Kinetic Study of Olefin Polymerization with a Supported Metallocene Catalyst. IV. Comparison of Bridged and Unbridged Catalyst in Gas Phase

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ABSTRACT: A kinetic study of ethylene/1-hexene (E/1-H) copolymerization is conducted with a supported bridged 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. On-line perturbation techniques are implemented to determine key kinetic parameters such as the activation energies for propagation and catalyst deactivation. A comparison of the kinetic parameters and behavior is made between the bridged and a previously studied unbridged catalyst. Finally, a two-site model is proposed to explain the observed kinetic behavior with changing reaction temperature and comonomer concentration. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 81: 1451–1459, 2001

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

INTRODUCTION

The advent of Group 4 metallocenes has facilitated the possibility to closely control the properties of the polymer being produced. Some of the benefits include[1]: (i) Narrow distribution in molecular properties, (ii) controlling polymer properties by modifying the ligand structure of the catalysts, and (iii) with this flexibility, being able to establish a correlation between the catalyst structure and polymer properties. LLDPE (Linear Low Density Polyethylene) is the fastest growing class of ethylene-based polymers. It has registered an annual growth rate of about 10% over the past 10 years.[2] The introduction of short branches on the linear chains enhances the processability proper-

ties while maintaining to some degree the toughness exhibited by HDPE (High Density Polyethylene). 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.

This is the fourth part in the series of articles on the kinetics of supported metallocenes. In Part I,[3] a kinetic study on ethylene homopolymerization and ethylene–propylene copolymerization in a laboratory scale gas phase reactor was conducted using an unbridged zirconocene on a silica support. The temperature and comonomer effects were investigated and perturbation techniques were implemented to estimate important kinetic parameters. Using POLYRED™, models were proposed and the predictions compared well with the experimental data under the various reaction conditions. Hence, a kinetic model adequate for continuous reactor design and scale-up was
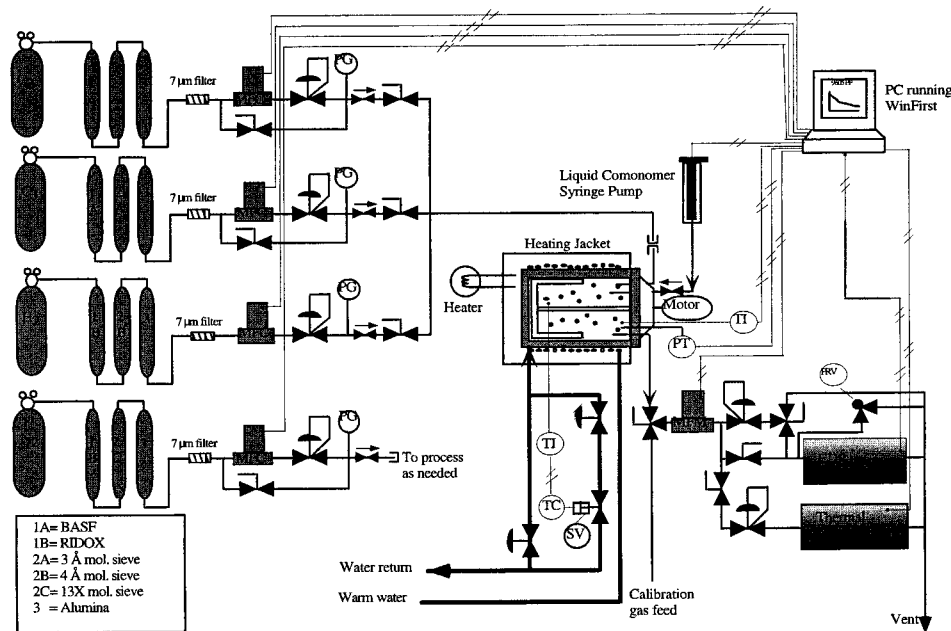

Figure 1   Reactor system.

achieved. In Part II,[4] ethylene–1-hexene copolymerization in the gas phase was investigated with the same catalyst used in Part I. Using a similar experimental methodology as in Part I, a comparison of the kinetic behavior and parameters of the two ethylene–comonomer systems was possible. In Part III,[5] the behavior of the unbridged catalyst was compared in different reactor systems. The kinetic parameters obtained from the gas phase reactor in Part I were used in a slurry reactor model to predict the behavior under various reaction conditions. The model predictions compared favorably to the experimental data obtained in the slurry reactor.

