

Fractal Approach for Modeling the Morphology Evolution of Olefin Polymerization with Heterogeneous Catalysts

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ABSTRACT: Fractal theory and methodology were used to investigate the morphology of titanium–magnesium-supported polyethylene catalysts and their relevant polymer particles. Through an analysis of the submicrostructures using scanning electron microscopy images, the surface fractal dimensions of the related particles were estimated with the box-counting method. With consideration given to the fact that the growth process of a polymer is an evolving fractal process, which is controlled on the one hand by the initial conditions, including the initial fractal dimensions of the catalysts and the initial reaction conditions, and on the other hand by the previous morphology characteristics of the system, a novel polymerization fractal growth model

was constructed. The simulation results showed good agreement with the experiment data. Moreover, the morphology evolution with the prepolymerization technique was predicted, and it was suggested that the duration of polymerization was 10–30 min. It was proven that the use of the surface fractal dimension as an important parameter describing the surface morphologies of the particles, either of catalysts or polymers, was real and effective. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 1463–1470, 2003

Key words: modeling; morphology; Ziegler–Natta polymerization

INTRODUCTION

Since the discovery of the titanium-based transition-metal catalysts known as Ziegler–Natta catalysts in the 1950s, significant progress has been made both in industrial α -olefin polymerization processes and in coordination polymerization theory. It is well known that for olefin polymerizations catalyzed by heterogeneous supported catalysts, the morphology of the polymer particle is a replica of the original catalyst particle, and so the morphology of the catalysts plays an important role in the growth of the polymers and their final morphology, which directly influences the properties of the polymers. Although many investigations have already been made of the particulate morphology of polyolefin catalysts and polymers, most of them concern only the phenomena and analyze them with respect to their quality.

Moreover, many polymerization models have been developed, such as the solid pore model,¹ the polymeric core model,² the polymeric flow model,^{3–5} the multigrain model,^{6,7} the improved multigrain model,^{8,9} and the multiactive center model.^{10,11} Of these models, the multigrain model is relatively close to the

reality of particle growth and has widely been accepted. It can explain the deactivation phenomena very well and can also predict the molecular weight distribution; describing the particulate morphology, however, it is weak quantitatively. Therefore, even though the representation and simulation of the polyolefin process have received considerable attention over the past 50 years, a numerical approach for predicting the interrelationship of the morphology structure and the polymerization process has yet to be developed; this is the motivation for the work presented here. Considering the fact of replica phenomena, we attempted to introduce the fractal point of view to construct a particle growth model.

Fractal objects are self-similar structures in which increasing magnifications reveal similar features on scales of different lengths.¹² A large number of natural and processed materials have been shown to have either fractal surfaces or fractal pore distributions. Since it was first introduced into the field of catalysts in 1983 by Pfeifer and Avnir,¹³ the concept of the fractal has received significant consideration from chemists and chemical engineers. Using a fractal subset, Gutfraind and Sheintuch¹⁴ successfully predicted the diffusion and reaction behaviors. Meanwhile, Giona¹⁵ applied a diffusion-limited aggregation fractal growth model to the study of the gas–solid first-order reaction. Later, Coppens and Froment¹⁶ proposed a fractal pore-net model to modify the transfer equations. Rigby and Gladden¹⁷ used cluster–cluster ag-

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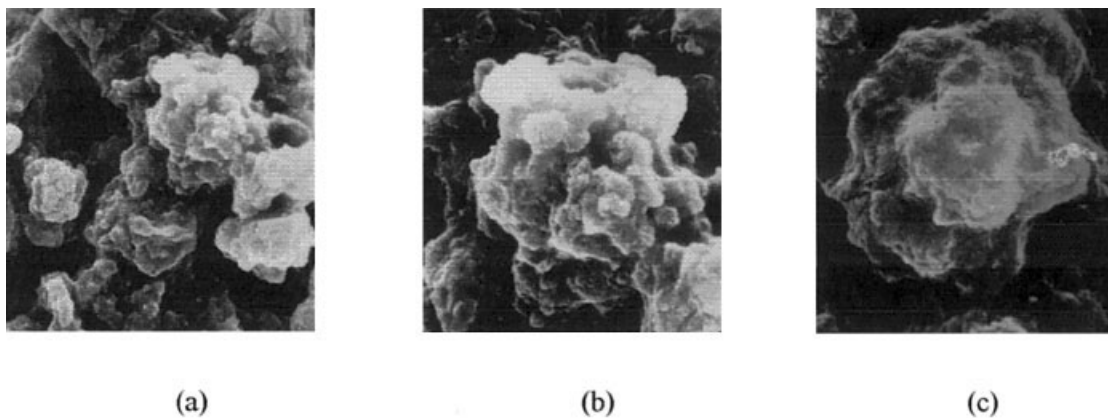


