

# Kinetic Study of Olefin Polymerization with a Supported Metallocene Catalyst. II. Ethylene/1-Hexene Copolymerization in Gas Phase

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**ABSTRACT:** A kinetic study of ethylene/1-hexene copolymerization is conducted with a supported metallocene catalyst in a gas-phase reactor. The investigation into the kinetics of ethylene/1-hexene copolymerization includes the effects of operational parameters such as the reaction temperature, pressure, and comonomer concentration. The large variations in gas-phase composition using only an initial charge of 1-hexene are illustrated by experiment. To remedy this, the ability to control the comonomer composition of 1-hexene online for the entire duration of the reaction is demonstrated. Online perturbation techniques are implemented to determine key kinetic parameters such as the activation energies for propagation and catalyst deactivation. From pressure perturbation results, a reaction rate order close to 1 is obtained for ethylene in the presence of 1-hexene. Finally, all the parameters obtained from the study are compared to those determined from ethylene–propylene (E–P) copolymerization. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 80: 1096–1119, 2001

**Key words:** ethylene/1-hexene copolymerization; metallocene catalyst; kinetic study; supported zirconium catalyst; gas phase; parameter estimation

## INTRODUCTION

The Group 4 metallocenes have provided major improvements over the traditional titanium catalysts in terms of their ability to more closely control the properties of the polymer being produced. Some of the benefits include<sup>1</sup> (i) a narrow distribution in molecular properties, (ii) controlling polymerization behavior and polymer properties by modifying the ligand structure of the catalysts, and (iii) with this flexibility in catalyst structure, being able to establish a correlation between the polymerization behavior and polymer properties. Linear low density polyethylene

(LLDPE) is a very important class of ethylene-based polymers. The introduction of short branches on the linear chains enhances the rheological properties while maintaining (to some degree) the toughness exhibited by high-density polyethylene (HDPE). LLDPE is predominantly produced in the presence of heavy comonomers like 1-hexene and 1-octene that facilitate the formation of the short-chain branches by random copolymerization.

There have been only a few reports on metallocene-catalyzed ethylene/1-hexene kinetics.<sup>2–7</sup> Quijada et al.<sup>7</sup> studied the effect of ethylene pressure on the copolymerization of ethylene with 1-hexene for  $\text{Et}[\text{Ind}]_2\text{ZrCl}_2$  in solution. When varying the pressure, the characteristics and properties of the formed copolymers were in accordance with the expectation for changes in the

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monomer concentration; increasing the pressure caused a decrease in comonomer incorporation, resulting in higher crystallinities and molecular weights. Chien and Nozaki<sup>4</sup> found that 1-hexene had a negative "comonomer effect," resulting in the reduction of the polymerization rate compared to ethylene homopolymerization for two homogeneous metallocenes. Koivumaki and Sepala<sup>5</sup> monitored ethylene consumption upon 1-hexene addition for homogeneous  $\text{Cp}_2\text{ZrCl}_2$  catalysts. They observed rate enhancement with 1-hexene when polyethylene was insoluble in the reaction medium. At higher temperatures, where the product was soluble, there was no rate enhancement but rather a rate decrease. Muhle<sup>6</sup> presented results from investigations into the role of the metallocene catalyst structure for supported catalysts in polyethylene gas-phase fluidized-bed reactor kinetics. Estimation of kinetic parameters was based on an evaluation of polymer product properties. In the present study, the kinetics of ethylene/1-hexene copolymerization was investigated with a supported metallocene catalyst in a stirred-bed reactor.

The stirred-bed reactor (SBR) system built at the UWPREL<sup>8</sup> is designed to study the gas-phase kinetics of ethylene-comonomer systems like ethylene/propylene and ethylene/1-hexene. It has been shown that by virtue of controlling the comonomer composition detailed investigations into the kinetics of traditional Ziegler-Natta<sup>9-11</sup> and metallocene catalysts are possible.<sup>12</sup> The ability to control the composition of 1-hexene was illustrated,<sup>8</sup> but there have not been any kinetic results reported on metallocene-catalyzed ethylene/1-hexene systems. In this study, the comonomer and temperature effects in ethylene/1-hexene kinetics were investigated. Important kinetic parameters such as the activation energies of propagation and deactivation, the reactivity ratios, and the reaction rate order with respect to ethylene in the presence of 1-H were determined. These results can be compared and contrasted to those obtained for the ethylene/propylene system which has been studied using the same unbridged supported zirconocene in Part I.<sup>12</sup>

## EXPERIMENTAL

The reactor system<sup>8</sup> used was well-described in previous investigations with supported metallocenes and traditional Ziegler-Natta catalysts.<sup>9-11</sup> The entire reactor system is shown in

Figure 1. Figure 2 depicts the various ports on the reactor. The opening and closing of the vent line determines the mode of the reactor operation. If the valve is closed, the reactor is said to be operating in the "no-purge" mode. In this mode of operation, it is not possible to control the composition of the comonomer since there is not an exit gas stream from the reactor entering the FTIR. The reactor is said to be operating in the "purge" mode when the valve is open, thereby facilitating effective control of the comonomer composition. The liquid comonomer feed system in the reactor setup is shown in Figure 3. The syringe is filled with 1-hexene from the storage bomb prior to the onset of the reaction. During the course of the polymerization reaction, a computer control algorithm is used to maintain the 1-hexene gas-phase composition constant by feeding 1-hexene from the syringe pump. This control scheme uses measurements from the FTIR gas analyzer. Figure 4 shows plots of the 1-hexene composition being controlled effectively at different levels.

## KINETICS AND COMONOMER COMPOSITION EFFECTS

The broad distribution observed in the molecular weight and comonomer composition distribution of the polymers made from traditional Ziegler-Natta catalysts is attributed to the presence of multiple sites. Metallocenes typically produce polymers which possess a narrow distribution in properties such as the molecular weight and comonomer composition. But broadening of these properties could occur if the comonomer composition is not controlled effectively over the entire duration of the reaction time. A drift in the gas-phase comonomer composition in the reactor can prove to be a likely reason for the heterogeneity observed in polymer properties such as the comonomer composition distribution. For kinetic studies, it is imperative that the comonomer composition be controlled effectively for the entire duration of the reaction. To illustrate the importance of this issue, reactions are carried out in the no-purge mode where the comonomer is injected into the system only at the beginning of the experiment. This mode of operation is often used in practice based on the hope that the consumption rate of the comonomer is relatively insignificant such that the 1-hexene composition in the gas phase does not change drastically over the entire

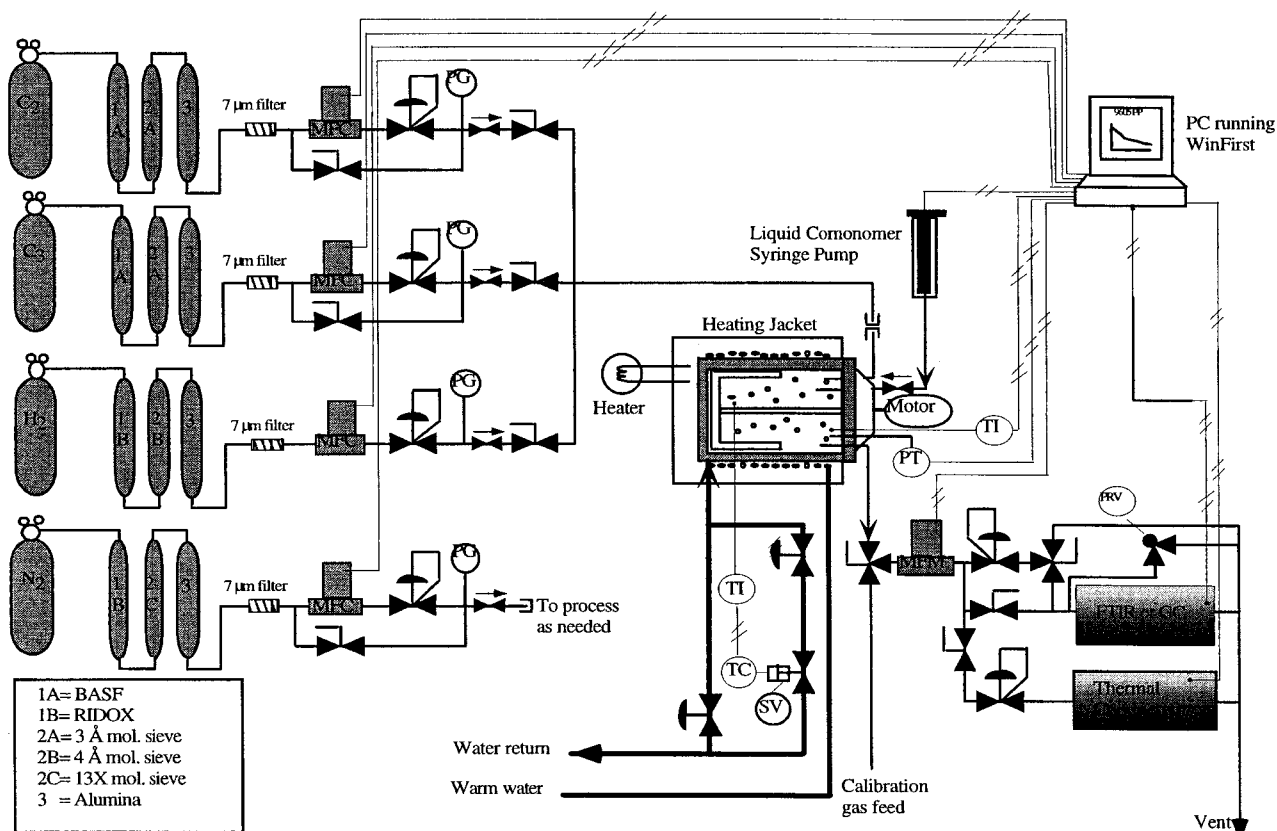


Figure 1 Horizontal stirred-bed gas-phase reactor system.

course of the reaction. However, we will test this assumption in what follows.

The following model tests the assumption by investigating the possible drift in the comonomer composition in the gas phase. Equations (1) and (2) summarize the material balances for ethylene and 1-hexene in the reactor (1: ethylene; 2: 1-hexene;  $r$  = reactor;  $g$  = gas;  $s$  = sorbed):

$$\frac{dn_{1r}}{dt} = \frac{dn_{1g}}{dt} + \frac{dn_{1s}}{dt} = -R_{p1} + F \quad (1)$$

$$\frac{dn_{2r}}{dt} = \frac{dn_{2g}}{dt} + \frac{dn_{2s}}{dt} = -R_{p2} \quad (2)$$

where

- $n_{1r}$  and  $n_{2r}$  are the moles of ethylene and 1-hexene in the reactor, respectively,
- $n_{1s}$  and  $n_{2s}$  are the moles of ethylene and 1-hexene sorbed into the polymer, and
- $n_{1g}$  and  $n_{2g}$  are the moles of ethylene and 1-hexene present in the gas phase.

- $F$  refers to the constant flow of ethylene being fed into the reactor.
- $R_{p1}$  and  $R_{p2}$  are related to the intrinsic reaction rates (defined in eqs. (3) and (4)) by

$$R_{p_i} = R_{pM_i} \frac{gcat}{\rho_{poly}}$$

$$Rp_{M_1} = A_1(kp_{11}C_1^* + kp_{21}C_2^*)[M_1]_{eq} \quad (3)$$

$$Rp_{M_2} = A_2(kp_{22}C_2^* + kp_{12}C_1^*)[M_2]_{eq} \quad (4)$$

In eqs. (3) and (4),  $A_i = 3.6 M_{w_i}$  and

- $[M_1]_{eq}$  and  $[M_2]_{eq}$  are the equilibrium concentrations of ethylene and 1-hexene sorbed in the polymer, respectively.
- $[M_1]_{eq} = k_1^*P_1$  and  $[M_2]_{eq} = k_2^*P_2$  as shown in eq. (18).
- $C_i^*$  is the active site concentration with monomer end-group  $i$ .

