crystallization elution fractionation (Cef)) have been developed based on similar principle but with the shorten analysis time. Although Tref requires a long analysis time, it was found that Tref analysis is more robust. Therefore, Tref remains the key CCD characterization technique, especially for polyolefins with complex chain microstructures (Anantawaraskul *et al.*, 2003a; Anantawaraskul *et al.*, 2005; Gabriel and Lilge, 2001). For certain polymer blends, Tref was also found to provide better separation resolution when compared to Crystaf (Anantawaraskul *et al.*, 2003a; Monrabal and Hierro, 2011).

Temperature rising elution fractionation (Tref) consists of two steps: crystallization and elution. During the crystallization step, a polymer solution is fed into a Tref column loaded with an inert support. The temperature is then slowly decreased at a constant cooling rate, allowing polymer chains to crystallize and fractionate from solution at the temperatures corresponded to their chain crystallizabilities. During the elution step, the temperature is slowly increased at a constant heating rate and a fresh solvent is continuously fed into the column. The concentration of eluted polymer solution at the end of Tref column as a function of the elution temperature is monitored to generate the Tref profile. (Wild, 1991; Soares and Hamielec, 1995a; Anantawaraskul, 2005). Figure 1 shows Tref results of some polyolefins.

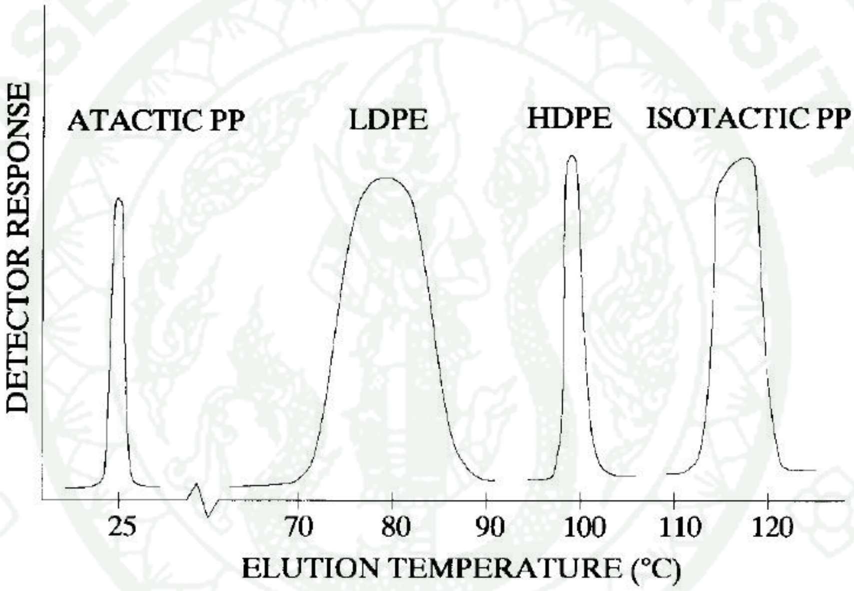


Figure 1 Tref profiles of some polyolefins.

Source: Soares and Hamielec (1995a)

Tref calibration curve, which is a relationship between average comonomer content and peak elution temperature, is required for converting Tref profile to CCD. However, the Tref results and calibration curve depend on polymer chain microstructures (e.g., molecular weight, comonomer type, comonomer content) and operating conditions (i.e., cooling rate, heating rate, solvent flow rate). Therefore, each calibration curve is adequate only for specific polymer types and specific operating conditions. Using general calibration curves for converting Tref profile to

CCD could lead to misinterpretation of CCD. Although a calibrations curve can be experimentally obtained by performing Tref analysis of a series of copolymers with various comonomer contents (Wild *et al.*, 1982; Pigeon and Rudin, 1994; Savitski *et al.*, 2003), such process is often very long and tedious.

To gain the quantitative understanding Tref fractionation mechanism and find the alternative approach for constructing Tref calibration curves, several researchers have attempted to propose Tref models. All previously proposed models can be categorized into two general approaches. The first approach assumes that the solid-liquid equilibrium between crystallized polymers and polymers in a dilute solution at each elution temperature governs the Tref fractionation process (Borrajo *et al.*, 1995; Elicabe *et al.*, 1996a, 1996b; Tomba *et al.*, 2005). The second approach describes Tref profiles based on the Stockmayer bivariate distribution assuming that all polymers with a specific comonomer content fractionated at corresponding elution temperatures (Soares and Hamielec, 1995b; da Silva Filho *et al.*, 2000; Alghyamah and Soares, 2009a, 2009b). As both modeling approaches are based on the concept of thermodynamic equilibrium, they could not describe the important kinetic roles in Tref analysis (i.e., effect of cooling rate, heating rate, and solvent flow rate) that have been experimentally observed (Anantawaraskul *et al.*, 2003a). Therefore, both modeling approaches cannot be used to construct Tref calibration curve at different operating conditions.

Recently, an alternative modeling approach for polymer characterization based on the concept of population balance has been developed and efficiently implemented for Crystaf (Anantawaraskul *et al.*, 2006, 2007a, 2007b). This approach is versatile with the important advantage that mathematical models for describing various kinetic processes can be easily incorporated. Although physical set-up of Tref (i.e., plug flow column) is distinct from set-up of Crystaf (i.e., well-mixed vessel), the model based on the population balance could be adapted for Tref when an appropriate discretization from a plug flow column to a series of small well-mixed controlled volume is employed.

In this work, a new mathematical Tref model based on population balance concept with the incorporation of crystallization and dissolution kinetics was developed. The proposed model was validated with experimental Tref profiles of ethylene homopolymers and ethylene/1-olefin copolymers at several operating conditions. Application of the proposed model in constructing the simulated Tref calibration curves as an alternative to experimental calibration curve, which requires tedious process, was preliminary illustrated.

The other objective is to apply the proposed Tref model for describing the Tref profiles of polymers with complex chain microstructures (i.e., copolymer blends and linear olefin block copolymers (OBCs)). The OBC is a new class of thermoplastic elastomers produced by chain shuttling polymerization which uses two catalysts with different comonomer reactivity ratios in combination with a chain shuttling agent (CSA). The CSA transfers a growing polymer chain from catalyst with a high comonomer reactivity ratio, which produces soft or low crystallinity blocks, to catalyst with a low comonomer reactivity ratio, which produces hard or high crystallinity blocks, as a reversible transfer agent (Arriola *et al.*, 2006). This leads the linear multi-block chain microstructures alternating between hard and soft blocks to have various end used properties providing advantages over random ethylene/α-olefin copolymers.

The proposed Tref model was applied with the information of OBCs obtained from Monte Carlo simulation to predict the Tref profiles of OBCs with various chain shuttling probabilities. Moreover, the simulated Tref profile of OBC was compared with those of random ethylene/α-olefin copolymer and copolymer blend.

OBJECTIVES

1. To develop a new mathematical model of Tref based on the concept of population balance with the incorporation of crystallization and dissolution kinetics for ethylene homopolymers and ethylene/1-olefin copolymers.

2. To validate the proposed Tref model with experimental Tref profiles and estimate Tref model parameters for ethylene homopolymers and ethylene/1-olefin copolymers at several operating conditions.

3. To develop a new strategy for constructing the Tref calibration curves of ethylene/1-olefin copolymers at specific operating conditions based on the proposed Tref model.

4. To predict the Tref profiles of OBCs at various chain shuttling probabilities using Monte Carlo simulation and the proposed Tref model and compare such profiles with the simulated Tref profiles of random ethylene/α-olefin copolymer and polymer blend.

Scope of the Investigation

In this thesis, a mathematical model of Tref based on the concept of population balance with the incorporation of crystallization and dissolution kinetics was proposed. The results were validated with experimental Tref profiles of ethylene homopolymers and ethylene/1-olefin copolymers at several operating conditions.

Polymer samples used are (1) ethylene homopolymer samples with the number average molecular weight of 19,100 and 52,100 g/mol, (2) a series of ethylene/1-hexene copolymers having the number average molecular weight of ~35,000 g/mol and a range of 1-hexene content of 0.68-3.14 mol%, and (3) an ethylene/1-octene copolymer sample having the number average molecular weight of 40,700 g/mol and 1-octene content of 2.19 mol%. All of polymer samples were produced with a single site type catalyst; therefore, they have the polydispersity index (PDI) close to 2.0. The investigated range of operating conditions are cooling rates of 0.1-0.5 °C/min, heating rates of 0.1-0.5 °C/min, and solvent flow rates of 0.1-0.5 mL/min.

The Tref model was performed using the number of population groups of 9,045 to represent chain length distribution of polymer. A Tref column was computationally discretized into 40 interconnecting, well-mixed control volumes. Such conditions were determined from the systematic independency test with the detailed outlined in Appendix A and B.

To predict the Tref profiles of OBCs using Monte Carlo simulation and the proposed Tref model, 200,000 polymer chains were generated to provide an adequate representation of OBC microstructure. The investigated CSA polymerization parameters are shuttling probability (P_s) in the range of 0-0.3, catalyst molar fraction (P_{cat}) of 0.5, and number average molecular weight of 30,000 g/mole. The results were then compared with those of random copolymer and copolymer blend with equivalent average comonomer content.

LITERATURE REVIEW

Temperature rising elution fractionation (Tref) and crystallization analysis fractionation (Crystaf) are characterization techniques which fractionate polymer chains according to their chain crystallizabilities in a dilute solution (Wild, 1991; Monrabal, 1994; Anantawaraskul *et al.*, 2005). These techniques are based on the continuous non-isothermal crystallization of polymer chains from a dilute solution. Chemical composition distribution (CCD) of copolymer, which describes the distribution of comonomer fraction in their chains, can be estimated using Tref or Crystaf profile together with calibration curves. Figure 2 shows the CCD of a typical linear low density polyethylene made from Ziegler-Natta catalysts, reflecting the composition heterogeneity of these copolymers.

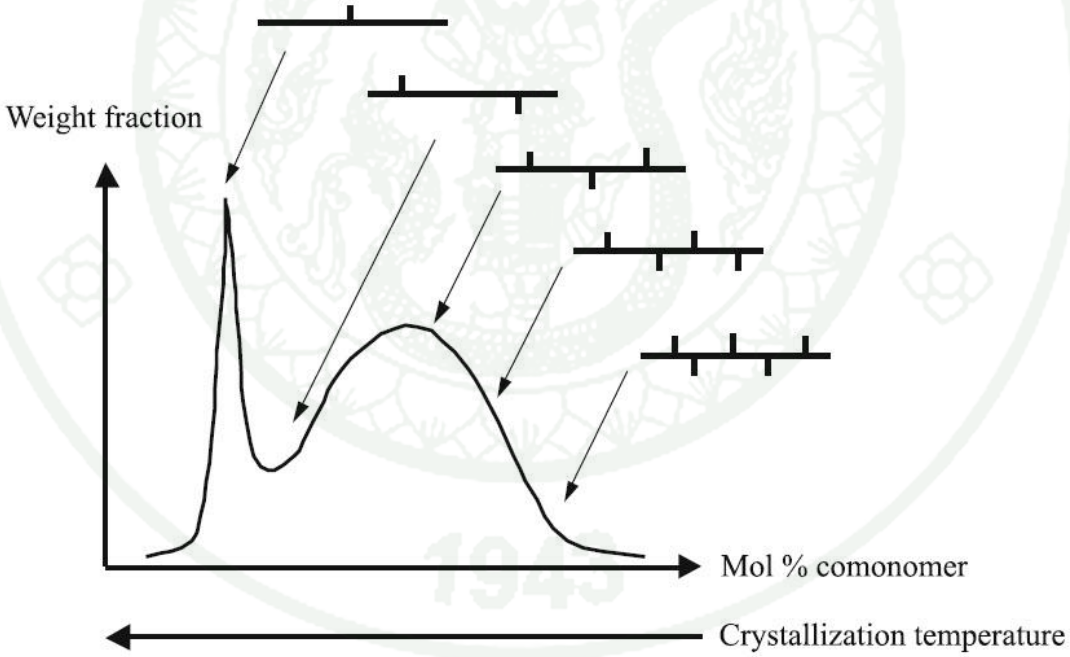


Figure 2 Chemical composition distribution of linear low density polyethylene.

Source: Anantawaraskul *et al.* (2005)

Tref analysis can be divided into two consecutive steps: crystallization and elution (Wild, 1982, 1991). In the first step, the polymer sample is dissolved in a good solvent and then loaded into a Tref column packed with an inert support. The crystallization step is carried out under a slow cooling rate. During this period, the polymer chains crystallize and coat onto the support in layers of different crystallizabilities, as illustrated in Figure 3. The internal layers that are closer to the surface of the support were crystallized at higher temperatures and, therefore, have higher crystallizabilities than those of the external layers. In the second step, the polymer layers are eluted from the support in the reverse order of crystallization. A fresh solvent flows through a Tref column while the temperature is slowly increased. The polymer eluted will be monitored by mass concentration detector. So the polymer fractions with lower crystallizabilities are eluted first at lower temperatures while the fractions with higher crystallizabilities are only eluted at higher temperatures.

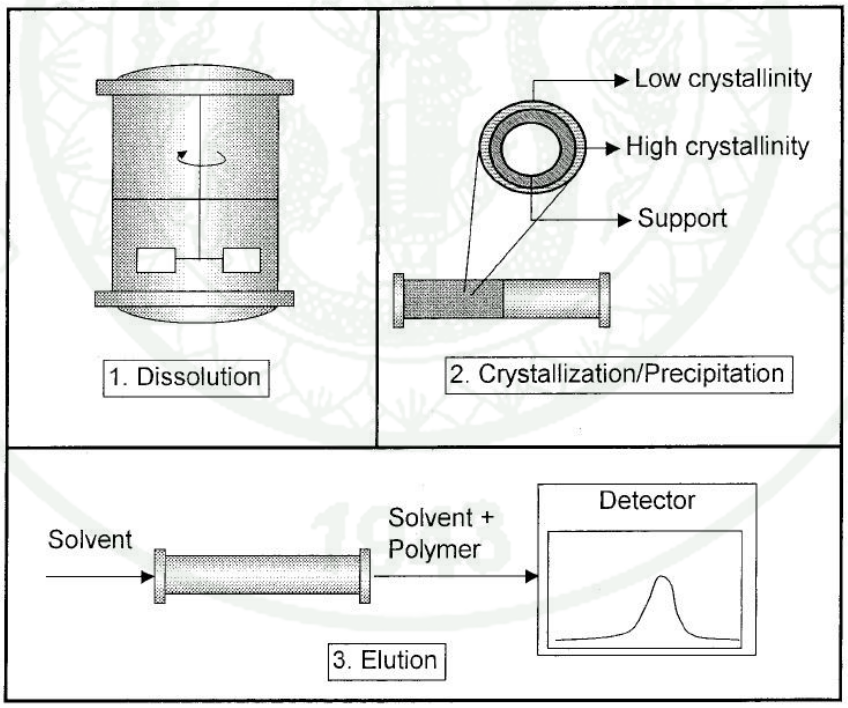


Figure 3 The schematic diagram of temperature rising elution fractionation (Tref).

Source: Anantawaraskul *et al.* (2003a)

1. Effect of Chain microstructures and operating conditions on Tref profiles

1.1 Effect of chain microstructures on Tref profiles

The previous investigations have shown that the polymer chain crystallizability is influenced by the molecular structures of polymer (i.e., molecular weight and comonomer content). As we knew that Tref technique fractionates polymer chains according to their crystallizabilities/solubilities, Tref profiles are understandably influenced by polymer microstructures to some degree.

Wild *et al.* (1982) studied the effect of molecular weight on Tref profiles using a series of narrow molecular weight distribution fractions of linear polyethylene over a wide range of molecular weight. Figure 4 shows the molecular weight dependence of elution temperature. It was found that the molecular weight significantly affect the elution temperature of fractionation for the polymers having low molecular weight (<10,000). For polymers having higher molecular weight, the effect becomes minimal.

The comonomer content is an important copolymer chain microstructure that significantly affects copolymer chain crystallizability and Tref profiles (Pigeon and Rudin, 1994). This can be observed by examining the Tref calibration curve, which is a relationship between comonomer content and peak elution temperature. Figure 5 shows an example of Tref calibration curve which was obtained from linear low density polyethylene fractions. It can be seen that the peak elution temperatures are lower as the comonomer content increases because the comonomer units interrupt their chain regularities, causing polymer chains to have lower chain crystallizabilities and elution temperature.

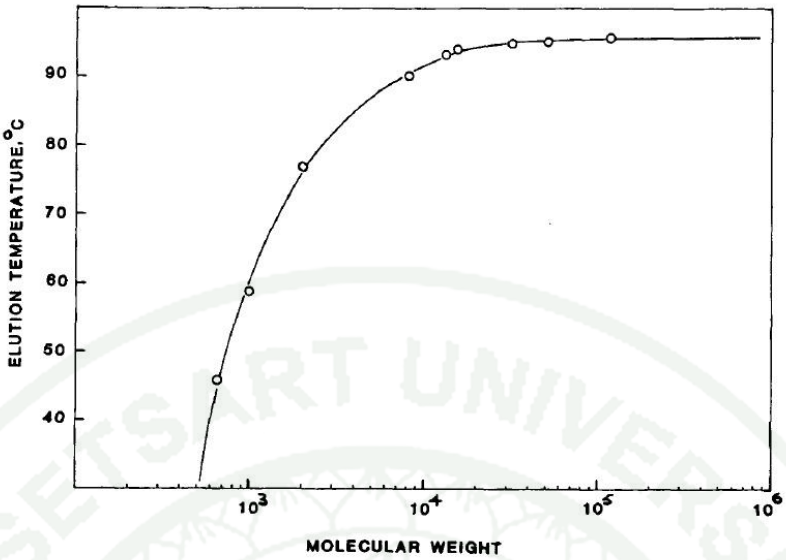


Figure 4 Molecular weight dependence of elution temperature for linear polyethylene fractions.

Source: Wild et al. (1982)

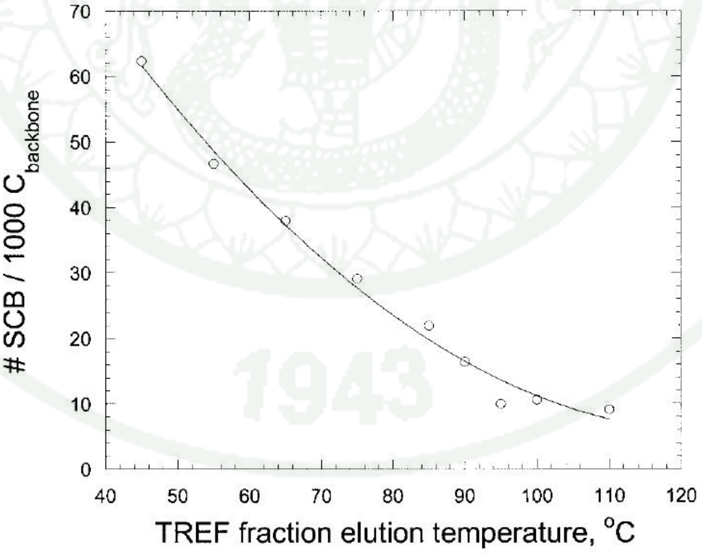


Figure 5 An example of Tref calibration curve of linear low density polyethylene.

Source: Savitski et al. (2003)

1.2 Effect of operating conditions on Tref profiles

In principle, polymer should be fractionated in the vicinity of thermodynamic equilibrium. But, in fact, the typical operating conditions of Tref analysis is found to be far from the thermodynamic equilibrium. The important evident are an important kinetic roles in Tref analysis, which was previously reported by Anantawaraskul *et al.* (2003a). Three effect of operating conditions on Tref profiles are the effects of cooling rate, heating rate, and solvent flow rate.

Anantawaraskul *et al.* (2003a) observed the effect of cooling rate during crystallization step on Tref profiles of ethylene/1-octene copolymer at various cooling rates in the range of 0.1-0.5 °C/min. A heating rate and a solvent flow rate were kept constants at 0.2 °C/min and 0.2 mL/min, respectively. The results show that Tref profiles become broader and the peak elution temperatures are rather similar when the cooling rate decreases as shown in Figure 6. This is because the slow cooling rates allow polymer molecules to have more times to rearrange and crystallize close to their equilibrium temperatures.