Figure 1 SEM images of the titanium–magnesium-supported catalyst at different magnifications: (a) 5000 \times , (b) 10,000 \times , and (c) 20,000 \times .

gregate structures to describe porous media and performed numerical simulations. Khorasheh, Khalede, and Grey¹⁸ simulated the diffusion process of a fractal Koch curve of reactant molecules of different sizes. In summary, most of the fractal models directed toward the formation of a fractal structure, in which a certain kind of fractal growth method is first determined, are not suitable for the simulation of olefin polymerization process, in which both physical and chemical fractal processes exist.

For the quantitative description of a fractal system, the fractal dimension should be introduced. Experimental determinations of the fractal dimensions have been obtained with scanning electron microscopy (SEM),¹⁹ small-angle X-ray scattering,^{20,21} adsorption,^{13,22} mercury porosimetry,^{23,24} magic-angle-spinning ²⁹Si NMR,²⁵ and nuclear magnetic relaxation of a fluid in a porous medium. In this study, SEM was used to measure the fractal dimensions of porous pellets, and an advanced box-counting method was developed to estimate the fractal dimensions from the SEM images.

FRACTAL CHARACTERISTICS OF POLYMERIZATION

The inner surfaces of the catalysts and their polymers are so rough and irregular that they cannot properly be described with two-dimensional characteristics, which are used in most traditional polymerization models. Comparing SEM images of titanium–magnesium-supported catalysts with different scales (Fig. 1), we find that the irregularities are similar: they are aggregated with a hierarchical structure from primitive granules, and this means fractal characteristics. Therefore, the fractal dimension can be used to describe the surface morphology quantitatively.

The same surface characteristics are found for the catalyst supports and the polymers. Moreover, comparing the morphology of the catalyst with that of its support and polymers (Fig. 2), we see that they are very similar, and this demonstrates the duplicate phenomena of morphology from supports to polymers. As a result, during heterogeneous catalyzed olefin polymerizations, both the particle morphology and

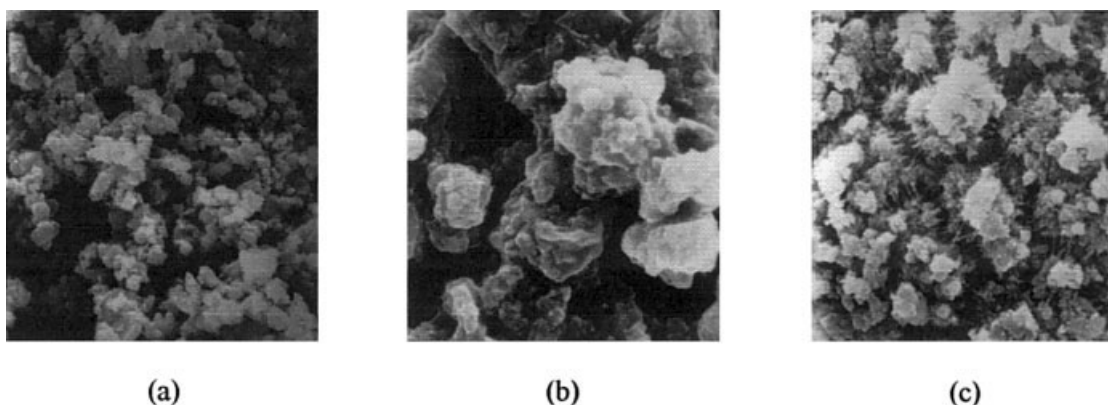


Figure 2 SEM images of the catalyst, its support, and the polymer at 5000 \times : (a) the Mg(OEt)₂ support, (b) the catalyst, and (c) the polymer.

