

Study on kinetics of propylene polymerization at different temperatures via Monte Carlo simulation

Luo Zhenghong¹ Huang Kai² Cao Zhikai¹

(¹Department of Chemical and Biochemical Engineering, Xiamen University, Xiamen 361005, China)

(²Department of Chemistry and Chemical Engineering, Southeast University, Nanjing 210096, China)

Abstract: The elementary reactions of propylene polymerization catalyzed by conventional Ziegler-Natta catalysts was proposed according to the comprehensive view and without considering the effect of any impurity in the material on propylene polymerization. The Monte Carlo simulation technique was employed to investigate the kinetics of propylene polymerization in order to determine the validity of the stationary state assumption and the effects of the polymerization temperature on the polymerization. The simulated total amount of active species, which only increases quickly at the beginning of the polymerization, indicates that the stationary state assumption in the studied system is valid. Moreover, significant effects of polymerization temperature on the polymerization conversion, and the molecular weight and its distribution were also analyzed. The simulated results show that the consumption rate of propylene increases with the increase of polymerization temperature; the maximum values of the number-average degree of polymerization are constant at different polymerization temperatures, however, the peak appears earlier with the higher temperature; as the polymerization temperature increases, the average molecular weight decreases and the molecular weight distribution changes greatly.

Key words: Monte Carlo simulation; propylene polymerization; kinetics; polymerization temperature

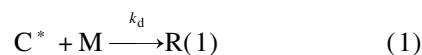
Polypropylene is a popular thermoplastic polymer, which is produced via bulk polymerization in the petroleum chemical industry. The molecular configuration of polypropylene and the characteristics of polymer can be controlled by the catalyst and polymerization method. Moreover, other factors, such as polymerization conditions, can also influence the industrial production. The catalyst influences the rate and the quality of the polymer, and it is a key factor in industrial production. Up to now the catalyst and reactor for propylene polymerization have been well developed in industry^[1,2]. There are also a series of publications on polymerization conditions^[3-6]. Based on the conservation equations, Zacca et al.^[3-5] presented a model for propylene polymerization to theoretically analyze the effects of polymerization conditions on the polymerization. Chaves et al.^[6] investigated the effects of polymerization conditions on propylene polymerization experimentally. In short, past studies were mostly concentrated on the polymerization itself and the resultant products by means of classic physical chemistry methods. However, little investigation on the effects of the polymerization conditions has been done by means of the stochastic method.

During the last decades, the Monte Carlo simulation has been shown to be a powerful stochastic method to investigate polymerization kinetics. It has been successfully applied in polymer science to study the complicated polymerization kinetics^[7-9], and it has attracted more and more attention recently. With the help of the Monte Carlo simulation, this paper focuses on the effects of polymerization temperature on propylene polymerization catalyzed by the conventional Ziegler-Natta catalyst.

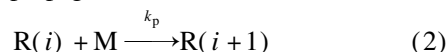
1 Polymerization Mechanism and Monte Carlo Simulation

Zacca et al.^[3-5] investigated the kinetics of propylene polymerization catalyzed by the conventional Ziegler-Natta catalyst. According to the view of Zacca et al., the mechanism proposed for the polymerization is as follows:

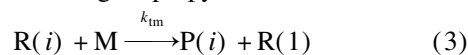
Propylene initiation reaction



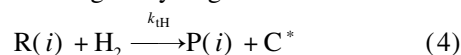
Propylene propagation reaction



Chain transferring to propylene



Chain transferring to hydrogen

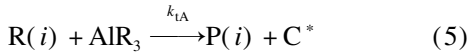


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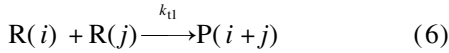
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Biography: Luo Zhenghong (1972—), male, doctor, luozh@xmu.edu.cn.

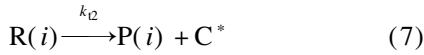
Chain transferring to cocatalyst (AlR_3)



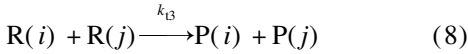
Deactivation reaction



Spontaneous deactivation reaction



Deactivation reaction



where C^* is the active catalyst site; M represents propylene; H_2 represents hydrogen; $\text{R}(i)$, $\text{R}(j)$ represent polypropylene chain radical with chain length i or j ($i, j = 1, 2, \dots$); $\text{P}(i)$, $\text{P}(j)$ represent polypropylene with chain length i or j ($i, j = 1, 2, \dots$); k_d is the propylene initiation rate constant; k_p is the chain propagation rate constant; k_{IA} is the rate constant of chain transferring to cocatalyst (AlR_3); k_{IH} is the rate constant of chain transferring to hydrogen; k_{im} is the rate constant of chain transferring to propylene; k_{II} is the chain termination rate constant according to Eq. (6); k_{I2} is the chain termination rate constant according to Eq. (7); k_{I3} is the chain termination rate constant according to Eq. (8).

