Modeling of the Propylene Polymerization Catalyzed by Single-/Multi-Active Site Catalyst: A Monte Carlo Study

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ABSTRACT: In the present study, a model is established to describe the propylene polymerization kinetics catalyzed by the typical catalysts with single-/multi-active site type in a liquid phase stirred-tank reactor using the Monte Carlo simulation method, regardless of the mass and heat diffusion effects within the polymer particles. Many kinetic data, including polypropylene yield, concentration transformation of catalyst active sites, number–average molecular weight, etc., are obtained by the model. The simulated kinetic results are found to be in agreement with the reference ones obtained in a population balance model. Furthermore, the comparisons of the kinetic data between the polymerization catalyzed by the catalyst with single-active site type (typically silica-supported metallo-cene) and the catalyst with multi-active site type (typically MgCl$_2$-supported Ziegler-Natta catalyst) have been studied using the model. Especially, the effects of hydrogen on the polymerization are studied using the model. The studied results show that the theory of catalyst active site can be used to explain the different propylene polymerization kinetics catalyzed by the typical catalyst with single-/multi-active site type. In addition, the role of hydrogen in the propylene polymerization needs to be emphasized. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 110: 3360–3367, 2008

Key words: Monte Carlo simulation; polypropylene; propylene polymerization catalyst; single-/multi-active site catalyst

INTRODUCTION

Polypropylene (PP) has attracted lots of attentions owing to its simple configuration but various applications. PP can be used to manufacture a series of industrial and civil products, such as gas pipeline, synthetic fiber, plastic film, etc. Practically, PP can be produced via propylene polymerization in various reactors. In the propylene polymerization field, most of the papers published are concerned with the heat and mass transfer behaviors inside the catalyst particles and of the reaction mechanism from meso-scale using the experimental technique.[1–4] The study on the propylene polymerization from microscale is not common.

Recently, the mathematical modeling applied in the polymerization field has been paid more attention with the development of computer technique and mathematical algorithm. The ability to model the complete polymerization process or even with product properties, facilitates a more rigorous examination of whether the assumed kinetic mechanism and coefficients provide an adequate representation of the polymerization itself. Up to now, aside from the Monte Carlo simulation technique, some mainstream mathematical modeling techniques may include well-known "method of moments,"[5,6] "Galerkin *h-p* finite element method (FEM),"[7,8] and "continuous variable approximation."[9] It should be noted that the Galerkin *h-p* FEM has been implemented in the commercial software package PREDICI, as developed by Wulkow.[10] The former two methods start with a population balance and meanwhile, they both suffer from the enclosure problem when dealing with higher dimensionality. The continuous variable approximation method seems to be encountered by modeling random scission more often. The Monte Carlo simulation is employed for problems where analytical or differential equations approaches are not feasible in view of high dimensionality, especially in the case of very complex reaction schemes where conventional methods require a high level of sophistication and include many simplified assumptions, Monte Carlo methods seem to be a simple and flexible alternative.

Platkowski and Reichert[11] have tested the validity of the Monte Carlo simulation method in modeling several specific polymerization reactions, including heterogeneous polycondensation, inverse emulsion polymerization, and thermal polymer degradation. For the propylene polymerization process, Luo et al.[12] proposed a novel kinetic scheme and studied

the effects of impurity on the propylene polymerization by using the Monte Carlo simulation method.
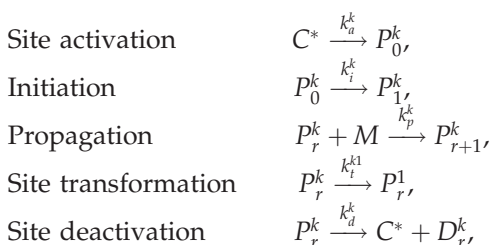
On the other hand, as to the polymerization itself, the catalyst active site theory has been developed almost all way along with the continuous upgrading of technology and improvement of product physical properties. Kakugo et al.[13] fractionated the PP prepared with Ti-based catalysts by using an elution column technique and proposed a new model for the active site types. Rincon-Rubio et al.[14] have studied a kinetic model involving two types of active sites for the propylene polymerization over a supported TiCl$_4$/MgCl$_2$ Ziegler-Natta catalyst. In short, the catalyst active site theory,[15–17] indicates that, for the case of single-site-type catalysts, such as most metallocenes, the polymerization scheme can be used with a single set of kinetic constants. And that for multiple-site-type catalysts, such as heterogeneous Ziegler-Natta catalysts, it is generally assumed that two or more active site types are present, each one with a distinct set of polymerization kinetics constants, monomer coming in contact with high activity sites leads to the production of relatively longer polymer chains while shorter chains are produced by low activity sites, and therefore making polymer chains with different average properties. However, the universal agreement between theoretical investigation and industrial manufacturing is far away from being reached yet.