In the experiment being conducted, due to the no-purge mode of operation, there is a constant

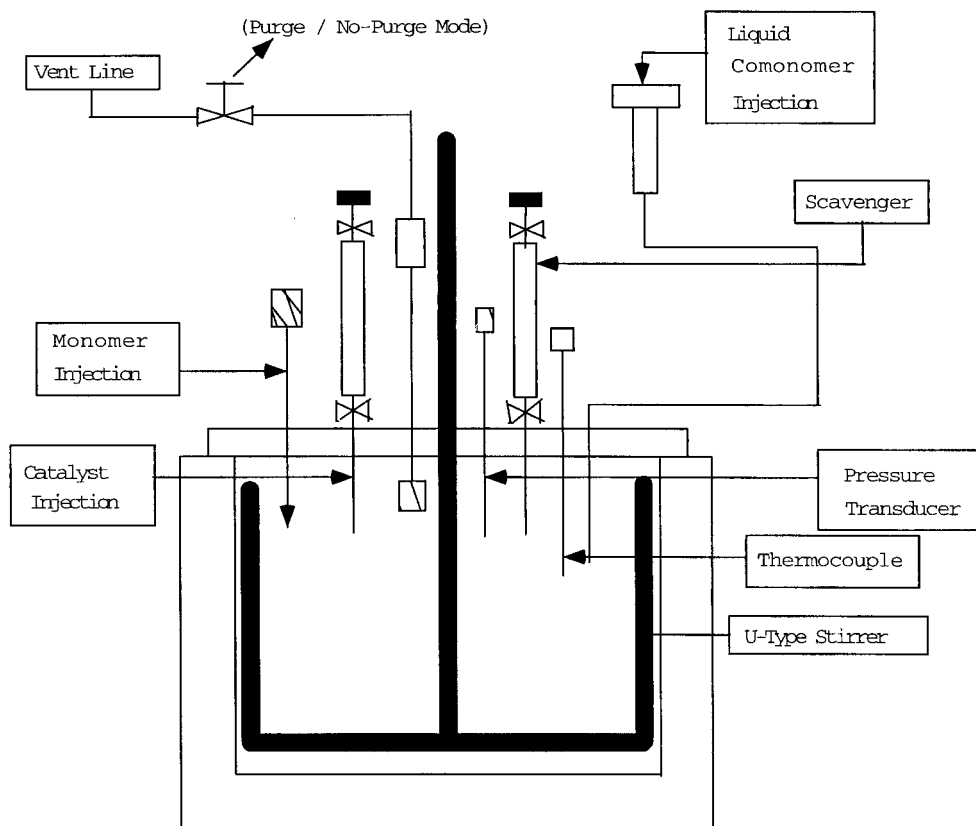


Figure 2 Reactor schematic.

flow of ethylene into the reactor to maintain the total pressure ( $P_t$ ) constant. Hence, the determination of the partial pressure of ethylene is quite trivial as shown in eq. (5):

$$P_1 = P_t - P_2 \quad (5)$$

To determine the change in the partial pressure of 1-hexene ( $P_2$ ) over the course of the reaction, the following analysis was implemented: Assuming ideal gas behavior and implementation of Henry's Law in eq. (2) results in eq. (6) and, subsequently, eq. (7):

$$\frac{dn_{2r}}{dt} = \frac{V_r}{RT} \frac{dP_2}{dt} + \frac{d(k_2^* P_2 V_{pol})}{dt} = -R_{p2} \quad (6)$$

$$\frac{dn_{2r}}{dt} = \frac{V_r}{RT} \frac{dP_2}{dt} + k_2^* P_2 \frac{dV_{pol}}{dt} + V_{pol} k_2^* \frac{dP_2}{dt} = -R_{p2} \quad (7)$$

$V_{pol}$ , the volume of polymer being produced, changes with time and is calculated using eq. (8):

$$\frac{dV_{pol}}{dt} = (R_{PM_1} + R_{PM_2}) \cdot \frac{g_{cat}}{\rho_{poly}} \quad (8)$$

Since the reaction is being conducted in the no-purge mode, it is not possible to obtain information on the intrinsic reaction rate of 1-hexene. Under no-purge conditions, only the rate of ethylene consumption is measured. Following the ethylene-propylene studies conducted on this particular catalyst, it was found that the catalyst did not display a high tendency toward comonomer incorporation. Hence, the number of sites with ethylene end groups is much greater than is those with comonomer end groups:

$$C_1^* \gg C_2^* \quad (9)$$

Using the assumption from eq. (9) in eqs. (3) and (4) results in eqs. (10) and (11):

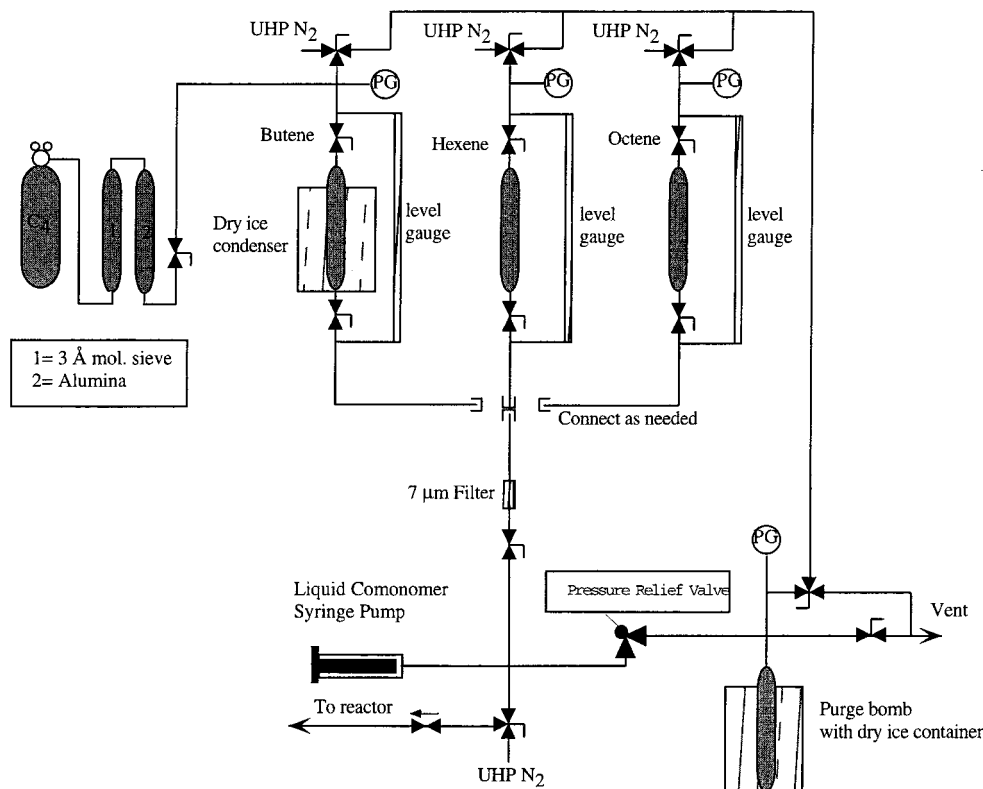


Figure 3 Liquid comonomer feed system.

$$R_{pM_1} = A_1(k_{p11}C_1^*)[M_1]_{eq} \quad (10)$$

$$R_{pM_2} = A_2(k_{p12}C_1^*)[M_2]_{eq} \quad (11)$$

Equation (11) is modified based on the knowledge of reactivity ratios as shown in eq. (12):

$$R_{pM_2} = A_2\left(\frac{k_{p11}}{r_1} C_1^*\right)[M_2]_{eq} \quad (12)$$

Hence, the model that is used to determine the drift in the 1-hexene composition in the gas phase contains eqs. (13) and (14):

$$\frac{dn_{2r}}{dt} = \left(k_2V_{pol} + \frac{V_r}{RT}\right) \frac{dP_2}{dt} + k_2^*P_2 \frac{dV_{pol}}{dt} = -R_{p2} \quad (13)$$

$$\frac{dV_{pol}}{dt} = k_{p11}C_1^* \left(k_1(P_t - P_2) + \frac{k_2^*P_2}{r_1}\right) \quad (14)$$

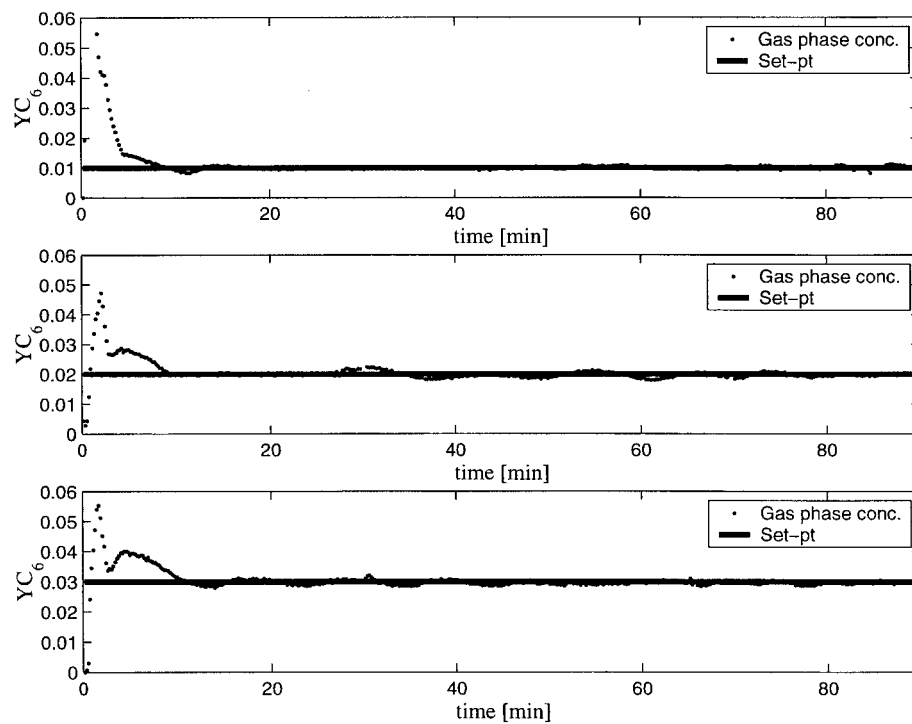
Based on the assumption from eq. (9),  $k_{p11}C_1^*$  can now be determined from the experimentally mea-

sured reaction rate of ethylene ( $R_{pM_1}$ ) as shown in eq. (15):

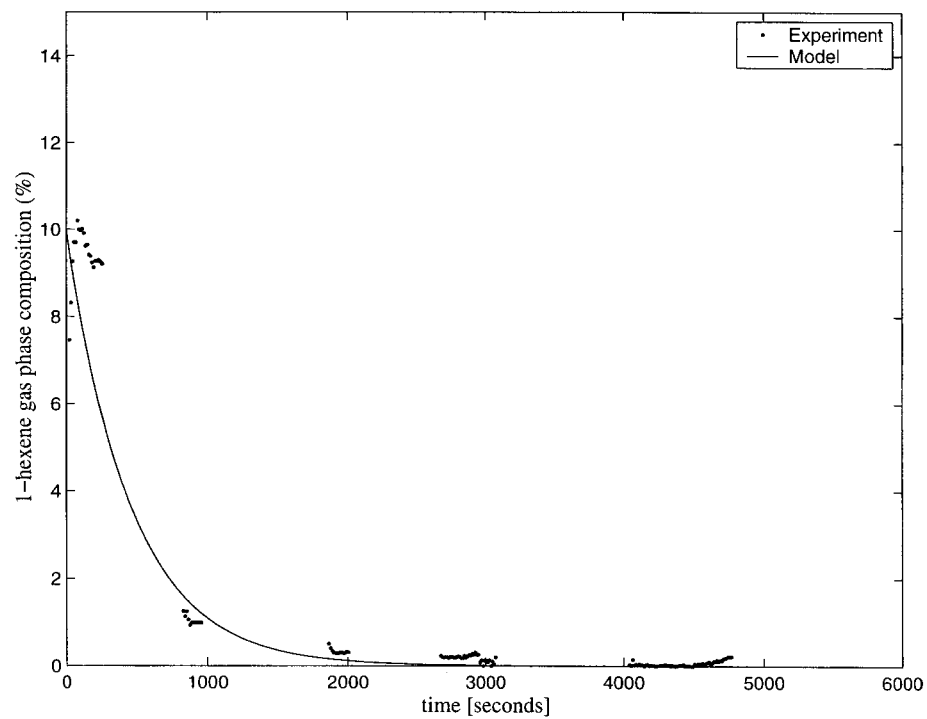
$$k_{p11}C_1^*|_t = \frac{R_{pM_1}|_t}{A_1[M_1]_{eq}} \quad (15)$$

