Model Development for Semicontinuous Production of Ethylene and Norbornene Copolymers Having Uniform Composition

Shaojie Liu
State Key Laboratory of Chemical Engineering (ZJU), Institute of Polymerization and Polymer Engineering,
Dept. of Chemical Engineering, Zhejiang University, Hangzhou 310027, China

Kun Cao
State Key Laboratory of Chemical Engineering (ZJU), Institute of Polymerization and Polymer Engineering,
Dept. of Chemical Engineering, Zhejiang University, Hangzhou 310027, China

State Key Laboratory of Chemical Engineering (ECUST), UNILAB Research Center of Chemical Reaction Engineering,
School of Chemical Engineering, East China University of Science and Technology, Shanghai 200237, China

Zhen Yao and Bogeng Li
State Key Laboratory of Chemical Engineering (ZJU), Institute of Polymerization and Polymer Engineering,
Dept. of Chemical Engineering, Zhejiang University, Hangzhou 310027, China

Shiping Zhu
Dept. of Chemical Engineering, McMaster University, Hamilton, ON L8S 4L7, Canada

DOI 10.1002/aic.11714

Terminal and penultimate models for controlling copolymer composition distribution (CCD) in ethylene and norbornene (NB) copolymerization were developed by taking into account the variation of active site concentration with the initial comonomer ratio. The models were validated by batch polymerization experimental data. The terminal model gave better correlation with the composition data whereas the penultimate model had a better fit to the rate data. The terminal model was then used to design NB feeding policies in semicontinuous processes for targeted CCD profiles. Based on the model results, a series of ethylene-NB copolymers with various NB contents were prepared. With the same NB content, the semicontinuous process produced a uniform composition, whereas the batch process yielded broad CCD. The batch samples had lower T_g values and broader transition ranges, even yielded crystalline materials. In contrast, the semicontinuous samples overcame the disadvantages. © 2009 American Institute of Chemical Engineers *AIChE J,* 55: 663–674, 2009

Keywords: cyclic olefin copolymer, ethylene, norbornene, copolymer composition drift, model, semicontinuous control

Introduction

Ethylene-norbornene copolymer (ENC) has excellent transparency, low moisture absorption, high heat resistance, etc. It is an important class of industrial materials with a broad

---

Correspondence concerning this article should be addressed to K. Cao at kcao@che.zju.edu.cn or S. Zhu at zhuship@mcmaster.ca.

range of applications in optical, electric, and medical fields.[1] The norbornene (NB) content is the key parameter for the properties of ENC materials. With increasing NB content, the copolymer changes from crystalline to amorphous substance while its glass transition temperature (T_g) can be adjusted in the range of 20–260°C by varying its NB content.[2–6]

The ethylene and NB copolymerization with homogeneous metallocene catalysts has been studied by many workers over the past decade.[1–33] Several groups have investigated the effects of copolymer composition on the ENC thermal properties and reported the linear T_g vs. NB content relationships.[1,4,6,16,26,27] However, T_g is not only determined by the average NB content, but also by the chain microstructure such as composition and sequence distributions. For example, random copolymers have higher T_g's than alternating stereoregular counterparts of similar NB contents.[28] Block NB sequences can improve chain stiffness and T_g.[29] The molecular dynamic simulations have been applied to calculate its T_g.[30] The molecular weight of ENC (if not very high) also plays an important role in the thermal behaviors of the materials.[31]

For the next generation optical applications, the ENC materials must have high NB content and uniformity in chain microstructure for higher T_g and better transparency. To achieve this goal, both sequence length distribution and copolymer composition distribution (CCD) must be carefully designed and controlled. The sequence distribution is mainly determined by structure and symmetry of metallocene catalyst, electronic effect and steric hindrance of ligand and relevant polymerization conditions. The most comprehensive analysis of the sequence length distribution of ENC was contributed by Tritto et al.[20–23] Another significant contribution was by Choi and coworkers[6–9] through modeling effort. Assuming no loss of the active sites, they employed classical first-order, second-order and reduced third order Markov models to describe copolymer composition and sequence distribution. Each model has advantages and weaknesses in predicting polymerization rate, average copolymer composition, and NB sequence length distribution.

There have been some investigations on the effects of CCD on the ENC's thermal properties.[8,33] The batch copolymerization experiments were often carried out in very short reaction times for reducing CCD effect. Choi and coworkers[8] found that the obtained copolymer's T_g decreased with the reaction time because less NB was incorporated into the copolymer at the late stage of reaction and then the melting peak of polyethylene began to appear in the samples. To produce the copolymer of uniform composition, the comonomer ratio should be kept constant during the polymerization. They proposed a continuous process operated at steady state for adding both ethylene and NB. These studies have opened a widow for designing more efficient copolymerization processes.

In general, there are three approaches for ENC productions: batch, semicontinuous, and continuous. This classification is based on the NB feeding strategy during copolymerization because ethylene is always continuously supplied to reactor. In the batch process, composition drift can be dramatic due to the different reactivity ratios and the resulting copolymer has a broad CCD if the reaction time is long. The uniform composition can only be achieved by semicontinuous and continuous processes. Compared with continuous process, semicontinuous process with adjustable adding rate is more flexible for the preparation of copolymers having different CCDs but similar average compositions.

Our hypothesis is that the ENC materials with uniform composition distribution prepared by semicontinuous process would have better properties than the ones having the same NB content but broader CCD by batch process. In other words, to obtain the same grade of ENC materials, the use of semicontinuous process would require less consumption of the costly NB monomer. In this work, we made a good effort to synthesize ENC samples with narrow CCD by semicontinuous process and to investigate the effects of CCD on ENC's thermal properties. Modified terminal and penultimate models for ethylene and NB copolymerization had been developed and compared. Some model parameters were estimated by correlating experimental data from the batch process and the others were from the literature. It was then extended to the semicontinuous process and was used to design NB feeding strategies for the targeted CCD profiles by systematic experimental investigation and detailed model development.

Model Development

For the model-based design and control of CCD of ENC, the challenge is to give an accurate prediction of polymerization rate and copolymer composition. In this work, we developed a terminal model and a penultimate model. The general reaction mechanisms, the mainframes of both models, and the kinetic parameters used in the stimulation were adopted from the literature.[6–9] However, we introduced a dependence function of active site concentration on NB/E ratio, to better correlate the experimental data. We found the correlation becomes poor without taking account into this dependence. The model was firstly verified by the batch process and then extended to design NB feeding profiles for uniform composition.

Terminal model

For the ethylene and NB copolymerization with metallocene catalysts, the rapid formation of active centers can be assumed. The polymerization rate and copolymer composition are determined by the following propagation reactions:

$$P_{r,1}^* + M_1 \xrightarrow{k_{p11}} P_{r+1,1}^* \tag{1}$$

$$P_{r,1}^* + M_2 \xrightarrow{k_{p12}} P_{r+1,2}^* \tag{2}$$

$$P_{r,2}^* + M_1 \xrightarrow{k_{p21}} P_{r+1,1}^* \tag{3}$$

$$P_{r,2}^* + M_2 \xrightarrow{k_{p22}} P_{r+1,2}^* \tag{4}$$

where M_1 is ethylene, M_2 is NB; $P_{r,1}^*$ and $P_{r,2}^*$ are growing polymer chains with ethylene and NB as the terminal unit, respectively. The kinetic parameters were shown in Table 1.

Applying the quasi-steady-state assumption to live polymers, we can have the following copolymer composition equation,

Table 1. Kinetic Parameters Used in the Terminal Model Stimulation

Parameter	Value	Parameter	Value
k_{p11}	1.67×10^7 L mol^{-1} h^{-1}	r_1	1.47
k_{p22}	7.80×10^4 L mol^{-1} h^{-1}	r_2	0.024
k_{p12}	1.14×10^7 L mol^{-1} h^{-1}		
k_{p21}	3.25×10^6 L mol^{-1} h^{-1}		

$$\left(\frac{M_2}{M_1}\right)_p = X\frac{(r_2X+1)}{(r_1+X)} \tag{5}$$

where $(\frac{M_2}{M_1})_p$ and $X = \frac{[M_2]}{[M_1]}$ are the NB/E mole ratios in polymer and monomer populations, respectively.