In this article, to investigate the effects of the elementary kinetic mechanism on the polymerization, we apply the Monte Carlo simulation technique to investigate the propylene polymerization catalyzed by two types of catalysts from microscale. The simulated data are compared with each other.

MODEL DESCRIPTION

Kinetic scheme

The widely accepted kinetic mechanism for the propylene homopolymerization is applied, which is shown as follows:

Site activation	$C^* \xrightarrow{k_a^k} P_0^k,$
Initiation	$P_0^k \xrightarrow{k_i^k} P_1^k,$
Propagation	$P_r^k + M \xrightarrow{k_p^k} P_{r+1}^k,$
Site transformation	$P_r^k \xrightarrow{k_t^{k1}} P_r^1,$
Site deactivation	$P_r^k \xrightarrow{k_d^k} C^* + D_r^k,$

where, C^* is the active site, D_r^k is the dead polymer of chain length r on the kth type of active site, M is the monomer, $P_r^{k(l)}$ is a living polymer chain of length r on kth(lth) type of active site.

With all these reaction equations, some assumptions are followed based on the literatures:[18–22]

1. the site activation reaction is assumed instantaneous,
2. the rate constant of the initiation reaction is treated equally as the rate constant of the propagation reaction,
3. the rate constants for all steps are independent upon the chain length,
4. the transfer reactions are assumed to form the same site type C^*.

As to the number and behavior of the active sites of industrial Ziegler-Natta catalyst, many researchers,[15,16] have studied by means of the "deconvolution" of existing experimental curve. However, the curve fitting task is merely a mathematical job expecting to prove the multi-site-type nature of the Ziegler-Natta catalyst but not helpful in industrial use. Zacca et al.[23,24] have attributed the different nature of active site types to different oxidation states of the titanium atom. Accordingly, Zacca et al. propose a two-site-type model for Ziegler-Natta catalyst, reflecting the oxidation state of the catalyst from Ti^{3+} to Ti^{2+}. The mechanism, which accords with Cossee's theory,[25,26] is also adopted in this article. In addition, some points must be emphasized according to the industrial situation.

1. There are two types of sites and only site of type 1 may transform into site type 2 which subsequently deactivates,
2. Site type 1 does not deactivate but transforms to site type 2. Site type 2 deactivate with time.

As to the single-site-type model for typically metallocene, the site transformation reaction is ignored. In practice, the site transformation reaction reflects the uniform type of active center of the catalyst, which is the main distinction different from the multi-site-type model.

Kinetic data

Since hundreds of variations of kinetic schemes owing to different polymerization systems and industrial conditions, it is extremely hard to get a complete set of industrial data on the propylene polymerization. The data in this article, mainly based on Refs. 22–24, are simultaneously selected from previous study with similar polymerization systems and operation conditions. Tables I and II list the selected parameters for one-site-type and two-site-type catalyst, respectively. Moreover, a few explanations need to be emphasized:

1. Monomer concentration used in this simulation is the concentration at the active site other than the normally measured concentration in the

TABLE I
Simulation Parameters Used for the One-Site-Type Model (Metallocene Catalyst)

Parameter	Unit	Value at 70°C	Reference
[Al]	mol/m^3	10	22
χ_{Ti}^*	–	0.40	23, 24
M_b	mol/m^3	9917	23, 24
φ	–	0.479	23, 24
k_p^1	m^3/mol/s	0.2691	23, 24
k_d^1	s^{-1}	1.811×10^{-4}	23, 24

bulk phase. Floyd et al.[18] obtain the relation of the two concentrations by introducing a sorption factor φ. Corresponding equation is as follows:

$$M_s = \varphi M_b, \tag{1}$$

where M_b and M_s represent monomer concentration in the bulk fluid and at the catalyst sites, respectively,

2. The mol concentration of Al is considered same as mol concentration of catalyst,
3. The total mol fraction of Ti available as active sites is equal to 40%. In the multi-site-type model the initial amounts of site type 1 and 2 are 80.64 and 19.36%, respectively. On the other hand, fraction of active site 1 accounts for 100% in the single-site-type model.