The SBR (stirred bed reactor) system developed in our laboratory[6] is designed to study the gas phase kinetics of ethylene–comonomer systems. It has been shown that by virtue of controlling the comonomer composition, detailed investigations into the kinetics of traditional Ziegler-Natta[7–9] and metallocene catalysts are possible.[3,4] The main objective of this study is the comparison of the kinetic behavior and parameters between the unbridged and bridged catalysts. To that extent, the experimental plan for the bridged metallocene can be outlined as:

1. Carry out an experimental design to determine temperature/comonomer effects. This facilitates the comparison of kinetic behavior under similar reaction conditions.

2. Estimate kinetic parameters (E_d, E_p, reactivity ratios). This provides (i) an opportunity to test the effectiveness of the previously established perturbation techniques[3,4] on different catalysts, and (ii) a comparison of the kinetic parameters.

3. Model the kinetic data. This tests the validity of the model proposed for this particular catalyst.

The results are compared to those obtained for ethylene/1-hexene copolymerization with the unbridged supported zirconocene in part II.[4]

EXPERIMENTAL DETAILS

The reactor system[6] used has been well described in previous investigations with supported metallocenes and traditional Ziegler-Natta catalysts.[7–9] 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 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 comonomer composition because 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
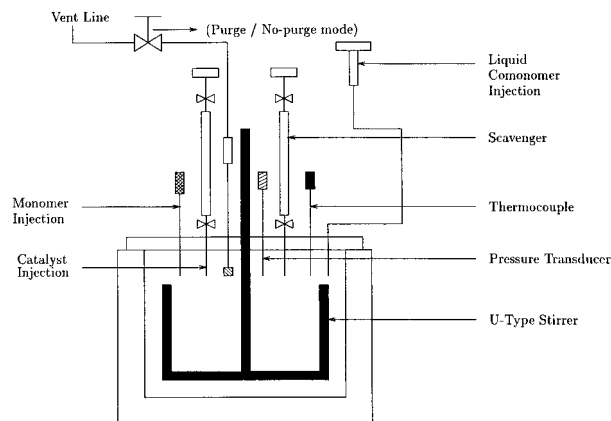
Figure 2 Reactor schematic.

Figure 4 Reproducibility obtained with kinetic results from the bridged catalyst ($T = 70°C$; $P = 52$ psia).

valve is open, thereby facilitating effective control of 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-controled 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. It has been shown previously that the 1-hexene composition can be controlled effectively at different levels.[4]

Experimental—Procedure and Data Analysis

Experimental Procedure

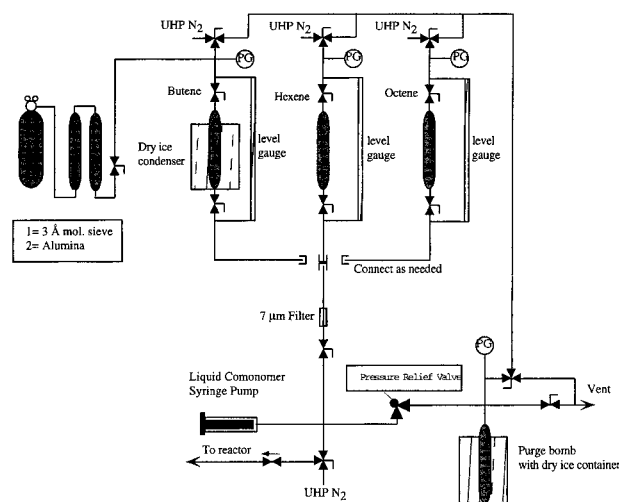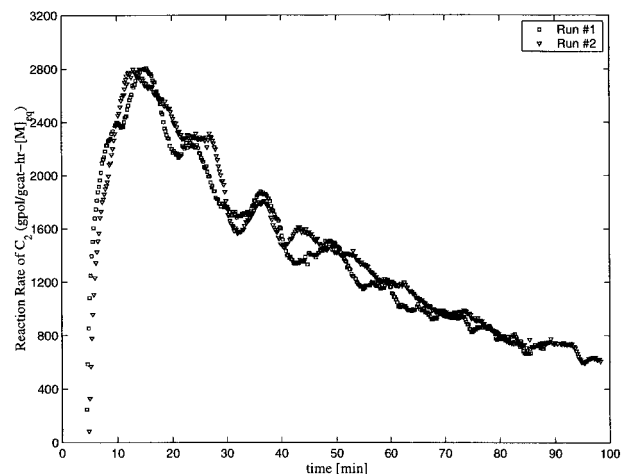The procedure implemented for conducting reactions with the bridged catalyst is not very differ-