The instantaneous NB content in copolymer can be calculated,

$$F_2 = \frac{\left(\frac{M_2}{M_1}\right)_p}{1+\left(\frac{M_2}{M_1}\right)_p} \tag{6}$$

If we assumed $c^* \approx Y_1^* + Y_2^*$, the live polymer could be expressed as follows:

$$Y_1^* = \frac{kp_{21}[M_1]}{kp_{21}[M_1]+kp_{12}[M_2]}c^*, \quad Y_2^* = \frac{kp_{12}[M_2]}{kp_{21}[M_1]+kp_{12}[M_2]}c^* \tag{7}$$

where c^* is the activated catalyst; Y_1^* and Y_2^*, the total concentration of growing polymer chains with ethylene and NB as the terminal unit. The ethylene and NB consumption rates are expressed as:

$$\frac{dM_1}{dt} = -VRp_1 + F_{1,\mathrm{in}} \tag{8}$$

$$\frac{dM_2}{dt} = -VRp_2 + F_{2,\mathrm{in}} \tag{9}$$

$$\frac{dV}{dt} = F_{1,\mathrm{in}}\frac{M_{\mathrm{w}_1}}{\rho_1} + F_{2,\mathrm{in}}\frac{M_{\mathrm{w}_2}}{\rho_2} \tag{10}$$

where $F_{1,\mathrm{in}}$ and $F_{2,\mathrm{in}}$ are the molar flow-in rates of ethylene and NB; $M_{\mathrm{w}1}$ and $M_{\mathrm{w}2}$, the molecular weights of monomer ethylene and NB; ρ_1 and $\rho_{2,}$ the densities of ethylene and NB in solvent; and R_{p1} and R_{p2}, the ethylene and NB polymerization rates, respectively: $Rp_1 = (k_{p11}Y_1^* + k_{p21}Y_2^*)[M_1]$, $Rp_2 = (k_{p12}Y_1^* + k_{p22}Y_2^*)[M_2]$.

The ethylene concentration can be kept constant by maintaining the total pressure constant, i.e.,

$$\frac{d[M_1]}{dt} = 0 \tag{11}$$

For the batch process, $F_{2,\mathrm{in}} = 0$, $F_{1,\mathrm{in}}$ can be given,

$$F_{1,\mathrm{in}} = \frac{Rp_1}{1-[M_1]\frac{M_{\mathrm{w}1}}{\rho_1}}V = K_0V, \quad \left(K_0 = \frac{Rp_1}{1-[M_1]\frac{M_{\mathrm{w}1}}{\rho_1}}\right) \tag{12}$$

Then,

$$\frac{dV}{dt} = K_0\frac{M_{\mathrm{w}1}}{\rho_1}V \tag{13}$$

$$\frac{d[M_2]}{dt} = -Rp_2 - [M_2]K_0\frac{M_{\mathrm{w}1}}{\rho_1} \tag{14}$$

Given the initial conditions, Eqs. 13 and 14 can be solved numerically. The composition profile, catalyst activity, NB conversion, polymerization rate and copolymer composition can then be predicted. It should be pointed out that Eqs. 11–14 are not needed in designing the NB feeding profile for the composition control.

The molar numbers of monomer unit ethylene and NB in copolymer, m_1 and $m_{2,}$ can be obtained by numerical integration. The cumulative NB content in copolymer is,

$$\overline{F}_2 = \frac{m_2}{m_1+m_2} \tag{15}$$

Penultimate model

For a penultimate model, the polymerization rate and copolymer composition are determined by the following propagation reactions:

$$P_{r,11}^* + M_1 \xrightarrow{k_{p111}} P_{r+1,11}^* \tag{16}$$

$$P_{r,11}^* + M_2 \xrightarrow{k_{p112}} P_{r+1,12}^* \tag{17}$$

$$P_{r,22}^* + M_1 \xrightarrow{k_{p221}} P_{r+1,21}^* \tag{18}$$

$$P_{r,22}^* + M_2 \xrightarrow{k_{p222}} P_{r+1,22}^* \tag{19}$$

$$P_{r,21}^* + M_1 \xrightarrow{k_{p211}} P_{r+1,11}^* \tag{20}$$

$$P_{r,21}^* + M_2 \xrightarrow{k_{p212}} P_{r+1,12}^* \tag{21}$$

$$P_{r,12}^* + M_1 \xrightarrow{k_{p121}} P_{r+1,21}^* \tag{22}$$

$$P_{r,12}^* + M_2 \xrightarrow{k_{p122}} P_{r+1,22}^* \tag{23}$$

where $P_{r,ij}^*$ *represents the propagating polymer* $M_iM_j^*$. The subscript notation r denotes the length of chain. The kinetic parameters were shown in Table 2.

The reactivity ratios are defined as follows,

$$r_{11} = \frac{k_{p111}}{k_{p112}}, \quad r_{22} = \frac{k_{p222}}{k_{p221}}, \quad r_{21} = \frac{k_{p211}}{k_{p212}}, \quad r_{12} = \frac{k_{p122}}{k_{p121}} \tag{24}$$

Applying the quasi-steady-state assumption to live polymers, we also have the copolymer composition equation for the penultimate model.

Table 2. Kinetic Parameters Used in the Penultimate Model Stimulation

Parameter	Value	Parameter	Value
k_{p111}	1.67×10^7 L mol^{-1} h^{-1}	r_{11}	1.47
k_{p112}	1.14×10^7 L mol^{-1} h^{-1}		
k_{p121}	3.07×10^6 L mol^{-1} h^{-1}	r_{12}	1.024
k_{p122}	7.37×10^4 L mol^{-1} h^{-1}		
k_{p211}	1.63×10^7 L mol^{-1} h^{-1}	r_{21}	0.887
k_{p212}	1.84×10^7 L mol^{-1} h^{-1}		
k_{p221}	1.78×10^5 L mol^{-1} h^{-1}	r_{22}	9.0×10^{-4}
k_{p222}	1.56×10^2 L mol^{-1} h^{-1}		

$$\left(\frac{M_2}{M_1}\right)_p = \frac{1 + \frac{r_{12}X(r_{22}X+1)}{(r_{12}X+1)}}{1 + \frac{r_{21}(r_{11}+X)}{X(r_{21}+X)}} \tag{25}$$

If we assumed $c^* \approx Y^*_{11} + Y^*_{12} + Y^*_{21} + Y^*_{22}$, the live polymer concentrations could be expressed as follows,

$$Y^*_{11} = ac^* \tag{26}$$

$$Y^*_{21} = aX\frac{k_{p112}}{k_{p211}}c^* \tag{27}$$

$$Y^*_{12} = aX\frac{k_{p112}}{k_{p121}}\frac{1+\frac{X}{r_{21}}}{1+r_{12}X}c^* \tag{28}$$

$$Y^*_{22} = ar_{12}X^2\frac{k_{p112}}{k_{p221}}\frac{1+\frac{X}{r_{21}}}{1+r_{12}X}c^* \tag{29}$$

where $a = (1 + \frac{k_{p112}}{k_{p211}}X + X\frac{k_{p112}}{k_{p121}}\frac{1+\frac{X}{r_{21}}}{1+r_{12}X} + r_{12}X^2\frac{k_{p112}}{k_{p221}}\frac{1+\frac{X}{r_{21}}}{1+r_{12}X})^{-1}$, ${Y_{ij}}^*$ is the total concentration of $M_iM_j^*$.

The ethylene and NB polymerization rates are,

$$Rp_1 = (k_{p111}Y^*_{11} + k_{p211}Y^*_{21} + k_{p121}Y^*_{12} + k_{p221}Y^*_{22})[M_1] \tag{30a}$$

$$Rp_2 = (k_{p112}Y^*_{11} + k_{p212}Y^*_{21} + k_{p122}Y^*_{12} + k_{p222}Y^*_{22})[M_2] \tag{30b}$$

Design NB feeding profile

Our objective is to control composition drift through semicontinuous operation. The strategy used in this work is to design NB feeding profile. For the copolymers with uniform composition, we can apply the following constraint: F_2 = constant. i.e., keeping the NB/E constant in the reactor.

With $\frac{d[M_1]}{dt} = 0$, i.e. to keep the NB/E constant, it is necessary to have $\frac{d[M_2]}{dt} = 0$. With these two conditions, the monomer feeding profile for the targeted uniform copolymer composition can be obtained.

$$F_{1,\text{in}} = \frac{VRp_1(1 - \frac{M_{\text{w2}}}{\rho_2}[M_2]) + VRp_2\frac{M_{\text{w2}}}{\rho_2}[M_1]}{(1 - \frac{M_{\text{w1}}}{\rho_1}[M_1])(1 - \frac{M_{\text{w2}}}{\rho_2}[M_2]) - \frac{M_{\text{w1}}M_{\text{w2}}}{\rho_1\rho_2}[M_1][M_2]} \tag{31}$$

$$F_{2,\text{in}} = \frac{VRp_2(1 - \frac{M_{\text{w1}}}{\rho_1}[M_1]) + VRp_1\frac{M_{\text{w1}}}{\rho_1}[M_2]}{(1 - \frac{M_{\text{w1}}}{\rho_1}[M_1])(1 - \frac{M_{\text{w2}}}{\rho_2}[M_2]) - \frac{M_{\text{w1}}M_{\text{w2}}}{\rho_1\rho_2}[M_1][M_2]} \tag{32}$$

$$V = V_0\exp\left(K_1\frac{M_{\text{w1}}}{\rho_1}t + K_2\frac{M_{\text{w2}}}{\rho_2}t\right) \tag{33}$$

where V_0 is the initial volume of reaction mixture; t is the reaction time.