Model methodology

The well-known Monte Carlo simulation method applied in the reaction is first introduced by Gillespie.[27] Figure 1 gives a main frame of Monte Carlo simulation for stochastic formulation of chemical kinetics. In this article, however, Monte Carlo simulation method is based on the basic theory of Gillespie with a few modifications. The modifications are

TABLE II
Simulation Data Used for the Two-Site-Type Model (TiCl$_4$/MgCl$_2$ Ziegler-Natta Catalyst)

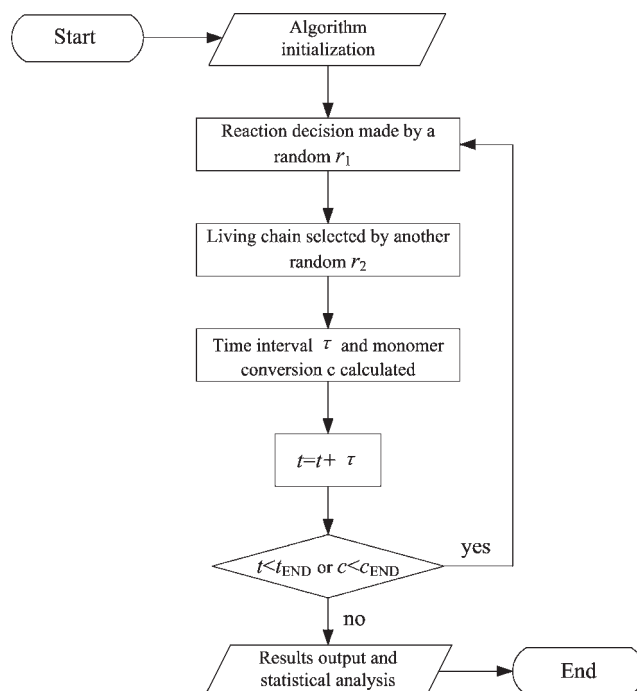| Parameter	Unit	Value at 70°C	Reference
[Al]	mol/m^3	10	22
χ_{Ti}^*	–	0.40	23, 24
μ_1	–	0.8064	23, 24
μ_2	–	0.1936	23, 24
M_b	mol/m^3	9917	23, 24
φ	–	0.479	23, 24
k_p^1	m^3/mol/s	0.3428	23, 24
k_p^2	m^3/mol/s	0.03428	23, 24
k_t^{12}	s^{-1}	2.835×10^{-4}	23, 24
k_d^2	s^{-1}	7.95×10^{-5}	23, 24

Figure 1 Monte Carlo simulation methodology applied in this article.

discussed by taking the multi-site-type catalyst for example (case of single-site-type is much easier) here.

To avoid the "deficient" or "overplus" sampling problem that usually takes place when some reaction possibilities are extremely larger than the others, a method of "bias sampling" is adopted to solve this problem.[28] The thought of "bias sampling" introduces a weighted adjustment to the probability of each reaction, making whose magnitude much closer to each other. In other words, the reaction with small probability is hypothetically magnified:

$$P_d^k = c a_d^k \Big/ \sum_k \left[c(a_d^k + a_t^k) + a_p^k \right], \tag{2}$$

$$P_t^k = c a_t^k \Big/ \sum_k \left[c(a_d^k + a_t^k) + a_p^k \right], \tag{3}$$

where, a_d^k is the rate of site deactivation on the "kth" type of active site, a_p^k is the reaction rate of propagation on the "kth" type of active site, a_t^k is the rate of site transformation on the "kth" type of active site. Correspondingly, P_d^k and P_t^k represent the probability of site deactivation and site transformation on the "kth" type of active site, respectively. Here c is set as 100.

In compensation for the comparative decrease of propagation reaction probability, once they are selected, the reaction should repeat c times and the relative time interval τ' equals c plus τ, while the time interval for the rest remains unchanged.
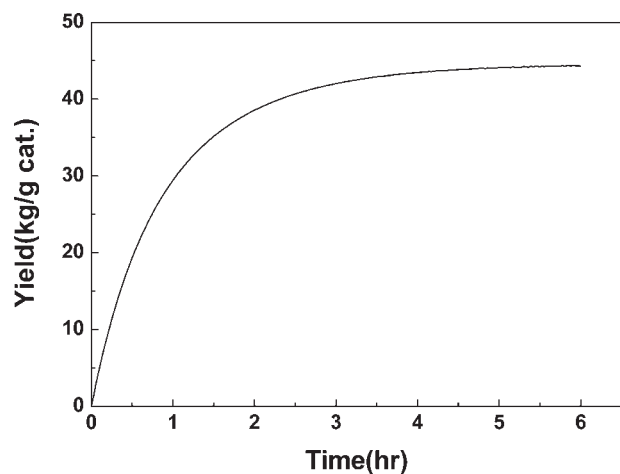
Figure 2 Polymerization yield vs. time under the single-site-type model.