To validate its predictions, the model was compared to the data collected from the FTIR. To obtain the measurements, the valve on the vent line was opened briefly at regular intervals. Figure 5 shows the model predictions to be quite consistent with the experimental data. Under these operating conditions, the calculated comonomer composition distribution appears to be quite broad as can be seen in Figure 6. The weight fraction of the total polymer,  $WF_{poly}$ , produced at time  $t$  is shown in eq. (16):

$$WF_{poly}(t) = \frac{\int_0^t (R_{pM_1} + R_{pM_2}) dt}{\int_0^{t_{\text{reac}}} (R_{pM_1} + R_{pM_2}) dt} \quad (16)$$



**Figure 4** Control of comonomer composition at different gas-phase concentrations.



**Figure 5** Model prediction versus experimental data for mol fraction of 1-hexene in the gas phase.

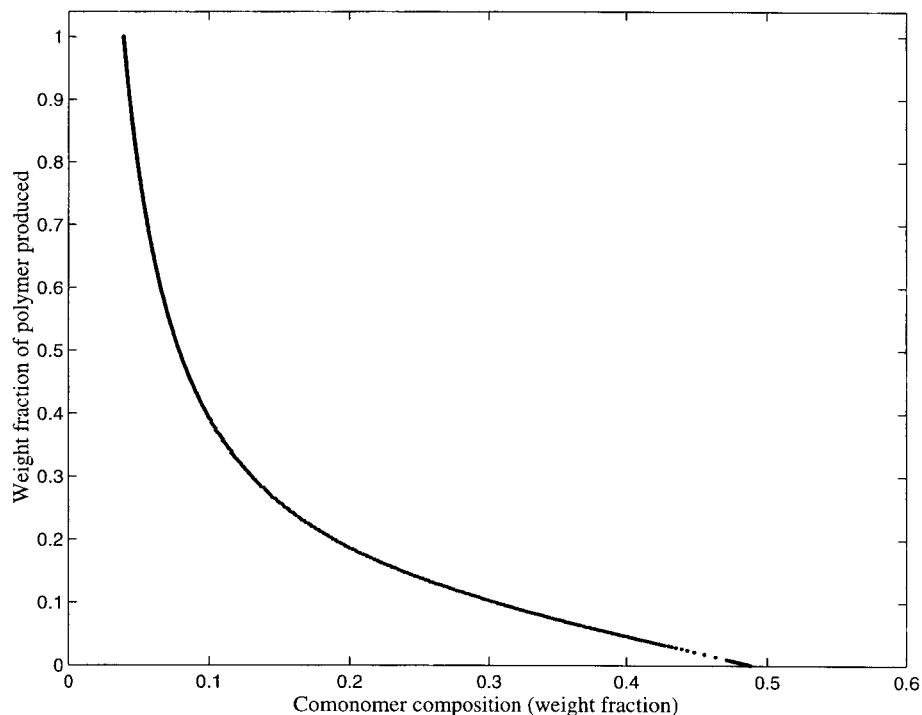


Figure 6 Calculated comonomer composition distribution.

where  $t_{\text{reac}}$  is the time for the entire duration of the reaction. Based on the model, it is possible to calculate the reaction rates of the two monomers. The calculation of the 1-hexene weight fraction in the polymer ( $Hex_{\text{poly.}}$ ) being produced at time  $t$  is shown in eq. (17):

$$Hex_{\text{poly.}}(t) = \frac{\int_0^t R_{pM_2} dt}{\int_0^t (R_{pM_1} + R_{pM_2}) dt} \quad (17)$$

Based on Figure 6, it can be said that the heterogeneity observed in the properties of polymers produced with an initial charge of the comonomer can be attributed to the inability in being able to control the comonomer composition in the gas phase for the entire duration of the reaction time. Figures 7 and 8 depict the predicted drifts under different reaction conditions. The drifts were calculated based on the experimentally measured reaction rates at the different operating conditions considered. From Figures 7 and 8, it is clear that strong composition variations will exist in experiments where there is only

an initial charge of the comonomer. Hence, it will be difficult to obtain accurate kinetic behavior or representative polymer properties from such experiments.

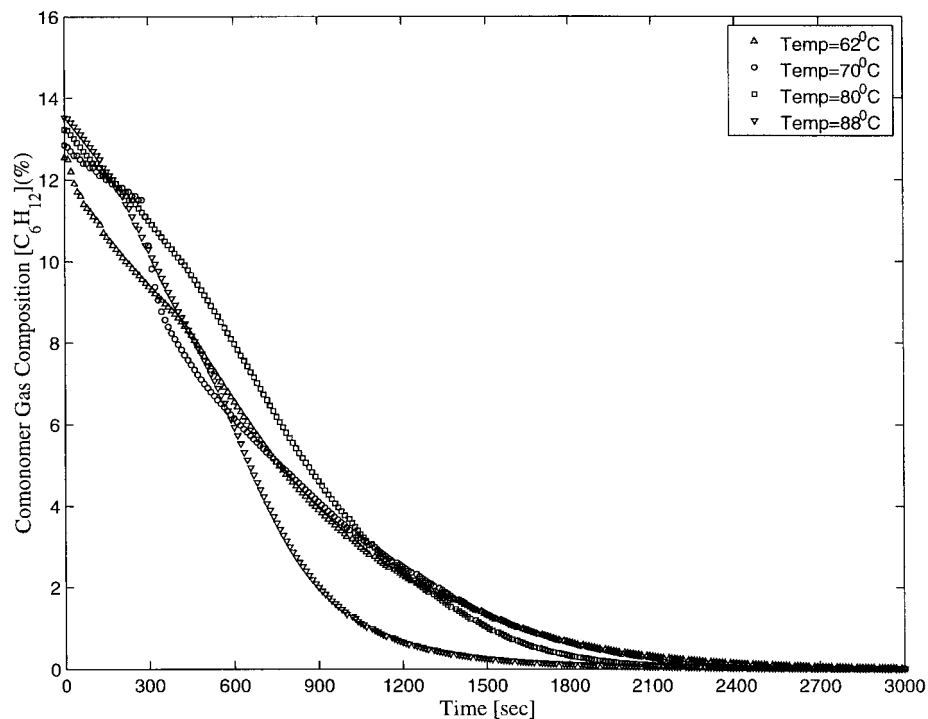
## EXPERIMENTAL DESIGN

### Data Representation

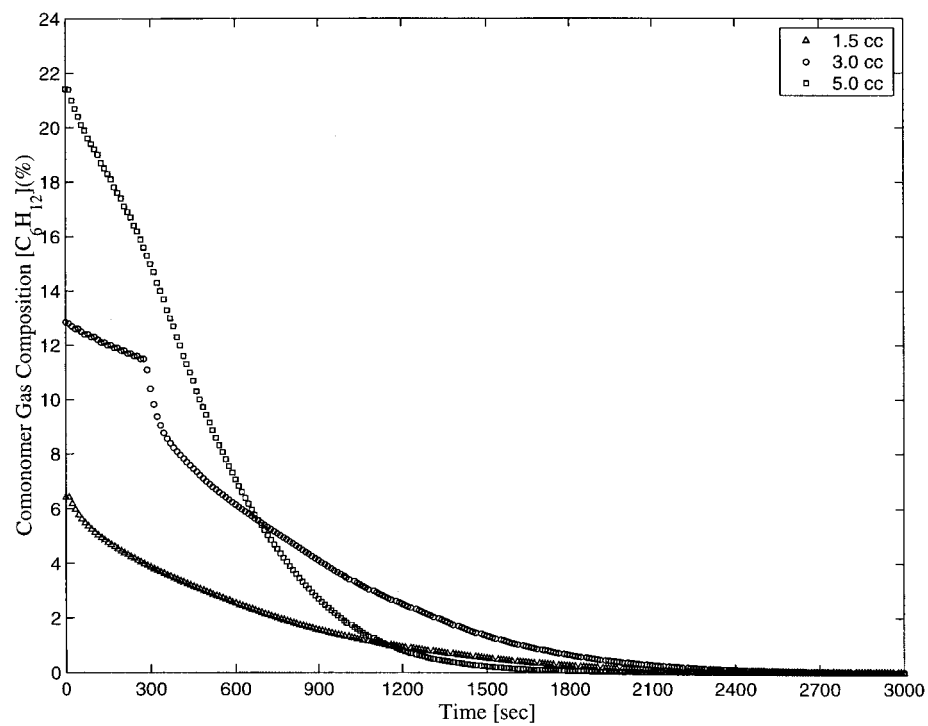
The kinetic data are presented as the intrinsic polymerization rate of monomers: (gPolymer)/(gcat, h,  $[M_i]_{\text{eq}}$ ). Based on the units used, it should be noted that the intrinsic reaction rate will depend on the monomer concentration only if the reaction rate order with respect to the particular monomer is different from 1. The reaction rates were normalized by the monomer concentration in the amorphous polymer ( $[M_i]_{\text{eq}}$ ) using the solubility equation proposed by Hutchinson and Ray.<sup>13</sup> It has the units of mol/(L amorphous polymer) and is calculated by the following equation:

$$[M]_{\text{eq}} = k_i^* P_i$$

where  $P_i$  is the partial pressure of species  $i$  in the gas. Parameter  $k^*$  is the so-called Henry's Law constant and is determined by Stein's correlation<sup>14</sup>:



**Figure 7** Observed drift for different temperatures. Initial 1-hexene amount: 3 cc; pressure: 5.24 atm.



**Figure 8** Observed drift for different initial amounts of 1-hexene.  $P = 5.24$  atm;  $T = 70^\circ\text{C}$ .



**Table I Pressures Above Which Deviations from Henry's Law Become Significant for 1-Hexene Sorption into a Polymer**

Temperature (K)	Pressure (atm)	Pressure (psia)
335	0.2	2.94
343	0.3	4.41
353	0.38	5.59

$$\log(k_i^*) = -2.38 + 1.08 \left( \frac{T_{c_i}}{T} \right)^2$$

where  $T_{c_i}$  is the critical temperature of species  $i$  and  $T$  is the reaction temperature. For heavier comonomers like 1-hexene, there is an upper limit on the pressure above which deviations from Henry's Law are observed. Under such conditions, Henry's Law underpredicts the amount of comonomer sorbed into the polymer. Based on the results presented by Hutchinson and Ray,<sup>13</sup> Table I shows the approximate upper limit of partial pressures for 1-hexene at temperatures of interest where deviations from Henry's Law are observed.

#### Determination of the Number of Experiments

Prior to conducting any kinetic investigation, it is imperative to ensure that the experimental design implemented will (i) capture the essential kinetic features of the catalyst and (ii) provide data that can be used for the purposes of kinetic parameter estimation. If the experiments shown in Table II are to be conducted (based on Hutchinson's results), a reactor pressure of 52 psia would prove to be appropriate for all the different operating conditions. Dew-point calculations have shown that 1-hexene will not condense for the different reaction conditions considered.