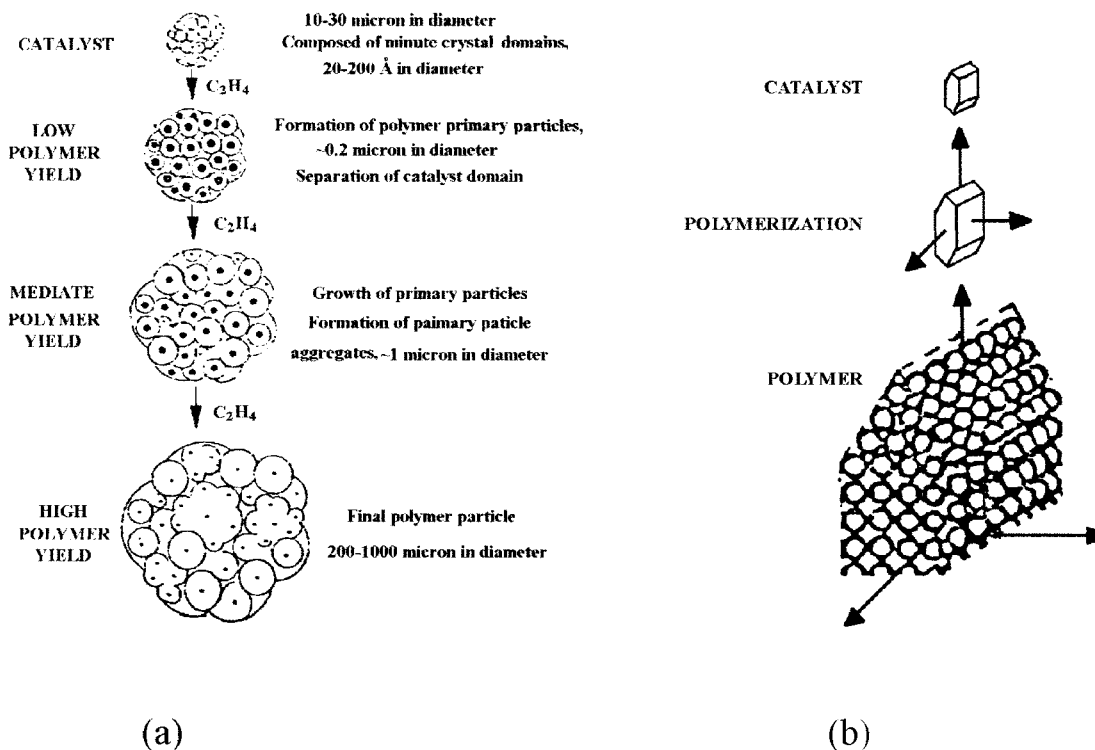


Figure 3 Catalyst duplication process: (a) particle morphology and (b) particle aggregation.

aggregation mode are duplicated, as shown in Figure 3.

CONSTRUCTION OF THE POLYMERIZATION FRACTAL MODEL

For olefin polymerizations catalyzed by heterogeneous supported catalysts, one of the most unique features is the breakup of the solid catalyst particles,^{26,27} so that active catalytic sites, which are mostly located in the inner pore surface, would be exposed to the bulk fluid by the disintegration of the original catalyst, and this would result in the enhancement of catalytic activity. Consequently, the entire olefin polymerization, from catalyst grains to polymer particles, includes a series of processes (not only propagation, transfer and accumulation, as for usual polymerizations, but also the breakup of particles). In the polymerization fractal model, such a process is suggested as a fractal evolution, which is performed in two ways: first, the fluctuation of the microcritical energy of the system is fractal-similar, and second, the morphology of the changing particles is fractal-similar. Figure 4 gives of the evolution of both at active site A.

With the diffusion of monomer C_2H_4 to the inner surfaces of catalysts, the reaction and chain propagation can be realized at active sites; meanwhile, the microenergy is increased until an energy barrier is overcome; this means a breakup of the particles and the exposure of new active sites. Then, the morphol-

ogy transfer between old and new substances is achieved. This microprocess is repeated until the end of the polymerization.

It is clear that the fluctuations of microenergy depend only on the system itself. It is controlled on the one hand by the initial conditions, which include the initial fractal dimension of the catalysts (D_{f0}) and the initial reaction condition [reaction temperature (T) and monomer concentration (M_b)], and on the other hand by the previous morphology characteristics of the system, which are described as inertial terms in the fol-

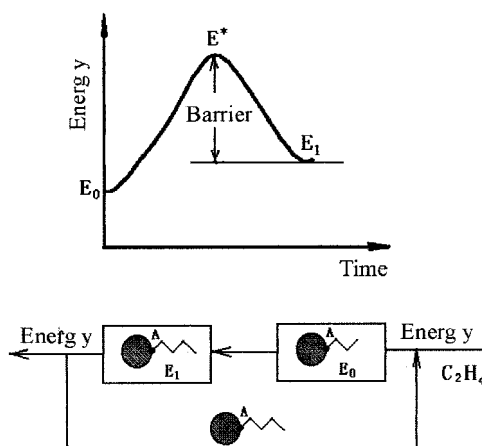


Figure 4 Microenergy and morphology evolution at active site A.

lowing model. Meanwhile, the fluctuations develop according to the Laplace equation, and the velocity of these fluctuations reflects the intensity of the morphology evolution, that is, the reaction rate. Moreover, the evolution process may follow the rule of the lowest energy because the system always tries to keep its morphology characteristics as steady as possible, and so a self-similar morphology must be evolved.