ent from that of the unbridged catalyst.[4] The only important difference from the previous procedure was the level of TEA introduced into the reactor during the scavenging procedure was reduced by about 10–20%. Figure 4 illustrates the reproducibility of results obtained for this particular catalyst.

Data Representation

The kinetic data are presented as the intrinsic polymerization rate of monomers:

$$\frac{g \text{ Polymer}}{\text{gcat, h}, [M_i]_{\text{eq}}}.$$

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 have been normalized by the monomer concentration in the amorphous polymer ($[M_i]_{\text{eq}}$) using the solubility equation proposed by Hutchinson et al.[10] It has the units of

$$\frac{\text{mol}}{\text{cc-amorphous polymer}}$$

and is calculated by the following equation,

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

Figure 3 Comonomer feed system.

Table I 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	—	—
343	52.0	0.01	0.008	0.005
353	52.0	0.01	—	—

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[11]:

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

where T_{ci} is the critical temperature of species i, and T is the reaction temperature. In the previous study of ethylene/1-hexene copolymerization with the unbridged catalyst,[4] it was shown that for heavier comonomers like 1-hexene, there is an upper limit on the pressure above which deviations from Henry's Law are observed. As with the reactions with the unbridged catalyst,[4] the reaction pressure in the current study was maintained at 52 psia for the different kinetic experiments. In this way, Henry's Law would be appropriate for determining the concentrations in the amorphous polymer at the different reaction conditions.

Experiments Performed

As in the previous studies, experiments were carried out at three different temperatures and three levels of comonomer composition. In addition, temperature perturbation experiments were used to estimate activation energies. The details are given in Tables I and II.

**Table II Perturbation Experiments Conducted**

Run Number	Pert. Type	Com. Comp.
Run #1	Step-up	1.0%
Run #2	Step-up	1.0%
Run #3	Step-up	1.0%
Run #4	Step-down	0.8%
Run #5	Step-down	1.4%
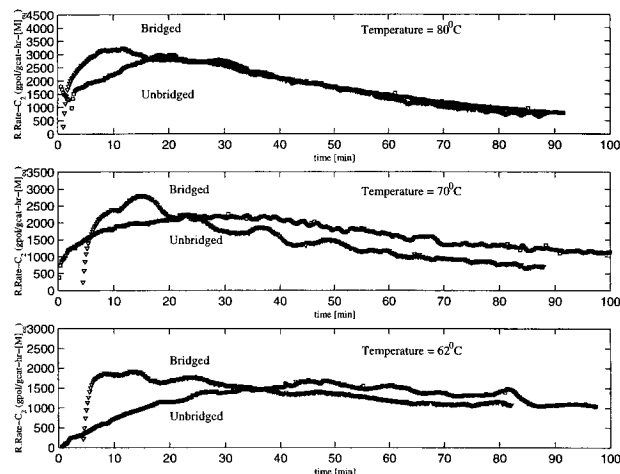
Figure 5 Comparison of kinetic behavior between the two catalysts (1-hexene gas phase comp.: 1%).