Based on our experience in Part I, it was found that reactions conducted at high temperatures in the presence of high comonomer concentrations in the gas phase were subject to the onset of diffusion caused by polymer sintering. Table III shows a comparison of the sorbed concentrations of the two comonomers under various operating conditions. For the experimental design implemented for the ethylene/1-hexene systems, it is noted that, by conducting runs with the 1-hexene concentration in the gas phase lying anywhere between 1 and 3%, a range of comonomer sorbed concentrations are obtained comparable to those

used in ethylene/propylene copolymerization. By doing so, it is now possible to conduct a valid comparison between the kinetics of the two ethylene-comonomer systems under similar operational conditions. This is important from the standpoint of being able to compare comonomer and temperature effects. Also, we are able to obtain information on conditions under which diffusion limitations become important based on what we have learned in Part I. With this knowledge, the experimental issues that would have to be considered include (i) studying comonomer effects (keeping the temperature constant at 62 or 70°C) and conducting reactions with the gas-phase concentration at 1, 2, and 3%; (ii) studying temperature effects—(with maintaining the 1-hexene composition in the gas phase at 1%) conducting reactions over a range of 62–80°C; and (iii) perturbation reactions for estimating activation energies of propagation and deactivation. The minimum number of experiments to be conducted is approximately nine (three comonomer effects, three temperature effects, and three perturbation reactions). The study of temperature effects and use of perturbation techniques to estimate the activation energies of propagation and deactivation account for the additional experiments.

#### DISCUSSION OF REACTION KINETICS: COMONOMER AND TEMPERATURE EFFECTS

The reactor temperature profiles for the experiments are provided in Figures 9 and 10. It is important to be aware of the reactor temperature profiles prior to drawing inferences about the comonomer and temperature effects. There can exist an initial temperature induction time that varies with the different reaction conditions.

- Reaction rate profiles—comonomer effects. Figures 11 and 12 show the various kinetic

**Table II Experiments for Studying Temperature and Comonomer Effects in Ethylene/1-Hexene Copolymerization**

Temperature (K)	Pressure (psia)	Gas-phase Composition of 1-Hexene		
335	52.0	0.01	0.02	0.03
343	52.0	0.01	0.02	0.03
353	52.0	0.01	—	—

**Table III Comparison of Sorbed Concentrations of Propylene and 1-Hexene in Polymer**

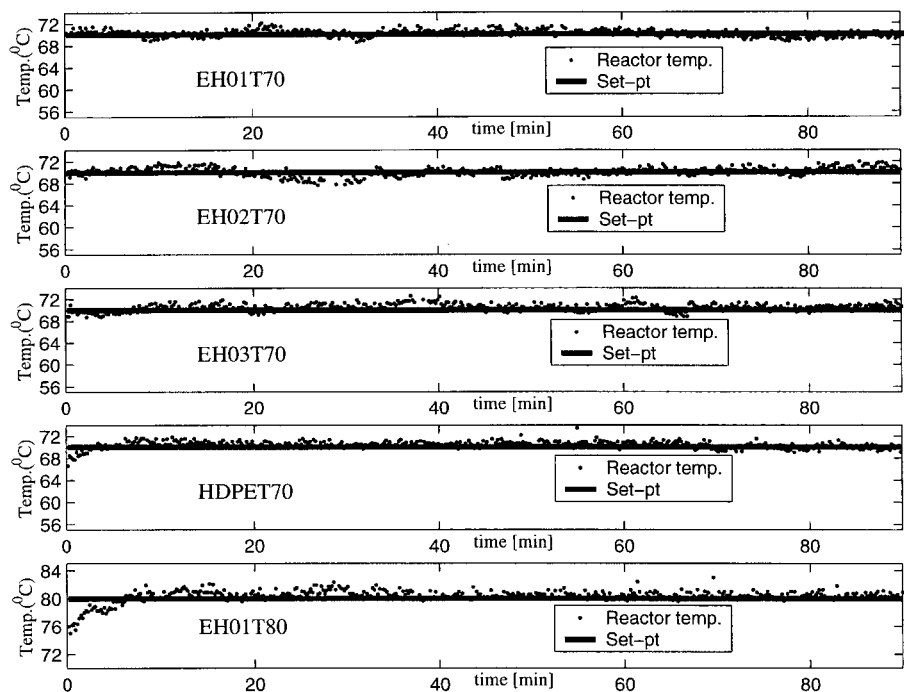
Temperature (°C)	$C_{6g}$	$C_{6s}$	$C_{2p}$	$C_{2s}$	$C_{3g}$	$C_{3s}$	$C_{2p}$	$C_{2s}$
62	0.01	0.040	63.9	0.084	0.1	0.038	50.49	0.106
62	0.02	0.080	56.8	0.083	0.2	0.078	49.98	0.094
62	0.03	0.120	49.7	0.082	0.3	0.115	49.47	0.082
70	0.01	0.031	63.9	0.077	0.1	0.033	50.49	0.098
70	0.02	0.063	56.8	0.076	0.2	0.067	49.98	0.087
70	0.03	0.093	49.7	0.075	0.3	0.100	49.47	0.076
80	0.01	0.023	63.9	0.070	0.1	0.028	50.47	0.089

$p$ : Partial pressure (psia);  $s$ : sorbed (gMon/L-amor.polym.);  $g$ : in gas, mole fraction.  
Total pressure: (i) ethylene/propylene, 71 psia; (ii) ethylene/1-hexene, 51 psia.

profiles associated with changing comonomer compositions at 62 and 70°C. The homopolymerization plots are provided for comparison. The presence of the comonomer has a significant effect on the reaction rate. When comparing the kinetic profiles to homopolymerization, it is observed that (i) the position of the peak has shifted, (ii) an increase in activity is observed, and (iii) the decay rate has decreased. Additionally, an incremental increase in the 1-hexene concentration fails to have a significant effect on the kinetics in terms of increased activity. This is found to occur at both 62 and 70°C. It is not possible to

provide a unique interpretation for the observed comonomer effects. For example, these effects could be due to more rapid site activation by the comonomer or could be attributed to the comonomer stabilizing the sites activated by ethylene, thereby slowing deactivation. Much more work is required to clarify this issue.

- Reaction rate profiles—temperature effects. Figure 13 shows the effect of temperature on the rate profiles when the composition has been maintained at 1%. Since an initial temperature induction time exists in reaching

**Figure 9** Reactor temperature profiles.

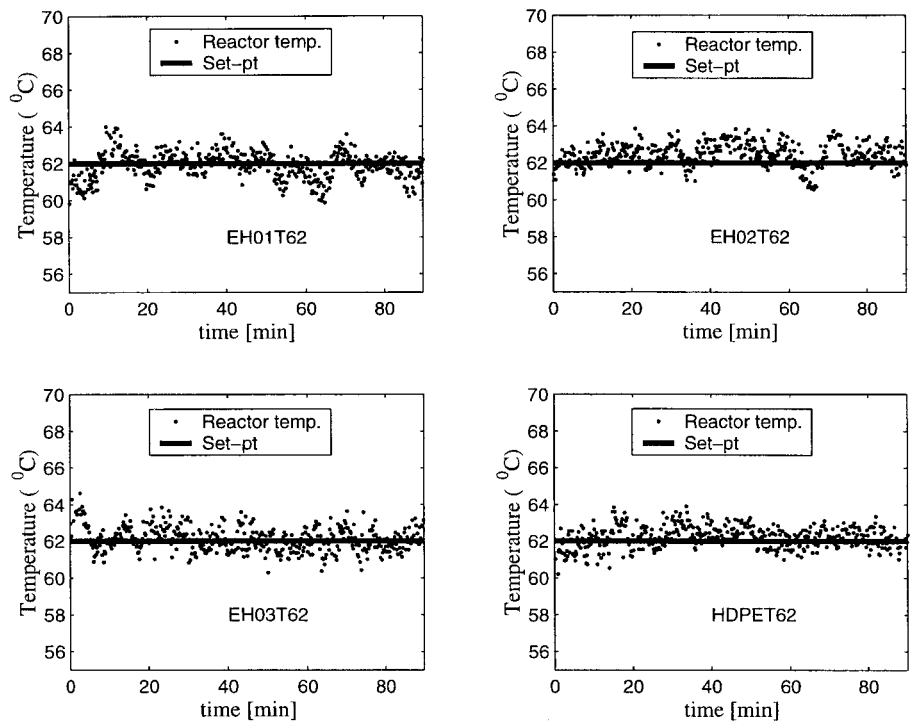


Figure 10 Reactor temperature profiles.

the reactor temperature setpoint, inferences cannot be made about a change in the peak position with changing temperature. How-

ever, by increasing the temperature, the peak magnitude increased and the decay rate became more rapid.

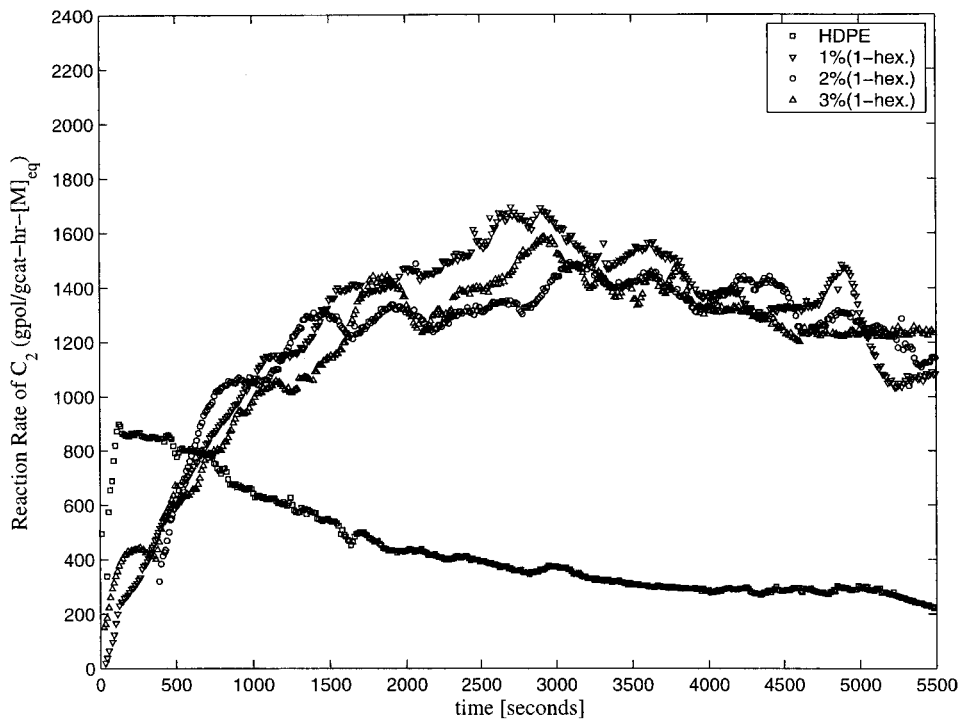
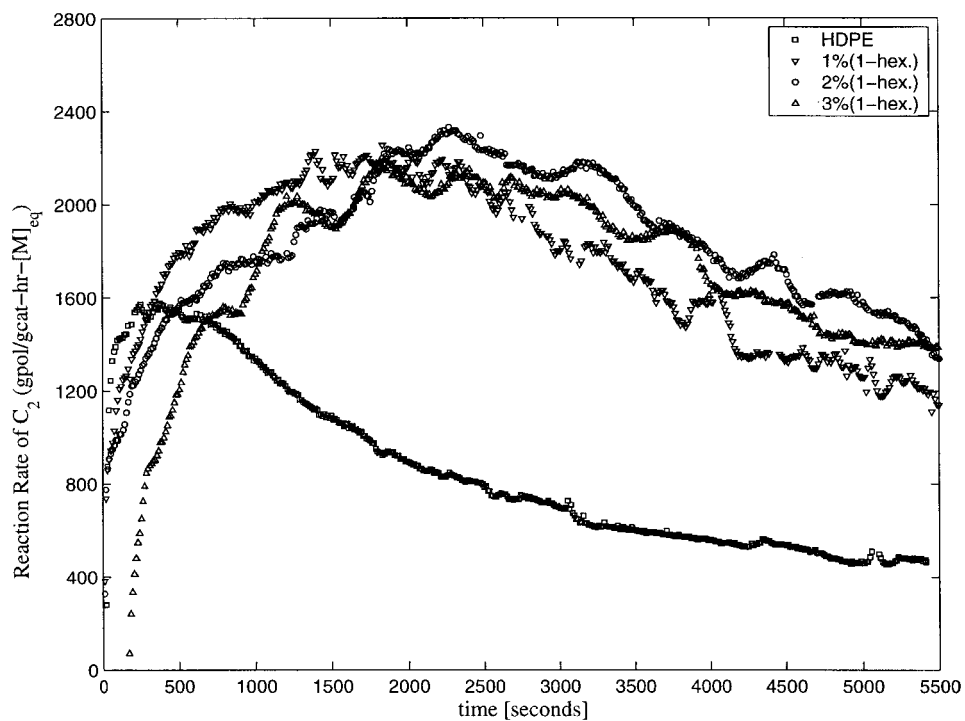
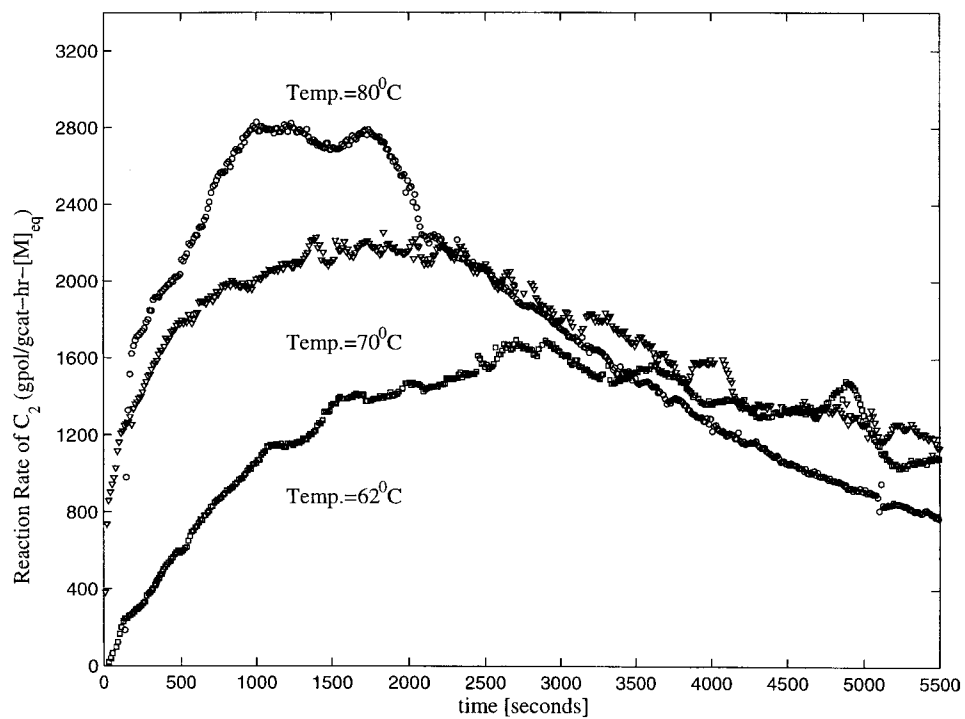