The effect of heating rate during the elution step on Tref profiles is shown in Figure 7. The experiments were carried out at various heating rates, while a cooling rate and a solvent flow rate were kept constants at 0.2 °C/min and 0.2 mL/min, respectively. The results shows that Tref profiles become broader as the heating rate increases because, at the same solvent flow rate, the solvent will elute the polymer over a wider range of solubilities when higher heating rates are used. Moreover, Tref peak temperature shifts to higher elution temperatures with increasing heating rates because polymer solutions reach the end of the column at higher elution temperatures.

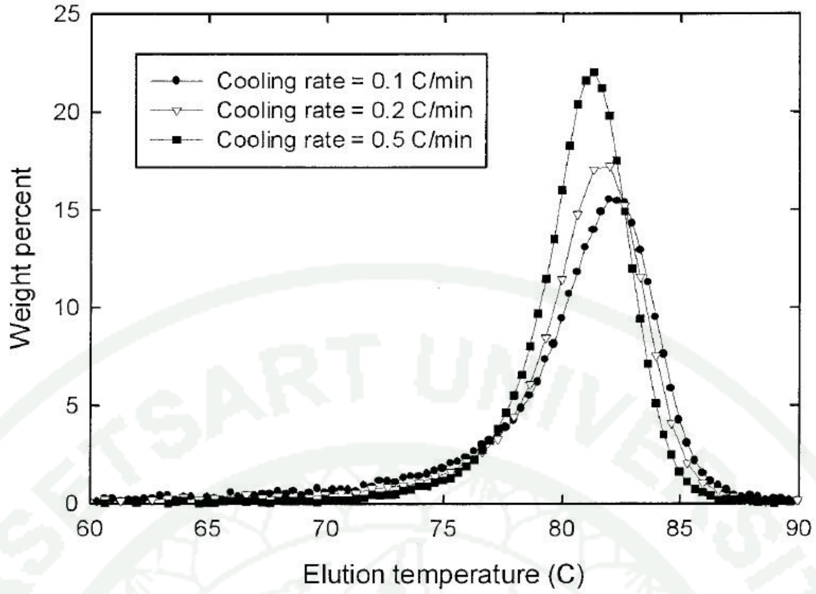


Figure 6 Effect of cooling rate on Tref profiles of ethylene/1-octene copolymer.

Source: Anantawaraskul *et al.* (2003a)

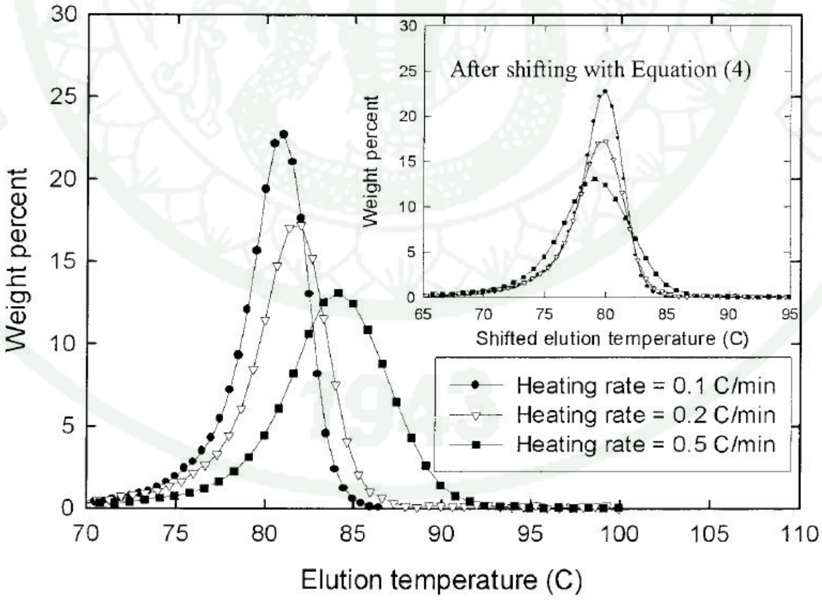


Figure 7 Effect of heating rate on Tref profiles of ethylene/1-octene copolymer.

Source: Anantawaraskul *et al.* (2003a)

The effect of solvent flow rate during elution step was investigated at a cooling rate of 0.2 °C/min and a heating rate of 0.2 °C/min. It was found that Tref profiles become broader as the solvent flow rate decreases, as shown in Figure 8. This is because the slow solvent flow rate increases the residence time of solvent in the column and broadens ranges of polymer molecules eluted per pass of solvent. Furthermore, higher residence times in the column imply that the polymer solution will reach the exit of Tref column at later times or at higher elution temperatures.

Interesting, the effect of all operating conditions on Tref profiles which was observed for ethylene/1-hexene copolymer is not significant when the ratios of cooling rate to heating rate to solvent flow rate were kept at a constant ratio of 1:1:1. Figure 9 shows comparison of the Tref profiles at several rates (with a constant ratio).

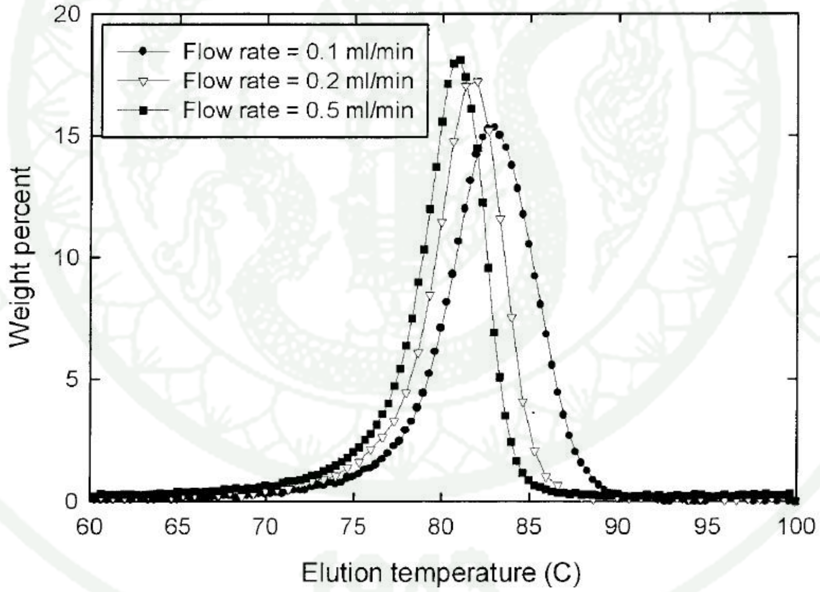


Figure 8 Effect of solvent flow rate on Tref profiles of ethylene/1-octene copolymer.

Source: Anantawaraskul *et al.* (2003a)

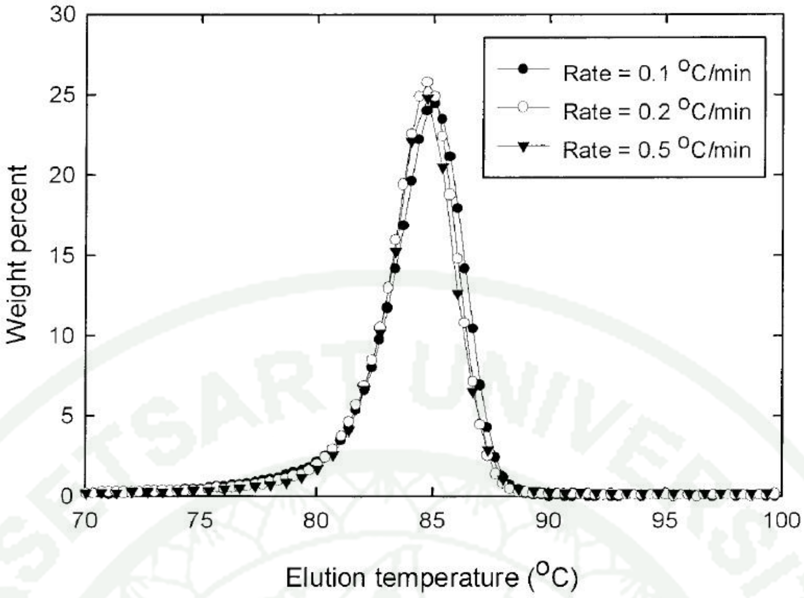


Figure 9 Comparison of Tref profiles of ethylene/1-hexene copolymer when the ratio of the cooling rate: the heating rate: the solvent flow rate is 1:1:1.

Source: Anantawaraskul *et al.* (2003a)

2. The previously proposed models of temperature rising elution fractionation (Tref)

Recently, several Tref models based on the concept of thermodynamic equilibrium have been proposed to describe the Tref fractionation mechanism. The previous Tref models could be classified into 2 groups: (1) Tref model based on a simple thermodynamic solid-liquid equilibrium (Borrajo *et al.*, 1995; Elicabe *et al.*, 1996a, 1996b; Tomba *et al.*, 2005) and (2) Tref model based on Stockmayer b ivariate distribution (Soares and Hamielec, 1995b; da Silva Filho, 2000; Alghyamah, 2009a, 2009b).

2.1 Tref model based on a simple thermodynamic solid-liquid equilibrium

Borrajo *et al.* (1995) applied the solid-liquid equilibrium relationship between crystallized polymers and polymers in a dilute solution at each elution temperature to describe Tref fractionation process. In this study, the model regards copolymer chains of x_i-size as alternating sequences of crystallizable homopolymers blocks, and noncrystallizable, highly branched copolymer blocks. Crystallizable blocks L_i participate in pure crystallites at melting point, T_{Fi}, and melting enthalpy, ΔH_{F_i} ,

$$T_{Fi} = 414.2\left(1 - \frac{6.27}{L_i}\right) \qquad (K) \tag{1}$$

$$\Delta H_{Fi} = 2.546\frac{L_i}{1.4} - 7.32 \qquad (KJ/mole) \tag{2}$$

To fractionate a copolymer fraction having average crystallinity fraction of C_i and crystallizable blocks L_i, a simple thermodynamic model based on an extension of Flory-Huggins theory was assumed to describe the elution temperature of its chain according to the solid polymer-liquid solution equilibrium temperature, T,

$$\frac{1}{T} = \frac{1}{T_{F_i}} - \frac{R}{\Delta H_{F_i}}\left\{1 + \ln\phi_i + x_i\left[-\left(\frac{\sum\phi_i}{\bar{x}_n} + \frac{\phi_0}{Y_0}\right) + \chi\phi_0^2\right]\right\} \tag{3}$$

where ϕ_i is a volume fraction for x_i-size species in the liquid solution, ϕ_0 is a volume fraction for a solvent in the liquid solution, $\sum\phi_i$ is the total polymer volume fraction in the liquid solution, $\bar{x}_n$ is a number average size for the species in the liquid phase, χ is the Flory-Huggins interaction parameter, R is the gas constant, and Y_0 is a molar volume ratio for the solvent/monomer.

This model shows that the fractionation process depends on melting temperature, melting enthalpy, average crystallinity, average crystallizable sequence length, and polymer-solvent interaction parameter. Moreover, this thermodynamic model was applied to describe the fractionation process of Tref in preparative mode with the lengths of crystallizable polymer blocks distributed as Gaussian functions.

Although this thermodynamic model based on the Flory-Huggins theory could be used to predict average elution temperature of homopolymer, it could not directly estimate Tref profiles.

Afterwards, Elicabe *et al.* (1996a) attempted to obtain the distribution of crystallizable lengths (DCL) of a linear ethylene homopolymer from Tref profile, which could be related to short-chain branching distribution (SCBD) if applied for the case of copolymers, using the inverse algorithm of the proposed thermodynamic model. This approach was validated for low molecular weight homopolymers and homopolymers blends (Elicabe *et al.*, 1996b; Tomba *et al.*, 2005). It was found that the thermodynamic model could be used to predict DCLs and the molecular weight of polymer sample used from Tref profiles without the use of calibration curves.

However, these proposed models for Tref were based on the concepts of thermodynamic without a consideration of crystallization kinetic and dissolution kinetic effects and, therefore, could not describe the important effect of operating conditions on Tref profiles discussed earlier.

2.2 Tref model based on Stockmayer bivariate distribution

Soares and Hamielec (1995b) proposed that the Stockmayer bivariate distribution can be used to qualitatively and quantitatively interpret Tref profiles of polyolefins made by each site-type of multiple site type catalysts. The instantaneous chain length and composition distribution proposed by Stockmayer (1945), which was corrected for difference in monomer molecular weights, is given by:

$$w(r,y)drdy = [1 + y\delta]\tau^2 r \exp(-\tau r)dr \cdot \frac{1}{\sqrt{2\pi\beta / r}} \exp\left(-\frac{y^2 r}{2\beta}\right)dy \tag{4}$$

$$\beta = \overline{F}_1\left(1-\overline{F}_1\right)\sqrt{1+4\overline{F}_1\left(1-\overline{F}_1\right)\left(r_1 r_2 - 1\right)} \tag{5}$$

$$\delta(j) = \frac{1 - M_1 / M_2}{M_2 / M_1 + \overline{F_1}\left(1 - M_1 / M_2\right)} \tag{6}$$

where r is chain length, y is deviation from average copolymer composition, $\overline{F_1}$ is average mole fraction of monomer type 1 of copolymer, r_1 and r_2 are reactivity ratios, M_1 and M_2 are molecular weights of monomers type 1 and 2, and τ is ratio between transfer rate and propagation rate.

The copolymer compositions of polymer chains were considered in this model to obtain the Tref results. Several researchers have attempted to apply this proposed model for deconvoluting the MWDs and CCDs of polyolefins made with heterogeneous Ziegler-Natta catalysts (da Silva Filho *et al.*, 2000; Alghyamah and Soares, 2009a, 2009b). They found that this methodology can be used to describe the Tref results of a polyolefin produced by multiple-site type catalysts and estimate the minimum number of site types required to describe the MWD and CCD of a polyolefin sample.

Although the previous results showed that the proposed model could be used to predict the Tref profiles of binary copolymers produced by each catalyst site type well, it still did not consider crystallization kinetic and dissolution kinetic effects during fractionation. Therefore, it still could not describe the important effect of operating conditions on Tref profiles.

3. Population balance concept for modeling

An alternative modeling approach based on a population balance concept has been used for describing fractionation mechanism of several polymer characterization techniques, such as chromatographic techniques (Glockner, 1987) and Crystaf technique (Anantawaraskul *et al.*, 2006, 2007a, 2007b). In the Crystaf model, this concept with the incorporation of the crystallization kinetics was found to effectively describe the effect of both chain microstructures and operating conditions. This Crystaf model is of particular interests because, similar to Tref, Crystaf also fractionates polymer chain based on chain crystallizability. Therefore, a population balance model for Tref might be developed based on the same concept.

Although the physical set-up of Tref (i.e., plug flow column) is clearly distinct from that of Crystaf (i.e., well-mixed vessel), the model based on the population balance could be adapted for Tref if an appropriate discretization from a plug flow column to a series of small well-mixed controlled volume is employed. Note that for Tref model, not only crystallization kinetic but also dissolution kinetic must be incorporated in the model.

Although dissolution kinetic has not been incorporated into a population balance model before, this should be done in the same manner as the case of crystallization kinetic. Avrami equation, which was previously applied for the dissolution kinetic of crystals in aqueous solution (Demirkiran *et al.*, 2007; Sun *et al.*, 2009), was used as an empirical equation for describing the dissolution kinetics of polymer crystals during elution step of Tref analysis.

In this work, a mathematical Tref model based on population balance concept with the incorporation of both crystallization and dissolution kinetics will be developed to describe the effects of chain microstructures (i.e., molecular weight and comonomer content) and operating conditions (i.e., cooling rate, heating rate, and solvent flow rate) on Tref profiles following the approach outlined above,

4. Characterization of linear olefin block copolymers (OBCs)

The OBC is a new class of polyolefins produced by chain shuttling polymerization which uses two catalysts with different comonomer reactivity ratios in combination with a chain shuttling agent (CSA), which is a metal alkyl complex. Figure 10 shows the mechanism of chain shuttling polymerization.

For an ethylene/α-olefin copolymer, the catalyst with a low comonomer reactivity ratio (Catalyst1) produces hard or high crystallinity blocks, while the catalyst with a high comonomer reactivity ratio (Catalyst2) produces soft or low crystallinity blocks. Shuttling takes place when hard block is exchanged with the CSA bearing a soft block at Catalyst1 or a soft block is exchanged with the CSA bearing a hard block at Catalyst2. Further chain growth at Catalyst1 then extend the soft segment with a hard segment, thus giving a block copolymer (Arriola *et al.*, 2006; Anantawaraskul *et al.*, 2009). These linear block olefin copolymers provide advantages compared to conventional polyolefins elastomers, such as higher heat and abrasion resistances (Wang *et al.*, 2009a, 2009b).

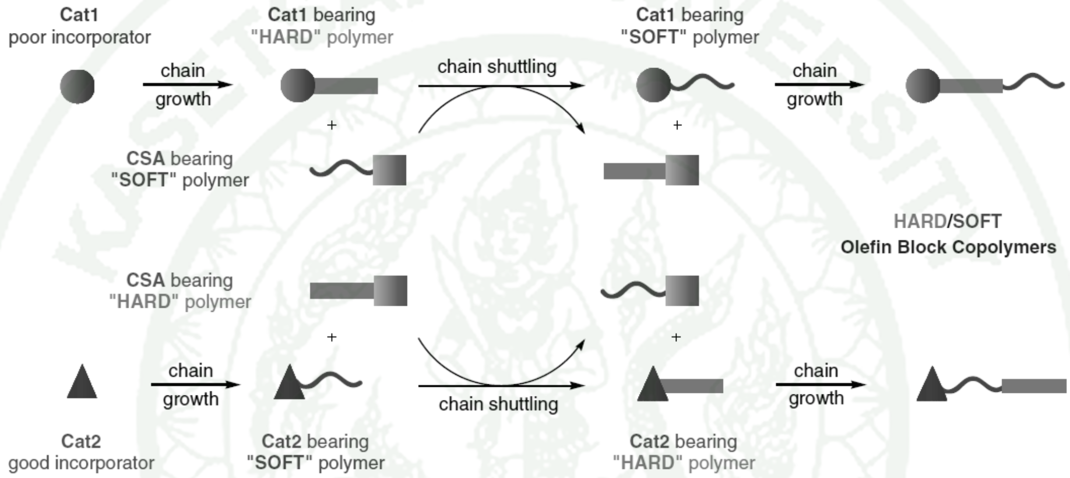


Figure 10 The mechanism of chain shuttling polymerization.

Source: Arriola et al. (2006)

While the crystallizations and rheological behaviors of OBCs have been investigated (Gupta *et al.*, 2007; Wang *et al.*, 2007; Khariwala *et al.*, 2008), the characterization of OBCs chain microstructures is a challenging task. Although the characterization results of OBCs using Tref and Crystaf techniques could be obtained as reported by Li Pi Shan *et al.* (2007), it could not describe their chain microstructural distributions because Tref and Crystaf techniques could not directly reflect the block length and chemical composition distributions of OBCs. The modeling of these characterization techniques may be a promising approach to help identify the link between Tref profile and OBC chain microstructures.

Recently, Anantawaraskul *et al*. (2009) attempted to modify the Crystaf model based on population balance concept for interpreting the Crystaf profiles of OBCs. A Monte Carlo simulation was used to model the information of chain microstructure of OBCs. This information was then used together with the modified Crystaf model to predict Crystaf results. Moreover, block index (*BI*) of OBCs, which had been observed as the differences of crystallizability between random copolymer and OBCs by Shan *et al.* (2007), was used to quantify the peak crystallization temperature of OBCs deviated from that of random ethylene/1-olefin copolymers at the same comonomer content. The Crystaf results obtained from the modified Crystaf model were shifted to higher crystallization temperatures by this deviated temperature for interpreting Crystaf profiles of OBCs. However, the reported results from the modified Crystaf model for OBCs were only preliminary and might be inaccurately because they assumed that the values of *BI* parameters of Crystaf is the same as that experimentally obtained from Tref analysis.

In this work, the proposed Tref model will be modified for OBC. The values of *BI* parameters obtained from Tref analysis will be directly used to correct the simulated Tref profiles. These results should be more reliable and better correlate to chain microstructures obtained from Monte Carlo simulation.