Experimental Section

Materials

Ethylene with 99.95% purity, supplied by Foshan Kedi Gas Chemical Industry Co., Ltd. of Guangdong Province in China, was dried by passing through columns filled with 3 Å molecular sieve and Cu catalyst. NB with 99% purity was purchased from ACROS and dried over CaH_2 and distilled for 6 h before use. Toluene was distilled for 6 h with a sodium/potassium alloy under dry nitrogen atmosphere prior to use. The metallocene catalyst was *rac*-$[Et(Ind)_2]ZrCl_2$ from ACROS. The cocatalyst was MAO (10 wt % in toluene, AKZO NOBEL).

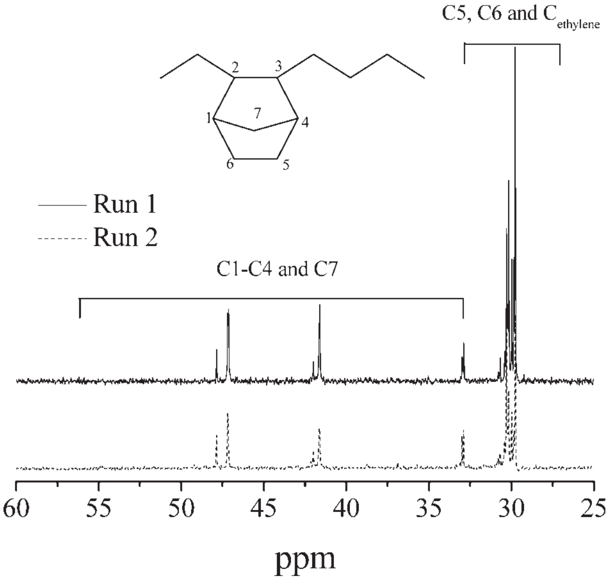

Figure 1. **^{13}C NMR spectra of typical ENC samples produced by batch and semicontinuous processes in this work (18–21 mol % NB).**

Polymerization

The polymerization procedures were similar to that reported in the previous work except for the addition of NB.[34] Ethylene consumption was measured with a flowmeter. Before the addition of cocatalyst and catalyst, certain amounts of NB determined by the initial NB/E, were added to the reactor. The additional NB was then added according to the designed feeding policy by a peristaltic pump controlled by computer. The NB federate profiles in Figure 11 calculated by the model were followed in the polymerization processes. The initial reactor volumes were the sum of added toluene (50 ml), MAO (1.8 ml) and initial added NB volume (varied with the initial NB/E ratio). We injected NB solution (20 vol % toluene and 80 vol % NB). The largest volume of the injected NB solution was <5.5 ml. The largest volume change was thus <10%. The NB feed rates in Figure 11 are the actual amount of neat NB fed to the reactor, not including the 20 vol % toluene in the values. The toluene amount fed was small (about 1 ml) and its effect on the reaction system can be neglected.

Characterization and measurements

The thermal behaviors of the produced ENC materials were investigated by a differential scanning calorimeter, Perkin-Elmer DSC 7. In each experiment, 9–10 mg of sample was used and the DSC was run under dry nitrogen. All the samples were first heated from 30 to 200°C at a rate of 10°C/min, held at 200°C for 3 min, cooled to 30°C at 10°C/

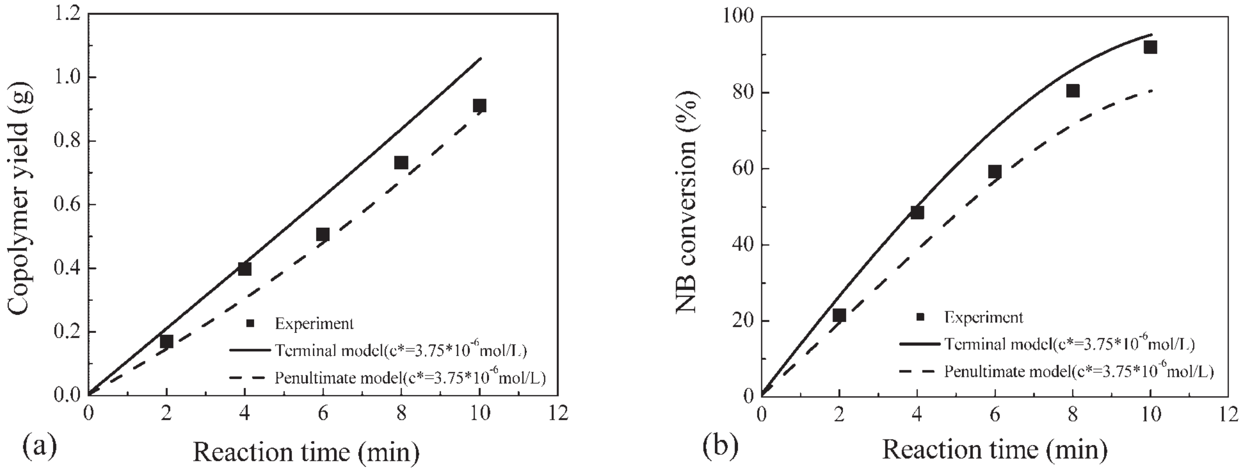

Figure 2. Copolymer yield/NB conversion vs. reaction time in the batch process for initial NB/E = 1.3 (c^* = constant).

(a) Copolymer yield vs. reaction time; (b) NB conversion vs. reaction time. Conditions: catalyst concentration = 4 × 10^{-5} mol/l, Al/Zr = 1500, toluene = 50 ml, P = 1 atm, T = 70°C, initial NB/E = 1.3, total reaction time = 10 min.

min, and held at 30°C for 3 min. The samples were then scanned from 30 to 200°C at a rate of 10°C/min. The second heat curve was used for analysis.

Varian Unity-400 nuclear magnetic resonance (NMR) instrument was used to estimate the NB content of ENC. The ^{13}C NMR spectra of the typical ENC samples produced in this work were shown in Figure 1. The method of Ruchatz and Fink was adopted for the chemical shift assignments and copolymer composition estimates:[3]

$$\text{mol \%Norbornene} = \frac{\frac{1}{5} I_{\mathrm{N(C1-C4,C7)}}}{\frac{1}{2}\left(I_{\mathrm{E,N(C5,C6)}} - \frac{2}{5} I_{\mathrm{N(C1-C4,C7)}}\right) + \frac{1}{5} I_{\mathrm{N(C1-C4,C7)}}} \times 100$$

where $I_{\mathrm{N(C1-C4,C7)}}$ = the integral of the C1–C4 and C7 signals of NB (33–56 ppm) and $I_{\mathrm{E,N(C5,C6)}}$ = the integral of the signals of ethylene and the C5 and C6 of NB (27–32.7 ppm).