Figure 11 Influence of changing comonomer composition on reaction kinetics at 62°C.



**Figure 12** Influence of changing comonomer composition on reaction kinetics at 70°C.



**Figure 13** Influence of changing temperature on reaction kinetics. (1-hexene gas phase composition: 1%.)

These observations are similar to those seen in ethylene/propylene copolymerization in Part I.

## PARAMETER ESTIMATION

### Online Perturbation Experiments

In the present gas-phase system, a variety of perturbation techniques<sup>9,10,15</sup> were implemented to estimate important parameters such as (i) the activation energies of propagation and deactivation and (ii) the reaction rate order with respect to ethylene in homopolymerization and copolymerization. In the current research effort, perturbations in temperature and pressure are enforced to determine the parameters for ethylene/1-hexene kinetics. The parameters obtained from ethylene/1-hexene kinetics are then compared to those obtained from ethylene/propylene kinetics.

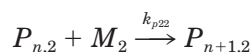
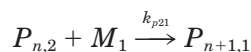
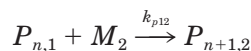
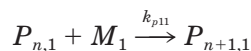
For the different perturbations, the 1-hexene gas-phase composition was maintained at 1%. A brief summary of the data analysis method is provided here. A detailed procedure in analyzing the data from the perturbation techniques was already presented in Part I.<sup>12</sup>

For homopolymerization, the monomer consumption rate can be described as

$$Rp \left[ \frac{g \text{ pol}}{g \text{ Cat}, h} \right] = A k_p C^* [M]_{\text{eq}} \quad (18)$$

where  $[M]_{\text{eq}}$  [=] (mol/L-amorphous polym.) is the monomer concentration at the catalyst site,  $A_i$  (conversion factor) = 3.6 MW<sub>*i*</sub>,  $k_p$  [=] (cc-amorphous polym./mol-act.sites.s), and  $C^*$  [=] (mol-act.sites/g.cat.).

The copolymerization rate expression is derived from the following equations:



The monomer consumption rates for copolymerization can be described as follows:

$$Rp \left[ \frac{g M_1 \text{ converted}}{g \text{ Cat}, h} \right] = A_1 k_{p,11} C_1^* \beta_1 [M_1]_{\text{eq}} \quad (19)$$

$$Rp \left[ \frac{g M_2 \text{ converted}}{g \text{ Cat}, h} \right] = A_2 k_{p,22} C_2^* \beta_2 [M_2]_{\text{eq}} \quad (20)$$

$$\frac{dC^*}{dt} = -k_d C^* t \quad (21)$$

where 1 and 2 correspond to ethylene and 1-hexene, respectively.  $C_i^*$  denotes the concentration of active sites with end group  $i$ .  $C^*$  ( $= \sum_i C_i^*$ ) is the total concentration of active sites. Parameters  $\beta_1$  and  $\beta_2$  are defined as

$$\beta_1 = 1 + \frac{1}{r_1} \frac{[M_2]_{\text{eq}}}{[M_1]_{\text{eq}}} \quad (22)$$

$$\beta_2 = 1 + \frac{1}{r_2} \frac{[M_1]_{\text{eq}}}{[M_2]_{\text{eq}}} \quad (23)$$

Here,  $r_1$  and  $r_2$  are reactivity ratios:

$$r_1 = \frac{k_{p,11}}{k_{p,12}} \quad r_2 = \frac{k_{p,22}}{k_{p,21}} \quad (24)$$

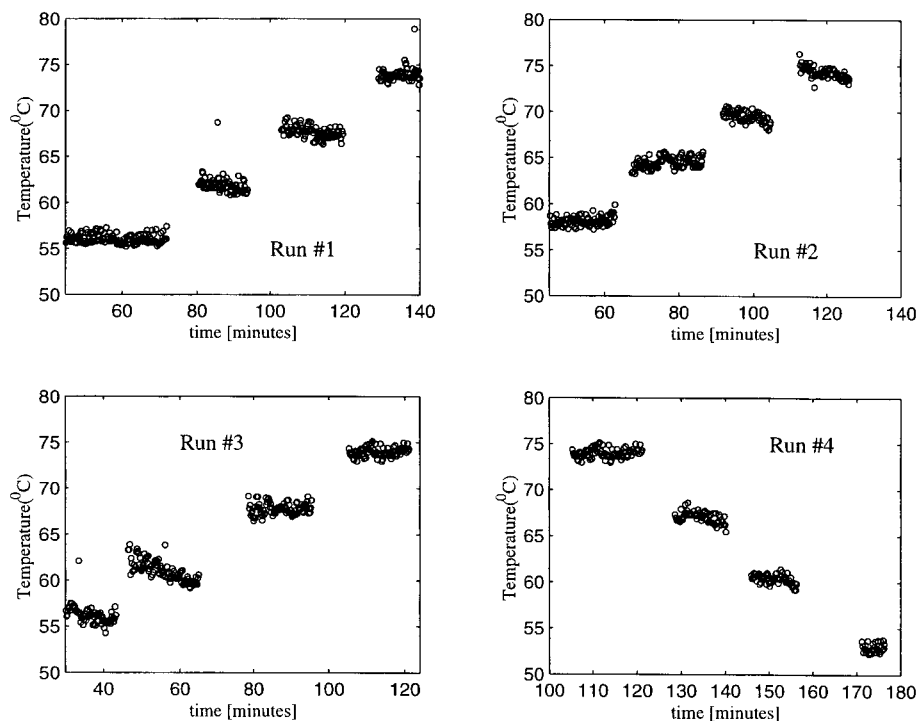
In arriving at the expressions for  $\beta_1$  and  $\beta_2$ , the following quasi-steady-state assumption was used:

$$k_{p,12} C_1^* [M_2]_{\text{eq}} = k_{p,21} C_2^* [M_1]_{\text{eq}} \quad (25)$$

In this study, the focus is on the ethylene reaction rate. To account for catalyst decay, the procedure implemented for the current investigation follows what has been conducted for ethylene/propylene kinetics in Part I. In the current study, step-up and step-down temperature and pressure perturbations are implemented.

#### • Temperature Perturbations

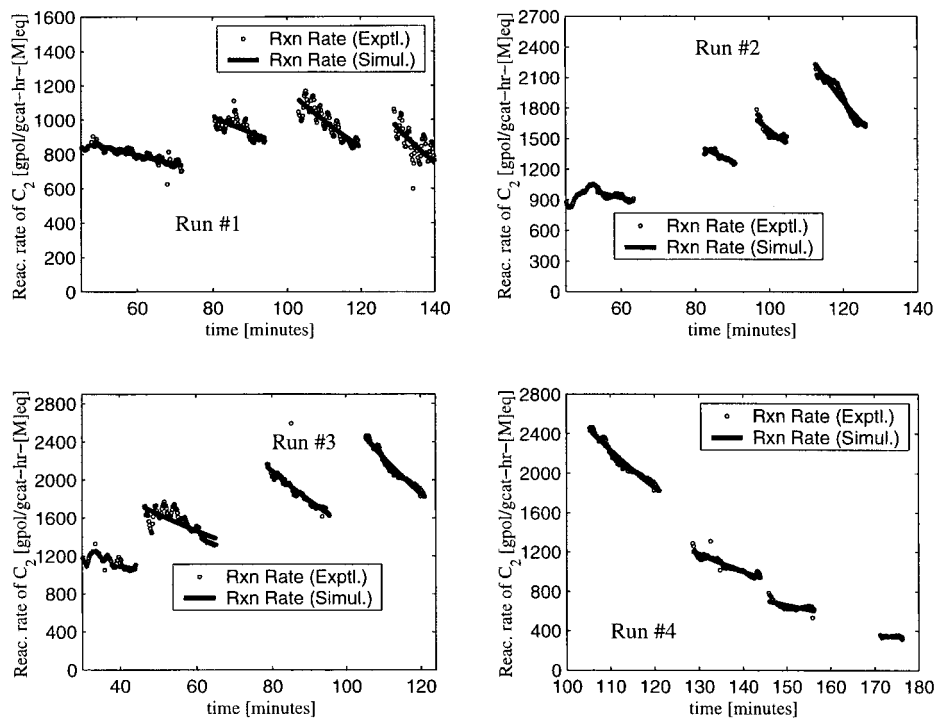
Step-up and step-down perturbations are conducted to determine the activation energies of propagation,  $E_p$ , and deactivation,  $E_d$ . The perturbations are conducted over a range of about 20–25°C, with each perturbation lasting for about 15–20 min. Figure



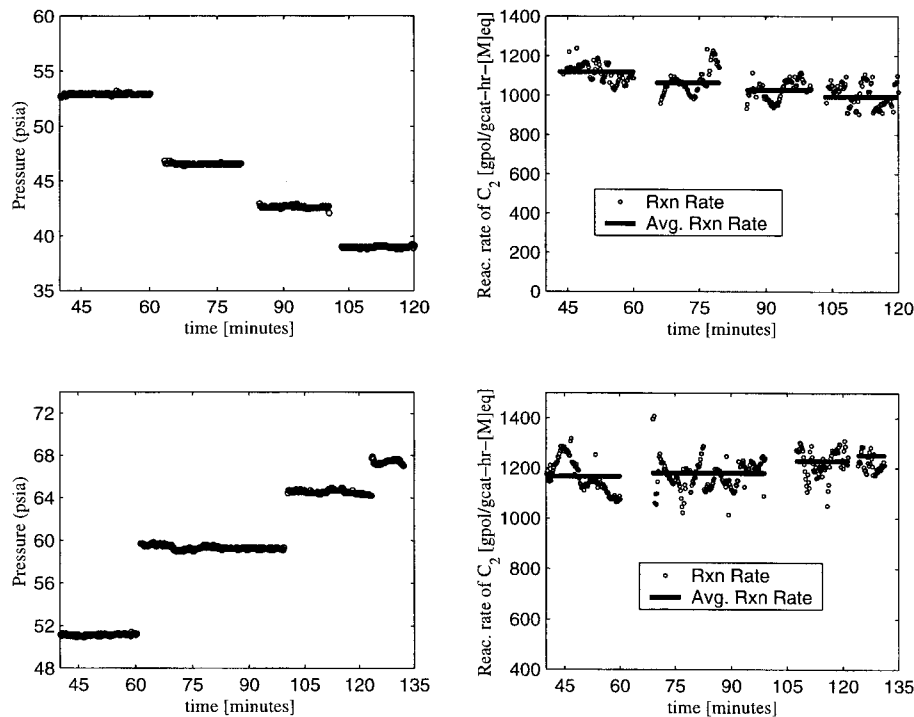
**Figure 14** Temperature perturbations implemented upon the system.