MATERIALS AND METHODS

This thesis proposed a mathematical Tref model based on population balance concept with the incorporation of crystallization and dissolution kinetics, which can be used for describing the Tref profiles of commercial polyolefins. The simulated Tref profiles will be validated with the experimental Tref profiles at several operating conditions. The part of materials and methods could be divided into 4 parts: (1) experimental Tref analysis, (2) Tref model development, (3) application of Tref model for simulating Tref calibration curves, and (4) application of Tref model for characterizing linear olefin block copolymers (OBCs).

1. Experimental Tref analysis

1.1 Materials

Table 1 summarizes polymer samples used in this investigation. Two ethylene homopolymers having different average molecular weights were used to examine the effect of molecular weight. A series of ethylene/1-hexene copolymers with different 1-hexene contents but similar number-average molecular weights (M_N) were used for investigating the effect of comonomer content. An ethylene/1-octene copolymer was used to investigate the effect of operating conditions. All samples were produced with a single site type catalyst; therefore, their MWDs and CCDs are narrow, and their polydispersity indices are close to 2.0.

1.2 Tref analysis

1.2.1 The Tref analysis for ethylene homopolymers

For ethylene homopolymers (E191 and E521), a Tref column with a volume of 2 mL was used in an automated crystallization elution fractionation (Cef) apparatus (PolymerChar S.A., Valencia, Spain) operating with the Tref mode. Figure 11 illustrates temperature program of Tref analysis for ethylene homopolymers.

Firstly, a polymer was dissolved in 1, 2, 4 trichlorobenzene (TCB) with a concentration of 1.25 mg/mL at 160 °C for 1 hour. The polymer solution was then introduced into the Tref column and the column temperature was reduced to 120 °C. During the crystallization step, the polymer chains were allowed to crystallize onto the support while a temperature was decreased to 35 °C at a constant cooling rate of 0.2 °C/min. In the elution step, a fresh TCB solvent was flowed through the Tref column at a constant flow rate of 0.5 mL/min and a temperature was increased to 120 °C at a constant heating rate of 1.0 °C/min, while the polymer chains coating on the support were dissolved back into the solvent. The concentration of polymer eluted was then monitored and recorded as a function of elution temperature to provide a Tref profile.

Table 1 Summary of polymer samples used in this investigation.

Sample No.	Polymer type	M_N (g/mol)	Comonomer content (mol %)
E191	Ethylene homopolymer	19,100	-
E521	Ethylene homopolymer	52,100	-
EH068	Ethylene/1-hexene copolymer	37,200	0.68
EH151	Ethylene/1-hexene copolymer	36,300	1.51
EH314	Ethylene/1-hexene copolymer	34,200	3.14
EO219	Ethylene/1-octene copolymer	40,700	2.19

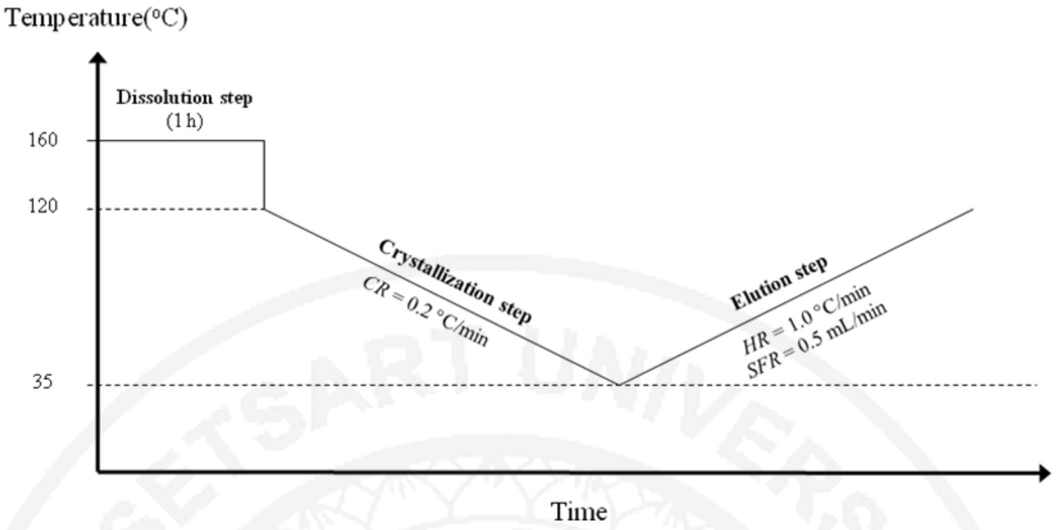


Figure 11 Temperature program of Tref analysis for ethylene homopolymers.

1.2.2 The Tref analysis for ethylene/1-olefin copolymers

The Tref analysis for ethylene/1-olefin copolymers (EH068, EH151, EH314, and EO219) was performed by *Anantawaraskul et al.* (2003a) with a Crystaf-Tref-V-LS manufactured by PolymerChar S.A. (Valencia, Spain). In this part, the previously reported Tref results were used for the model validation. Figure 12 illustrates the temperature program of Tref analysis for ethylene/1-olefin copolymers.

Firstly, the polymer sample was dissolved in TCB in a Crystaf vessel at a concentration of 1 mg/mL at 160 °C for 1 hour. The polymer solution was then loaded into a Tref column packed with an inert support and held for stabilization at 95 °C for 45 minutes before a crystallization step. In the crystallization step, the polymer chains crystallized and precipitated onto the support by a slow reduction of the temperature to 30 °C at a constant cooling rate (0.1-0.5 °C/min). The column temperature was kept at 30 °C for 45 minutes for stabilization before the elution step. In the elution step, a pure solvent (TCB) flowed through the column at a constant flow rate (0.1-0.5 mL/min) while the temperature was slowly increased to 100 °C at a constant heating rate (0.1-0.5 °C/min). The concentration of polymer being eluted was monitored by an infrared detector and was plotted as a function of the elution temperature, Tref profile.

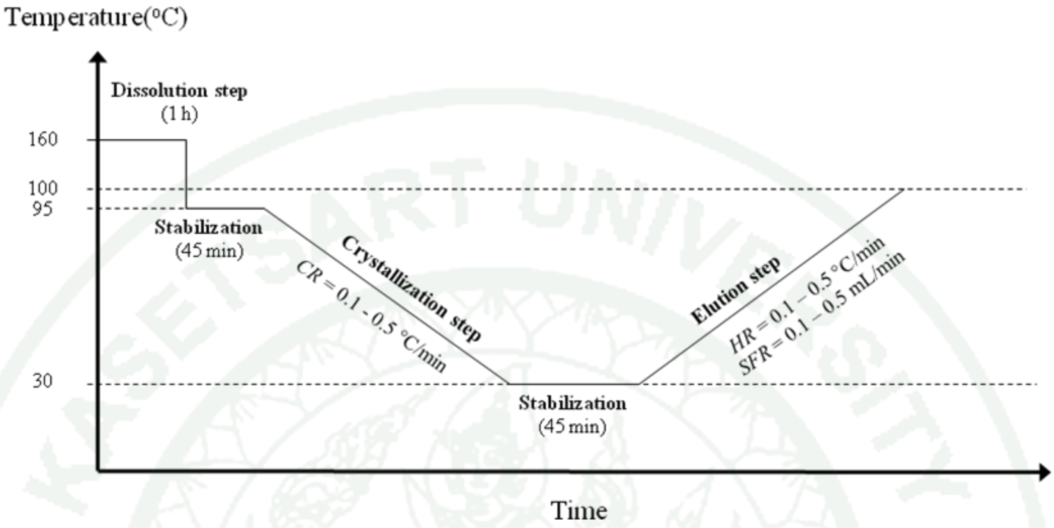


Figure 12 Temperature program of Tref analysis for ethylene/1-olefin copolymers.

2. Tref model developments

A new mathematical Tref model based on the concept of population balance that takes crystallization kinetic and dissolution kinetic into account was developed to quantitatively clarify the fundamental fractionation mechanism in Tref analysis and describe Tref profiles for ethylene homopolymers and ethylene/1-olefin copolymers at several operating conditions. In the model, a Tref column was computationally discretized into *N* interconnecting control volumes and polymer molecules introduced into Tref column were assumed to distribute uniformly throughout the Tref column (i.e., all control volumes contain a polymer solution with the same MWD and CCD).

During crystallization, polymer chains crystallized within each control volume following their crystallization kinetics. During elution, the dissolution kinetics were used to describe polymer molecules dissolved back at each elution temperature. The population balance was then used for tracking polymer eluted within, flowing into, and flowing out of each control volume. The fraction of polymers eluted out of the Tref column was monitored to establish the Tref profile.

2.1 Tref model development for homopolymers

Figure 13 illustrates the computational steps to simulate the Tref profiles for homopolymers. For the Tref analysis of homopolymers, the chain length of polymer is considered to be a key factor reflecting chain crystallizability. The Tref model development for homopolymers was divided into 4 steps: (1) discretization, (2) crystallization, (3) dissolution, and (4) population balance during the elution step.

2.1.1 Discretization

Initially, the mass of polymer along the Tref column would be modeled by discretizing the chain length distribution as similar as molecular weight distribution, hence, the chain length influencing the molecular weight of polymer molecule is used to be a key factor controlling polymer chain crystallizability. Figure 14 illustrates the Discretization concept of Tref model. The Flory's distribution could be used to model the chain length distribution of ethylene homopolymers having polydisperse indices of 2.0, made with a single site type catalyst (Soares and Hamielec, 1995; Alghyamah and Soares, 2009a, 2009b). A relationship between the weight of chain length, $w(r)$, and the polymer chain length, r, representing a number of repeating units in a polymer chain, can be written as following

$$w(r) = \tau^2 r \exp(-\tau r) \tag{7}$$

$$\tau = \frac{mw}{M_N} \tag{8}$$

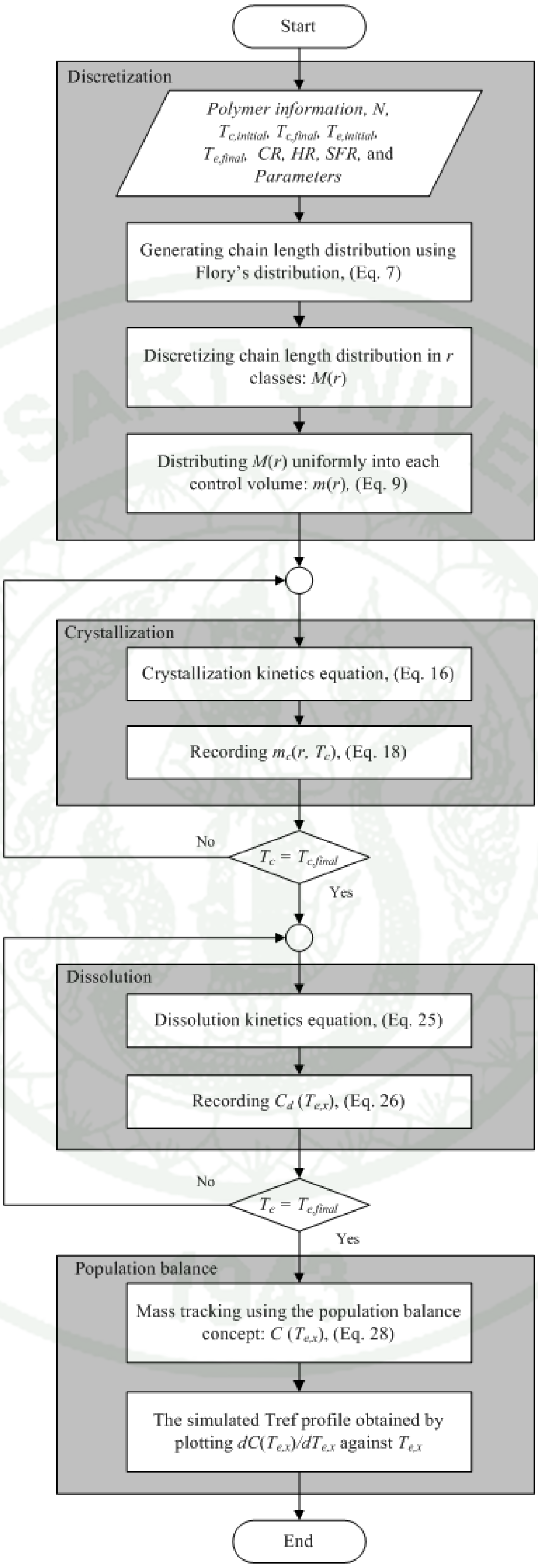


Figure 13 Illustration of the computational steps to simulate Tref profiles for homopolymers.

where τ is the ratio of all chain transfer rates to the propagation rate, parameter *mw* is molecular weight of the repeating unit, and M_N is the number average molecular weight of polymer chain.

The chain length distribution obtained from Flory's distribution was discretized into several population groups according to chain length r. The total mass of each population group, $M(r)$, was considered to be uniformly distributed into N control volumes along the Tref column. The polymer fraction of population group with chain length of r in each control volume can simply be calculated from

$$m(r) = \frac{M(r)}{N} \tag{9}$$

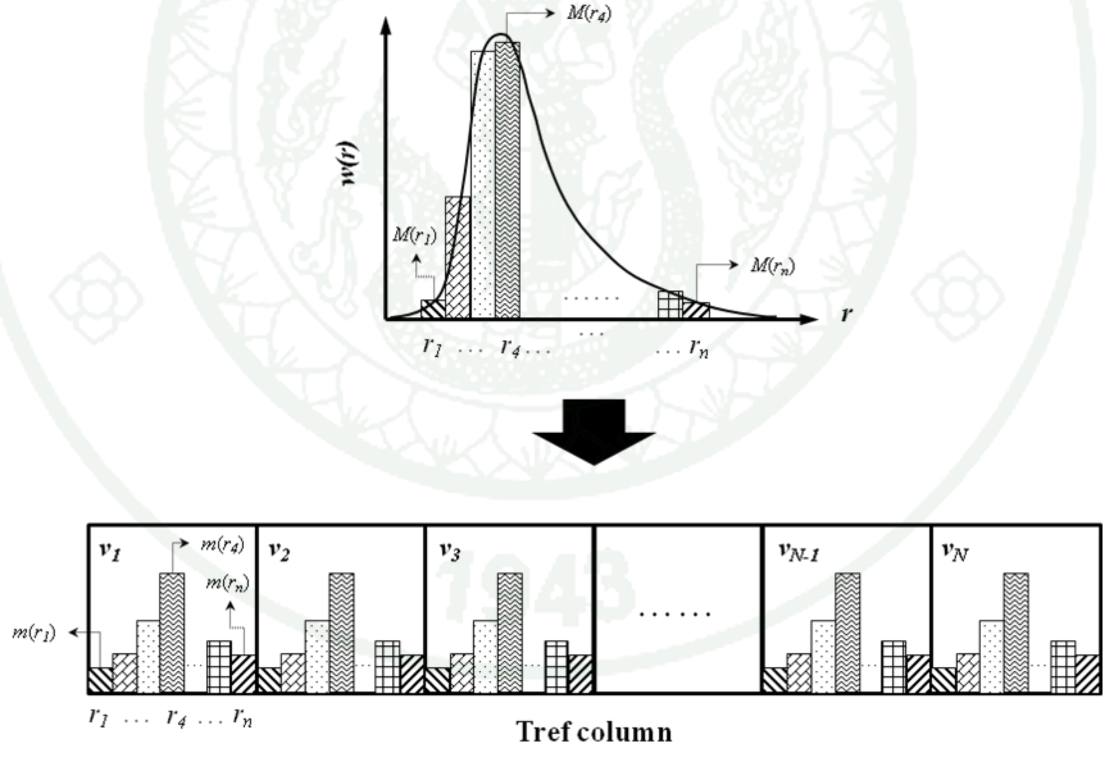


Figure 14 The discretization concept of Tref model.

2.1.2 Crystallization

The conceptual model for describing polymer crystallization is illustrated in Figure 15. For illustration, we consider a model polymer consisting of three population groups, each with different polymer chain lengths (i.e., chain crystallizabilities) obtained from the discretization of the chain length distribution as shown in Figure 14. At the initial, high temperature ($T_{c,0}$), a model polymer is completely dissolved in a solvent. After that, each polymer population group crystallizes and coats on the support according to their crystallizabilities and following their crystallization kinetics as the column temperature decreases at a constant cooling rate.

Although, the crystallization of all population groups is occurred under non-isothermal conditions, we assume that crystallization of each population group is occurred within such a small temperature range that the crystallization kinetics of each population group can be assumed to follow the Avrami equation, which was used to determine for homopolymers with specific chain length, r, as a relationship between crystallinity, X_c, and time, t_c, (Anantawaraskul *et al.*, 2006, 2007a):

$$X_c(t_c) = 1 - \exp(-k_c t_c^{n_c}) \tag{10}$$

where n_c and k_c are Avrami parameters during crystallization step. The parameter n_c is generally assumed to be constant, while the parameter k_c is a function of the crystallization temperature.

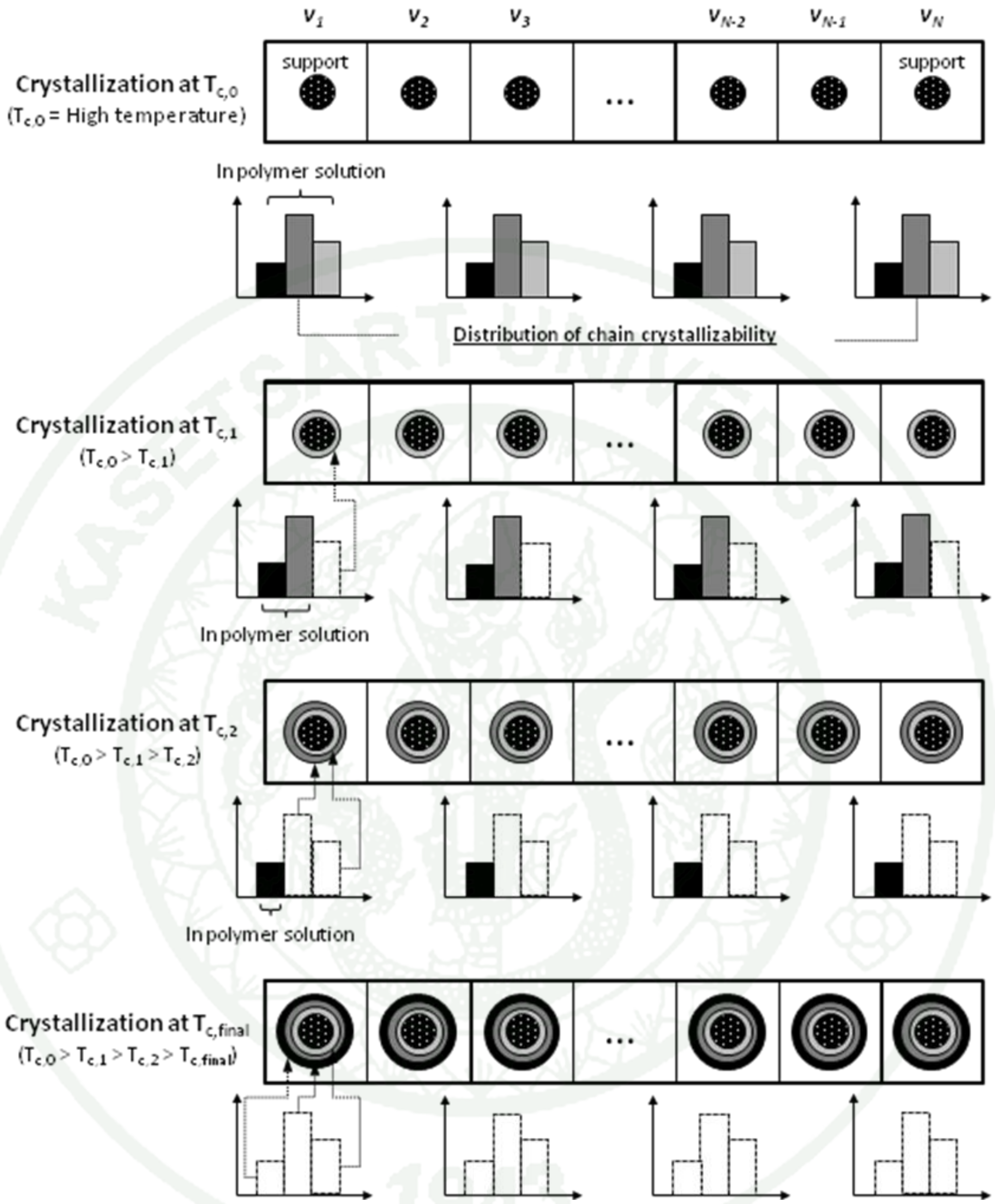


Figure 15 Conceptual model for the Tref crystallization step.