The molecular weight and molecular weight distribution were measured at 150°C in 1,2,4-trichlorobenzene using a Waters GPCV 2000 with a combined refractive index and viscosity detector.[35]

Results and Discussion

Batch process

Firstly, we assume an independence of the active site concentration (c^*) on the NB/E ratio. The model results of the copolymer yield and NB conversion vs. reaction time using

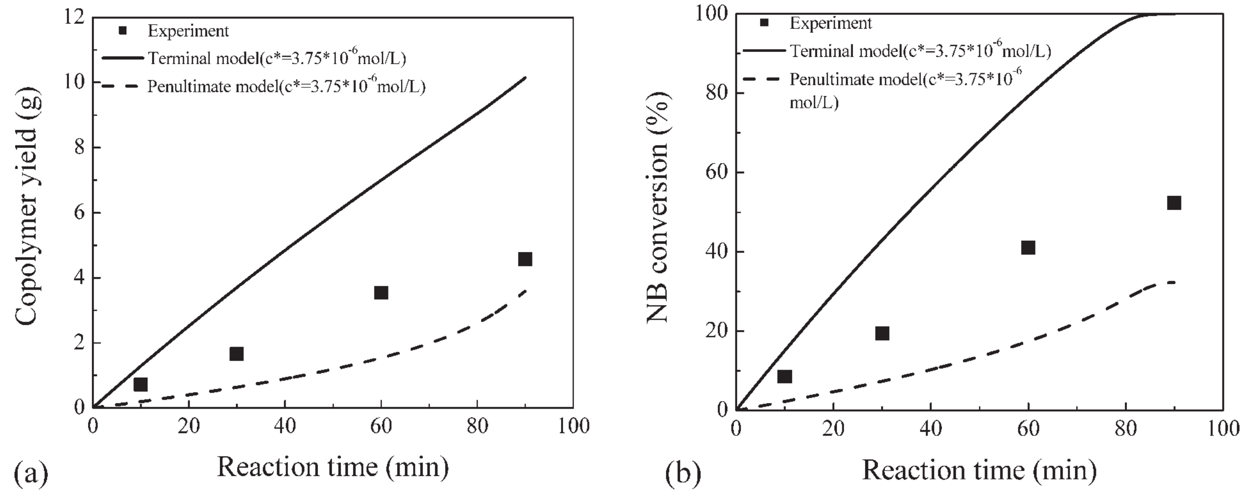

Figure 3. Copolymer yield/NB conversion vs. reaction time in the batch process for initial NB/E = 19.6 (c^*=constant).

(a) Copolymer yield vs. reaction time; (b) NB conversion vs. reaction time. Conditions: catalyst concentration = 4 × 10^{-5} mol/l, Al/Zr = 1500, toluene = 50 ml, P = 1 atm, T = 70°C, initial NB/E = 19.6, total reaction time = 90 min.

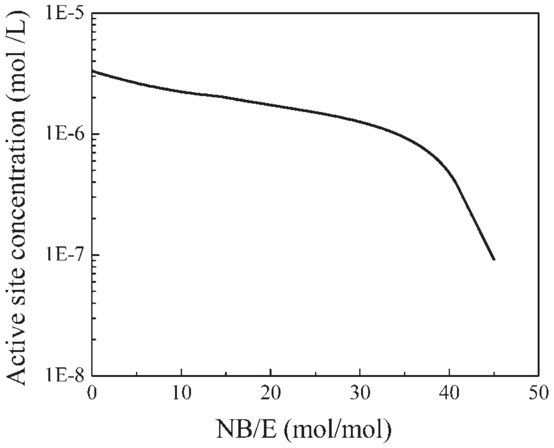

Figure 4. Active site concentration vs. initial NB/E in the batch processes.

Conditions: catalyst concentration = 4 × 10^{-5} mol/l, Al/Zr = 1500, toluene = 50 ml, P = 1 atm, T = 70°C.

this assumption are shown in Figures 2 and 3. Large discrepancies can be seen between the model calculation and experimental data, particularly at high NB/E values. The models can underestimate or overestimate the yield and conversion values, depending on the active site concentration used in the calculation. However, their trends cannot be caught if the active site concentration remains unchanged. With the same set of parameters, the penultimate model underestimates whereas the terminal model overestimates their values.

We then assume the active site concentration is not only a function of the catalyst concentration but also affected by the initial monomer ratio. This concept may be explained by the effect of NB concentration on the efficiency of catalyst activation. That is, $c^* = f([c]_0, [\mathrm{MAO}]_0/[c]_0, [M_2]_0/[M_1]_0)$. Based on this concept, we develop a relationship between c^* and the initial NB/E ratio as described by the following equations (also shown in Figure 4).

$$c^* = \frac{2.0365\times10^{-6}}{2.1353}(3.5016 - 0.1778X + 0.007570X^2 - 1.1926\times10^{-4}X^3), \quad X \le 15 \quad (34)$$

$$c^* = \frac{2.0365\times10^{-6}}{1.0996}(1.9704 - 0.09221X + 0.002972X^2 - 4.1568\times10^{-5}X^3), \quad 15 < X < 45 \quad (35)$$

This relationship is evaluated by correlating experimental copolymer yields and compositions with the terminal model. It has been reported that the terminal model gave better composition prediction than the penultimate model.[6–9] The major objective of this work is to control the composition drift. Therefore, we chose the terminal model in Eq. 36 for finding the dependence function. The experimental data were from the literature.[34] A nonlinear least-square criterion is used. The object function is as follows

$$F = w_1\sum\left(\frac{\mathrm{Act}_{\mathrm{exp}} - \mathrm{Act}_{\mathrm{cal}}}{\mathrm{Act}_{\mathrm{exp}}}\right)^2 + w_2\sum\left(\frac{\overline{F}_{2\mathrm{exp}} - \overline{F}_{2\mathrm{cal}}}{\overline{F}_{2\mathrm{exp}}}\right)^2 \quad (36)$$

where w_i is the weighting factor of each term in the function. Act is the catalyst activity and $\overline{F}_2$ is the cumulative NB composition in copolymer.

Using the developed relationship between c^* and NB/E ratio in Figure 4, the copolymer yield and NB conversion could be readily predicted by the terminal model, shown in Figures 5 and 6. The penultimate model appears to give slightly better prediction if the k_{222} value is increased by 20 times with the reactivity ratios remaining unchanged. It should be pointed out that k_{222} is treated as an adjustable

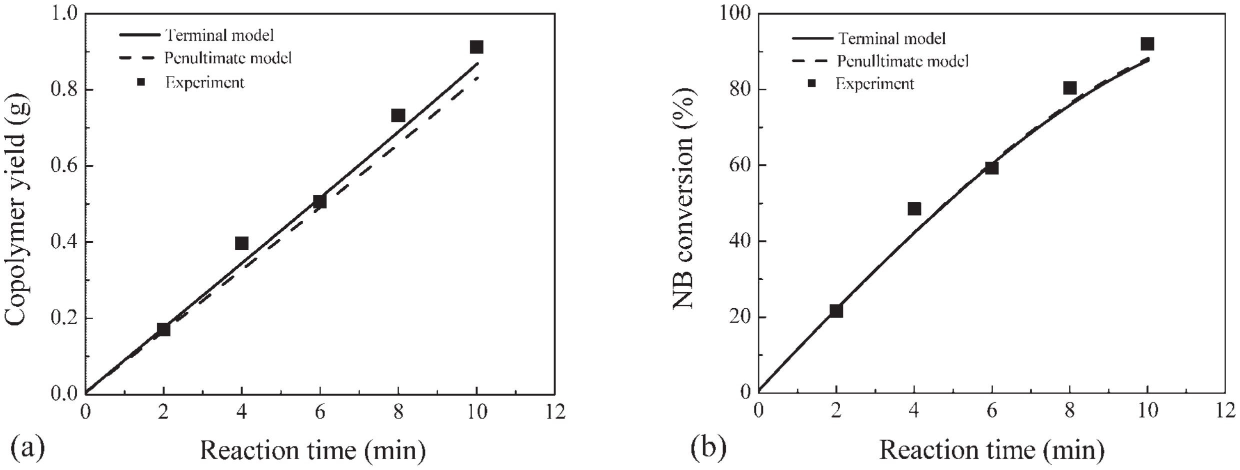

Figure 5. Copolymer yield/NB conversion vs. reaction time in the batch process for initial NB/E = 1.3 (For the model calculation, c^* varies with the initial NB/E according to Figure 4).

(a) Copolymer yield vs. reaction time; (b) NB conversion vs. reaction time. Conditions: catalyst concentration = 4 × 10^{-5} mol/l, Al/Zr = 1500, toluene = 50 ml, P = 1 atm, T = 70°C, initial NB/E = 1.3, total reaction time = 10 min.