14 shows examples of the perturbations implemented for the catalyst system. It should be noted that the transition time

between perturbations does not last very long. The deactivation rate constant,  $k_d$ , was determined by assuming first-order de-



**Figure 15** Reaction rate response to the temperature perturbations implemented on the system (with the simulation results). Mol fraction of  $C_6$  in the gas phase: 0.01.

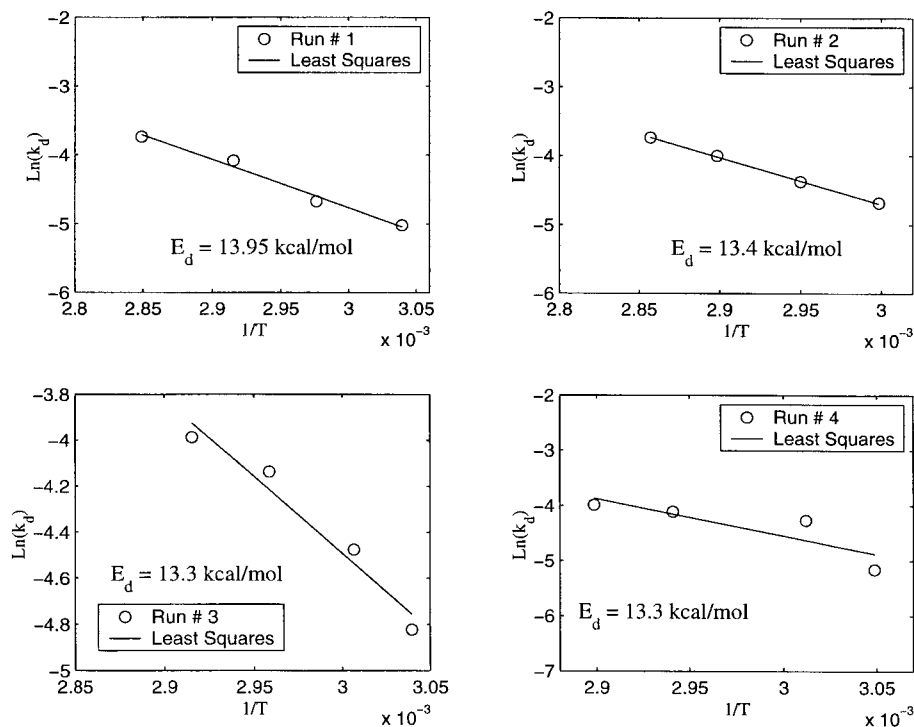


**Figure 16** Reaction rate response (corrected for catalyst decay) to the pressure perturbations implemented on the system.

cay. The plots of the experimental data are in good agreement with the model predictions (see Fig. 15).

• Pressure Perturbations

Figure 16 shows the step-up and step-down perturbations implemented with the accom-



**Figure 17** Activation energy of deactivation (obtained from each run).

**Table IV** Estimates for  $E_d$  from the Different Perturbations

Run No.	$E_d$ (kcal/mol)
Run #1	$13.95 \pm 0.34$
Run #2	$13.4 \pm 1.3$
Run #3	$13.3 \pm 1.14$
Run #4	$13.3 \pm 1.12$

panying reaction rate responses for this particular system. The transition time between perturbations is found to be negligible.

### Kinetic Parameters Estimated

#### Catalyst Deactivation

Figure 17 and Table IV show the results obtained for the activation energy of deactivation. The difference in values obtained is not very significant. They lie in the range of 13.0–14.0 kcal/mol.

#### Propagation Reaction

Figure 18 and Table V show the results obtained for the activation energy of propagation based on the Arrhenius plots for the different techniques.

The values lie between 10.5 and 11.2 kcal/mol. This is within the expected range of 10–13 kcal/mol for reactions involving carbon–carbon double-bond openings.<sup>16</sup>

#### Reactivity Ratios

The reactivity ratios are obtained by the Fineman–Ross method. Table VI summarizes the results:

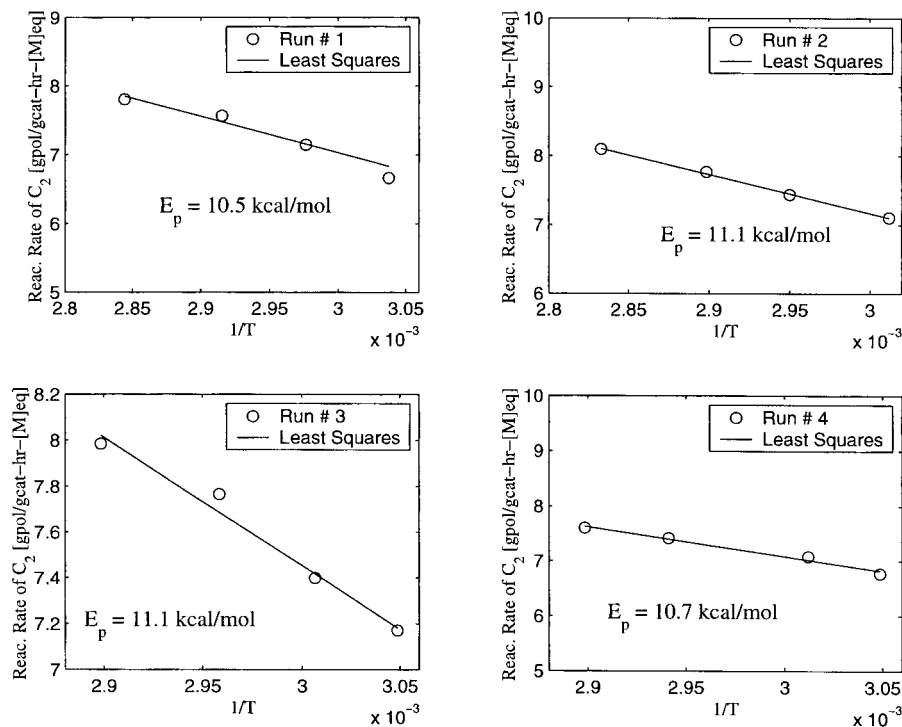
$$\frac{F(f-1)}{f} = \frac{F^2}{f} r_1 - r_2 \quad (26)$$

where

$$F = \frac{[M_1]_{\text{eq}}}{[M_2]_{\text{eq}}} \quad (27)$$

$$f = \frac{\text{monomer 1 in polymer}}{\text{monomer 2 in polymer}} \quad (28)$$

Monomers 1 and 2 represent ethylene and 1-hexene in this study, respectively. The reactivity ratios are determined from the Fineman–Ross plot shown in Figure 19. Figure 19 depicts plots obtained at different temperatures and also shows a



**Figure 18** Activation energy of propagation (obtained from each run).



**Table V** Estimates for  $E_p$  from the Different Perturbations

Run No.	$E_p$ (kcal/mol)
Run #1	10.5 ± 0.92
Run #2	11.1 ± 0.36
Run #3	11.1 ± 1.23
Run #4	10.7 ± 1.15

plot of the cumulative results. It is found that the values of  $r_1$  and  $r_2$  are approximately 18.8 and 0.046, respectively. The values do not display a discernible change when increasing the temperature from 62 to 70°C.

### Reaction Rate Order

The least-squares results obtained from step-up and step-down perturbations are shown in Figure 20. The reaction rates were corrected for catalyst decay. The slopes obtained from both step-up and step-down results have values of  $0.24 \pm 0.025$  and  $0.24 \pm 0.048$ , respectively. Therefore, the reaction rate order of ethylene in the presence of 1-hexene is 1.24. This is similar to the reaction rate order obtained for ethylene in the presence of propylene in Part I. The results are consistent with the theory put forth by Karol et al.<sup>17</sup>

## MODEL PREDICTIONS

- Kinetic Scheme

For copolymerization, where there is rate enhancement in the presence of the  $\alpha$ -olefin, a two-site model was proposed to explain the observed kinetics. The model used is the same as the one used to describe ethylene/propylene copolymerization kinetics in Part

I. The elementary reactions in the kinetic scheme are summarized in Table VII. As in Part I, this two-site kinetic scheme is embedded into a comprehensive kinetic model which is available for transition-metal-catalyzed olefin polymerization in the polymerization modeling package POLYRED<sup>TM</sup>.

- Parameter Estimation from POLYRED<sup>TM</sup>

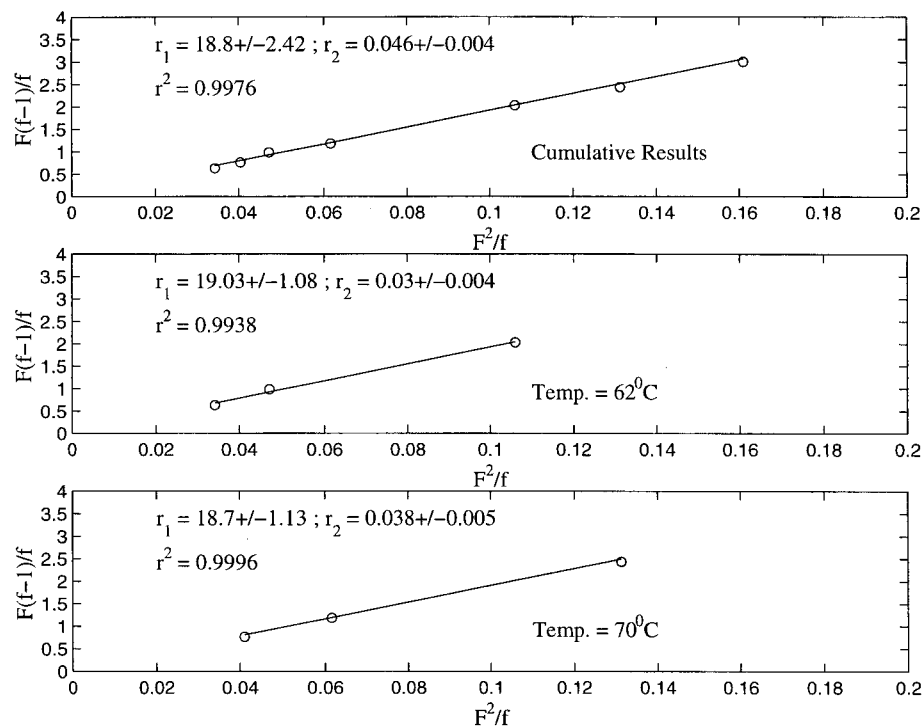
With the consistency of the perturbation techniques having been proved in Part I, average values of  $E_p$  and  $E_d$  obtained from the perturbation methods were used in the current estimation effort. The strategy implemented here is very similar to what was conducted in Part I. A total of five preexponential factors need to be estimated in the proposed kinetic model for ethylene/1-hexene copolymerization. They are associated with the propagation of monomer 1 at both sites  $k_{p,110}^1$  and  $k_{p,110}^2$ , site transformation from 1 to 2 due to the introduction of comonomer (1-hexene)  $k_{tr,0}^{1 \rightarrow 2}$ , and deactivation at both sites  $k_{d,0}^1$  and  $k_{d,0}^2$ . In addition, the activation energy of site transformation is estimated. The centering-point technique<sup>18,19</sup> is implemented in estimating the necessary parameters. The parameters not included in the estimation are the kinetic rate constants of activation of site 1 by the two monomers and the propagation rate constants for 1-hexene at the two sites. When it was found that the values failed to change during estimation calculations, they were excluded from the set of parameters being estimated.