A relationship between the crystallization temperature, T_c, and the crystallization time, t_c, was established by relating to a constant cooling rate, *CR*, during crystallization step in Tref fractionation process:

$$\frac{dT_c}{dt_c} = -CR \tag{11}$$

At the beginning of crystallization (t_c = 0), the crystallization temperature is assumed to be equal to the equilibrium dissolution temperature of chain length *r*. Therefore, integrating equation (11) with $T_c(0) = T_d(r)$, a relationship between crystallization temperature and time can be obtained:

$$t_c = \frac{T_d(r) - T_c}{CR} \tag{12}$$

The effect of kinetic chain length on the equilibrium dissolution temperature of chain length *r*, $T_d(r)$, can be described by the Gibbs-Thomson equation proposed by Beigzadeh *et al.* (2001) as following:

$$T_d(r) = T_d^o\left[\frac{r - \alpha_d}{r}\right] - T_{sc} \tag{13}$$

where T_d^o is the equilibrium dissolution temperature of chain with infinite lengths, T_{sc} is a supercooling temperature for Tref analysis, α_d is a constant that is inversely proportional to the enthalpy of fusion. To reduce the number of parameters, equation (13) could be reduced to:

$$T_d(r) = A_c - \frac{B_c}{r} \tag{14}$$

where,

$$A_c = T_d^o - T_{sc} \text{ and } B_c = T_d^o \cdot \alpha_d \tag{15}$$

where the parameter A_c, B_c should generally be a constant due to both T_d^o and T_{sc} are constant for a given polymer/solvent combination. α_d is a constant that is inversely proportional to the enthalpy of fusion. The A_c and B_c are in degree Celsius.

Finally, a crystallization kinetics equation for homopolymer with specific r can be obtained by incorporating equation (10), (12), and (14):

$$X_c(r,T_c) = \begin{cases} 0, & T_c \geq T_d(r) \\ 1 - \exp\left\{ -k_c \left[\frac{\left(A_c - B_c / r\right) - T_c}{CR} \right]^{n_c} \right\}, & T_c < T_d(r) \end{cases} \tag{16}$$

where CR is a constant cooling rate during crystallization step, n_c is the Avrami exponent, and k_c is the apparent Avrami prefactor averaging over a range of crystallization temperature.

The total crystalline mass fraction of a population group with a chain length of r at specific crystallization temperature of T_c, $M_c(r,T_c)$, in Tref column can be calculated from a product between $m(r)$ and X_c:

$$M_c(r,T_c) = m(r) \cdot X_c(r,T_c) \tag{17}$$

Therefore, the crystalline mass fraction of a population group with a chain length of r during the small temperature interval between $T_c + \Delta T_c$ and T_c, $m_c(r,T_c)$, can be calculated:

$$m_c(r,T_c) = M_c(r,T_c) - M_c(r,T_c + \Delta T_c) \tag{18}$$

2.1.3 Dissolution

Figure 16 illustrated the conceptual model describing the elution step of Tref analysis. For the illustration, we consider the elution of a model polymer with three population groups previously considered in the conceptual model of crystallization step as shown in Figure 15. When the column temperature increases, each population group in a control volume is dissolved back to the solution according to its solubility and following its dissolution kinetics. At the same time, a fresh solvent flows into the column and, therefore, polymer solutions pass between the interconnecting control volumes along the Tref column.

Avrami equation has been previously applied as an empirical equation for describing the dissolution kinetics of crystals in aqueous solution under isothermal conditions (Demirkiran and Künkül, 2007; Sun *et al.*, 2009). Similar to the model development in the crystallization step, we assume that each population groups of polymer is dissolved over such a small temperature range that the dissolution kinetics for each population group follows an empirical Avrami equation, which describes relationship between dissolved fraction, X_d, and time, t_d as following:

$$X_d(t_d) = 1 - \exp(-k_d t_d^{\,n_d}) \qquad (19)$$

where n_d and k_d are adjustable parameters. Similar to the Avrami equation for describing crystallization kinetics, n_d is expected to be constant for a given polymer while k_d is expected to be a function of temperature.

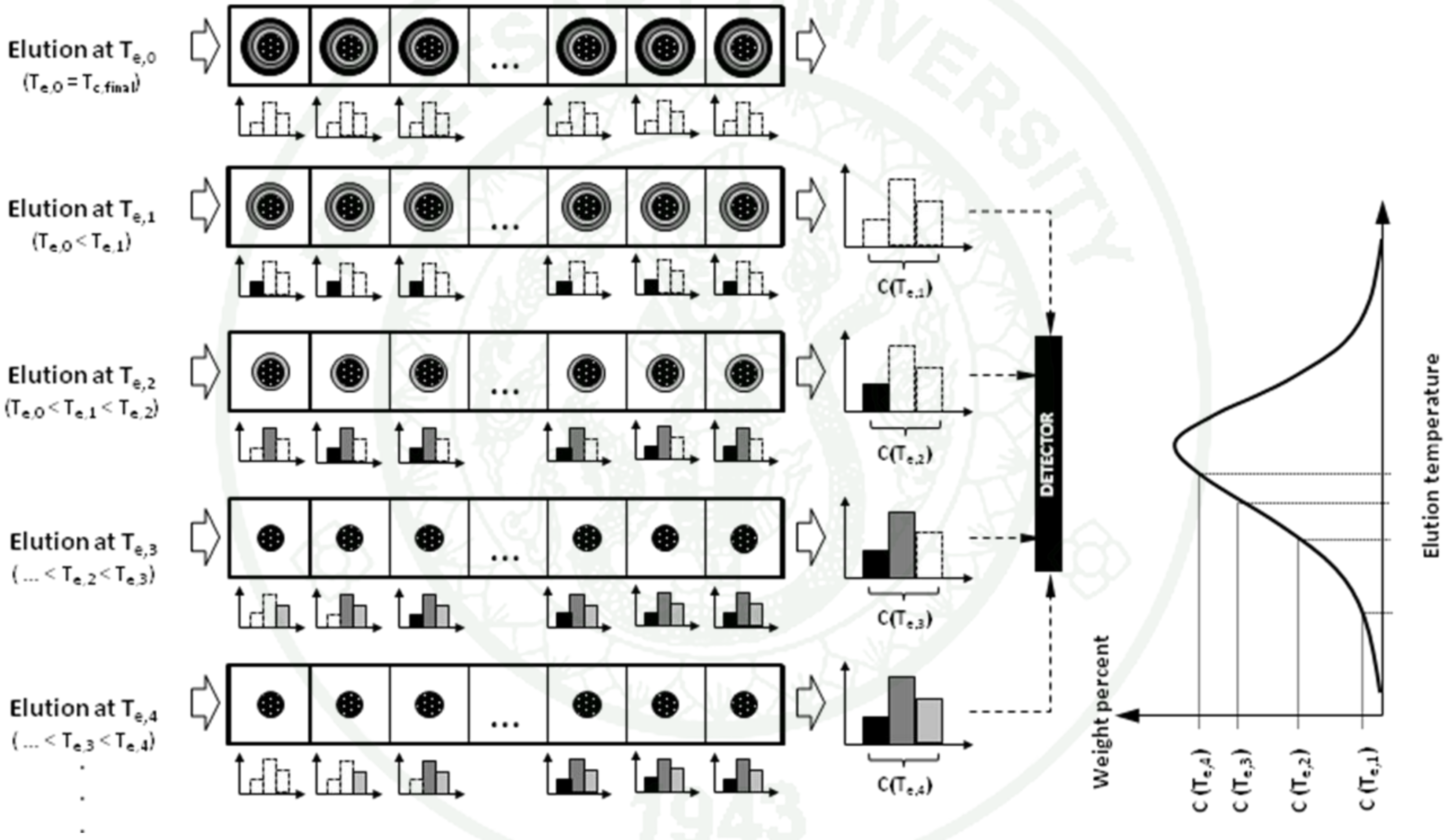


Figure 16 Conceptual model for the Tref elution step.

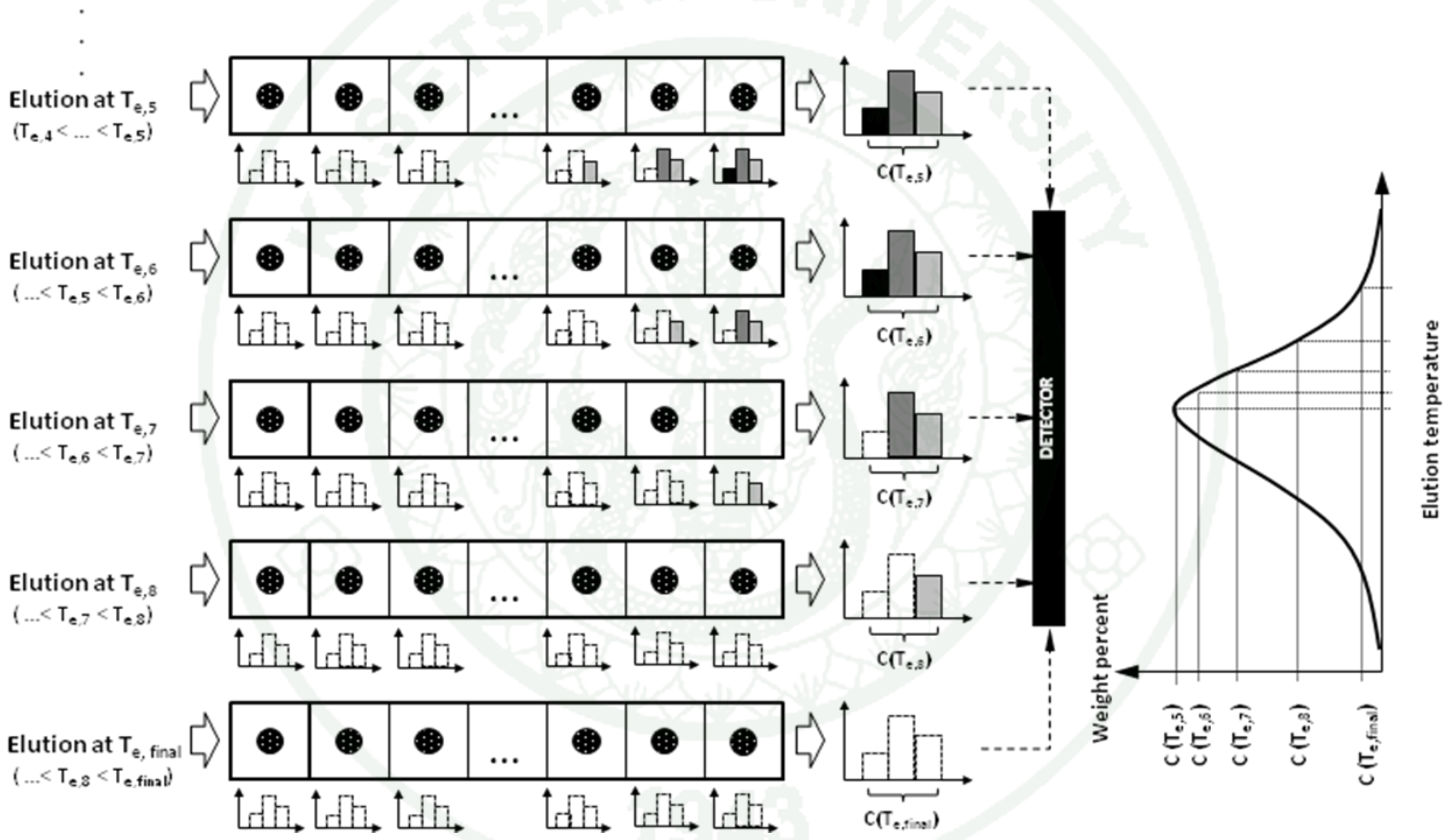


Figure 16 (Continued).

As the dissolution occurred at a constant heating rate (*HR*), a relationship between the dissolution temperature, T_d, and dissolution time, t_d, can be written as equation (20). In the Tref analysis, the dissolution temperature is the temperature of Tref column or elution temperature, T_e.

$$\frac{dT_d}{dt_d} = \frac{dT_e}{dt_d} = HR \tag{20}$$

For a population group with a chain length *r*, the initial elution temperature $T_{e,0}$ at $t_d = 0$ is equal to the equilibrium crystallization temperature of chain length *r*, $T_c(r)$. Integrating equation (20) with this initial condition gives a relationship between elution temperature at a time step *x*, $T_{e,x}$, and dissolution time.

$$t_d = \frac{T_{e,x} - T_c(r)}{HR} \tag{21}$$

The $T_c(r)$ is a function of polymer chain length and can be obtained by the modified Gibbs-Thomson equation (Beigzadeh *et al.*, 2001), as shown in equation (22),

$$T_c(r) = T_d^o \left[\frac{r - \alpha_c}{r}\right] - T_{sh} \tag{22}$$

where T_{sh} is a superheating temperature, and α_c is inversely proportional to the enthalpy of fusion.

To reduce the number of parameters in equation (22), we can rearrange this equation to:

$$T_c(r) = A_d - \frac{B_d}{r} \tag{23}$$

$$A_d = T_d^o - T_{sh} \quad \text{and} \quad B_d = T_d^o \times \alpha_c \tag{24}$$

As both T_d^o and T_{sh} are constant for a given polymer/solvent combination, both A_d and B_d are expected to be constants.

Finally, we can obtain a relationship between dissolved fraction and elution temperature by combining equation (19), (21) and (23):

$$X_d(r, T_{e,x}) = \begin{cases} 0 & , T_{e,x} < T_c(r) \\ 1 - \exp\left\{ -k_d \left[\dfrac{T_{e,x} - (A_d - B_d / r)}{HR} \right]^{n_d} \right\} & , T_{e,x} \geq T_c(r) \end{cases} \tag{25}$$

where $X_d(r,T_{e,x})$ is the dissolved fraction of polymer with chain length r when the temperature reaches $T_{e,x}$.

Consequently, the concentration of polymer dissolved at $T_{e,x}$ in each control volume, $C_d(T_{e,x})$, can be calculated by following equation:

$$C_d(T_{e,x}) = \sum_{r=1}^{\infty} \sum_{T_c = T_{c,0}}^{T_{c,final}} \left[m_c(r, T_c) \cdot X_d(r, T_{e,x}) \right] \tag{26}$$

where $m_c(r,T_c)$ is the crystalline mass fraction of a population group with a chain length of r crystallized at T_c, which can be calculated from equation (18).

2.1.4 Population balance during the elution step

Following the assumption that the polymer uniformly distributed along the column, the concentration of polymer dissolved at $T_{e,x}$ in i^{th} control volume, $C_d(v_i, T_{e,x})$, can be determined by following equation:

$$C_d(v_i, T_{e,x}) = C_d(T_{e,x}) \tag{27}$$

Figure 17 illustrates the conceptual idea of population balance calculation. The concentration of eluted polymer at the exit of Tref column at $T_{e,x}$, $C(T_{e,x})$, can be calculated by the population balance of every control volumes using the general formulas as following:

$$C(T_{e,x}) = \begin{cases} \sum_{i=j}^{N} \left[C_d(v_i, T_{e,i-j}) \right] & \text{, when } j = N\text{-}x+1, \quad \text{and} \quad 0 < x \leq N \\ \sum_{i=1}^{N} \left[C_d(v_i, T_{e,i-j}) \right] & \text{, when } j = N\text{-}x+1, \quad \text{and} \quad x > N \end{cases} \tag{28}$$

where $T_{e,x}$ is the elution temperature at a time step x, which can be calculated from

$$T_{e,x} = T_{e,x-1} + \Delta T_e \tag{29}$$

The initial elution temperature, $T_{e,0}$, is the final crystallization temperature, $T_{c,final}$. The increment of elution temperature for Tref analysis, ΔT_e, can be calculated as follows

$$\Delta T_e = \frac{V_c}{SFR} \times \frac{HR}{N} \tag{30}$$

where SFR is the solvent flow rate during elution step. V_c is a volume of Tref column.

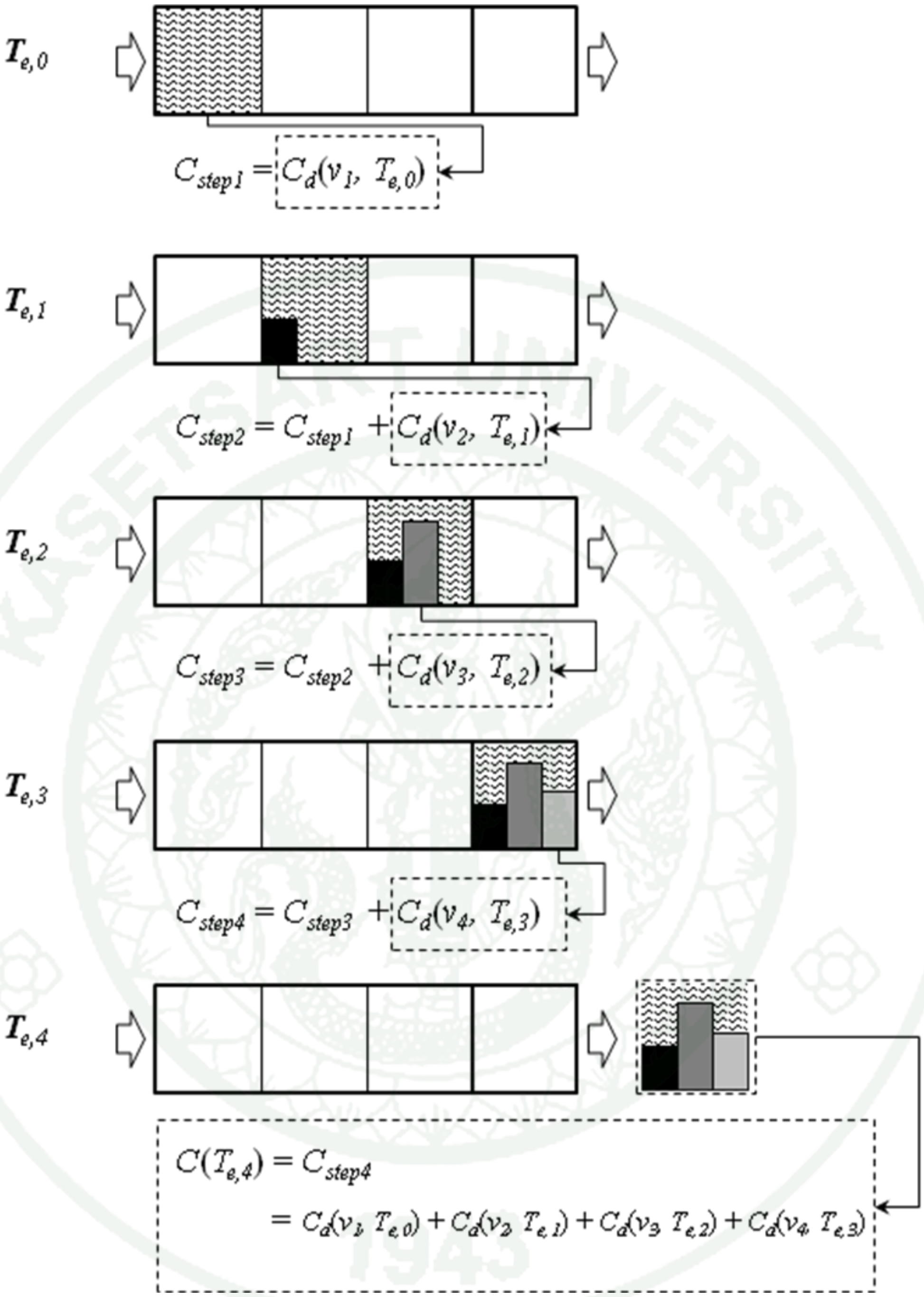


Figure 17 The conceptual idea of population balance calculation.