Temperature/Comonomer Effects

Figures 5 and 6 depict the temperature and comonomer effects observed for the bridged catalyst.

1. Temperature effects—comparison of kinetic behavior between the two catalysts. Figure 5 compares the kinetic rate profiles of the two catalysts at three different reaction temperatures. The reaction rate peak magnitude obtained with the bridged catalyst is higher compared to the unbridged catalyst, and the bridged catalyst has a steeper gradient of decay at the three reaction temperatures. The bridged catalyst also displays decay-type kinetics at the three reaction temperatures, while the un-
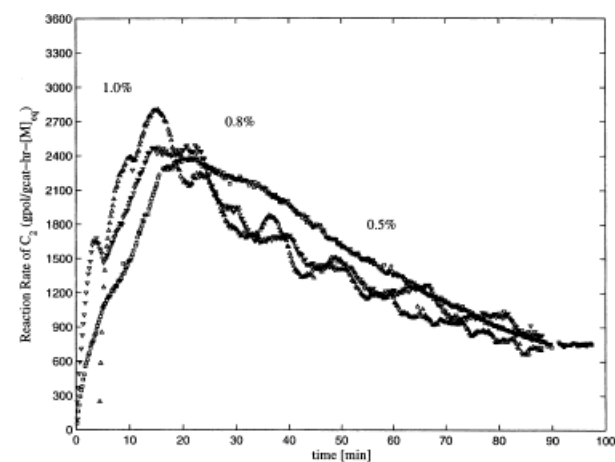
Figure 6 Comonomer effects observed with the bridged metallocene ($T = 70°C$).

bridged catalyst shows a transition from build up to decay-type as the reaction temperature is raised from 62 to 80°C.
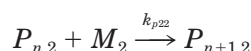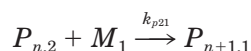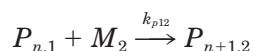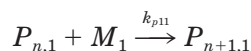
2. Comonomer effects—Figure 6 depicts the change in the kinetic rate profiles as the comonomer concentration is increased from 0.5 to 1.0%. Note that varying the comonomer gas phase composition results in only a small change in activity; however, increasing the comonomer gas phase composition decreases the induction time associated with reaching the peak and increases peak magnitude. As shown below, the bridged catalyst was much more effective in incorporating comonomer than the un-bridged catalyst. In fact, the maximum possible level of comonomer composition in the gas phase that was possible, such that sticking problems could be prevented, was about 1.0%. This observation seems to agree with what other researchers[12] have found when comparing bridged and unbridged catalysts.

Estimation of Kinetic Parameters

In the present gas phase system, a variety of perturbation techniques[3,4,7,9] have been 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 are carried out to determine the parameters for ethylene/1-hexene kinetics. The parameters obtained for this particular catalyst are then compared to those obtained from the unbridged catalyst.

The 1-hexene gas phase composition was maintained at different levels for the different perturbations (see Table II). A detailed procedure in analyzing the data from the perturbation techniques has already been presented.[3]

The copolymerization rate expression is derived from the following equations:

$$P_{n,1} + M_1 \xrightarrow{k_{p11}} P_{n+1,1}$$

$$P_{n,1} + M_2 \xrightarrow{k_{p12}} P_{n+1,2}$$

$$P_{n,2} + M_1 \xrightarrow{k_{p21}} P_{n+1,1}$$

$$P_{n,2} + M_2 \xrightarrow{k_{p22}} P_{n+1,2}$$

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

$$Rp\left[\frac{g\ M_{1\ \text{converted}}}{\text{gCat, h}}\right] = A_1 k_{p,11} C_1^* \beta_1 [M_1]_{\text{eq}} \quad (1)$$

$$Rp\left[\frac{g\ M_{2\ \text{converted}}}{\text{gCat, h}}\right] = A_2 k_{p,22} C_2^* \beta_2 [M_2]_{\text{eq}} \quad (2)$$