Nevertheless, it needs to be noted that, in terms of sensitivity, modest changes in these parameters do not influence the results; however, order-of-magnitude changes in these default parameters would alter model predictions. The pa-

**Table VI** 1-Hexene Composition in the Polymer

Sample	Temperature (°C)	$C_6$ in Gas	$C_6$ Sorbed	$C_6$ in Polymer
EH-01H-62C	62	0.01	0.32	0.024
EH-02H-62C	62	0.02	0.49	0.042
EH-03H-62C	62	0.03	0.59	0.069
EH-01H-70C	70	0.01	0.29	0.022
EH-02H-70C	70	0.02	0.45	0.039
EH-03H-70C	70	0.03	0.55	0.059
EH-01H-80C	80	0.01	0.25	0.017

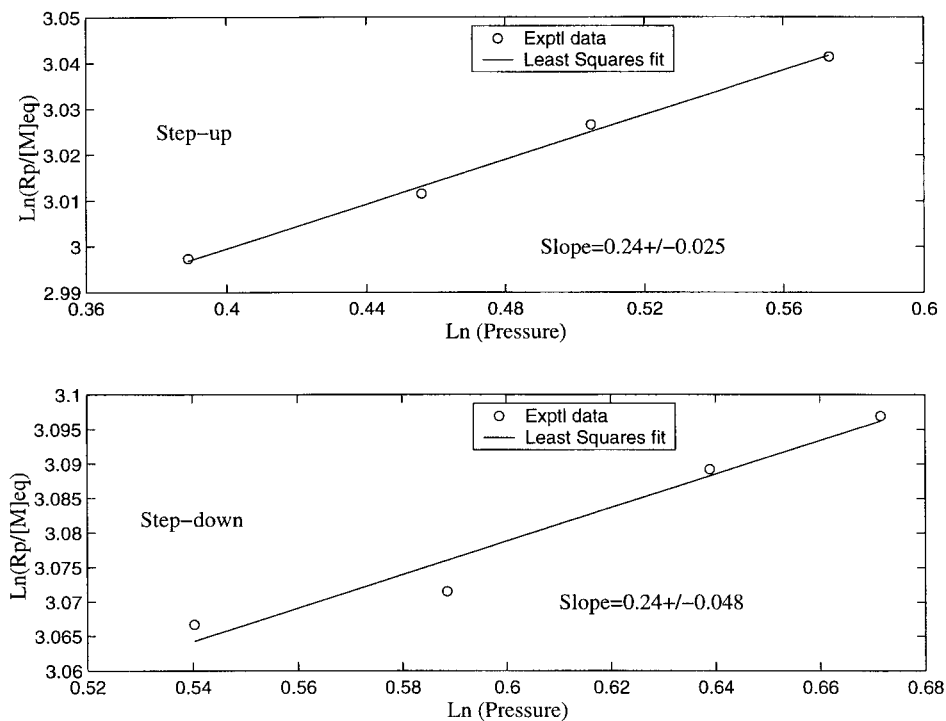
All the data are presented in mol fractions.



**Figure 19** Determination of reactivity ratios using the Fineman–Ross method.

rameters were multiplied by  $C_{pot}$  since the exact site concentration of the catalyst is unknown. To obtain the exact values of the preexponential fac-

tors, the products need to be divided by the site concentration of the catalyst. The value of  $C_{pot}$  used in the POLYRED simulations was 1.04



**Figure 20** Reaction rate order of ethylene (in the presence of 1-hexene).

**Table VII Elementary 2-Site Reaction Rate Model for Ethylene/1-Hexene Copolymerization**

Name	Reaction
Activation	$C_{pot} + M_i \rightarrow C_i^{*,1}$
Propagation	$C_i^{*,k} + M_j \rightarrow C_j^{*,k}$
Deactivation	$C_i^{*,k} \rightarrow C_d + D_n^k$
Site transformation	$C_i^{*,1} + M_2 \rightarrow C^{*,2}$

$k = 1$  or  $2$ ;  $i =$  monomer 1 or 2.

$\times 10^{-4}$ . The relationship between  $C_{pot}$  and  $C^*$  is provided in Table VII. Since the activation energy of propagation for the two monomers was the same, the reactivity ratios obtained are a ratio of the preexponential factors of the propagation rate constants. Hence, they are independent of temperature. Table VIII shows the values obtained for the reactivity ratios following the estimation of the preexponential factors. The values obtained for the reactivity ratios for the two sites differ marginally, but lie within the confidence intervals obtained in Figure 19. Figures 21 and 22 illus-

trate the change in the instantaneous ethylene weight fraction in the polymer and instantaneous  $r_1$  over the entire duration of the reaction. Instantaneous  $r_1$  was calculated from a simplified form of the Mayo equation<sup>13,20,21</sup>:

$$\left(\frac{M_1}{M_2}\right)_{\text{polymer}} = \frac{1}{r_1} \left(\frac{M_1}{M_2}\right)_{\text{sorb}} \quad (29)$$

From Figure 22, it is observed that the change in the instantaneous value of  $r_1$  is very minimal over the entire course of the reaction. This provides a plausible explanation for the reactivity ratios of the two sites being very similar.

The current reactor model in POLYRED<sup>TM</sup> assumes the absence of any monomer diffusion limitations. Since the experiments were not conducted in the region where the onset of diffusional limitations might have been important, data from all the copolymerization experiments were used in the parameter estimation procedure. The results obtained are shown in Table VIII. Note that the set of kinetic parameters estimated

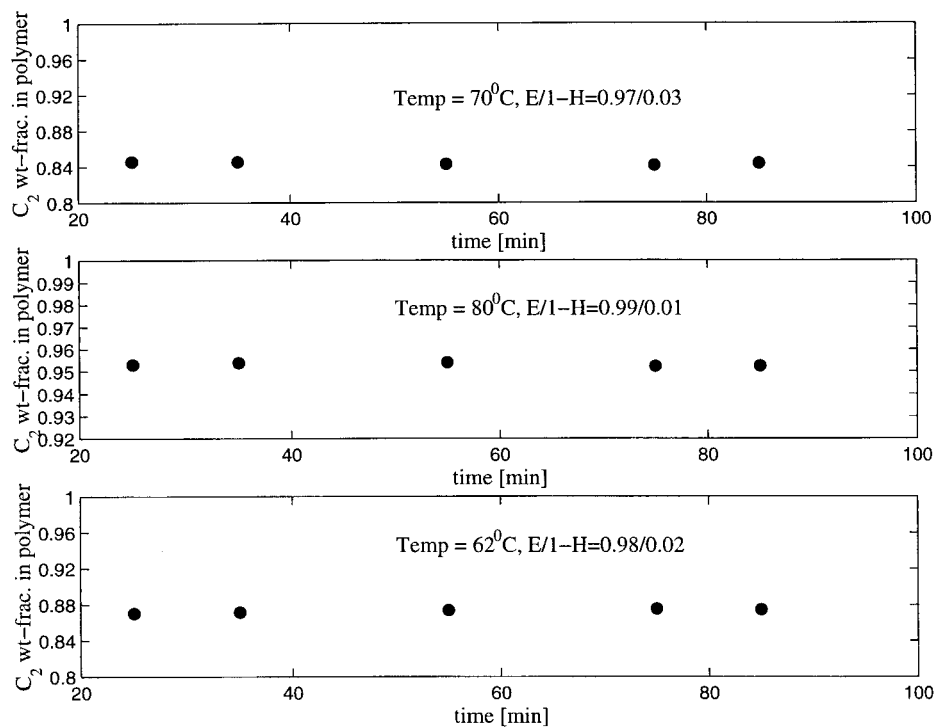
**Table VIII Kinetic Parameters for Copolymerization**

Parameter	Estimated Value		Units
	Site 1	Site 2	
Preexponential Factors			
Site activation, $k_{ao,1}C_{pot}^a$	$1.25 \times 10^3$	—	(cc-amor.polym./gcat.s)
Site activation, $k_{ao,2}C_{pot}^a$	$1.88 \times 10^2$	—	(cc-amor.polym./gcat.s)
Propagation, $k_{po,11}C_{pot}^b$	$4.22 \times 10^8$	$7.48 \times 10^{10}$	(cc-amor.polym./gcat.s)
Propagation, $k_{po,12}C_{pot}^a$	$2.24 \times 10^7$	$4.13 \times 10^9$	(cc-amor.polym./gcat.s)
Propagation, $k_{po,21}C_{pot}^a$	$4.51 \times 10^7$	$1.56 \times 10^8$	(cc-amor.polym./gcat.s)
Propagation, $k_{po,22}C_{pot}^a$	$1.81 \times 10^6$	$6.32 \times 10^6$	(cc-amor.polym./gcat.s)
Site transformation, $k_{tro}^{1 \rightarrow 2}C_{pot}^b$	$1.07 \times 10^2$	—	(cc-amor.polym./gcat.s)
Deactivation, $k_{do}^b$	$2.3 \times 10^5$	$8.24 \times 10^4$	$s^{-1}$
Activation Energies			
Site activation, $E_a^a$	10.0	10.0	kcal/mol
Propagation, $E_p^c$	10.6	10.6	kcal/mol
Site transformation, $E_{tr_{S1 \rightarrow S2}}^b$	13.12	—	kcal/mol
Deactivation, $E_d^c$	13.5	13.5	kcal/mol
Reactivity Ratios			
$r_1$	18.94	18.09	—
$r_2$	0.04	0.04	—

<sup>a</sup> Default value in POLYRED<sup>TM</sup>.

<sup>b</sup> Estimated using POLYRED<sup>TM</sup>.

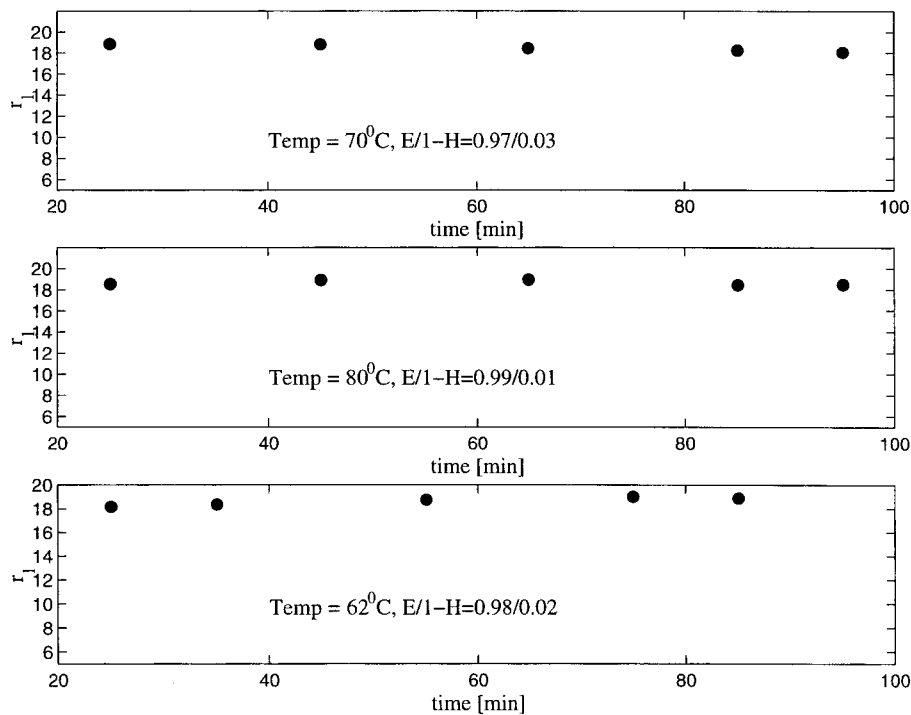
<sup>c</sup> Estimated via online perturbation.