The simulated Tref profiles can be obtained by differentiating $C(T_{e,x})$ and then plotting $dC(T_{e,x})/dT_{e,x}$ against $T_{e,x}$. For parameters estimation, all parameters involved in this model (A_c, B_c, n_c, k_c, A_d, B_d, n_d, and k_d) were minimized the summation of the square of the differences between the simulated and experimental Tref profiles:

$$\Phi = \sum_{T_e=T_{initial}}^{T_{final}} \left[\frac{dC_{\mathrm{model}}(T_{e,x})}{dT_{e,x}} - \frac{dC_{\exp}(T_{e,x})}{dT_{e,x}} \right]^2 \qquad (31)$$

2.2 Tref model development for binary copolymers

Figure 18 illustrates the computational steps to simulate Tref profiles for binary copolymers. The proposed model was extended to describe Tref profile for case of ethylene/1-olefin copolymers. For Tref analysis of binary copolymers, the longest ethylene sequence of polymer is considered to be a key factor reflecting chain crystallizability. The Tref model development for binary copolymers was divided into 4 steps as that for homopolymers: (1) discretization, (2) crystallization, (3) dissolution, and (4) population balance during the elution step.

2.2.1 Discretization

The mass of polymer along the Tref column could be modeled by discretizing the longest ethylene sequence distribution (LES distribution), hence, the longest ethylene sequence, *LES*, which is influenced by both molecular weight and comonomer content, was considered to be the key factor controlling polymer chain crystallizability (Anantawaraskul *et al.*, 2003b, 2007a, 2007b). The weight distribution function of *LES*, *W(LES)*, was derived by Costeux *et al.*, (2002):

$$W(LES) = \frac{(1-P_a)(1-pp)}{P_a}\left[F(1-pm^{LES}) - F(1-pm^{LES-1})\right] \qquad (32)$$

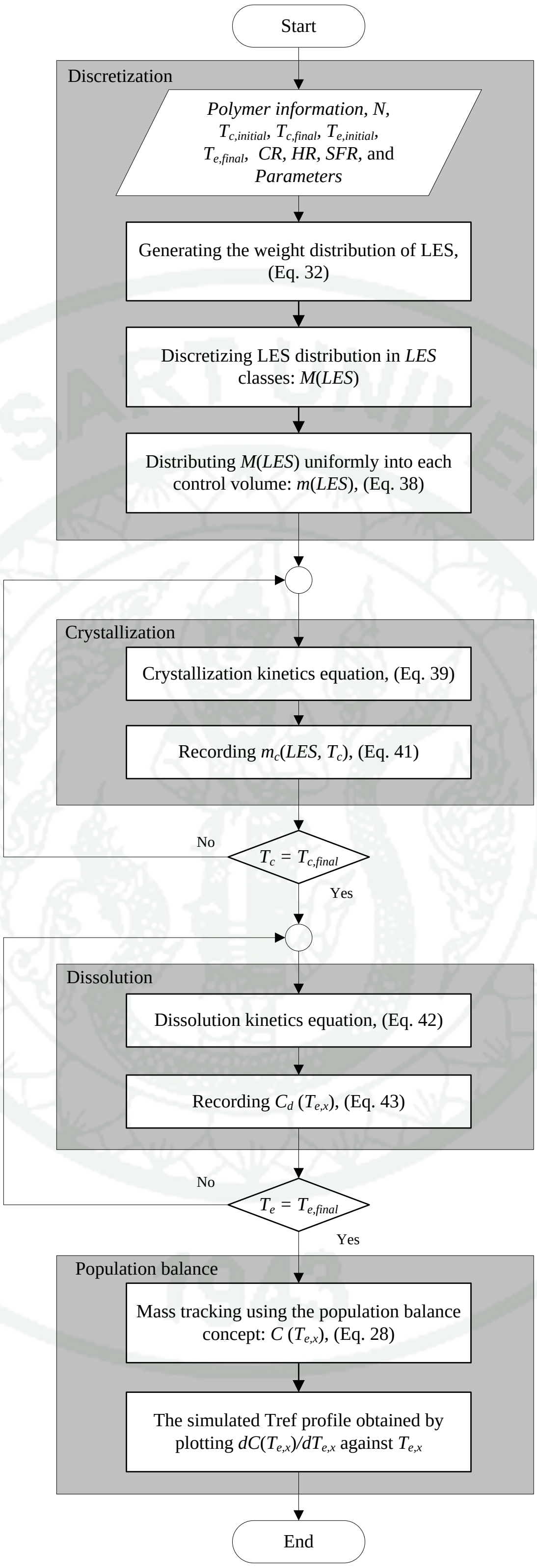


Figure 18 Illustration of the computational steps to simulate Tref profiles for binary copolymers.

The function *F(x)* and parameter P_a are expressed as,

$$F(x)=\frac{P_a x}{(1-P_a x)^2}\left[LES\left(1-\frac{P_a x}{1-pm^{LES}}\right)+\frac{P_a x}{1-pm}\right] \tag{33}$$

$$P_a=\frac{pp(1-cp)}{1-(cp\cdot pp)} \tag{34}$$

$$pm = pp\cdot cp \text{ and } cp=1-cpp \tag{35}$$

where *pm* is the probability of ethylene propagation, *cp* is ethylene/1-olefin choice probability, *cpp* is the 1-olefin propagation probability (normally *cpp* is equal to the average 1-olefin molar fraction for random copolymer), and *pp* is the overall propagation probability. Although, the overall propagation probability, *pp*, can be calculated from the number average chain length (r_N) and average 1-olefin fraction as follows:

$$pp=\frac{r_N-1}{r_N} \tag{36}$$

$$r_N=\frac{M_N}{(M_{CO}\cdot cpp)+(M_{MO}\cdot cp)} \tag{37}$$

where M_N is the number average molecular weight of ethylene/1-olefin copolymer, M_{CO} is the molecular weight of 1-olefin (84 g/mol for 1-hexene, 112 g/mol for 1-octene), and M_{MO} is the molecular weight of ethylene (28 g/mol).

The LES distribution obtained from equation (32) was discretized into several population groups according to *LES*. The total mass of each population group, *M*(*LES*), was considered to be uniformly distributed into *N* control volumes along the Tref column. The polymer fraction of population group with *LES* in each control volume can be calculated as

$$m(LES) = \frac{M(LES)}{N} \tag{38}$$

2.2.2 Crystallization kinetics equation

The crystallization kinetics equation for binary copolymers could be derived in the same way as the derivation of crystallization kinetics equation for homopolymers, as shown in equation (16), but a kinetic chain length r was substituted by LES. The crystallinity of specific LES and crystallization temperature, $X_c(LES,T_c)$, can be calculated as,

$$X_c(LES,T_c) = \begin{cases} 0, & T_c \geq T_d(LES) \\ 1 - \exp\left\{ -k_c \left[\frac{(A_c - B_c / LES) - T_c}{CR} \right]^{n_c} \right\}, & T_c < T_d(LES) \end{cases} \tag{39}$$

The total crystalline mass fraction of a population group with a LES at specific crystallization temperature of T_c, $M_c(LES,T_c)$, in Tref column can be calculated as,

$$M_c(LES,T_c) = m(LES) \cdot X_c(LES,T_c) \tag{40}$$

Hence, the crystalline mass fraction of a population group with a LES during the small temperature interval between $T_c + \Delta T_c$ and T_c, $m_c(LES,T_c)$, can be calculated:

$$m_c(LES,T_c) = M_c(LES,T_c) - M_c(LES,T_c + \Delta T_c) \tag{41}$$

2.2.3 Dissolution

A dissolution kinetics equation for binary copolymers could be derived as similar as a dissolution kinetics equation for homopolymers. Equation (25) can be modified to express a dissolution kinetics equation for binary copolymers by replacing a kinetic chain length of *r* with *LES* as shown in equation (42),

$$X_d(LES, T_{e,x}) = \begin{cases} 0 & , T_{e,x} < T_c(LES) \\ 1 - \exp\left\{ -k_d \left[\dfrac{T_{e,x} - (A_d - B_d / LES)}{HR} \right]^{n_d} \right\} & , T_{e,x} \geq T_c(LES) \end{cases}$$

(42)

where $X_d(LES,T_{e,x})$ is the dissolved fraction of polymer with *LES* when the temperature reaches $T_{e,x}$.

Consequently, the concentration of polymer dissolved at $T_{e,x}$ in each control volume, $C_d(T_{e,x})$, can be calculated by following equation:

$$C_d(T_{e,x}) = \sum_{r=1}^{\infty} \sum_{T_c = T_{c,0}}^{T_{c,final}} \left[m_c(LES, T_c) \cdot X_d(LES, T_{e,x}) \right] \qquad (43)$$

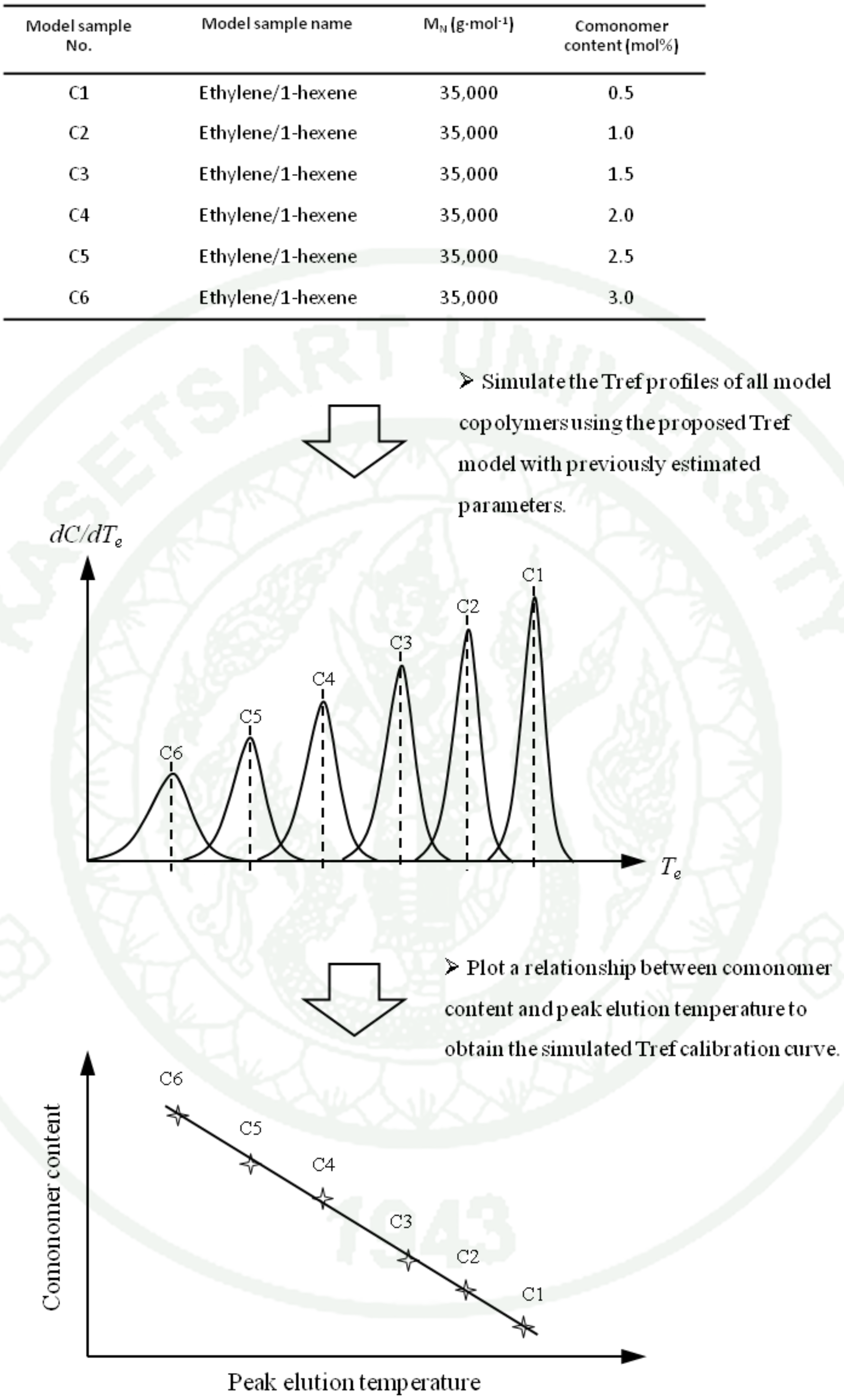
2.2.4 Population balance during the elution step

Finally, the Tref profile can be simulated by performing the population balance similar to the population balance step for homopolymers. Figure 17 and equation (28) show how to calculate the concentration of eluted polymer at the exit of Tref column at $T_{e,x}$, $C(T_{e,x})$.

Note that parameters A_c, B_c, A_d, and B_d, which are obtained by minimizing the summation of the square of the differences between the simulated and experimental Tref profiles as in equation (31), are not expected to be constants because the equilibrium crystallization/dissolution temperature is a function of comonomer content.

3. Application of Tref model for simulating Tref calibration curves

Figure 19 illustrates the computational steps to simulate Tref calibration curve for ethylene/1-hexene copolymers at a specific operating condition. Tref profiles of a series of model ethylene/1-hexene copolymers having different comonomer contents (0.5-3.0 mol%) but the same molecular weight (35,000 g/mol) were simulated using the proposed Tref model with previously estimated parameters. The peak temperatures of simulated Tref profiles were plotted as a function of the comonomer content. Tref calibration equations were obtained from the linear regression analysis.



Model sample No.	Model sample name	M_N (g·mol^{-1})	Comonomer content (mol%)
C1	Ethylene/1-hexene	35,000	0.5
C2	Ethylene/1-hexene	35,000	1.0
C3	Ethylene/1-hexene	35,000	1.5
C4	Ethylene/1-hexene	35,000	2.0
C5	Ethylene/1-hexene	35,000	2.5
C6	Ethylene/1-hexene	35,000	3.0

- Simulate the Tref profiles of all model copolymers using the proposed Tref model with previously estimated parameters.

- Plot a relationship between comonomer content and peak elution temperature to obtain the simulated Tref calibration curve.

Figure 19 Illustration of the computational steps to simulate calibration curve for ethylene/1-hexene copolymers at specific operating condition.

4. Application of Tref model for characterizing linear olefin block copolymers (OBCs)

The modeling of Tref characterization technique was explored as an alternative approach to describe Tref profiles of OBCs. The information of chain microstructures of OBCs was first simulated using Monte Carlo simulation developed by Anantawaraskul *et al.* (2009). The Tref model was modified and then applied with this chain microstructural information to simulate Tref profiles of OBCs. In this topic, the methodology was divided into 2 parts: (1) investigation of OBCs chain microstructures via Monte Carlo simulation and (2) modification of proposed Tref model for OBCs characterization.

4.1 Investigation of OBCs chain microstructures via Monte Carlo simulation

Anantawaraskul *et al.* (2009) proposed the Monte Carlo simulation for examining the chain microstructure of OBCs (*e.g.*, number average molecular weight, average comonomer content, molecular weight distribution, longest ethylene sequence distribution, etc.). Moreover, the effect of polymerization conditions (*i.e.*, chain shuttling probability, propagation probability, and catalyst ratio) on OBCs chain microstructure was investigated.

The chain shuttling polymerization mechanism for OBC chains was illustrated in Figure 20. Figure 21 shows a simplified algorithm of Monte Carlo simulation for simulating the chain microstructure of OBCs reported by Anantawaraskul *et al.* (2009). During the formation of a polymer chain, the random number, *R*, was generated to select the polymerization steps that are catalyst selection, monomer selection, chain propagation, chain shuttling, or even chain transfer. For each chain, a random number of *R* was first generated to select the catalyst type for chain formation. Catalyst 1 was assumed to produce ethylene rich chains, while Catalyst 2 produced α-olefin rich chains. If *R* is less than the mole fraction of Catalyst 1 in the reactor (P_{cat1}), the polymer chain will start growing on Catalyst 1; otherwise, it will start growing on Catalyst 2. In this study, two catalyst types were assumed to have the same overall activity ($P_{cat1} = P_{cat2} = 0.5$). The first monomer added for growing on the catalyst, which is ethylene molecule or α-olefin molecule, was selected by examining another random number of R. If $R \le P_m/(P_m + P_c)$, ethylene unit is first added to catalyst; otherwise, the α-olefin unit.

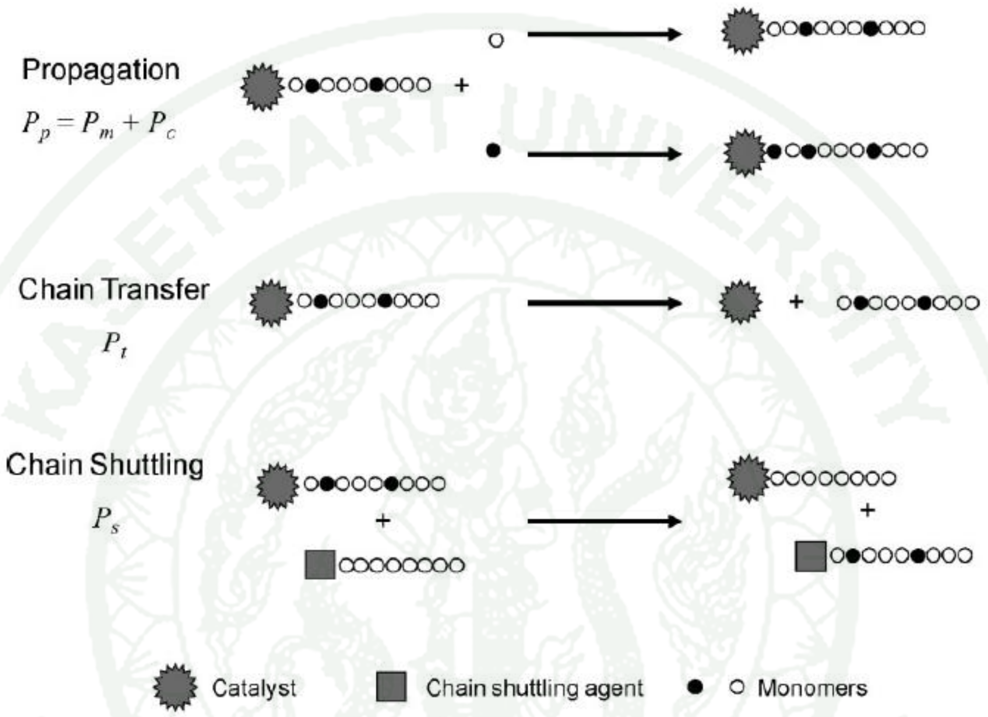
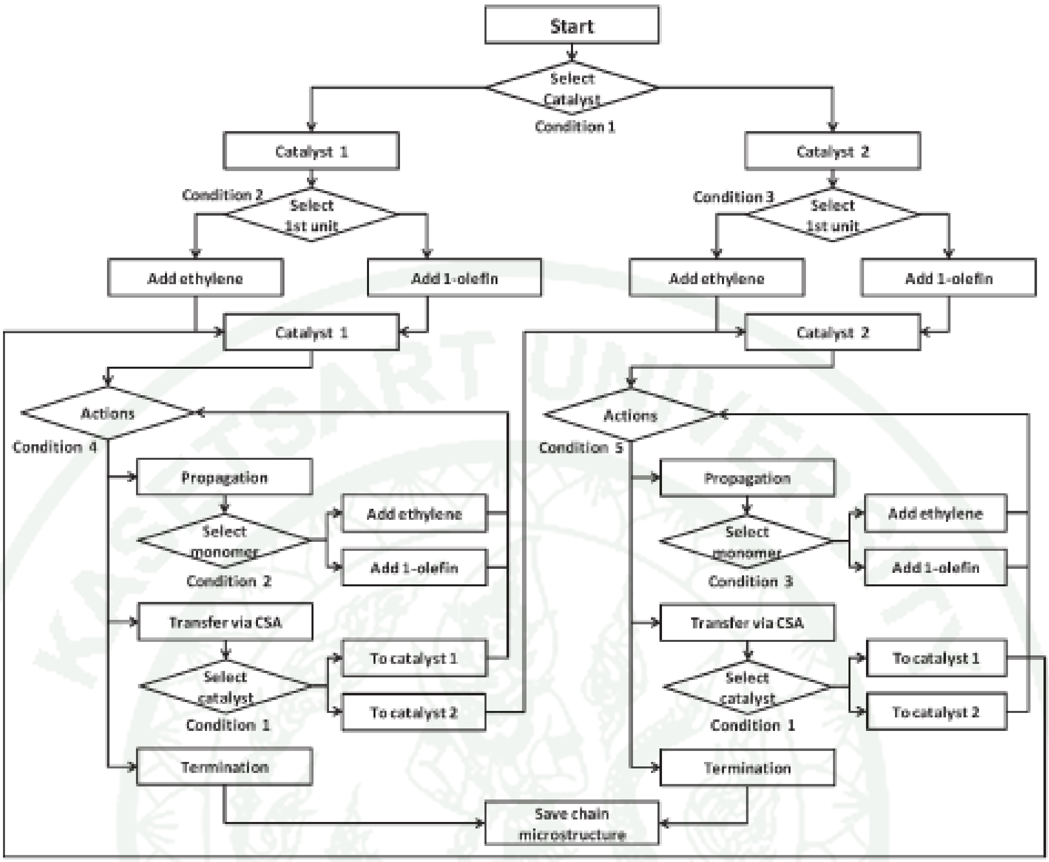


Figure 20 A simplified chain shuttling polymerization mechanism.