The simulation of Monte Carlo in our study is programmed in C++ language. A series of pseudo-random numbers between 0 and 1 are generated by the starting point seeded by the CPU clock and with the help of another random number, the period of the generated number is prolonged. Considering the limitation of the computer, initial monomer molecule number m is fixed at 1×10^9 and the monomer concentration is 1.0 mol/m^3, i.e. the total volume of the polymerization system, V, is about 1.66×10^{-15} m^3, the other parameters are analogically obtained. Living chain with length of 0 (considering instantaneous initiation reaction) of active site type 1 and 2 are 6.79×10^6 and 1.63×10^6, respectively. It lasts almost 11 h for the simulation of the reaction time up to 6 h on an Inter 2.13 GHz computer.

The simulation work of the single-site-type model is almost the same except that compared to different site types in the multi-site-type model, we take into consideration of both living and dead polymer chains of the only type of site and compare these two to each other, expecting to find out the main dissimilarity with the multi-site-type one.

RESULTS AND DISCUSSION

Kinetic study of propylene polymerization

Since the parameters used in this model are mainly selected from Refs. 22–24, the results derived from our model are firstly quantitatively compared with the original ones. We simulate the polymerization kinetics at 70°C using above Monte Carlo method. A series of simulation results including the polymer yield, the number–average molecular weight, and the fraction of active center, etc., are obtained and as follows.

Figure 2 gives the yield data (calculated based on the monomer consumption) over time under the sin-

gle-site-type model. The simulated polymerization yield data of multi-site-type model, which is also based on the monomer consumption, is compared with the referenced one,[23] in Figure 3. Although the correlation coefficient between these two figures can be up to 0.9923, actually there is some unobvious difference between our simulation results and the referenced one. Lack of the diffusion resistance consideration can be the main reason for this difference. Since we intend to investigate the different behaviors that single-/multi-site type catalyst has in the polymerization system from the microscale viewpoint, our model sticks to the kinetic mechanism without the diffusion consideration.

According to the yield curve shown in Figures 2 and 3, the polymerization process can be divided into three intervals. During the first hour of polymerization (i.e. the 1st interval), the PP yield almost increases straight to around 25 kg/g cat. In the next 3 h (the 2nd interval), the polymer yield shows a distinct change from the former and the polymerization rate tends to be slowed down. After the polymer yield achieved 43 kg/g cat. (the 3rd interval), the propylene yield remains almost constant with the time. The rapid increase of PP yield at the beginning can be ascribed to the rapid propagation rate and the high catalyst activity. The fast monomer consumption after an interval promotes the other reactions' probability of being selected and therefore, resulting in a mild decrease of the polymerization rate and eventual "pseudostability" of polymerization in the reactor. Other than the yield data, our model is able to provide a series of much more helpful information for industrial use, which can be referred to in the following text. Besides, Figures 2 and 3 show that the yield curves of single- and multi-site-type models exhibit almost no difference
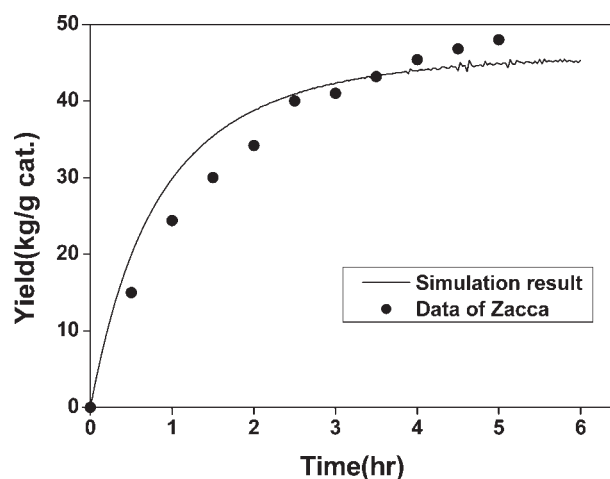