$$\frac{dC^*}{dt} = -k_d C^* t \quad (3)$$

where 1 and 2 correspond to ethylene and 1-hexene, respectively. $[M_i]_{\text{eq}}$ [=] (mol/L-amorphous polym.) is the concentration of monomer i at the catalyst site, A_i(conversion factor) $= MW_i*3.6$, k_{pij} [=] (cc-amorphous poly./mol-act $\cdot$ sites $\cdot$ sec) and C_i^* denotes the concentration of active sites with end group i. C^* $(=\Sigma_i C_i^*)$ is the total concentration of active sites. Parameters β_1 and β_2 are defined as

$$\beta_1 = 1 + \frac{1}{r_1}\frac{[M_2]_{\text{eq}}}{[M_1]_{\text{eq}}} \quad (4)$$

$$\beta_2 = 1 + \frac{1}{r_2}\frac{[M_1]_{\text{eq}}}{[M_2]_{\text{eq}}} \quad (5)$$

Here, r_1 and r_2 are reactivity ratios:

$$r_1 = \frac{k_{p,11}}{k_{p,12}} \qquad r_2 = \frac{k_{p,22}}{k_{p,21}} \quad (6)$$

In arriving at the expressions for β_1 and β_2, the following quasi-steady state assumption was used.

$$k_{p,12}C_1^*[M_2]_{\text{eq}} = k_{p,21}C_2^*[M_1]_{\text{eq}} \quad (7)$$

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 previous kinetic studies.[3,4] In the current study, step-up and step-down temperature perturbations are implemented.

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
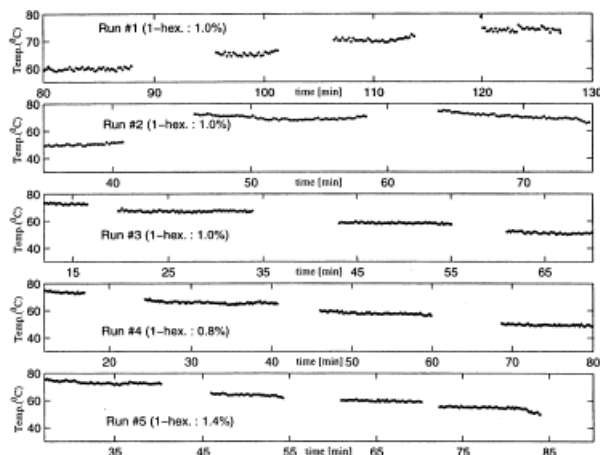
Figure 7 Temperature perturbations implemented (bridged catalyst).

Figure 9 Determination of E_p.

15–20 min. Figures 7 and 8 show the temperature perturbations and the resulting reaction rate responses obtained with this particular catalyst. The accompanying least-squares Arrhenius plots obtained from the experimental data are shown in Figures 9 and 10. Table III summarizes the values obtained for E_p and E_d from the various perturbation reactions.

Figure 11 shows the Fineman-Ross plot obtained to determine the reactivity ratios for this particular catalyst. The comonomer content in the polymer was determined by NMR.

Comparison of Kinetic Behavior and Parameters between Catalysts

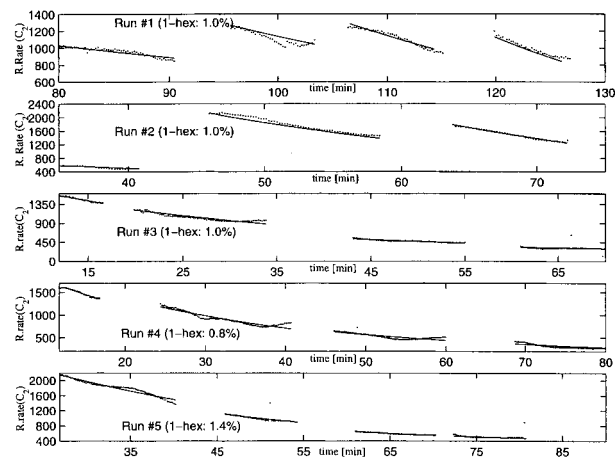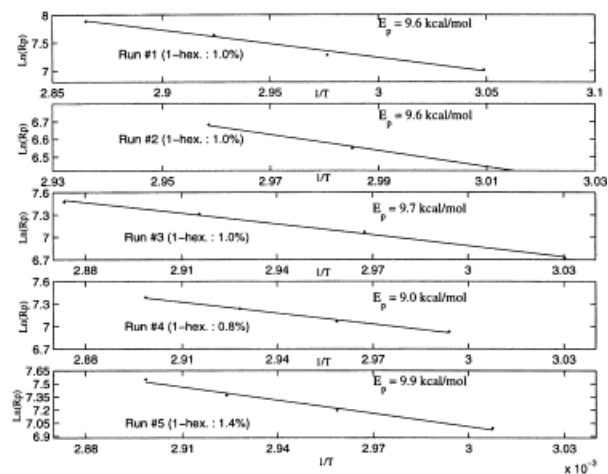Table IV shows a comparison of the different kinetic parameters of the two catalysts.