Source: Anantawaraskul *et al.* (2009)



Summary of conditions in the simplified OBC algorithm

Condition 1:	If $R \le P_{cat1}$ then chain starts with Catalyst 1, else chain starts with Catalyst 2
Condition 2:	If $R \le P_{m,1}/(P_{m,1}+P_{c,1})$ then add ethylene unit, else add α-olefin unit
Condition 3:	If $R \le P_{m,2}/(P_{m,2}+P_{c,2})$ then add ethylene unit, else add α-olefin unit
Condition 4:	If $R \le P_{p,1}$ then chain propagates, else if $R \le P_{p,1} + P_{s,1}$ then chain transfers, else chain terminates
Condition 5:	If $R \le P_{p,2}$ then chain propagates, else if $R \le P_{p,2} + P_{s,2}$ then chain transfers, else chain terminates

Figure 21 A simplified Monte Carlo algorithm for simulating the chain microstructure of OBCs.

Source: Anantawaraskul *et al.* (2009)

Subsequent reactions taking place at the catalyst, chain propagation, chain shuttling, or chain termination, were determined by comparing other random numbers of *R* with the propagation probability (P_p), chain shuttling probability (P_s), and chain transfer probability (P_t). A polymer chain propagates if $R \le P_p$, is shuttled if $P_p < R < P_p + P_s$, and terminates otherwise. Note that $P_p + P_s + P_t = 1$ for each catalyst type, since these three probabilities encompass all the possible events taking place during the life time of a polymer chain, as proposed in Figure 20. The parameter P_t is related to the number average chain length, r_N, of polymer produced with a given catalyst type by the relation $P_t = 1/r_N$.

Consideration chain propagation, another random number of *R* was generated to decide which monomer type is added into the polymer chain. Similar to the first monomer unit selection, if $R \le P_m / (P_m + P_c)$, ethylene unit is incorporated into the polymer chain; otherwise, α-olefin molecule. Assuming the copolymerization followed Bernoullian statistics, that is, the propagation probability of a given monomer is equal to its average mole fraction in the copolymer. First or higher order Markovian statistics can be easily incorporated into this Monte Carlo algorithm if necessary.

Consideration chain shuttling, another random number of *R* was generated to decide which catalyst type is selected according to the molar fractions of Catalyst 1 and Catalyst 2 in the reactor for chain transfer. The polymer chain is shuttled to another Catalyst 1 if $R \le P_{cat1}$; if $R > P_{cat1}$, the polymer chain is shuttled to Catalyst 2.

This process is repeated until the chain terminates. After chain termination, information on the chain microstructure is recorded. Note that all probabilities (P_p, P_s, P_t, P_m, and P_c) considered in this simulation are assumed to be different for each catalyst type. In this study, the 200,000 polymer molecules are simulated to adequately represent OBC microstructures.

4.2 Modification of proposed Tref model for OBCs characterization

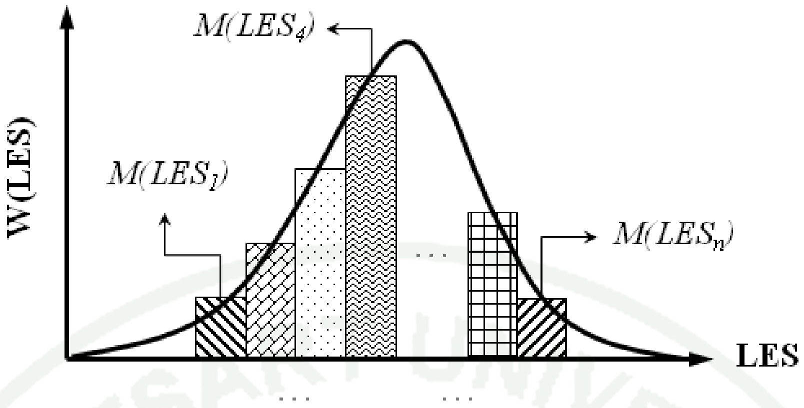
The LES of OBC chain was assumed to be a key factor reflecting its chain crystallizability similar to the case of random ethylene/1-olefin copolymer. The LES distributions of OBCs were obtained from Monte Carlo simulation.

Although the procedure for interpreting Tref profiles of OBCs is rather similar to that of random ethylene/1-olefin copolymers, the proposed Tref model must be modified. Starting, the LES distribution of OBC was discretized into several population groups according to *LES*. The total mass of each population group, *M(LES)*, and average 1-olefin molar fraction of each population group, *cc(LES)*, were recorded as shown in Figure 22.

The *M(LES)* was then distributed uniformly into N control volumes along the Tref column. The polymer fraction of a *LES* group in each control volume, *m*(*LES*) can be calculated by equation (38).

In the crystallization step, OBC polymer chains crystallized and coated onto the support following their crystallization kinetics. The crystalline mass fraction of a population group with a *LES* during the small temperature interval between $T_c+\Delta T_c$ and T_c, $m_c(LES,T_c)$, can be calculated from equation (39) to equation (41).

In the elution step, the concentration of OBC polymer dissolved at elution temperature of $T_{e,x}$, $C_d(T_{e,x})$, can be calculated by equation (42) and (43). Note that the parameters A_c, B_c, k_c, A_d, B_d, and k_d corresponding to average 1-olefin fraction of each population group, *cc(LES)*, were determined by the values of estimated parameters.



LES	M(LES)	cc(LES)
LES_1	$M(LES_1)$	$cc(LES_1)$
LES_2	$M(LES_2)$	$cc(LES_2)$
LES_3	$M(LES_3)$	$cc(LES_3)$
LES_4	$M(LES_4)$	$cc(LES_4)$
...	...	...
LES_n	$M(LES_n)$	$cc(LES_n)$

Figure 22 The discretization of LES distribution for OBC.

Moreover, the elution temperature of each OBC population group was expected to shift to a temperature higher than that of random ethylene/1-olefin copolymer fractions at the same equivalent 1-olefin molar fraction as experimentally observed by Shan and Hazlitt (2007). They proposed the block index (*BI*) parameter to quantify how the elution temperature of OBC fraction deviates from that of random copolymer fraction as,

$$BI = \frac{\frac{1}{T_x} - \frac{1}{T_{x0}}}{\frac{1}{T_A} - \frac{1}{T_{AB}}} \tag{44}$$

where T_x is the elution temperature of OBC fraction (i.e., OBC population group) with narrow CCD, T_{x0} is the elution temperature of random copolymers with the equivalent narrow CCD, T_A is the elution temperature of ethylene homopolymers, and T_{AB} is the elution temperature of a random copolymer with the same average composition as that of the whole OBC.

For each population group, the value of BI parameter was estimated to be a linear function of the average 1-olefin molar fraction (Anantawaraskul *et al.*, 2009),

$$BI = (4.783 \times cc) + 0.143 \tag{45}$$

where cc is the average 1-olefin molar fraction of each population group, $cc(LES)$.

The parameter T_A, T_{AB}, and T_{x0} based on the analytical Tref analysis can be evaluated using equation (46), introduced by Shan and Hazlitt (2007),

$$T_A \text{ or } T_{AB} \text{ or } T_{x0} = \frac{-237.83}{\ln(1-cc) - 0.639} \tag{46}$$

where cc is the 1-olefin molar fraction. For T_A, cc is assumed to be zero; for T_{AB}, cc is equivalent to average 1-olefin molar fraction of whole OBC; for T_{x0}, cc is equivalent to average 1-olefin molar fraction of each OBC population group.

The elution temperature of OBC population group, T_x, can be obtained using equation (46) with given BI, T_A, T_{AB}, and T_{x0}. A shift temperature of each OBC population group based on experimental observation, can be quantified as,

$$T_{shift} = T_x - T_{x0} \tag{47}$$

For each population group, the T_{shift} was applied to shift the elution temperature obtained from the case of random copolymers with the equivalent average comonomer content. After that, the Tref profile of OBC can be simulated by performing the population balance similar to the population concept for binary copolymers. Figure 17 and equation (28) show how to calculate the concentration of eluted polymer at the exit of Tref column at $T_{e,x}$, $C(T_{e,x})$.

RESULTS AND DISCUSSIONS

This topic is divided into 3 parts. The first part is the Tref model validations. The second part is application of Tref model for simulating Tref calibration curves. The third part is application of Tref model for characterizing linear olefin block copolymers (OBCs).

1. The Tref model validations

1.1 Effect of chain microstructures on Tref profiles

1.1.1 Effect of molecular weight on Tref profiles

E191 and E521 homopolymer samples were used to investigate the effect of molecular weight on Tref profiles. Figure 23 shows the chain length distribution of these samples calculated from equation (7). Figure 24 compares the experimental and simulated Tref profiles of both samples at a cooling rate of 0.2 °C/min, a heating rate of 1.0 °C/min, and a solvent flow rate of 0.5 mL/min. The results show that the simulated Tref profiles can reasonably describe the peak elution temperature and elution temperature range.

The results also indicated that at the same operating condition the peak elution temperatures of both E191 and E521 samples are practically the same. This observation agrees with the previous publication reported by Wild *et al.* (1982) that the peak elution temperature of Tref profile is independent of molecular weight when its molecular weight is more than 10,000 g/mol.

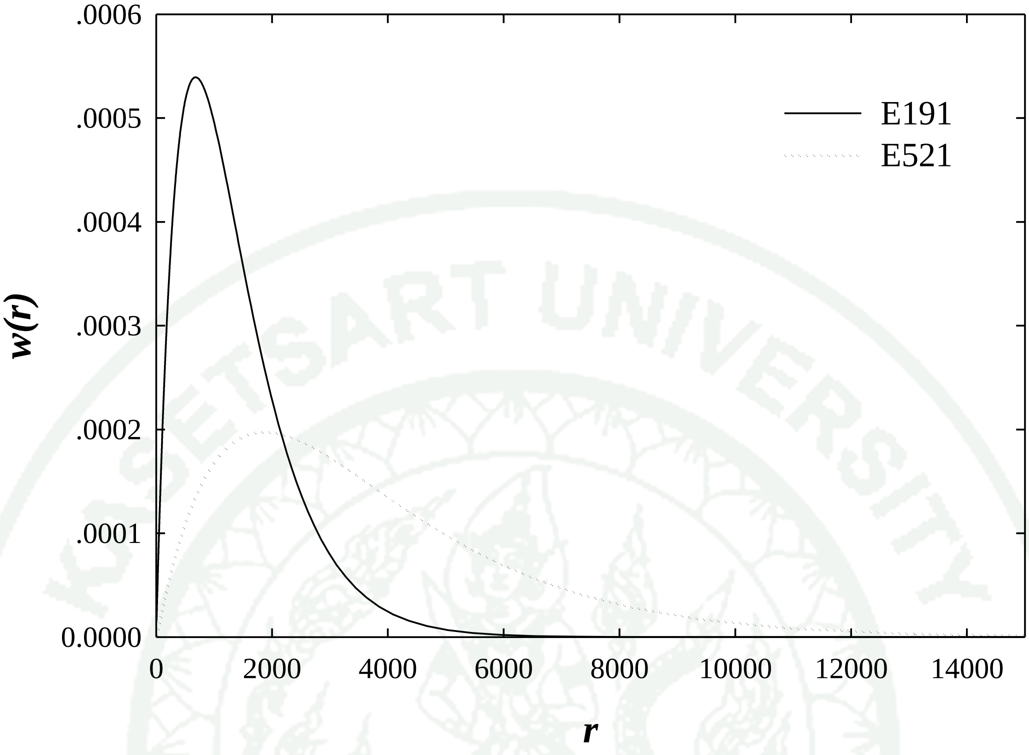


Figure 23 The chain length distributions of ethylene homopolymers.

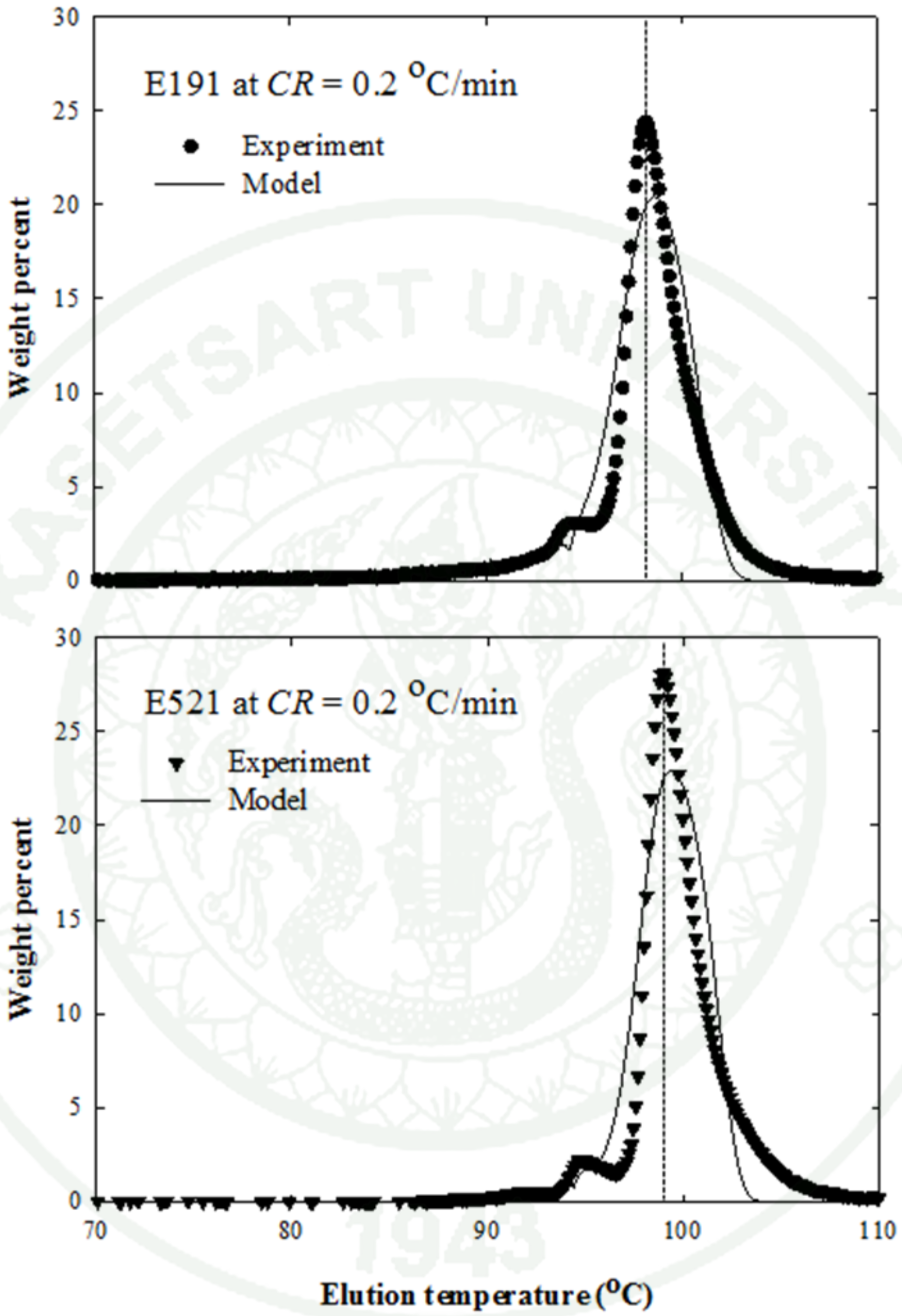


Figure 24 Comparison between experimental and simulated Tref profiles of E191 and E521 samples.

The estimated parameters (A_c, B_c, n_c, k_c, A_d, B_d, n_d, and k_d) for Tref model of ethylene homopolymers obtained by minimizing the function Φ in equation (31) are shown in Table 2. The values of parameters of crystallization kinetic equation in the proposed Tref model agree well with those in the Crystaf model of ethylene homopolymers (A = 90.45, B = 654.75, n = 3.96, and k = 2.469E-6) reported earlier by Anantawaraskul *et al.* (2006, 2007a). Unfortunately, we cannot directly validate the values of parameters describing dissolution kinetics because these values in the similar setting have not been previously reported. However, this issue will be reexamined later from the trends of these estimated values at various comonomer contents and operating conditions for the case of ethylene/1-olfin copolymers.

Table 2 The estimated parameters for the Tref model of ethylene homopolymers

Sample	Parameters describing the crystallization kinetics				Parameters describing the dissolution kinetics			
	A_c	B_c	n_c	k_c	A_d	B_d	n_d	k_d
E191	90.4	655	3.96	2.47E-6	94.0	1,245	3.44	1.30E-3
E521	90.4	655	3.96	2.47E-6	94.5	2,026	5.41	4.78E-4

1.1.2 Effect of comonomer content on Tref profiles

Figure 25 shows the LES distributions of all ethylene/1-hexene copolymers (i.e., EH068, EH151, and EH314 samples) investigated in this study. Figure 26 compares the experimental and simulated Tref profiles of these samples at a cooling rate of 0.1 °C/min, a heating rate of 0.2 °C/min, and a solvent flow rate of 0.2 mL/min.

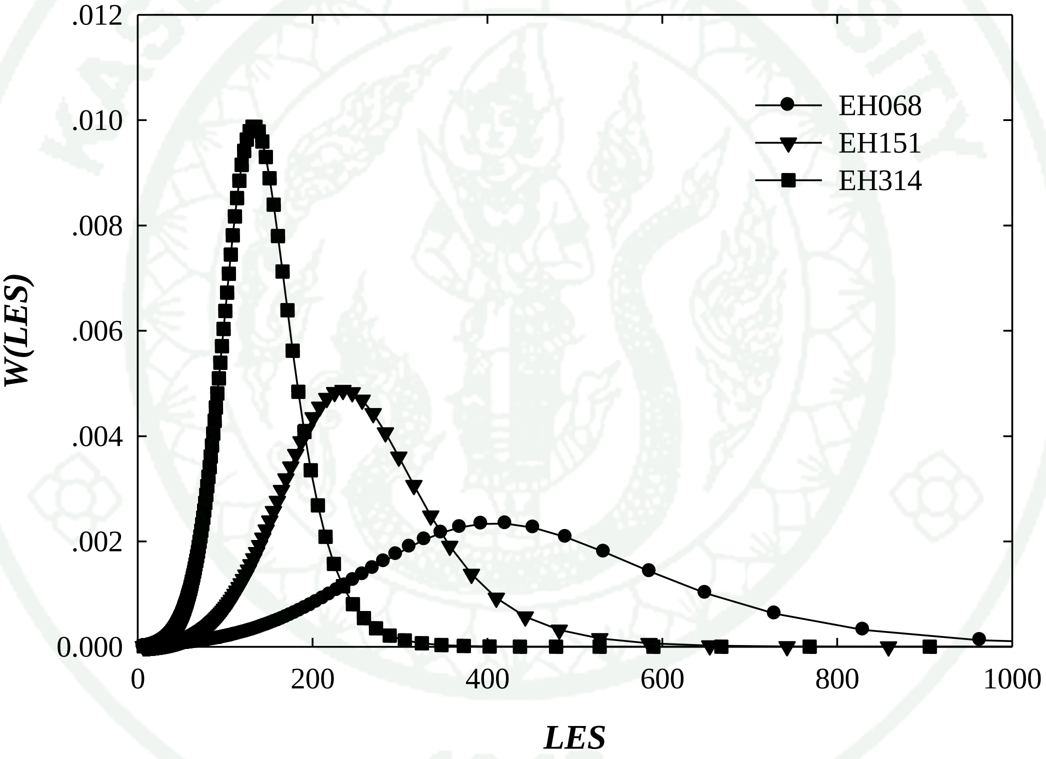


Figure 25 The longest ethylene sequence distributions of ethylene/1-hexene copolymers.