Figure 3 The simulated polymerization yield vs. time under the multi-site-type model and the comparison with the data obtained from Ref. 23.
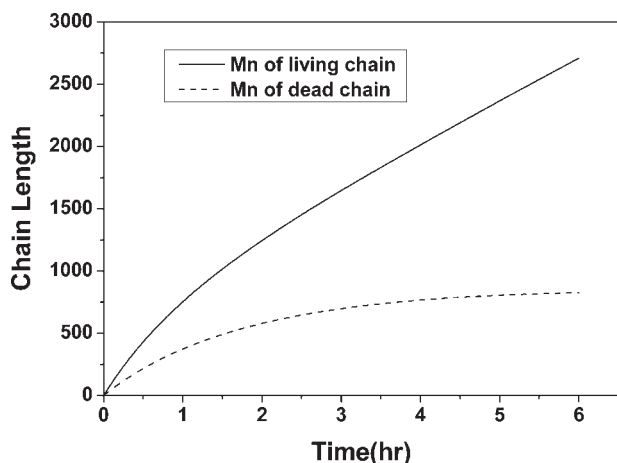
Figure 4 Number–average chain length changes with time under the single-site-type model.

to each other, owing to the fact that the single- and multi-site nature of catalyst has little influence on the yield data during the propylene polymerization.

Figures 4 and 5 illustrate that the number–average chain length changes with the time under different active site type models. As shown in Figures 4 and 5, due to the common nature of nondeactivation for the living chain in single-site-type model and site type 1 in the two-site-type model, the number–average chain length of these two displays almost a linear increase with the time and reach up to 2800 and 4000 after 6 h, respectively. On the contrary, as a result of deactivation reaction for the dead chain length of the single-site-type model and chain length of site type 2, Figures 4 and 5 indicate an asymptotic increase along with the time approaching their maximum values, both up to round about 800. The detailed descriptions on Figures 4 and 5 are shown
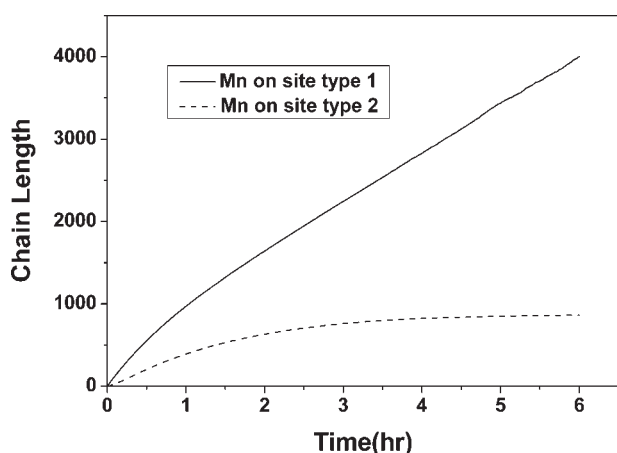
in "The effects of hydrogen on propylene polymerization" section.

To study the kinetic mechanism from the microscale, the active site concentration transformation is of remarkable importance. Since there is no transformation reaction among the active sites in the single-site-type model, as shown in Figure 6, the concentration of the active centers which are assumed uniformly distributed in the reactor drops down with time owing to the deactivation reaction. The descend rate slows down over time and at around 6 h after the polymerization, the active center fraction equals almost 0. Meanwhile, the multi-site-type model assumes that the first site type Ti^{3+} transforms to a lower oxidation state Ti^{2+} over time, which is less reactive to propylene. The assumption gives rise to the fact that fraction of active site type 1 decreases rapidly to 0 after 5 h of polymerization (faster than the single-site-type model) and promotes the fraction of active site type 2 to a maximum value of about 24% after 2 h of polymerization. The fraction of active site type 2 then declines to about 5% in the next 4 h of polymerization owing to its deactivation reaction. Figure 7 shows that the simulated concentration of each site type and overall amount of active sites are changing with time. The slight difference between the simulated result of active sites fraction and the referenced one,[23] can be seen in Figure 7, which indeed, has emphasized our model validity again.

The kinetic results given above are merely comparative work with the former ones. In addition, we are not able to investigate the molecular weight distribution of the two-site-type model for there are no deactivation reactions for both site types. This kind of reaction is made by hydrogen, which are discussed in the next section.
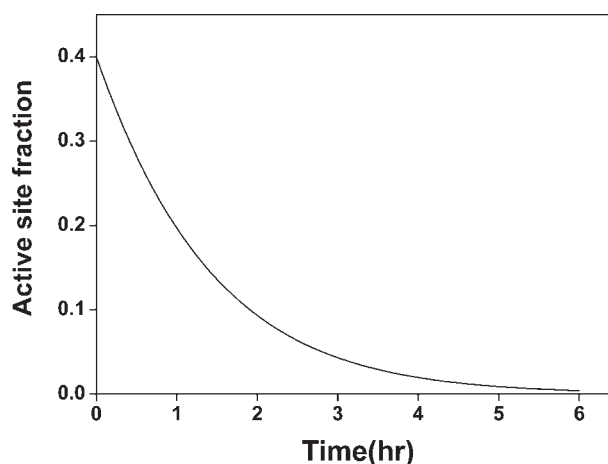

Figure 5 Number–average chain length changes with time under the multi-site-type model.