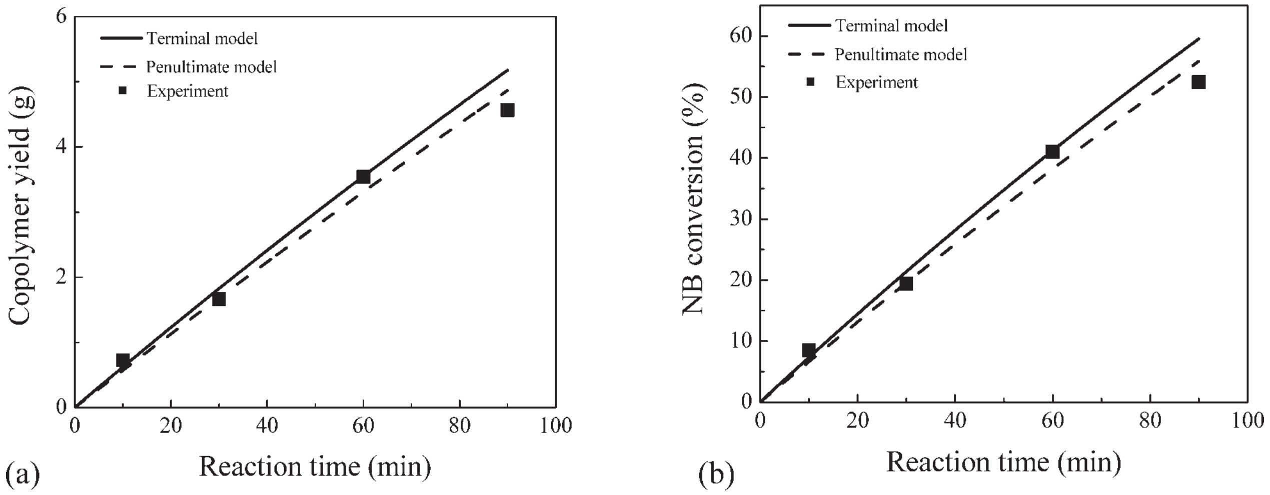

Figure 6. Copolymer yield/NB conversion vs. reaction time in the batch process for initial NB/E = 19.6 (For the model calculation, c^* varies with the initial NB/E according to Figure 4).

(a) Copolymer yield vs. reaction time; (b) NB conversion vs. reaction time. Conditions: catalyst concentration = 4 × 10^{-5} mol/l, Al/Zr = 1500, toluene = 50 ml, P = 1 atm, T = 70°C, initial NB/E = 19.6, total reaction time = 90 min.

parameter here. We can also keep the literature value k_{222} but adjust the NB/E ratio dependence function of active site concentration for the purpose of data correlation. The catalyst activity, polymerization rate and copolymer composition are also calculated using the modified terminal model and penultimate model.

Figure 7 shows the predicted and experimental catalyst activity for the batch process with various initial monomer ratios (NB/E). The model prediction agrees well with the experimental data. In general, the penultimate model gives slightly better result. The activity decreases with increasing NB/E, especially at high NB/E.

In addition, the polymerization rates of ethylene and NB are also well predicted (Figures 8 and 9). Figure 8 shows similar fits for both models. For the NB reaction rate (Figure 9), the penultimate model is also better than the terminal model. The experimental ethylene and NB polymerization rates are the 10 min averages of the initial stage of polymerization. The ethylene polymerization rate decreases with the increase of NB/E. There is a maximum in the NB polymerization rate. Similar results have been reported by Fink and coworker[2] and Choi and coworkers.[6] The main difference is the NB/E range that the max NB rate occur. This NB/E mole ratio is about 4 in our work, and the result of Fink is about

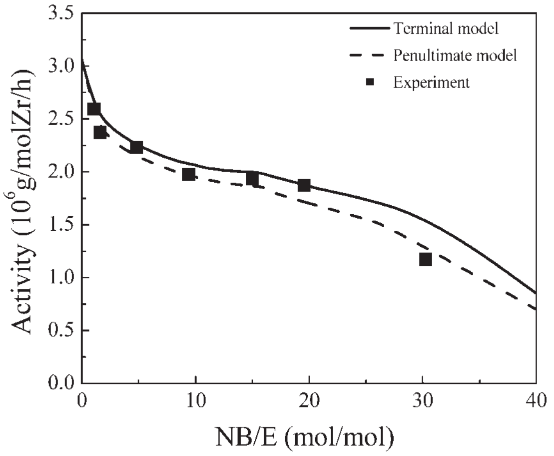

Figure 7. Catalyst activity vs. initial NB/E in the batch process (For the model calculation, c^* varies with the initial NB/E according to Figure 4).

Conditions: catalyst concentration = 4 × 10^{-5} mol/l, Al/Zr = 1500, toluene = 50 ml, P = 1 atm, T = 70°C, reaction time = 10 min.

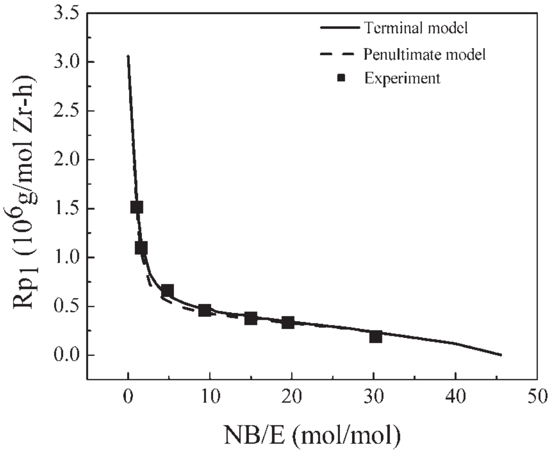

Figure 8. R_{p1} vs. initial NB/E in the batch process (For the model calculation, c^* varies with the initial NB/E according to Figure 4).

Conditions: catalyst concentration = 4 × 10^{-5} mol/l, Al/Zr = 1500, toluene = 50 ml, P = 1 atm, T = 70°C, reaction time = 10 min.

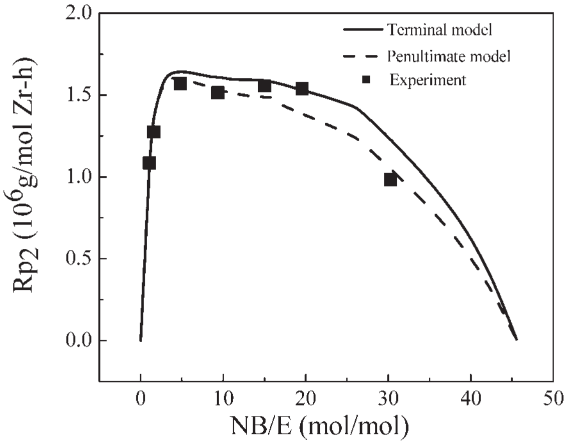

Figure 9. R_{p2} vs. initial NB/E in the batch process (For the model calculation, c^* varies with he initial NB/E according to Figure 4).

Conditions: catalyst concentration = 4×10^{-5} mol/l, Al/Zr = 1500, toluene = 50 ml, P = 1 atm, T = 70°C, reaction time = 10 min.

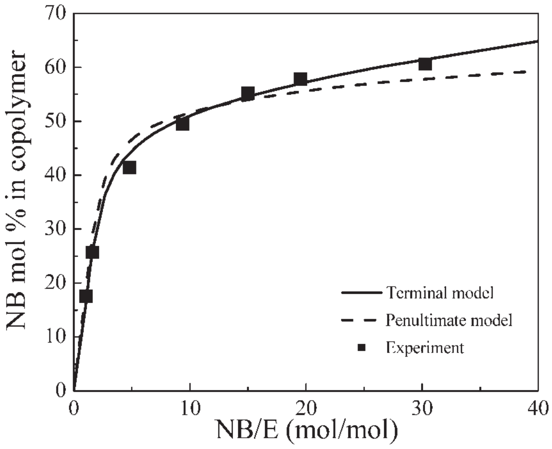

Figure 10. NB mol % in copolymer vs. initial NB/E in the batch process (For the model calculation, c^* varies with the initial NB/E according to Figure 4).

Conditions: catalyst concentration = 4×10^{-5} mol/l, Al/Zr = 1500, toluene = 50 ml, P = 1 atm, T = 70°C, reaction time = 10 min.

0.8–1. This may be due to the difference of the used catalysts and reaction conditions.

Figure 10 shows the predicted and experimental NB mol % in copolymer vs. initial NB/E in batch process. The terminal model gives better prediction of the copolymer composition than the penultimate model. NB mol % in copolymer increases significantly with increasing NB/E when NB/E is <10. However, with further increase in NB/E, the NB content increases slowly since longer NB blocks are difficult to form due to large steric hindrance.

Based on the results shown above, it is reasonable to conclude that the terminal model gives better prediction for the copolymer composition than the penultimate model, although the latter gives a slightly better prediction of the polymerization rates. Furthermore, the terminal model is also much simpler. Therefore, we select the terminal model to design NB feeding policies for the targeted CCD profiles in this work.

Control CCD using semicontinuous NB feeding policy

In the batch process of ethylene and NB copolymerization, composition drift can be dramatic and resulting copolymer has a broad CCD. A broad CCD may lead to a reduction in heat resistance of the ENC materials. In this section, we try to control the composition drift through a designed NB feeding rate. The effects of CCD on thermal properties of ENC are also investigated.