Let us assume that the energy fluctuation gives a sine wave as follows:

$$\left. \frac{dE}{dt} \right|_{t=t_k} = k' r_p(t_k) \sin(\omega t_k + \phi) \quad (1)$$

where E is the microenergy of the system; k' denotes the exchange coefficient between the energy and polymerization reaction rate, which determines the amplitude of energy fluctuation; $r_p(t_k)$ is the transient reaction rate; ω is the fluctuation frequency; and ϕ is the phase angle.

At the beginning of the polymerization, the initial morphology of the catalyst and the initial reaction conditions have a significant effect on the change in the system morphology, but this kind of influence becomes weaker and weaker with the progress of the reaction. Meanwhile, the influence of the morphology of the previous system becomes considerable. From this point of view, the morphology evolution of the system can be described as follows:

$$D_f(t_k) = [g(T, M_b) D_{f0} + k_1 r_p(t_k) \sin(\omega t_k + \phi)] \times e^{-k_2(T, M_b)t_k} + D_f(t_{k-1})(1 - e^{-k_3 t_k}) \quad (2)$$

where t_k is equal to $k\Delta t$ ($k = 0, 1, 2, \dots$), Δt is the sampling length, and $D_f(t_k)$ denotes the fractal dimension of the system (i.e., polyethylene particles) at time t_k . At $k = 0$, $D_f(t_k) = D_{f0} = D_{fc}$; here D_{fc} is the fractal dimension of the catalyst. At $k = \infty$, $D_f(t_k)$ is equal to $D_f(t_{k1})$.

$g(T, M_b) \times D_{f0} + k_1 \times r_p(t_k) \times \sin(\omega t_k + \phi)$ expresses the sensitive term of the initial condition, where $g(T, M_b)$ concerns T and M_b :

$$g(T, M_b) = a_1 + a_2 \left(\frac{T}{M_b + a_3} \right) + a_4 \left(\frac{T}{M_b + a_3} \right)^2 \quad (3)$$

a_1 – a_4 are coefficients experimentally determined.

k_1 is equal to $k'k''$ where k'' denotes the exchange coefficient between the critical microenergy and morphology characteristics of the system. $k_2(T, M_b)$ is the decay coefficient for the sensitive term of the initial conditions, which indicates the decay of the influence of the initial conditions on the characteristics of the system. This coefficient can be expressed as follows:

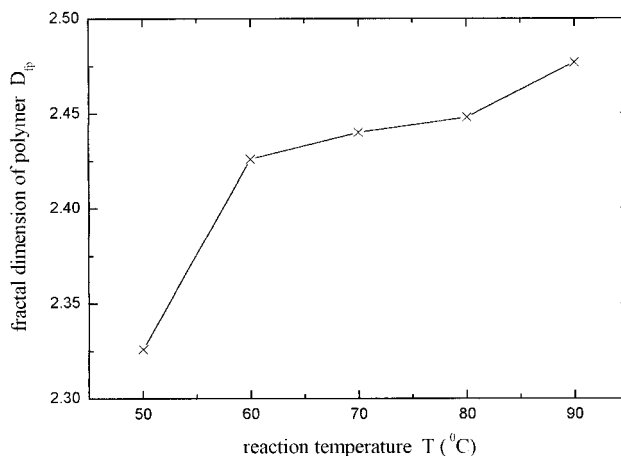


Figure 5 Influence of the reaction temperature on the fractal dimensions of the polymer (polymerization conditions: partial pressure of $C_2H_4 = 0.62$ MPa, partial pressure of $H_2 = 0$, and $Al/Ti = 45$).

$$k_2(T, M_b) = b_1 + b_2 \frac{M_b}{T} \quad (4)$$

where b_1 and b_2 are coefficients experimentally determined.

$D_f(t_{k-1})$ expresses the previous fractal dimension of the system, so $D_f(t_{k-1})(1 - e^{-k_3 t_k})$ indicates the inertia term of the system during the evolution, which tries to maintain the previous morphology characteristics of the system. k_3 is the intrinsic parameter of the catalyst.