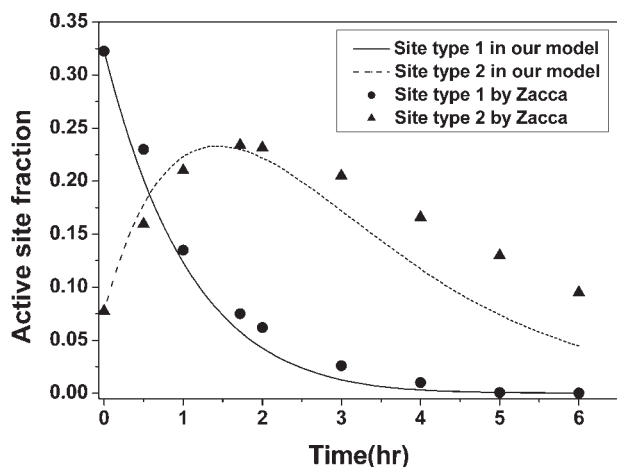**Figure 6** Fraction of active site vs. time under the single-site-type model.

Figure 7 The simulated fraction of active site vs. time under the multi-site-type model and the comparison with the data obtained from Ref. 23.

The effects of hydrogen on propylene polymerization

Many researchers have emphasized the role of hydrogen in the propylene polymerization.[29,30] For the in-site operations, hydrogen acts not only as a kind of transfer agent, since it can take good control of the molecular weight distribution and other properties of the product, but also increases the polymerization rate. Theoretically, the transfer to hydrogen reaction makes a living chain of length r turning into a dead chain of length r and brings an active center, the former can regulate the molecular weight distribution and the latter raises the reaction rate ($R_p = k_p[M][C^*]$).

Transfer to hydrogen $P_t^k + \frac{1}{2}H_2 \xrightarrow{k_{tH}^k} C^* + D_r^k$

To investigate the significance of hydrogen during the propylene polymerization, reaction of transfer to

hydrogen is added to our model. Additional parameters for reaction of transfer to hydrogen are selected from Refs. 31 and 32, which are also published by Zacca and coworkers.

The simulated polymerization is carried out at 70°C in absence of hydrogen and at two different hydrogen concentrations, one is the value derived from reference (i.e. $k_p/k_{tH} = 20.4$, $[H_2]/[M] = 3.2 \times 10^{-4}$), the other is hypothetical magnified by two times of the original (i.e. $k_p/k_{tH} = 20.4$, $[H_2]/[M] = 6.4 \times 10^{-4}$). Monomer and catalyst concentrations are the same for all runs.

As shown in Figures 8 and 9, the increase of polymerization rate made by hydrogen is not so clear. However, the quantitative values are different from each other to some extent, especially during the 2nd interval of the reaction. Owing to too many monomer molecules at the early stage of polymerization, the large probability of propagation indirectly prevent the occurrence of transfer reaction to hydrogen. That is the main reason why propylene yield with hydrogen is almost same as the one without hydrogen in the 1st interval. The effect of hydrogen on polymerization rate is revealed when monomer molecules decrease in the 2nd interval. In the 3rd interval, the yield of polymer remain almost unchanged, hydrogen plays a more effective role in regulating the molecular weight distribution.

Figures 10 and 11 compare the number–average molecular weight to each other with and without the existence of hydrogen. The simulation results show that higher hydrogen concentration at active sites can lower the chain length of the polymer. In one-site-type model, M_n reaches almost 480 after 6 h with the original hydrogen concentration and 360 with the two times magnified one. While in two-site-type model, M_n gets to around 490 after 6 h with the
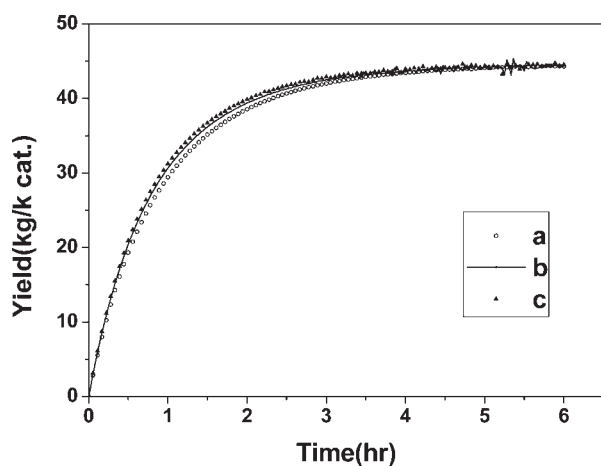