1. Reactivity ratios—the estimated reactivity ratios quantify the fact that the bridged catalyst incorporates the comonomer more efficiently than the unbridged catalyst. The experimental comonomer incorporation capability is shown in Figure 12 along with the theoretical predictions for the two catalysts. All the experimental data over different temperature and comonomer levels have been included. Temperature effects on r_1 and r_2 are expected to be small.

2. Activation energies, E_p and E_d—the slightly lower range of values obtained for E_p could explain the higher peak values obtained with the bridged catalyst. The marginally lower range of values obtained
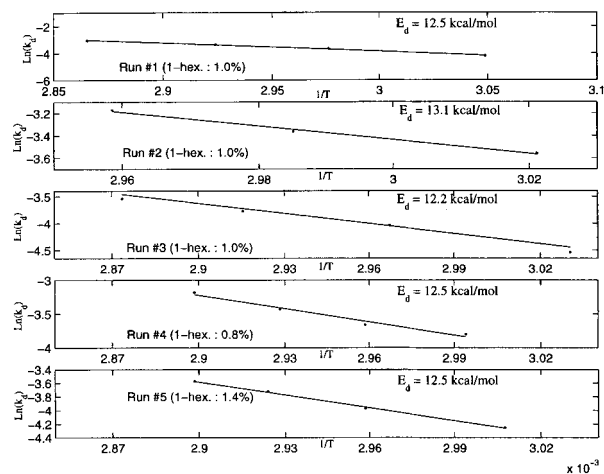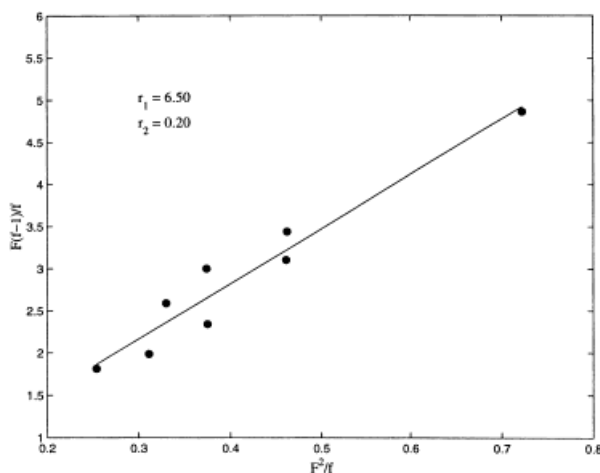

Figure 8 Reaction rate response to the temperature perturbations (−: model; .: experimental data).

Figure 10 Determination of E_d.