In summary, ω , ϕ , k_1 , and k_3 are intrinsic characteristics of the catalyst, and they are independent of the polymerization conditions. $g(T, M_b)$ and $k_2(T, M_b)$ are parameters concerning exterior reaction conditions.

EXPERIMENTS AND RESULTS

A typical supported $TiCl_4/Mg(OEt)_2$ catalyst was selected for studying the changes in the morphology characteristics during the ethylene polymerization process. All the polymerizations were carried out in an agitated 1-L stainless autoclave jacket reactor operated in the semibatch mode. SEM images of particles were acquired with a Hitachi S-570 scanning electron microscope. The reaction temperature, the concentration of the monomer ethylene, the Al/Ti ratio, the method of feeding H_2 , and the prepolymerization were considered.

Reaction temperature

The influence of the reaction temperature on the surface fractal dimensions of polyethylene is shown in Figure 5. At lower temperatures, because of the lower initial reaction rate, the accumulation of primary particles was relatively slow and compact, and this led to

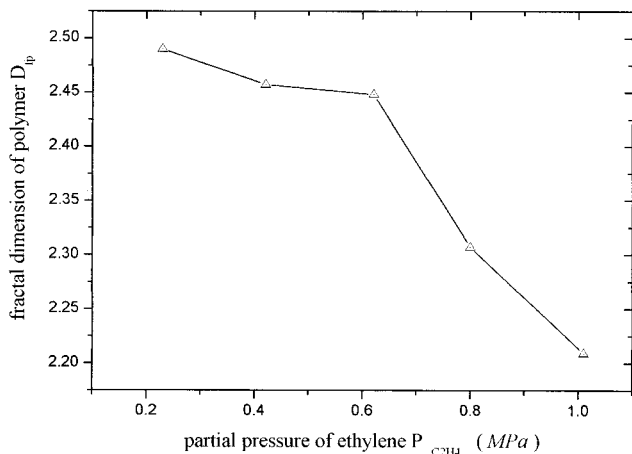


Figure 6 Influence of the partial pressure of C_2H_4 on the fractal dimensions of the polymer (polymerization conditions: $T = 80^\circ C$, partial pressure of $H_2 = 0$, and $Al/Ti = 45$).

a small surface fractal dimension of the particles. With an increase in the reaction temperature, the reaction rate increased rapidly, and the polyethylene chains folded and twisted so quickly that primary particles and subparticles could not aggregate closely; we regarded this as a shield effect. As a result, the irregularity of the inner surface of the polymer increased, and this was expressed as an increase in the fractal dimension.

Partial pressure of C_2H_4

The relationship between the surface fractal dimension and the partial pressure of ethylene, that is, the concentration of the monomer ethylene, is given in Figure 6, which shows an inverse proportion. Although the increase in the ethylene concentration sped up the reaction rate as well, the shield effect for accumulation was greatly weakened. Because, with an increase in the ethylene concentration, more reactant molecules made it easier for primary particles and subparticles to accumulate compactly, the roughness of the inner surface of the polymer became smaller. For the moment condition, the concentration of ethylene played a dominating part. Therefore, the increase in the partial pressure of C_2H_4 not only accelerated the polymerization but also modified the morphology of the particles.

Al/Ti ratio

The relationship between the Al/Ti ratio and the surface fractal dimension is not linear (Fig. 7). On the basis of both the reaction rate and polymer morphology, we selected an Al/Ti ratio of 30–60 ($T = 80^\circ C$, partial pressure of $C_2H_4 = 0.62$ MPa, and partial pressure of $H_2 = 0$).

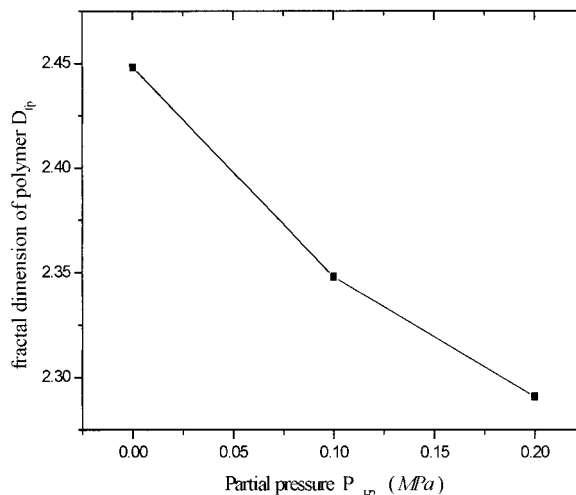


Figure 7 Influence of the partial pressure of H_2 on the fractal dimensions of the polymer (polymerization conditions: $T = 80^\circ C$, partial pressure of $C_2H_4 = 0.62$ MPa, and $Al/Ti = 45$).