Figure 8 Effects of hydrogen on the polymerization yield under the single-site-type model: (a) without hydrogen; (b) $k_p/k_{tH} = 20.4$, $[H_2]/[M] = 3.2 \times 10^{-4}$; (c) $k_p/k_{tH} = 20.4$, $[H_2]/[M] = 6.4 \times 10^{-4}$.
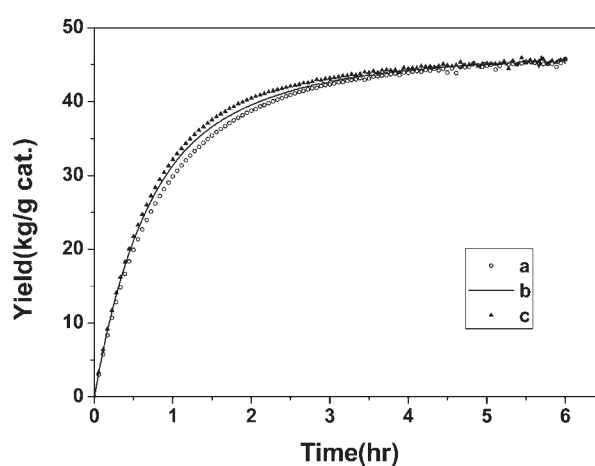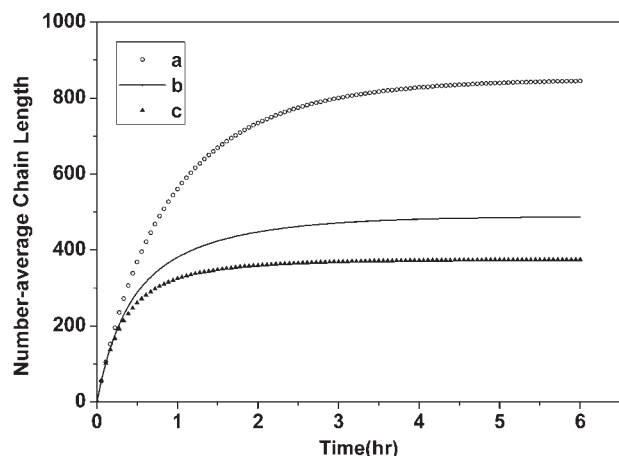

Figure 9 Effects of hydrogen on the polymerization yield under the two-site-type model: (a) without hydrogen; (b) $k_p/k_{tH} = 20.4$, $[H_2]/[M] = 3.2 \times 10^{-4}$; (c) $k_p/k_{tH} = 20.4$, $[H_2]/[M] = 6.4 \times 10^{-4}$.

Figure 10 Effects of hydrogen on the polymer number–average molecular weight under the single-site-type model: (a) without hydrogen; (b) $k_p/k_{tH} = 20.4$, $[H_2]/[M] = 3.2 \times 10^{-4}$; (c) $k_p/k_{tH} = 20.4$, $[H_2]/[M] = 6.4 \times 10^{-4}$.
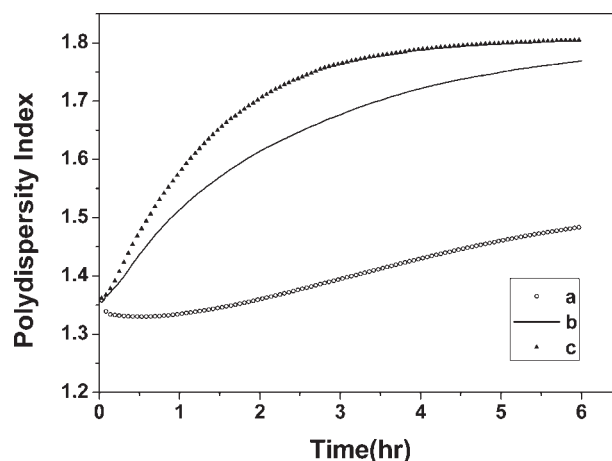

Figure 12 Effects of hydrogen on the PDI under the single-site-type model: (a) without hydrogen; (b) $k_p/k_{tH} = 20.4$, $[H_2]/[M] = 3.2 \times 10^{-4}$; (c) $k_p/k_{tH} = 20.4$, $[H_2]/[M] = 6.4 \times 10^{-4}$.

original hydrogen concentration and 370 with the doubled one. The two models exhibit a slight difference compared to each other. Together with Figures 4 and 5, it can be concluded that due to the accumulation of dead polymer chains in the polymerization system, higher percentage of dead polymer chains leads to a phenomenon that the growth of chain length decelerates and the system gets closer to the pseudostable situation. And with the existence of hydrogen, this phenomenon becomes more evident.