ENCs with five different targeted NB contents are prepared about 20, 35, 45, 55, and 60 mol %. The designed NB feeding profiles are shown in Figure 11. All runs using the different NB feeding policies in this work are summarized in Table 3. For the NB content in copolymer, the good agreement between model calculation and NMR data is evident (Table 3, Figures 12–16). The polydispersity (PDI) values in Table 3 are the experimental data. In theory we assumed a single active site. A possible reason for the high PDI's in the batch processes is the cumulative population of chains generated at different times having different molecular weights (Table 4).

Figure 12 shows the calculated NB mol % vs. time and the DSC curves for the samples with 20% NB content prepared by batch and semicontinuous processes. It is found that the copolymers with uniform CCD prepared by the semicontinuous process are amorphous. However, the samples with broad CCD from the batch process are crystalline. Their average NB contents are very similar. On the other hand, the crystallinity could not be attributed to the molecular weight effect. Since the molecular weight of Run 2 sample is even larger than that of Run 1. The only reason for the crystallinity is that some ENC chains in Run 2 sample have <18.3% NB. Although Run 1 sample contains only 18.3% NB, it is amorphous because of its uniform CCD.

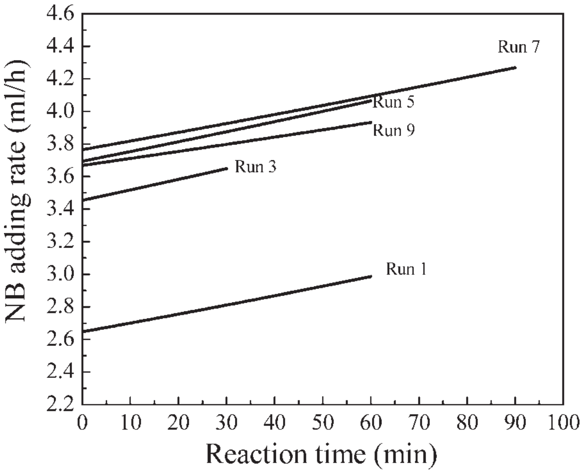

Figure 11. Designed NB feeding profiles for preparing copolymers with uniform composition.

Table 3. Copolymerization of Ethylene with Norbornene Using Different Norbornene Feeding Policies

Run	NB/E (at $t = 0$)	Polymerization Process	Reaction Time	NB mol % in Copolymer		M_n	PDI
				Model	Experiment		
1	0.6	Semicontinuous	60	20.8	18.3	8600	2.02
2	1.5	Batch	10	21.5	20.4	9200	3.43
3	1.7	Semicontinuous	30	35.7	34.7	30700	1.57
4	4.8	Batch	30	35.7	34.1	28800	2.38
5	4.1	Semicontinuous	60	44.8	44.1	40300	1.84
6	9.4	Batch	60	44.8	43.6	41200	2.21
7	12.3	Semicontinuous	90	53.4	52.8	70400	1.64
8	19.6	Batch	90	54.0	53.3	74100	3.11
9	25.8	Semicontinuous	60	60.5	59.1	105100	2.37
10	30.3	Batch	60	60.5	59.8	99200	3.01

Other conditions: catalyst concentration = 4×10^{-5} mol/l, Al/Zr = 1500, toluene = 50 ml, P = 1 atm, T = 70°C.

Figure 13 shows the comparison for the samples with 35% NB content prepared through batch and semicontinuous processes. The two samples have similar upper limits of T_g. However, Run 4 sample has broader CCD than Run 3 sample. The portion with lower NB content would lower T_g and lead to the broader T_g range. As a result, the average T_g of Run 4 sample is 10°C lower than that of Run 3. The similar T_g reduction can be found in the samples with 45% NB content (Runs 5 and 6), as shown in Figure 14.

Figure 15 shows the calculated time evolution of copolymer content and the corresponding DSC curves for the samples with 53% NB content prepared by batch and semicontinuous processes. These samples have similar NB contents (52.8–53.3%). The major difference is their CCD. It can be seen that the sample with uniform composition by semicontinuous process (Run 7) has only one T_g and the range of T_g is very narrow. When the CCD becomes broader (Run 8), the range of T_g becomes broader and a crystallization peak appears in the DSC cooling curve. The appearance of crystallization is very interesting, considering the high NB content in Run 8 sample (53.3%). The copolymer composition drift significantly in the batch process operated for a long time.

Figure 16 shows the calculated time evolution of copolymer content and the corresponding DSC curves for the samples with 60.5% NB content prepared by batch and semicontinuous processes. The T_g range of the sample with broad CCD is slightly broader than the sample with uniform composition. Its T_g is slightly lower than the uniform counterpart. The broad CCD does not significantly reduce the ENC thermal properties as in the other NB content samples. The reasons are two-fold: First, the CCD is not very broad, only from 61.8 to 59.1%; Second, in this case, the NB content is so high that all the individual chains from the batch process contain adequately high NB content and thus the variation of the average NB content would have no much influence on the copolymer's T_g.

Conclusions

In the batch process of ethylene and NB copolymerization, the composition drift can be significant due to their different reactivity ratios and the resulting copolymer has a broad CCD. The broad CCD would reduce thermal and other properties of the ENC materials. In this work, we developed a

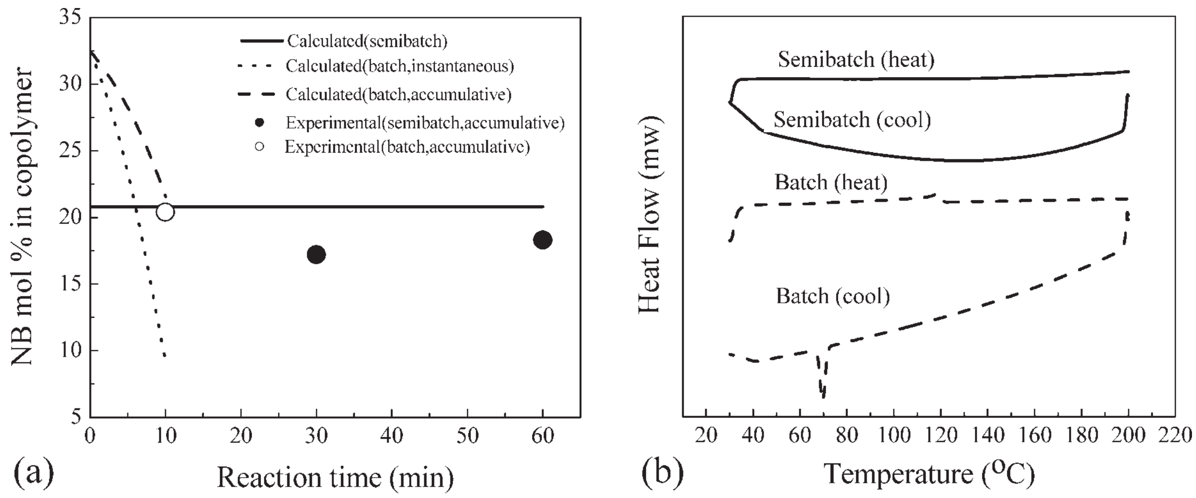

Figure 12. Terminal model simulation and experimental data for Runs 1 and 2.

(a) Composition drift; (b) DSC curves. Run 1: semicontinuous process, initial NB/E = 0.6; Run 2: batch process, initial NB/E = 1.5. Other conditions: catalyst concentration = 4×10^{-5} mol/l, Al/Zr = 1500, toluene = 50 ml, P = 1 atm, T = 70°C.

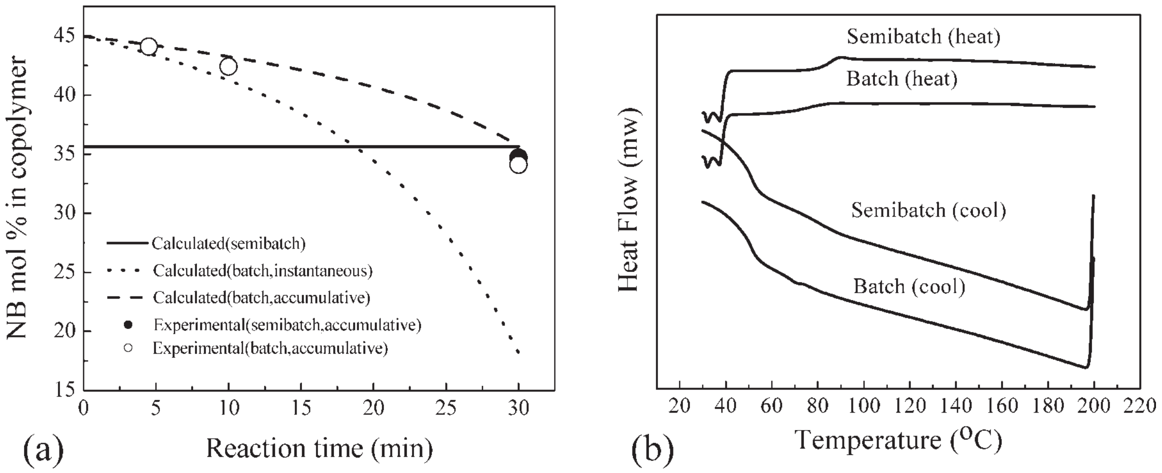

Figure 13. Terminal model simulation and experimental data for Runs 3 and 4.