Feeding of H_2

When H_2 was added during the polymerization, the reaction rate decreased, and the primary particles were modified uniformly. Accordingly, with an increase in the partial pressure of H_2 , the submicrosurface roughness of polyethylene became smaller with a compact aggregation of particles, and the surface fractal dimension was then reduced (Fig. 8).

Prepolymerization

For controlling and modifying the morphology of polymers, the prepolymerization technique is always being suggested in industry, and so we also have studied prepolymerization. The prepolymerization was carried out at $60^\circ C$ with a total C_2H_4 pressure of

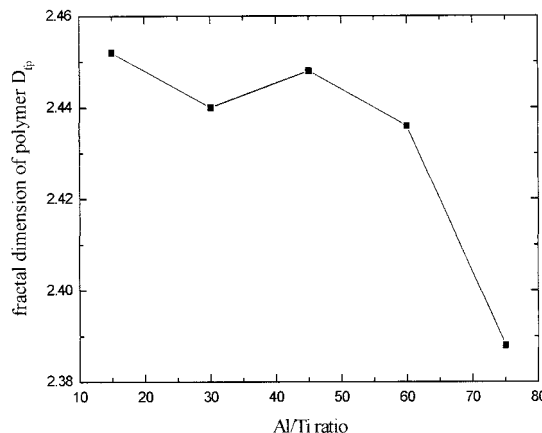


Figure 8 Influence of the partial pressure of Al/Ti on the fractal dimensions of the polymer (polymerization conditions: $T = 80^\circ C$, partial pressure of $C_2H_4 = 0.62$ MPa, and partial pressure of $H_2 = 0$).

TABLE I
Parameters in PFGM

$k_1 (\times 10^6)$	k_3	ω	φ	a_1
1.3761	0.011	0.2471	97.3	0.5186
$a_2 (\times 10^3)$	a_3	$a_4 (\times 10^6)$	b_1	b_2
3.683	1.0741	-5.6089	0.011	0.4714

0.41 MPa for 30 min, and then the feeding of C_2H_4 was stopped until the reaction temperature was increased to $90^\circ C$. The polymerization was performed at $90^\circ C$ and 0.81 MPa. Because the prepolymerization initial reaction conditions were very mild, primary particles and secondary particles of polyethylene could twist and fold more closely, and so the morphology of the system should be better. Our experiment showed that after the entire 150-min reaction, the fractal dimension of the polymer (D_{fp}) had already reached 2.409, which was smaller than that of the polymer without prepolymerization. The morphology of the system was indeed modified.

SIMULATION AND DISCUSSION

Experimental data were used to fit the parameters of the polymerization fractal growth model (PFGM) by the Marquart method. The parameters are shown in Table I.

The morphology evolution of polyethylene simulated by PFGM [given by eq. (2)] is shown in Figure 9, in which open circles denote the experiment data. During the polymerization, the morphology of the system changes continuously.

During the initial stage of the polymerization, polyethylene chains propagate at active sites of the catalyst with folding and twisting until the primary polyethylene particles are formed, whose shape and size (i.e., the degree of compactness) are primarily determined by D_{f0} and the initial reaction rate. With a large specific area, the catalyst usually has a high D_{f0} value, and the reaction conditions are relatively violent. Consequently, the fluctuation of the system microenergy is severe, and the particles are irregular with high fractal dimensions. During this period, changes in the initial reaction conditions greatly influence the morphology evolution. We say that it is a sensitive period of initial value. After that, the primary particles aggregate, continually accumulating in their surrounding spaces, and the fractal dimension becomes smaller. This is an inherited period or replica period, during which the previous morphology characteristics play an important role in the evolution. With the accumulation of the particles, the mechanism strength of the system becomes stronger until that the breakup occurs; meanwhile, the fractal dimension of the system becomes

greater. When the particles are fully broken, the fractal dimension reaches its highest point. Then, a new cycle from the sensitive period to the inherited period begins. These alternative accumulation and breakup processes accomplish the evolution from catalyst to polymer and bring on the self-similar morphology of the system. Both the sensitive period and inherited period, as well as the breakup, may happen according to Laplace lowest energy theory.