Figures 12 and 13 illustrate the different MWDs with different hydrogen concentrations. The polydispersity index (PDI) changes with polymerization time as well as the hydrogen concentration. The single-site-type assumption has guaranteed the narrow

MWD that even with doubled hydrogen concentration the PDI can only reach to 1.8, smaller than the theoretical value predicted by Flory.[33] The case is totally different for the multi-site-type model that with the original hydrogen concentration PDI is promoted to almost 2.2 and with the doubled one PDI can reach up to 2.5, both larger than the theoretical value of 2. Nature of catalyst multicenter makes contributions to broader molecular weight distribution in our simulation. Namely, higher hydrogen concentration can lead to higher PDI. Since what has been mentioned above, hydrogen can make a living chain with length r becoming a living chain with length 0. Higher concentration of hydrogen can enhance this effect and as a result, the molecular weight distribution becomes broader.
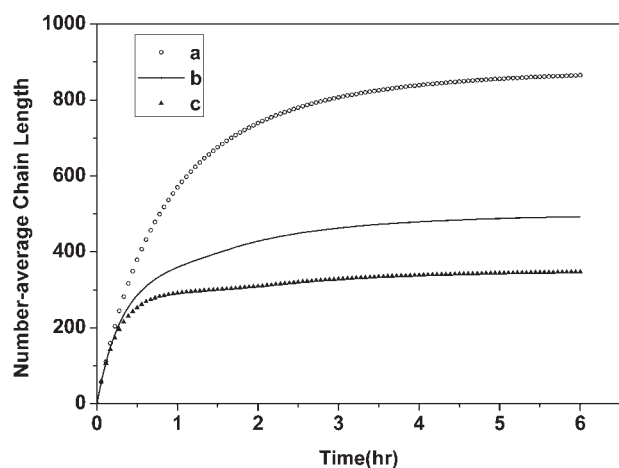

Figure 11 Effects of hydrogen on the polymer number–average molecular weight under the two-site-type model: (a) without hydrogen; (b) $k_p/k_{tH} = 20.4$, $[H_2]/[M] = 3.2 \times 10^{-4}$; (c) $k_p/k_{tH} = 20.4$, $[H_2]/[M] = 6.4 \times 10^{-4}$.

Figure 13 Effects of hydrogen on the PDI under the two-site-type model: (a) without hydrogen; (b) $k_p/k_{tH} = 20.4$, $[H_2]/[M] = 3.2 \times 10^{-4}$; (c) $k_p/k_{tH} = 20.4$, $[H_2]/[M] = 6.4 \times 10^{-4}$.
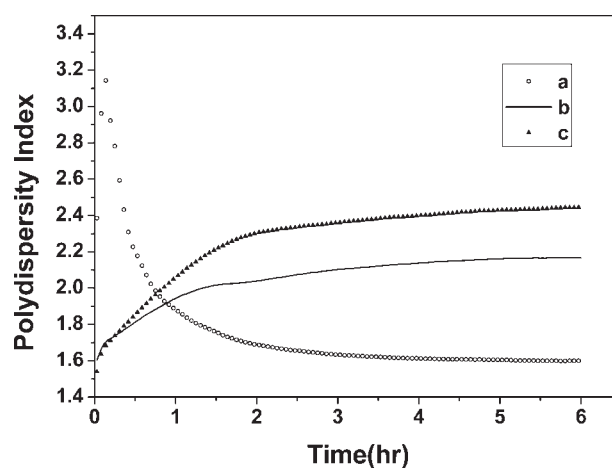
CONCLUSIONS

With respect to the wide application of Monte Carlo method, the algorithm in our study cannot be considered an innovative work. But as to the propylene homopolymerization study from the microscopic catalyst active site point of view, we have made the first attempt. The single-site-type model for metallocene and the two-site-type model for Ziegler-Natta catalyst are introduced, respectively. The theory of catalyst active site proves to be an effective way explaining the fact that the property of product yielded on an individual active site type is commonly unlike with the others. The multi-site-type nature of the catalyst, on the other hand, can make important contribution to the broadness of molecular weight distribution, even regardless of the mass and heat transfer resistance within the polymer particles. In addition, the role of hydrogen in propylene polymerization needs to be emphasized again according to the performance it has made in this simulation work. Industrially, it is considered as a molecular weight regulator. Further studies on the Monte Carlo simulation technique used in the propylene polymerization are in progress in our group.

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