(a) Composition drift; (b) DSC curves. Run 3: semicontinuous process, initial NB/E = 1.7; Run 4: batch process, initial NB/E = 4.8.

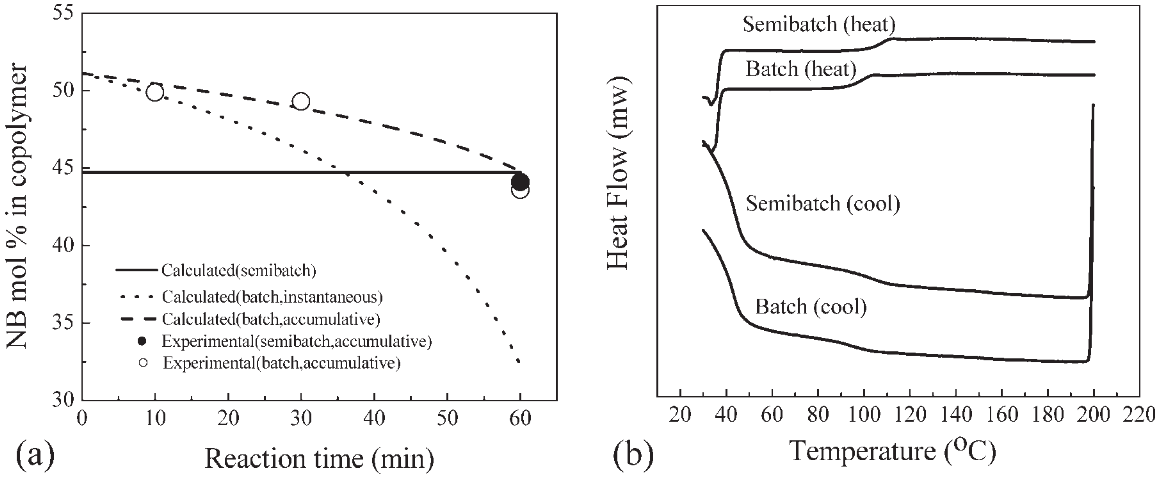

Figure 14. Terminal model simulation and experimental data for Runs 5 and 6.

(a) Composition drift; (b) DSC curves. Run 5: semicontinuous process, initial NB/E = 4.1; Run 6: batch process, initial NB/E = 9.4.

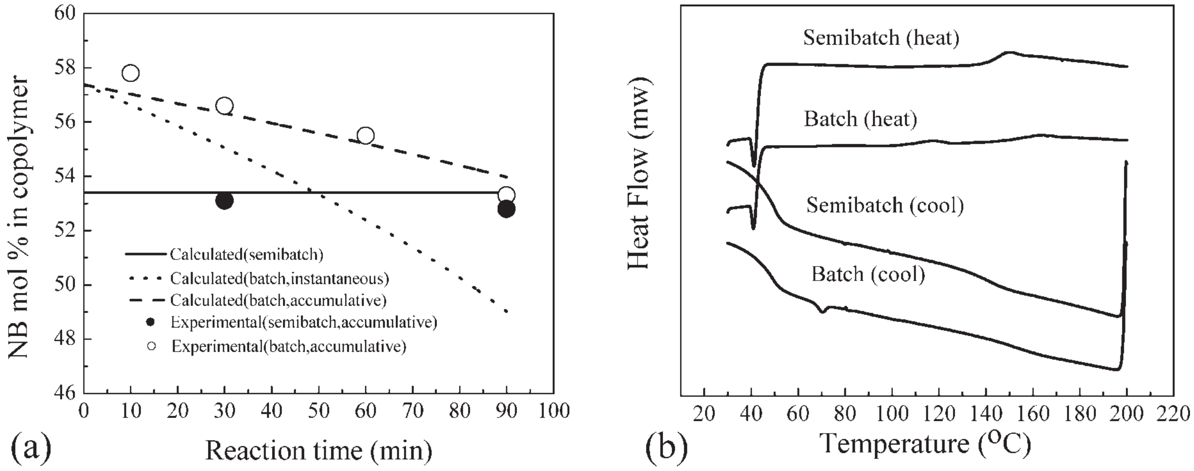

Figure 15. Terminal model simulation and experimental data for Runs 7 and 8.

(a) Composition drift; (b) DSC curves. Run 7: semicontinuous process, initial NB/E = 12.3; Run 8: batch process, initial NB/E = 19.6.

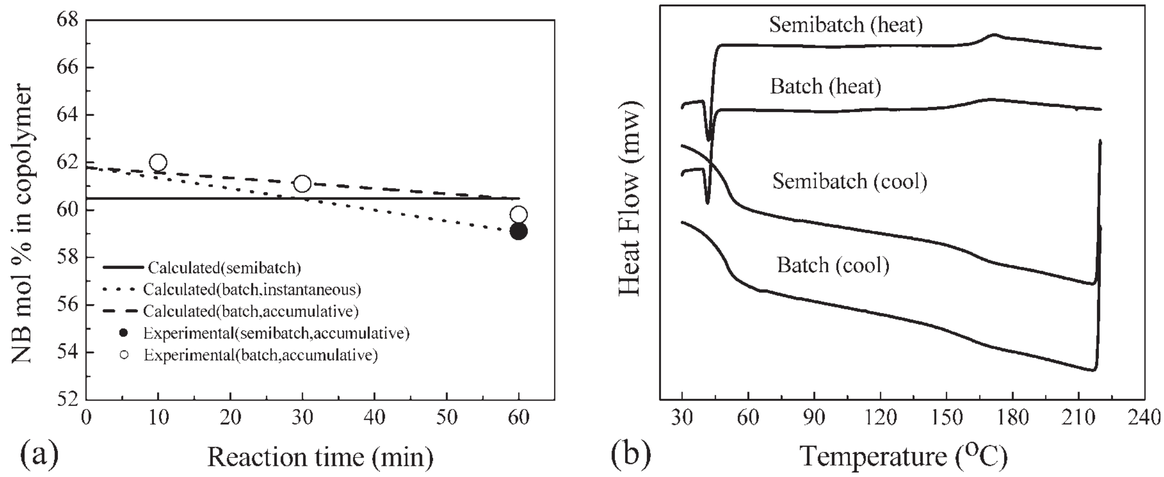

Figure 16. Terminal model simulation and experimental data for Runs 9 and 10.

(a) Composition drift; (b) DSC curves. Run 9: semicontinuous process, initial NB/E = 25.8; Run 10: batch process, initial NB/E = 30.3.

mathematical model for the purpose of controlling CCD. The model was first verified with the batch experimental data. The model predictions of the batch polymerization and the copolymer properties are in good agreement with the experimental results. The model was then extended to the semicontinuous process and was used to design NB feeding policies for the control of CCD.

The effects of CCD on thermal properties of the resulting ENC materials were investigated. The 20% NB content copolymers prepared by the batch process contained chains of lower than 18% NB and thus became crystalline materials. In contrast, the samples prepared by the semicontinuous process were amorphous due to their uniform CCD's. For the 35 and 45% NB content copolymers, the T_g values of the broad CCD samples were 10°C lower than the uniform samples. The broad CCD samples of 55% NB gave both T_g and T_m whereas the uniform copolymers of the same NB content had only one T_g and a narrower range of glass transition. Although the broad CCD did not reduce the ENC thermal properties significantly when the NB content in copolymer was 60%, the sample still had a slightly lower T_g and a broader range of glass transition. The CCD showed a significant effect on the glass transition properties of ENCs. The model-based design and control of CCD through semicontinuous process provides a powerful tool for producing new high-quality ENC materials, and cost-saving in renovating existing grades.