As a comonomer fraction increases, the Tref profiles shift to lower elution temperatures and become broader. This is because comonomer units incorporated into polymer chains disrupt the chain regularities, make it more difficult for polymer chain to fold in the crystallite unit, and thus lower their chain crystallizabilities and elution temperature. Further, an increase in comonomer fraction lead to shorter LES and, therefore, broadened Tref profiles because polymer chains having shorter LES can be dissolved back over a wider range of elution temperatures. The proposed Tref model can describe the effect of comonomer content on Tref profiles very well because LES, which effectively reflects chain crystallizability, was used in the model.

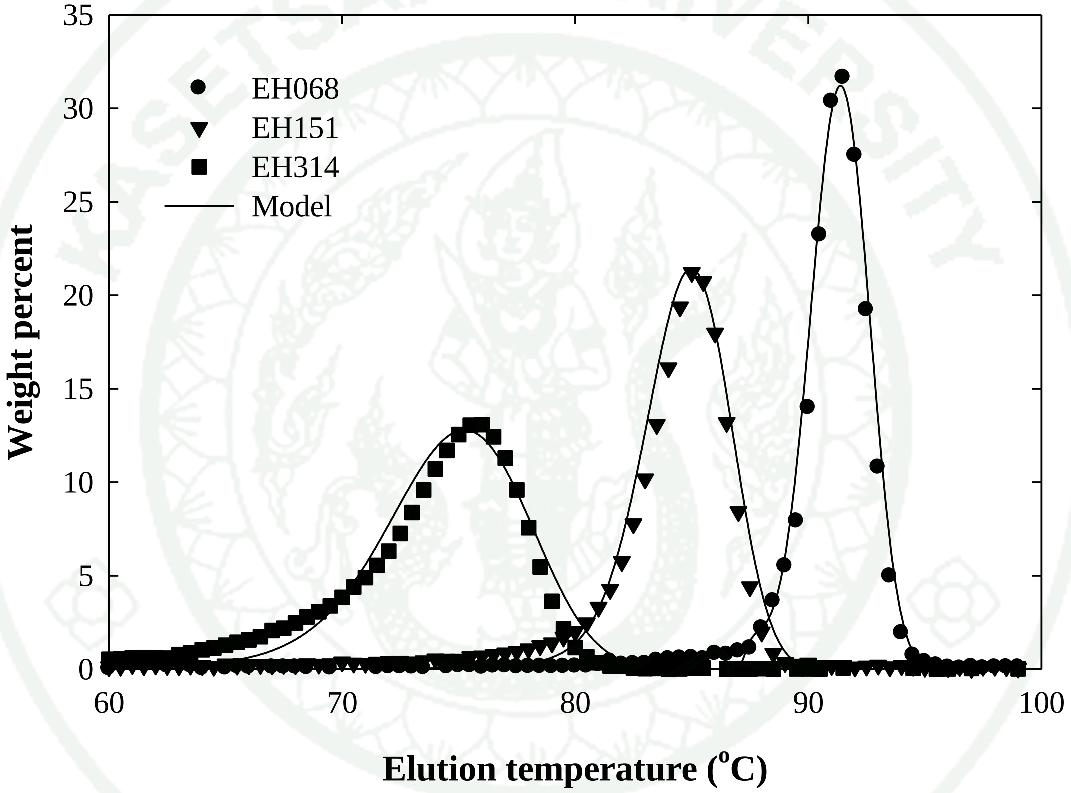


Figure 26 Effect of comonomer content on Tref profiles.

The estimated parameters for a series of ethylene/1-hexene copolymers (i.e., EH068, EH151, and EH314) at various comonomer contents are shown in Table 3. The results indicate that parameters A_c, B_c, A_d, and B_d depend on the comonomer molar fraction because it affects the equilibrium crystallization/dissolution temperature as discussed earlier. The parameters n_c and n_d are almost constant at 4.49 similar to the estimated value of Avrami component in the Crystaf model reported by Anantawaraskul *et al.* (2007a, 2007b). The values of parameters k_c and k_d decreases with an increase in comonomer content because the comonomer units disrupt the regularity of chain, lower their chain crystallizabilities/solubilities, and rates of crystallization/dissolution (Perez *et al.*, 1997).

Table 3 also shows the equations for approximating the value of each model parameter as a function of comonomer content. These empirical equations obtained from the estimated data; therefore, they are reliable only within the comonomer content range of 0.68-3.14 mol%.

Table 3 The estimated parameters for the Tref model of ethylene/1-hexene copolymers at various comonomer contents

Parameters	Estimated values of parameters for sample			Empirical equation *
	EH068	EH151	EH314	
Parameters describing the crystallization kinetics				
A_c	85.9	80.9	71.1	$A_c = 90.0 - (6.0 \cdot CC)$
B_c	597	550	507	$B_c = 614 - (35 \cdot CC)$
n_c	4.49	4.48	4.49	$n_c \approx 4.49$
k_c	2.30E-3	1.59E-3	3.41E-4	$k_c = 0.0045 \exp(-0.8 \cdot CC)$
Parameters describing the dissolution kinetics				
A_d	88.8	80.9	71.2	$A_d = 92.8 - (7.0 \cdot CC)$
B_d	566	671	877	$B_d = 480 + (126 \cdot CC)$
n_d	4.49	4.51	4.49	$n_d \approx 4.49$
k_d	7.35E-5	2.07E-7	2.38E-8	$k_d = 0.0001 \exp(-3.0 \cdot CC)$

* *CC* = comonomer content (mol %)

1.2 Effect of operating conditions on Tref profiles

1.2.1 Effect of cooling rate on Tref profiles

The effect of cooling rate during crystallization step on Tref profiles of EO219 sample is shown in Figure 27. In these cases, the heating rate and solvent flow rate were kept constant at 0.2 °C/min and 0.2 mL/min, respectively.

The result shows that Tref profiles become broader and slightly shifted to higher elution temperature when a cooling rate decreases. The simulated Tref profiles were found to be in a good agreement with the experimental Tref profiles at several cooling rates, as also shown in Figure 27. This model is the first that can adequately describe the effect of cooling rate because crystallization kinetics were incorporated in the model, while other previous models cannot describe such an effect because they are all based on the thermodynamic equilibrium assumption. The presence of crystallization kinetics is consistent with the previous experimental observation (Anantawaraskul *et al.*, 2003a) that Tref fractionation process is far from the thermodynamic equilibrium and, therefore, the crystallization kinetics play an important role, especially at the fast cooling rate.

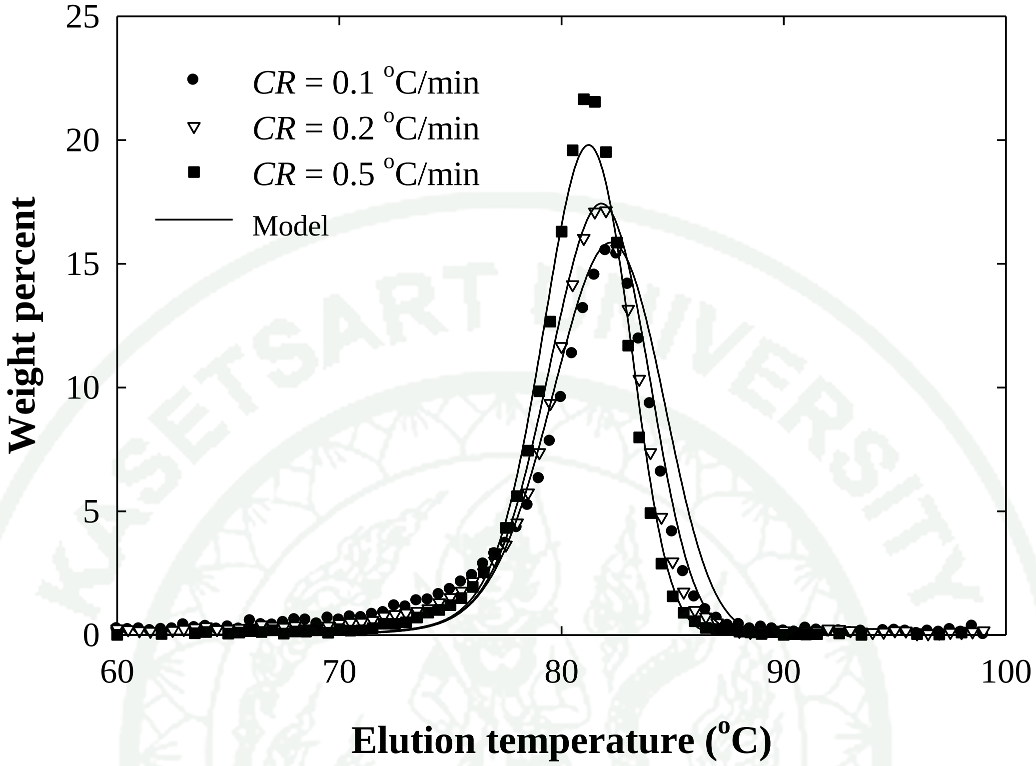


Figure 27 Effect of cooling rate (*CR*) on Tref profiles of EO219 sample.

1.2.2 Effect of heating rate on Tref profiles

Figure 28 shows how the heating rate affects the Tref profiles of EO219 sample, while a cooling rate and a solvent flow rate were kept constants at 0.2 °C/min and 0.2 mL/min, respectively.

We can observe that the Tref profiles become broader and shift to higher elution temperature as a heating rate increases. The simulation results show that this model incorporating with dissolution kinetics can be used well to describe the broadening and peak temperatures of experimental Tref profiles at several heating rates, as shown in Figure 28. It is because, at the same solvent flow rate, an increase in heating rates causes polymer molecules to dissolve back to a fresh solvent following their dissolution kinetics over a wider range of their solubilities and, then, polymer solutions reach the end of the column at higher elution temperatures as observed earlier by Anantawaraskul *et al.* (2003a).

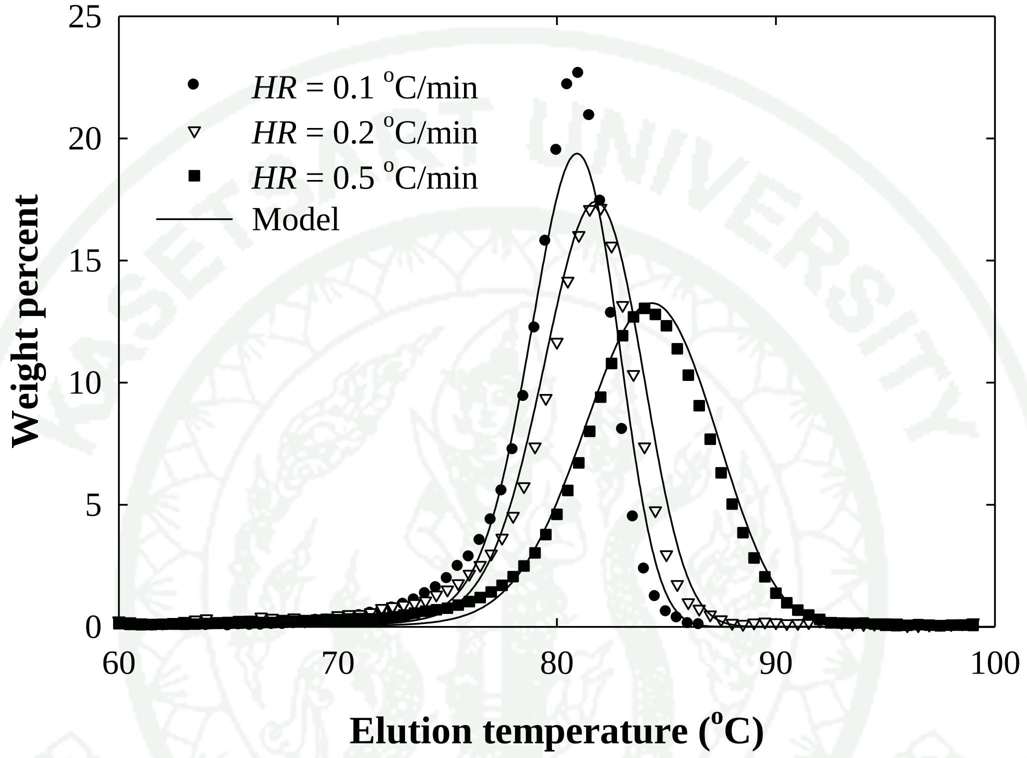


Figure 28 Effect of heating rate (*HR*) on Tref profiles of EO219 sample.

1.2.3 Effect of solvent flow rate on Tref profiles

The effect of solvent flow rate on Tref profiles of EO219 sample was investigated at a cooling rate of 0.2 °C/min and a heating rate of 0.2 °C/min as shown in Figure 29. The results show that, the Tref profiles shift to lower elution temperatures and become narrower when solvent flow rate increases. The simulated Tref profiles agree very well with the experimental Tref profiles at several solvent flow rates.

Considering an arbitrary control volume in Tref column at a constant heating rate, equation (30) shows that the elution temperature increment is inversely proportional to the solvent flow rate. This causes the shift of Tref peak temperature to lower elution temperatures when a solvent flow rate increases. Moreover, an increase in solvent flow rates causes polymer chains to dissolve back to a solution over a narrower elution temperature range and, therefore, the Tref profiles become narrower.

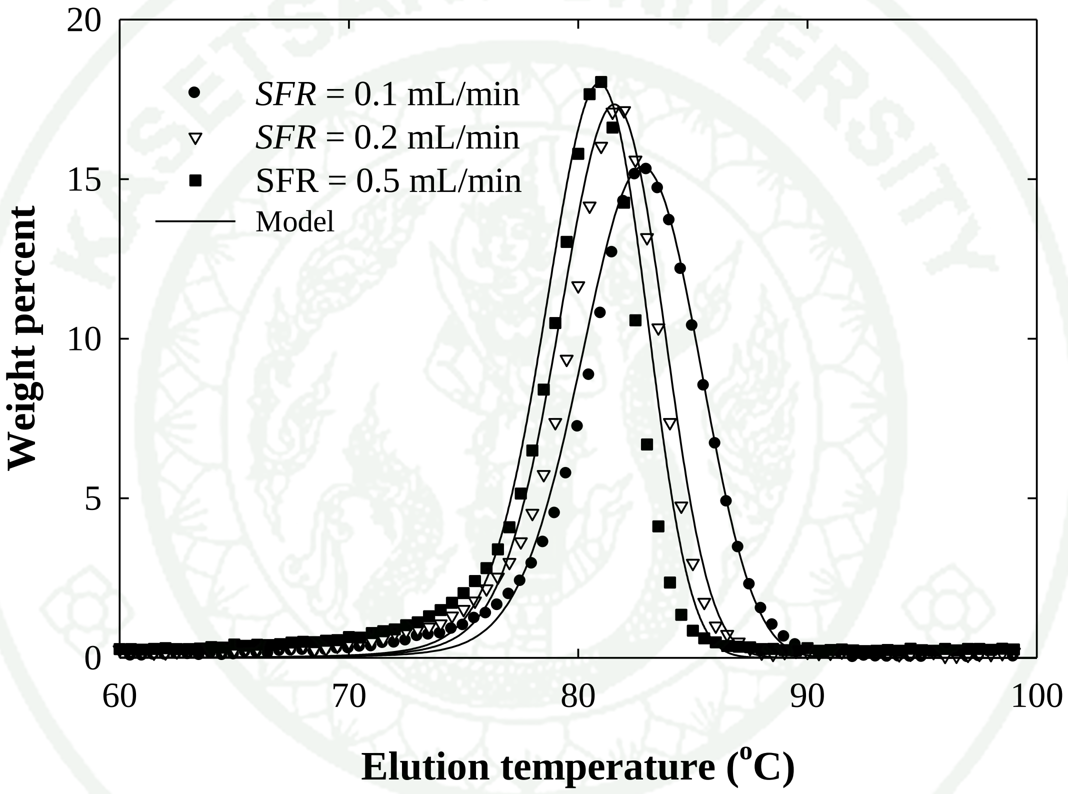


Figure 29 Effect of solvent flow rate (*SFR*) on Tref profiles of EO219 sample.

The estimated parameters for EO219 sample at various operating conditions are shown in Table 4. We found that the cooling rate significantly affects parameter k_c as previously observed in the Crystaf model (Anantawaraskul *et al.*, 2007a, 2007b), the heating rate influences the values of parameter k_d because the polymer crystallites can easily dissolve back to a solution when the heating rate increases, and the solvent flow rate does not significantly affect the values of any parameters. Parameters n_c and n_d for ethylene/1-olefin copolymers at various operating conditions are practically constant and agree well with the parameter in the Crystaf model (n = 4.49) as reported previously by Anantawaraskul *et al.* (2007a, 2007b). Parameters A_c, B_c, A_d, and B_d are found to be relatively constants. This can be theoretically expected because the equilibrium dissolution temperature is independent of the operating conditions.

Table 4 The estimated parameters for the Tref model of a ethylene/1-octene copolymer at various operating conditions

Rate	Parameters describing the crystallization kinetics				Parameters describing the dissolution kinetics			
	A_c	B_c	n_c	k_c	A_d	B_d	n_d	k_d
Cooling rates *								
0.1 °C/min	76.9	526	4.49	1.04E-3	76.4	680	4.49	3.80E-8
0.2 °C/min	76.9	526	4.49	1.64E-2	77.0	680	4.49	6.88E-8
0.5 °C/min	74.5	526	4.49	1.93E-1	77.7	680	4.49	1.64E-7
Heating rates **								
0.1 °C/min	76.9	526	4.49	1.64E-2	77.4	684	4.49	5.10E-9
0.2 °C/min	76.9	526	4.49	1.64E-2	77.0	684	4.49	6.88E-8
0.5 °C/min	74.5	526	4.59	1.64E-2	76.1	684	4.69	7.60E-7
Solvent flow rates ***								
0.1 mL/min	76.9	526	4.49	1.64E-2	76.9	695	4.49	5.72E-8
0.2 mL/min	76.9	526	4.49	1.64E-2	76.9	695	4.49	6.88E-8
0.5 mL/min	76.9	526	4.49	1.64E-2	76.9	695	4.49	7.26E-8

* A heating rate and a solvent flow rate were kept constants at 0.2 °C/min and 0.2 mL/min, respectively.

** A cooling rate and a solvent flow rate were kept constants at 0.2 °C/min and 0.2 mL/min, respectively.

*** A cooling rate and a heating rate were kept constants at 0.2 °C/min and 0.2 °C/min, respectively.

2. Application of Tref model for simulating Tref calibration curves

Figure 30 compares the simulated Tref calibration curves of ethylene/1-hexene copolymers having M_N = 35,000 g/mol with the experimental Tref peak temperatures of EH068, EH151, and EH314 samples at cooling rates of 0.1 °C/min and 0.2 °C/min, a heating rate of 0.2 °C/min, and a solvent flow rate of 0.2 mL/min. The simulated Tref calibration curves were found to be in a good agreement with experimental results, which indicate that the Tref calibration curve is slightly shift to lower elution temperatures when a higher cooling rate increases due to the same reason discussed on the effect of cooling rate on Tref profiles. Figure 30 also shows the approximated calibration equations which were constructed for a comonomer range of 0.5-3.0 mol%.

This new approach for constructing the simulated Tref calibration curves can potentially replace the tedious process of constructing experimental Tref calibration curves at the desired conditions, leading to a more efficient way for interpreting chemical composition distribution from Tref profiles.