Table III   Estimates for E_d and E_p from the Different Perturbations for the Bridged Catalyst

Run Number	Pert. Type	Com. Comp.	E_d (kcal/mol)	E_p (kcal/mol)
Run #1	Step-up	1.0%	12.5 ± 1.03	9.6 ± 0.60
Run #2	Step-up	1.0%	13.1 ± 1.60	9.6 ± 0.53
Run #3	Step-up	1.0%	12.2 ± 0.77	9.7 ± 0.85
Run #4	Step-down	0.8%	12.5 ± 0.43	9.0 ± 0.43
Run #5	Step-down	1.4%	12.5 ± 1.12	9.9 ± 0.56

Table IV   Comparison of Kinetic Parameters between the Two Catalysts

	Bridged Catalyst	Unbridged Catalyst
E_p (kcal/mol)	9.0–10.0	10.4–11.2
E_d (kcal/mol)	12.0–13.5	13.3–14.0
r_1	6.5	18.0–19.0
r_2	0.20	0.03–0.05

for E_d would explain the steeper gradient of decay obtained at the different reaction temperatures for the bridged catalyst.

Model Predictions/Parameter Estimation

The kinetic scheme used to describe the observed the temperature/comonomer effects is shown in Table V. The model consists of two sites, with the second site being formed by a site transformation reaction in the presence of the comonomer. Table VI shows the set of parameters that have been estimated using latest POLYRED™, which allows "known" parameters such as the reactivity ratios obtained from the polymer analysis to be fixed. This results in fewer parameters having to be estimated since k_{p12} and k_{p21} are k_{p11}/r_1 and k_{p22}/r_2, respectively. The results obtained for E_p and E_d from the perturbation techniques were

used in the parameter estimation procedure. The value of C_{pot} used in the simulations was 1.38 $\times 10^{-4}$.

Figures 13 and 14 show comparisons of model predictions with experimental data. The actual reactor temperature profiles from each experiment including fluctuations about the nominal value have been used in the simulations for the model predictions (see Figs. 13 and 14). The proposed model is quite appropriate for the bridged catalyst, as it has captured the kinetic features associated with changing comonomer composition and temperature.

CONCLUSIONS

Employing an experimental plan similar to that of the unbridged metallocene, the kinetics of a

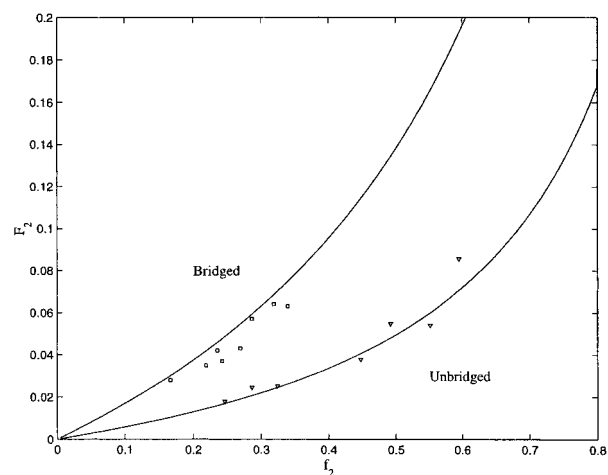**Figure 11**   Determination of reactivity ratios (bridged catalyst).

Figure 12   Comparison of comonomer incorporation between the two catalysts; f_2: mol fraction of 1-hexene sorbed in polymer; F_2: mol fraction of 1-hexene incorporated into the polymer.
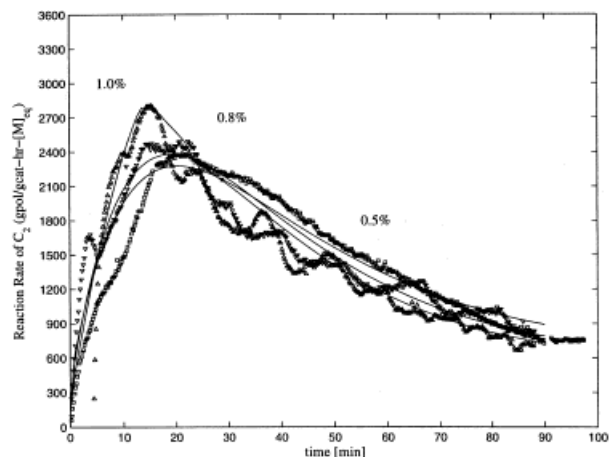
Table V   Elementary Two-Site Reaction Rate Model for Ethylene/1-Hexene Copolymerization

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

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

Figure 13   Comparison of model predictions with experimental data for changing comonomer concentrations ($T = 70°C$).

bridged metallocene were analyzed. Both comonomer and temperature effects were studied. The peak in the reaction rate profile appears earlier, and the peak magnitude is larger for the bridged catalyst compared to the unbridged catalyst. The cumulative activity over the reaction time is approximately the same for the two catalysts.