With PFGM, the effects of the initial reaction conditions can now be explained very well. With an increase in the reaction temperature, $g(T, M_b)$ increases, and $k_2(T, M_b)$ decreases. Therefore, a high reaction temperature results in a big fluctuation of the critical microenergy at the beginning of polymerization, and this causes a severe breakup of the polymer particles. As a result, the surface fractal dimension increases. When the polymerization is carried out under a relatively low temperature, the fluctuation of the critical microenergy is smaller, and the morphology evolution of the system is also slow, so that the morphology of the polymer particles is better. However, a low temperature leads in addition to a decrease in the reaction rate. Therefore, it is better to select the prepolymerization technique so that a polymer with an appropriate morphology can be formed during the initial stages.

Moreover, with PFGM, the morphology evolutions of polymerization with different durations of prepolymerization can be predicted, as shown in Figure 10. After prepolymerization, the system morphology remains unchanging during the caletactive period of the system until polymerization begins. Meanwhile, the changing tendency of morphology evolution is contin-

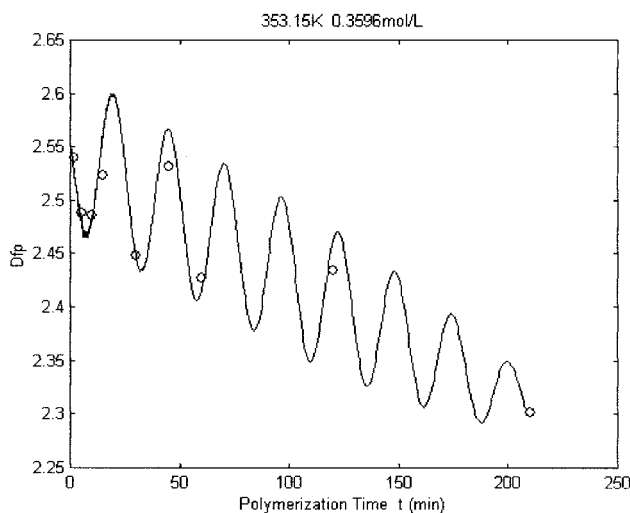


Figure 9 Simulation of the morphology evolution with PFGM (polymerization conditions: $T = 80^\circ C$, partial pressure of $C_2H_4 = 0.62$ MPa, partial pressure of $H_2 = 0$, and $Al/Ti = 45$). The open circle represent the experimental results.