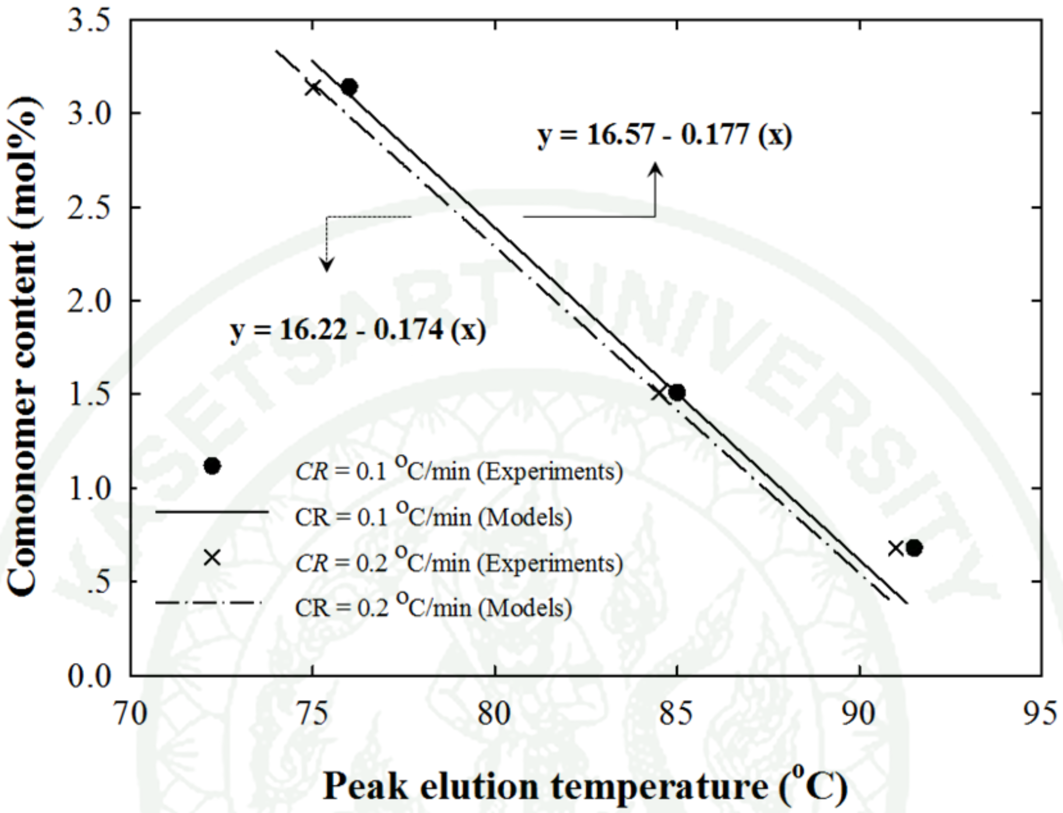


Figure 30 The simulated Tref calibration curves for ethylene/1-hexene copolymers at various operating conditions.

3. Application of Tref model for characterizing linear olefin block copolymers (OBCs)

To verify Monte Carlo simulation, the LES distribution of OBC was simulated with P_{cat1} = P_{cat2} = 0.5, $P_{c,1}$ = 0.01, $P_{c,2}$ = 0.03, P_t = 0.001 (M_N = 30,000 g/mol), and P_s = 0.0000 (no chain shuttling) and compared with the LES distributions of two random ethylene/1-hexene copolymers having 1-hexene content of 1 mol% and 3 mol% (LLDPE blend) simulated from equation (32). The results show that the LES distribution obtained from both simulations are similar, as shown in Figure 31. Therefore, the Monte Carlo simulation can be used well to generate the information of OBC.

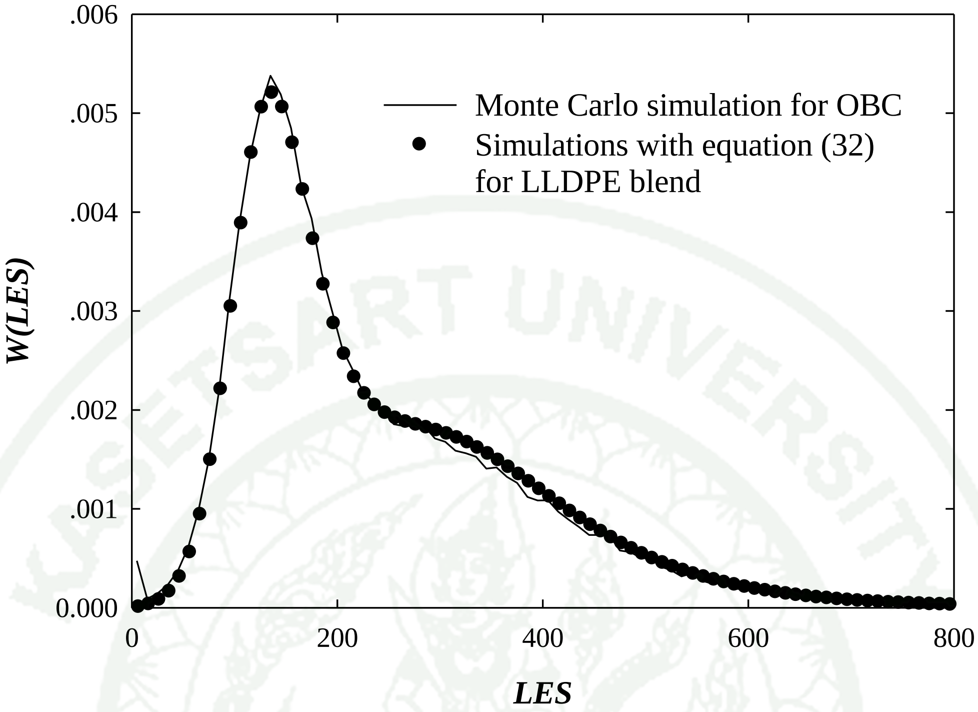


Figure 31 Comparison between the LES distributions obtained from Monte Carlo simulation for OBC and simulations with equation (32) for LLDPE blend.

Figure 32 shows the effect of the chain shuttling probability (P_s) on the LES distribution of OBCs. The LES distributions of OBCs at various P_s were simulated with $P_{cat1} = P_{cat2} = 0.5$, $P_{c,1} = 0.01$, $P_{c,2} = 0.03$, and $P_t = 0.001$ (M_N = 30,000 g/mol). The LES distributions of OBCs were also compared with that of a random copolymer with the same equivalent overall 1-hexene molar fraction of 2 mol%.

Note that Catalyst 1 produces ethylene rich copolymers which have longer LES, while Catalyst 2 produces ethylene poor copolymers which have shorter LES. At P_s = 0.0000 (no chain shuttling), two peaks of LES distribution, each corresponding to copolymers produced with the different catalysts, can be clearly observed. With increasing P_s, the LES distributions of polymer chains produced from both catalysts are starting to merge and generating a unimodal LES distribution, as shown in Figure 32. It can be observed that the LES distribution becomes narrow and approaches the LES distributions of a random copolymer because the increase in chain shuttling frequency will eventually lead to the formation of progressively shorter polymer blocks.

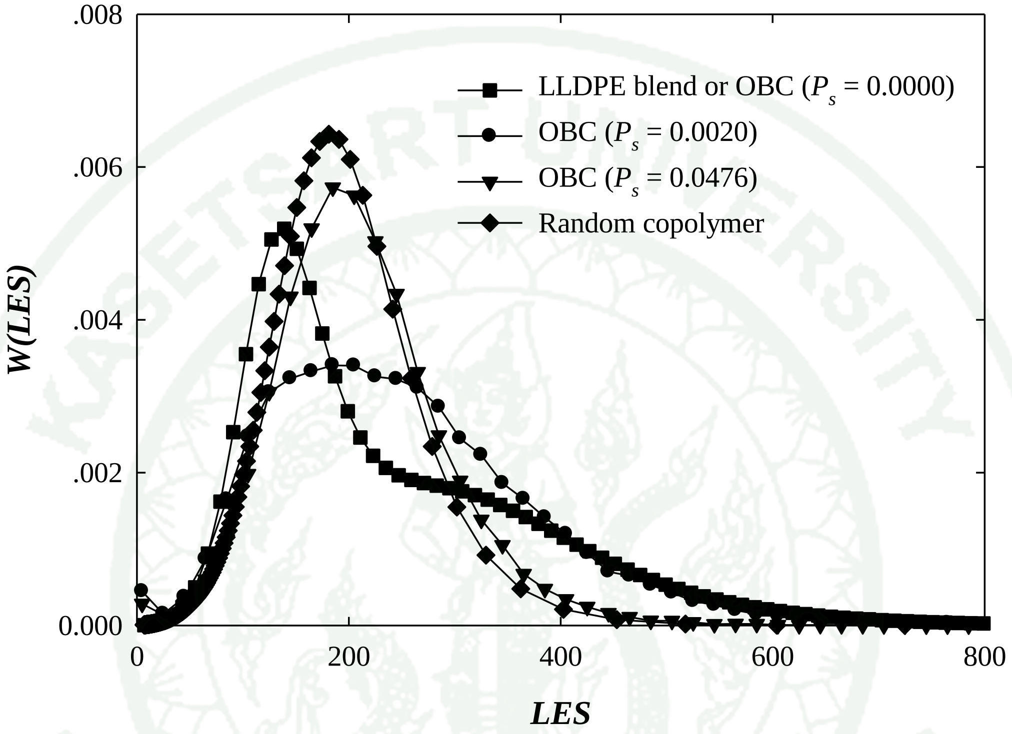


Figure 32 The LES distributions of LLDPE blend, OBCs, and a random copolymer.

The effect of the chain shuttling probability (P_S) on the simulated Tref profile of these model OBCs is illustrated in Figure 33. With increasing chain shuttling frequency, the bimodal Tref profiles (P_S = 0.0000) will start to merge and generate a unimodal Tref profiles and also shift to lower elution temperature. Figure 33 also compares the simulated Tref profiles of LLDPE blend, an OBC, and a random copolymer. The results show that the Tref profile of an OBC locates between that of a random copolymer and LLDPE blend. The Tref profiles of OBCs were found to approach that of a random copolymer, while the chain shuttling frequency increases. This agrees well with the experimentally results observed by Shan and Hazlitt (2007).

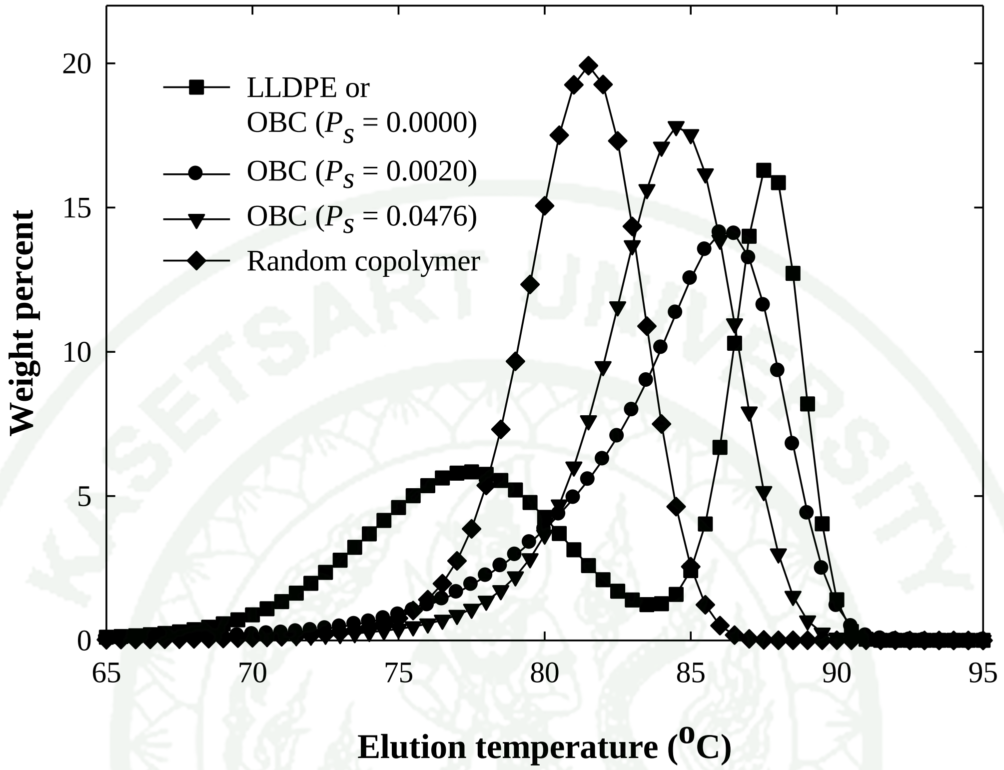


Figure 33 The simulated Tref profiles of LLDPE blend, OBCs, and a random copolymer.

This Tref modeling approach can be useful to interpret Tref profiles of polymers with more complex chain microstructures (e.g., polymer blends or linear olefin block copolymers). However, the experimental results are needed for model validations.

CONCLUSION AND RECOMMENDATION

Conclusion

A new approach of Tref modeling based on the concept of population balance model with the incorporation of crystallization and dissolution kinetics was developed to describe the experimental Tref profiles of ethylene homopolymers and ethylene/1-olefin copolymers at several operating conditions. The proposed Tref model can describe the effects of molecular weight, comonomer content, and operating conditions (e.g., the cooling rate, heating rate, and solvent flow rate) well. The model parameters also agree well with previously reported values and follow the expected theoretical trends. In addition, the values of all parameters, which were estimated by minimizing the summation of the square of the differences between the simulated and experimental Tref profiles, agree well with previously reported values and follow theoretical considerations.

A new approach for constructing the simulated Tref calibration curves based on the proposed model for ethylene/1-hexene copolymers at specific operating conditions was developed as an alternative to the tedious experimental approach.

As an alternative approach to experiments, Monte Carlo simulation and the modified Tref model were developed to describe the Tref profiles of OBCs at various chain shuttling probabilities. This approach was also used as the qualitative tool for comparing Tref profiles of OBCs with those of random copolymer and LLDPE blend. However, the results presented here is still preliminary; further experimental Tref results are required for quantitative validation.

Recommendation

The modeling concept used to describe the Tref fractionation mechanism can also be applied for developing the mathematical models of other new characterization techniques with similar fractionation principles (i.e., dynamic crystallization, crystallization elution fractionation).

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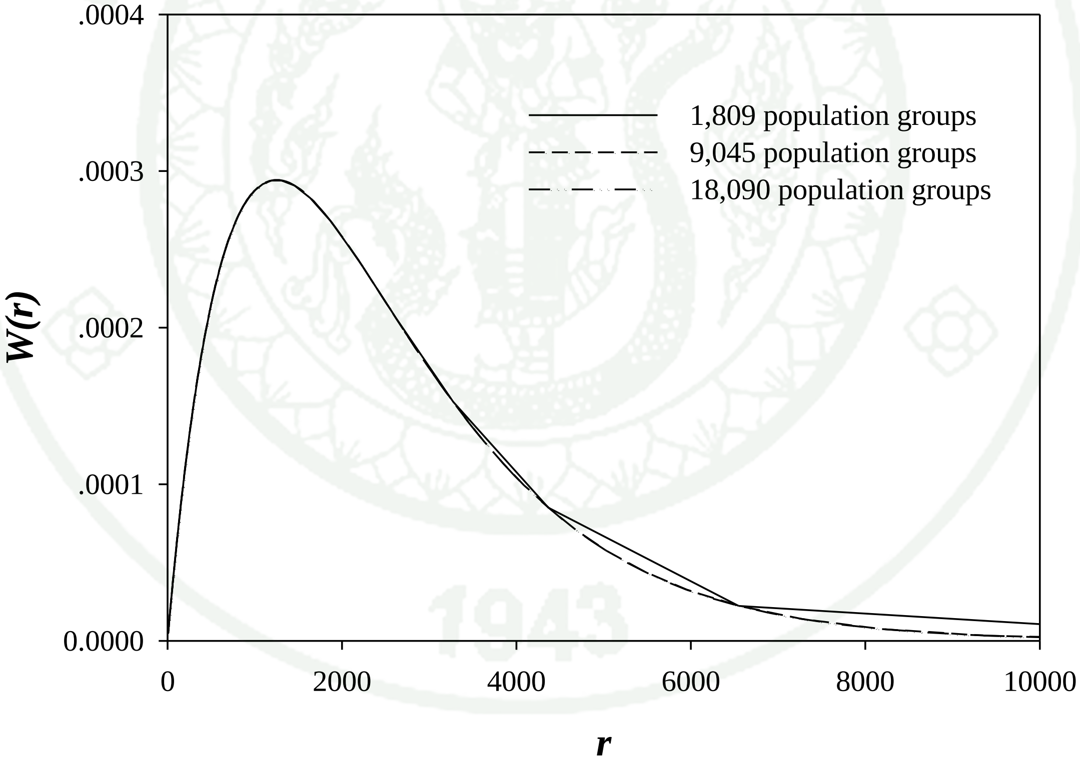
APPENDICES

Appendix A

The number of population groups

As described earlier, Tref column is computationally discretized into *N* interconnecting control volumes for population balance. A model ethylene homopolymer with M_N of 35,000 g/mol was used to determine an appropriate number of population groups. Discretization is performed in such a way that polymers in each population group are crystallized within the same temperature interval. Appendix Figure A1 shows that the number of population groups of 9,045 is sufficient to appropriately represent chain length distribution. For this number of population groups, polymers in each group are crystallized within the temperature interval of 0.01^{o}C. Note that this model polymer has the equilibrium dissolution temperature of 90.45^{o}C (Anantawaraskul *et al.*, 2006).

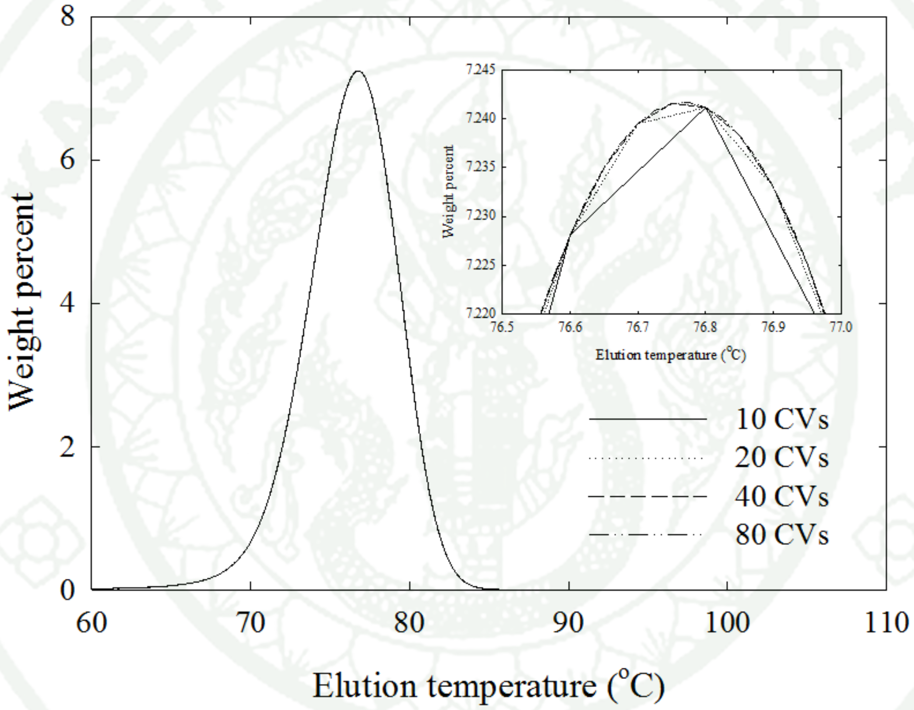


Appendix Figure A1 The chain length distributions with various numbers of population groups.

Appendix B

The number of control volumes

To determine an appropriate number of control volumes, Tref profiles of a model ethylene/1-hexene copolymer having M_N of 35,000 g/mol and 1-hexene content of 3 mol% were simulated with various numbers of control volumes at a cooling rate of 0.2°C/min, a heating rate of 0.2°C/min, and a solvent flow rate of 0.2 mL/min. Appendix Figure B1 indicates that 40 control volumes are already sufficient to simulate the Tref profile.



Appendix Figure B1 The simulated Tref profiles with various numbers of control volumes.

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