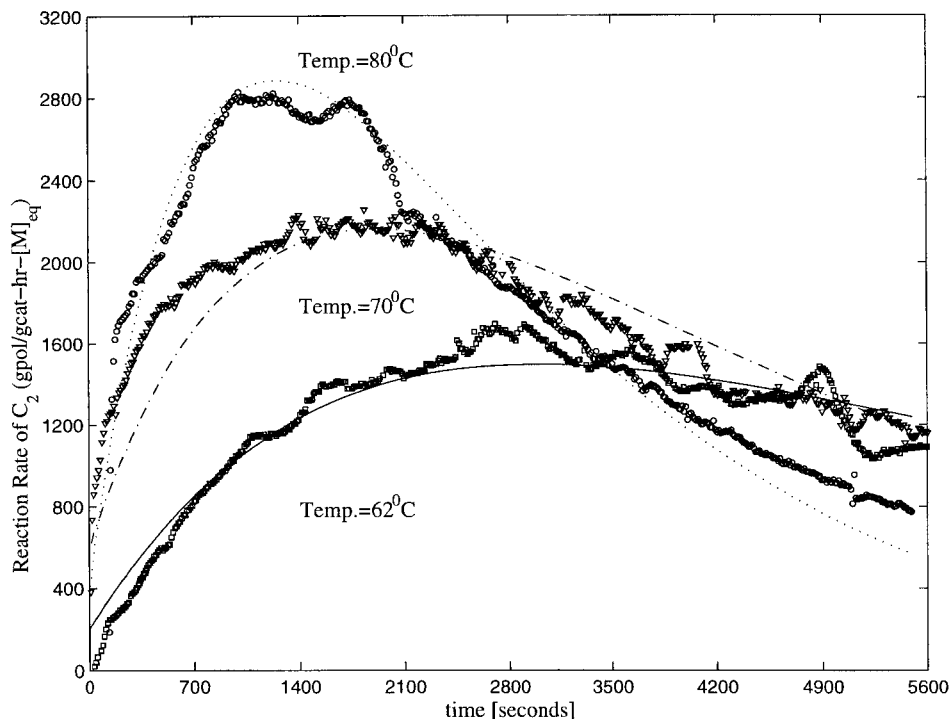
**Figure 21** Change in the weight fraction of ethylene in the polymer versus reaction time.

here is by no means a unique set. However, they are physically plausible and do represent the data well.

- Model Prediction  
 Figures 23–25 show the model predictions and experimental data from the ethylene/1-



**Figure 22**  $r_1$  versus reaction time.



**Figure 23** Comparison of experimental results and model predictions at different temperatures. 1-Hexene: 1%.

hexene copolymerization runs. The kinetics predicted by the model provide a reasonable fit and capture the trends observed in the experiments at 62, 70, and 80°C. Based on the observed consistency between the model predictions and the reaction rate data, it is noted that the reactions were not conducted in the regime where diffusion limitations become important.

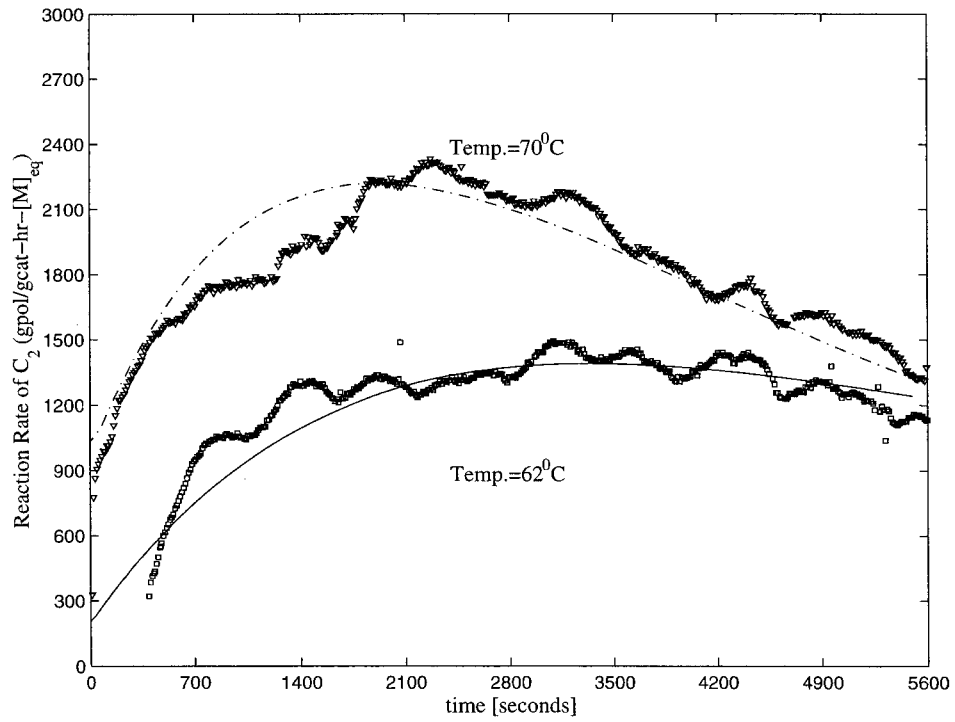
### COMPARISON OF PROPYLENE AND 1-HEXENE AS COMONOMERS

Table IX provides a comparison of the parameters obtained from the two ethylene/comonomer systems using the same supported metallocene catalyst. The estimated parameters for  $E_d$  lie in the same range, while for  $E_p$ , values obtained from ethylene/1-hexene kinetics are slightly lower than those from ethylene/propylene kinetics. The average value used in the parameter estimation procedure for ethylene/1-hexene is about 1.5 kcal/mol less than that used for ethylene/propylene. In both systems, the reactivity ratios were studied as a function of temperature. There were no dis-

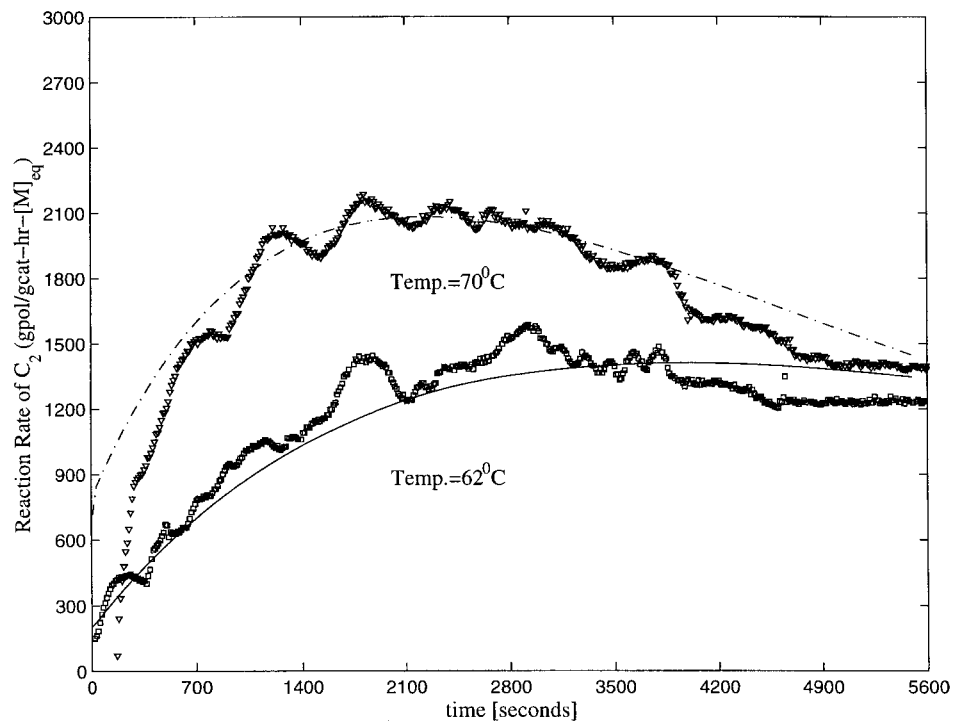
cernible changes in the values of  $r_1$  and  $r_2$  for the ethylene/1-hexene system as the temperature was increased from 62 to 70°C. The value of  $r_2$  is approximately the same for the two systems, while for  $r_1$ , the value for ethylene/1-hexene is higher than that obtained for ethylene/propylene. This is a trend that has been observed in traditional Ziegler–Natta catalysts, where  $r_1$  increases as the  $\alpha$ -olefin becomes heavier.<sup>16</sup> The reaction rate order of ethylene is found to be close to 1 in the presence of the two comonomers. It appears that this is the first investigation where the reaction rate order with respect to ethylene was determined in the presence of two types of comonomers using supported metallocene catalysts.

The trends observed for the temperature and comonomer effects are quite similar for the two systems. But ethylene shows higher reactivity in the presence of propylene as opposed to 1-hexene at similar comonomer-sorbed concentrations.

The monomer consumption rate for ethylene in the presence of the comonomer was defined in eq. (19), whereas  $\beta_1$  was defined in eq. (22). In Figures 11–13, the reaction rates normalized with respect to  $[M]_{eq}$  were plotted as a function of time. Hence, the dependence on the pressure exists



**Figure 24** Comparison of experimental results and model predictions at different temperatures. 1-Hexene: 2%.



**Figure 25** Comparison of experimental results and model predictions at different temperatures. 1-Hexene: 3%.

only if the reaction rate order with respect to the particular monomer is different from 1. Our copolymerization results showed that the reaction rate order with respect to ethylene is close to 1 in the presence of the comonomer. Let us define  $R_p^{ph}$  as the ratio of this normalized, intrinsic ethylene polymerization rate in the presence of propylene to the rate obtained in the presence of 1-hexene at the same sorbed comonomer concentrations and approximately the same ethylene-sorbed concentration. Using the results of comonomer-sorption calculations in Table III, the experimental results in Table X show that  $R_p^{ph}$  varies anywhere between 1.04 and 2.07 for very similar sorbed comonomer concentrations. Thus, over a wide range of conditions, the lower  $\alpha$ -olefin leads to higher ethylene polymerization rates. This is likely due to an intrinsically faster rate of propagation for lower  $\alpha$ -olefins similar to that found for Ziegler–Natta catalysts.<sup>16</sup>

## CONCLUSIONS

The comonomer and temperature effects observed in ethylene/1-hexene kinetics were found to be qualitatively similar to that observed for ethylene–propylene. The reactivity for ethylene, in the presence of propylene, was found to be higher than what was observed in the presence of 1-hexene.  $E_p$  and  $E_d$  were obtained from temperature-perturbation reactions.  $E_d$  did lie in the range of values obtained for the ethylene–propylene system, while the value of  $E_p$  was a little lower than was the corresponding set of values obtained for ethylene–propylene copolymerization. From the obtained reactivity ratios, it was found that  $r_2$  was approximately the same for the two systems, while  $r_1$  for ethylene/1-hexene was larger than was the corresponding value for ethylene/pro-

**Table IX Comparison of Results from Ethylene/Propylene and Ethylene/1-Hexene Kinetics**

	Ethylene/ 1-Hexene	Ethylene– Propylene
$E_p$	10.4–11.2	11.5–12.5
$E_d$	13.3–14.0	13.0–14.0
Reactivity ratios		
$r_1$	18.0–19.0	14.0–15.0
$r_2$	0.03–0.05	0.04–0.05
Reaction rate order	1.24	1.17–1.19

**Table X Ratios of Normalized Ethylene Reaction Rates Using Propylene Versus 1-Hexene**

Temperature	Ethylene/ 1-Hexene (Gas-phase composition)	Ethylene– Propylene (Gas-phase composition)	$R_p^{ph}$
62°C	1%	10%	1.04
62°C	2%	20%	1.29
62°C	3%	30%	1.52
70°C	1%	10%	1.57
70°C	2%	20%	1.64
70°C	3%	30%	1.54
80°C	1%	10%	2.07

pylene. The reaction rate order with respect to ethylene was found to be close to 1 in the presence of 1-hexene.

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