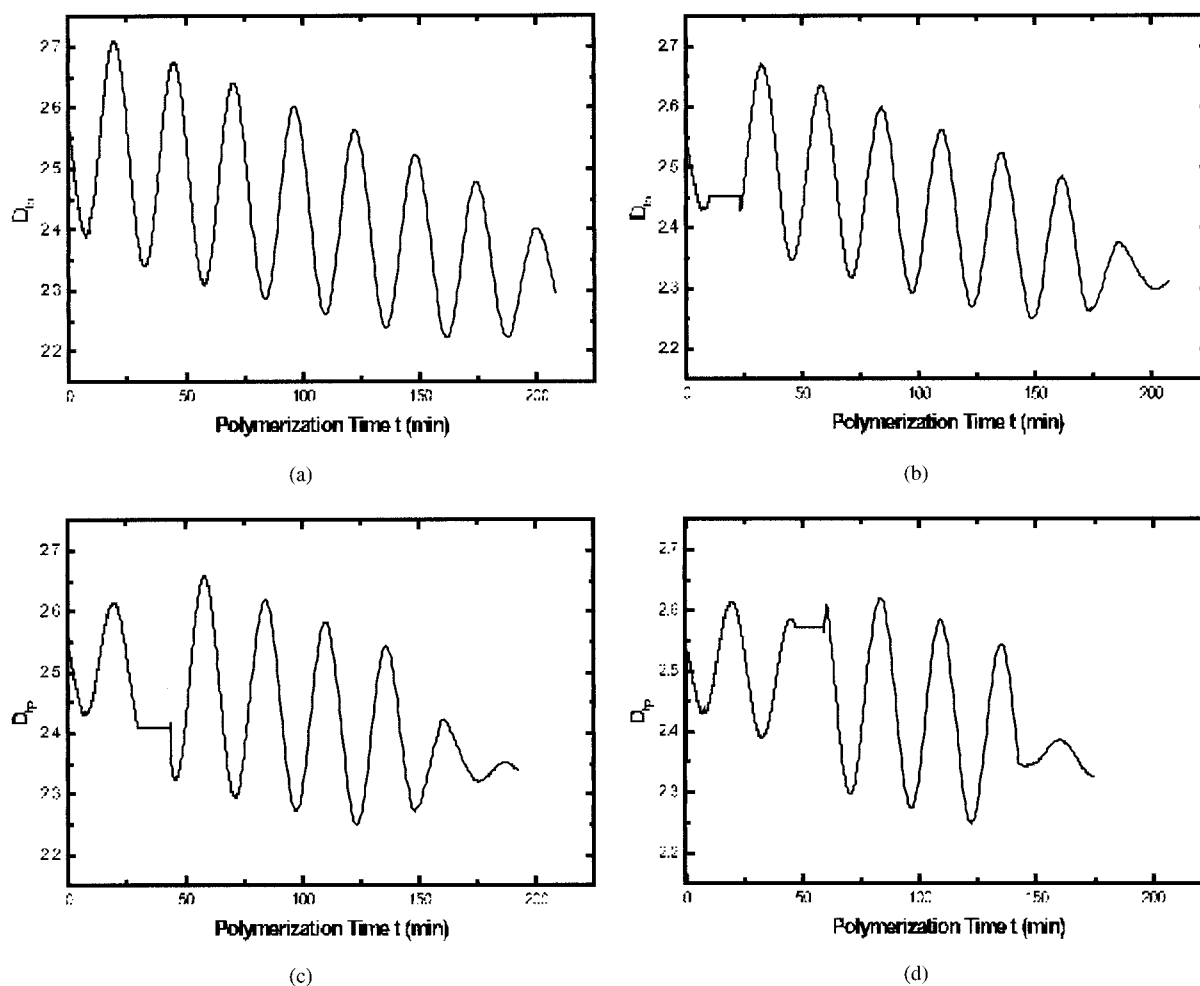


Figure 10 Prediction of the evolution of the system morphology with the prepolymerization (prepolymerization conditions: $T = 60^{\circ}\text{C}$ and partial pressure of $\text{C}_2\text{H}_4 = 0.41$ MPa; polymerization conditions: $T = 90^{\circ}\text{C}$ and partial pressure of $\text{C}_2\text{H}_4 = 0.81$ MPa).

ued. Both demonstrate the inheritable characteristics of the system morphology. The simulation results indicate also that the effect of prepolymerization on the final morphology of the polymer increases with the length of its duration. Because with an excessive prepolymerization the breakup of particles during late polymerization will be greatly restricted, this affects the exposure of active sites, expedites the deactivation, and worsens the final morphology of the particles. Therefore, it is suggested that the duration of polymerization be 10–30 min.

CONCLUSIONS

The morphology evolutions of polymerization on a titanium–magnesium-supported polyethylene catalyst have been studied in this work. It has been proven not only that catalysts and polyethylene particles possess fractal characteristics but also that the growth process of polymer grains is an evolving fractal process. Based on such a novel concept, PFGM has been constructed,

in which the system morphology can be determined by a combination of the initial conditions and the inertial characteristics of the system. For modifying the morphology of the particles, the selection of a prepolymerization technique and the feeding of H_2 have been suggested; moreover, a decrease in the reaction temperature or Al/Ti ratio has also been proposed with the precondition of a sufficient reaction rate.

Such a combination of the system's macrophe-nomena and its microfractal mechanism would enable us to understand the dynamic characteristics of the processes and to predict the final morphology of the grains, either of catalysts or polymers, under given operation conditions. This approach has successfully been used in this work, and it is likely that it completes a blank space in this field. Therefore, it could give us valuable guidance in our investigations and be applied to industrial production in the future.

NOMENCLATURE

a_1 – a_4	experimentally determined coefficients
b_1 and b_2	experimentally determined coefficients
$D_f(t_k)$	fractal dimension of a system at time t_k
D_{f0}	initial fractal dimension of a catalyst
D_{fc}	fractal dimension of a catalyst
D_{fp}	fractal dimension of a polymer
E	microenergy of system
k'	exchange coefficient between energy and polymerization rate
k''	exchange coefficient between microenergy and morphology characteristics of system
k_1	$k' \times k''$
k_2	decay coefficient for the sensitive term
k_3	intrinsic parameter of a catalyst
M_b	monomer concentration
$r_p(t_k)$	transient reaction rate
T	reaction temperature
Δt	sampling length
ϕ	phase angle of microenergy fluctuation
ω	fluctuation frequency

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