On-line temperature perturbation techniques were used to determine E_p and E_d. The values for E_p and E_d were lower for the bridged catalyst compared to the unbridged catalyst. NMR was used to determine comonomer content. Based on this, reactivity ratios were determined. The bridged catalyst showed significantly higher comonomer incorporation compared to the unbridged catalyst, and this was reflected in the reactivity ratios estimated. Finally, a proposed two-site model was able to

Table VI   Kinetic Parameters for Copolymerization-Bridged Catalyst

Parameter	Estimated Value		Units
	Site 1	Site 2	
Preexponential Factors			
Site activation, $k_{\text{ao},1}C_{\text{pot}}$[a]	4.53×10^2	—	(cc-amor · poly./g · cat s)
Site activation, $k_{\text{ao},2}C_{\text{pot}}$[a]	7.24×10^2	—	(cc-amor · poly./g · cat s)
Propagation, $k_{\text{po},11}C_{\text{pot}}$[a]	1.36×10^8	2.88×10^{11}	(cc-amor · poly./g · cat s)
Propagation, $k_{\text{po},12}C_{\text{pot}}$[a]	2.03×10^7	4.19×10^{10}	(cc-amor · poly./g · cat s)
Propagation, $k_{\text{po},21}C_{\text{pot}}$[a]	1.23×10^{10}	1.97×10^9	(cc-amor · poly./g · cat s)
Propagation, $k_{\text{po},22}C_{\text{pot}}$[a]	2.46×10^9	3.94×10^8	(cc-amor · poly./g · cat s)
Site transformation, $k_{\text{tro}}^{1 \rightarrow 2}C_{\text{pot}}$[a]	6.46×10^1	—	(cc-amor · poly./g · cat s)
Deactivation, k_{do}[a]	1.053×10^5	1.50×10^2	s^{-1}
Activation Energies			
Site activation, E_a[b]	9.0	9.0	kcal/mol
Propagation, E_p[c]	9.9	9.9	kcal/mol
Site transformation, $E_{\text{tr}_{\text{S1} \rightarrow \text{S2}}}$[a]	10.52	—	kcal/mol
Deactivation, E_d[c]	12.5	12.5	kcal/mol
Reactivity Ratios			
r_1[d]	6.53	6.53	—
r_2[d]	0.20	0.20	—

[a] Estimated using POLYRED™.
[b] Default value in POLYRED™.
[c] Estimated via on-line perturbation.
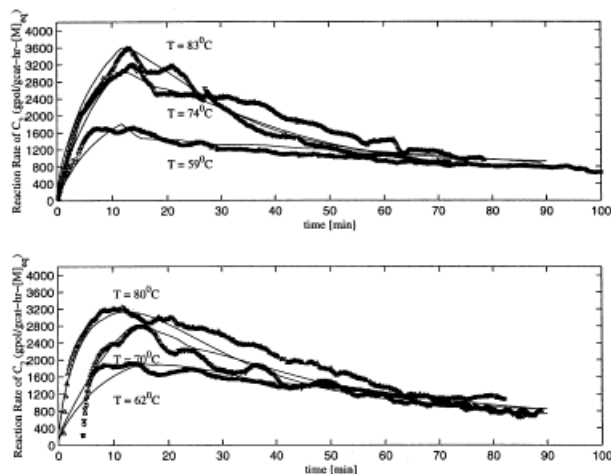[d] Estimated via polymer analysis.

Figure 14 Comparison of model predictions with experimental data at different reaction temperatures (1-hexene gas phase comp.: 1%).

capture the trends observed experimentally with changing temperature and comonomer composition in the reactor.

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