Table 4. Thermal Properties of ENC Prepared by Different NB Feeding Policies Obtained from DSC

Run	NB Content (mol %)	T_g (°C)	ΔT_g (°C)	T_m (°C)
1	18.3	–	–	–
2	20.4	–	–	119
3	34.7	85	17	–
4	34.1	75	34	–
5	44.1	107	17	–
6	43.6	98	24	–
7	52.8	145	16	–
8	53.3	158	20	118
9	59.1	165	15	–
10	59.8	162	20	–

Acknowledgments

This work was supported by the National Natural Science Foundation of China (No. 20576115) and the Key Project of Chinese Ministry of Education (No.104095). S.Z. thanks the Chinese Ministry of Education's Changjiang Scholarship for supporting his visit to Zhejiang University.

Literature Cited

1. Young MJ, Chang WS, Ma CC. Polymerization kinetics and modeling of a metallocene cyclic olefin copolymer system. *Eur Polym J*. 2003;39:165–171.
2. Ruchatz D, Fink G. Ethene-norbornene copolymerization using homogenous metallocene and half-sandwich catalysts: kinetics and relationships between catalyst structure and polymer structure. *Macromolecules*. 1998;31:4669–4673.
3. Ruchatz D, Fink G. Ethene-norbornene copolymerization using homogenous metallocene and half-sandwich catalysts: kinetics and relationships between catalyst structure and polymer structure. *Macromolecules*. 1998;31:4674–4680.
4. Ruchatz D, Fink G. Ethene-norbornene copolymerization using homogenous metallocene and half-sandwich catalysts: kinetics and relationships between catalyst structure and polymer structure. *Macromolecules*. 1998;31:4681–4683.
5. Ruchatz D, Fink G. Ethene-norbornene copolymerization using homogenous metallocene and half-sandwich catalysts: kinetics and relationships between catalyst structure and polymer structure. *Macromolecules*. 1998;31:4684–4686.
6. Park SY, Choi KY, Song KH, Jeong BG. Kinetic modeling of ethylene-norbornene copolymerization using homogeneous metallocene catalysts. *Macromolecules*. 2003;36:4216–4225.
7. Park SY, Choi KY. Modeling of ethylene-norbornene copolymer microstructure in solution polymerization with homogeneous metallocene catalysts. *Macromol Mater Eng*. 2005;290:353–362.
8. Park SY, Choi KY, Jeong BG. Modeling and analysis of ethylene/norbornene copolymerization with *ansa*-zirconocene/methylaluminoxane catalysts in a continuous polymerization reactor. *Ind Eng Chem Res*. 2005;44:6496–6503.
9. Park SY, Lee J, Choi KY. A reduced third order Markov model for ethylene-norbornene copolymerization kinetics with homogeneous metallocene catalysts. *Macromol React Eng*. 2007;1:68–77.
10. Bergström CH, Vänäänen TL, Seppälä JV. Influence of polymerization conditions on microstructure of norbornene-ethylene copolymers

made using metallocene catalysts and MAO. *J Appl Polym Sci*. 1997;63:1071–1076.

11. Kaminsky W, Noll A. Copolymerization of norbornene and ethene with homogenous zirconocenes/methylaluminoxane catalyst. *Polym Bull*. 1993;31:175–182.
12. Kaminsky W. Isotactic polymerization of olefins with metallocene MAO catalysts. *Polymer*. 1997;42:587–590.
13. Kaminsky W, Beulich I, Arndt RM. Copolymerization of ethane with cyclic and other sterically hindered olefins. *Macromol Symp*. 2001;173:211–226.
14. Kaminsky W, Tran P, Werner R. New polymers by copolymerzation of ethylene and norbornene with metallocene catalysts. *Macromol Symp*. 2004;213:101–108.
15. Donner M, Fernandes M, Kaminsky W. Synthesis of copolymers with sterically hindered and polar monomers. *Macromol Symp*. 2006;236:193–202.
16. Tran PD, Kaminsky W. Ethene/norbornene copolymerization by [Me$_2$Si(3-^{tert}BuCp)(N^{tert}Bu)]TiCl$_2$/MAO-catalyst. *J Zhejiang Univ Sci*. 2003;4:121–130.
17. Wendt RA, Mynott R, Hauschild K, Ruchatz D, Fink G. ^{13}C NMR studies of ethene-norbornene copolymers: assignment of sequence distributions using ^{13}C-enriched monomers and determination of the copolymerization parameters. *Macromol Chem Phys*. 1999;200: 1340–1350.
18. Wendt RA, Mynott R, Fink G. Ethene/norbornene copolymerization using the Catalyst system Pr^i[(3-Pr^i-Cp)Flu]ZrCl$_2$: determination of the copolymerization parameters and mechanistic considerations. *Macromol Chem Phys*. 2002;203:2531–2539.
19. Wendt RA, Angermund K, Jensen V, Thiel W, Fink G. Ethene copolymerization with trialkylsilyl protected polar norbornene derivates. *Macromol Chem Phys*. 2004;205:308–318.
20. Tritto I, Marestin C, Boggioni L, Sacchi MC, Brintzinger HH, Ferro DR. Stereoregular and stereoirregular alternating ethylene-norbornene copolymers. *Macromolecules*. 2001;34:5770–5777.
21. Tritto I, Boggioni L, Ferro DR. Alternating isotactic ethylene-norbornene copolymers by C_1-symmetric metallocenes: determination of the copolymerization parameters and mechanistic considerations on the basis of pentad analysis. *Macromolecules*. 2004;37:9681–9693.
22. Tritto I, Boggioni L, Zampa C, Ferro DR. Ethylene-norbornene copolymers by C-s-symmetric metallocenes: determination of the copolymerization parameters and mechanistic considerations on the basis of tetrad analysis. *Macromolecules*. 2005;38:9910–9919.
23. Tritto I, Boggioni L, Ferro DR. Metallocene catalyzed ethene- and propene co-norbornene polymerization: mechanisms from a detailed microstructural analysis. *Coord Chem Rev*. 2006;250:212–241.
24. Nomura K, Wang W, Fujiki M, Liu JY. Notable norbornene (NBE) incorporation in ethylene-NBE copolymerization catalysed by nonbridged half-titanocenes: better correlation between NBE incorporation and coordination energy. *Chem Commun*. 2006;25: 2659–2661.
25. Benavente R, Scrivani T, Cerrada ML, Zamfirova G, Perez E, Perena JM. Glass-transition temperature determination by microhardness in norbornene-ethylene copolymers. *J Appl Polym Sci*. 2003;89: 3666–3671.
26. Huang WJ, Chang FC, Chu PJ. Copolymerization of norbornene with ethylene: a high-resolution liquid NMR,DSC and solid state NMR study. *J Polym Res*. 2000;7:51–56.
27. Rische T, Waddon AJ, Dickinson LC, MacKnight WJ. Microstructure and morphology of cycloolefin copolymers. *Macromolecules*. 1998;31:1871–1874.
28. Harrington BA, Crowther DJ. Stereoregular, alternating ethylene-norbornene coolymers from monocyclopentadienyl catalysts activated with non-coordinating discrete anions. *J Mol Catal A: Chem*. 1998;128:79–84.
29. Forsyth J, Perena JM, Benavente R, Perez E, Tritto I, Boggioni L, Brinzinger H. Influence of the polymer microstructure on the thermal properties of cycloolefin copolymers with high norbornene contents. *Macromol Chem Phys*. 2001;202:614–620.
30. Katajisto J, Linnolahti M, Pakkanen TA. Properties of modified cyclo-olefin copolymers predicted by ab initio and molecular simulation techniques. *Theor Chem Acc*. 2005;113:281–286.
31. Ekizoglou N, Thorshaug K, Cerrada ML, Benavente R, Pérez E. Influence of the molecular weight on the thermal and mechanical properties of ethylene/norbornene copolymers. *J Appl Polym Sci*. 2003;89:3358–3363.
32. Delfolie C, Dickinson LC, Freed KF, Dudowicz J, MacKnight WJ. Molecular factors affecting the miscibility behavior of cycloolefin copolymers. *Macromolecules*. 1999;32:7781–7789.
33. Blochowiak M, Pakula T, Butt HJ, Floudas G. Miscibility of binary blends of ethylene/norbornene copolymers: comparison to a lattice cluster theory. *Polymer*. 2007;48:6010–6017.
34. Yao Z, Lv F, Liu SJ, Cao K. Synthesis of ethylene and norbornene copolymer with metallocene catalysts and characteristic analysis. *J Appl Polym Sci*. 2008;107:286–291.
35. Yao Z, Liu SJ, Lv F, Cao K. Determination of Mark-Houwink parameters of ethylene-norbornene copolymers and molecular characteristics estimation. *J Appl Polym Sci*. 2008;109:4010–4014.

Manuscript received Jan. 29, 2008, revision received July 12, 2008, and final revision received Sept. 19, 2008.