By the mechanism involved with all the elementary reactions, the kinetics of propylene polymerization can be studied through simulation. According to Refs. [1–3], we assume that: ① All the active radicals have the same activation energy; ② The efficiency of initiator and all the kinetic parameters of the elementary reactions are constant in reactions. Here we review the fundamental principles of the Monte Carlo method briefly, which were reported in Refs. [7–9].

First, a small control volume from the reaction system containing 10^8 molecules is specified, and we consider the control volume containing 10^8 molecules as 1 mol/L. Secondly, we calculate the reaction probabilities of eight elementary reactions and the time interval between two reactions in the simulation. Finally, we arrange $\text{P}_1, \text{P}_2, \dots, \text{P}_8$ in a confirmed sequence, produce a random number and determine the reaction order according to a certain rule.

All the programs were written in C++ language, debugged and executed in a Pentium IV 2.4 GHz personal computer.

2 Results and Discussion

The values of the kinetic rate constants of the Monte Carlo simulation are listed in Tab. 1. Those parameters are calculated by $k = k_0 \exp(-E_0/RT)$, where R_0, E_0 are taken from Refs. [1–3]. The other simulation parameters—the initial molecular numbers of propylene, hydrogen, catalyst (initiator) and cocatalyst

(AlR_3)—are $10^8, 2\,000, 2\,000, 1\,000$, respectively. The polymerization temperatures depend on the simulation conditions.

Tab. 1 Kinetic rate constants

Type of constant	$k_0/(\text{L} \cdot (\text{mol} \cdot \text{s})^{-1})$	$E_0/(\text{kJ} \cdot (\text{g} \cdot \text{mol})^{-1})$
$k_d/(\text{L} \cdot (\text{mol} \cdot \text{s})^{-1})$	4.97×10^7	50.16
$k_p/(\text{L} \cdot (\text{mol} \cdot \text{s})^{-1})$	4.97×10^7	50.16
$k_{\text{im}}/(\text{L} \cdot (\text{mol} \cdot \text{s})^{-1})$	6.16×10^3	50.16
$k_{\text{IH}}/(\text{L} \cdot (\text{mol} \cdot \text{s})^{-1})$	4.4×10^6	50.16
$k_{\text{IA}}/(\text{L} \cdot (\text{mol} \cdot \text{s})^{-1})$	7.04×10^2	50.16
$k_{\text{II}}/(\text{L} \cdot (\text{mol} \cdot \text{s})^{-1})$	7.92×10^3	50.16
$k_{\text{I2}}/\text{s}^{-1}$	7.92×10^3	50.16
$k_{\text{I3}}/(\text{L} \cdot (\text{mol} \cdot \text{s})^{-1})$	7.92×10^3	50.16

Using the Monte Carlo simulation, at first, the relationship between the polymerization time and the total amount of $\text{R}(1)$ of the studied system was simulated and plotted in Fig. 1. Fig. 1 shows that the total amount of active species of the system increases in the period of 0 to 0.04 s, and reaches its maximum value, and remains unchanged after about 0.04 s, which is short enough in comparison with the whole reaction times of reaching high conversion. So the stationary state assumption is valid.

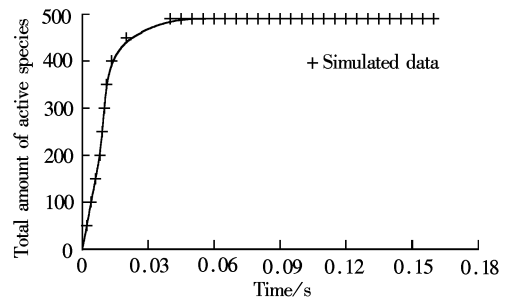


Fig. 1 Simulated amount of active species vs. time at 348 K

Fig. 2 illustrates the time-dependent amount of the propylene at different polymerization temperatures. The curves in Fig. 2 show that the amount of monomer decreases as the polymerization time increases. It means that the polymerization conversion increases with the increase of polymerization time. From Fig. 2, we can also determine that the consumption

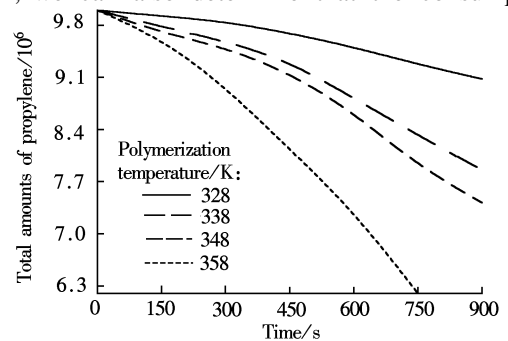


Fig. 2 Simulated amount of propylene vs. time at different temperatures

rate of the propylene increases with the increase of polymerization temperature, which may be due to the increase of the values of the kinetic rate constants with the increase of polymerization temperature.

Fig. 3 illustrates that the relationship between the polymerization time and the number-average degree of polymerization at different polymerization temperatures.

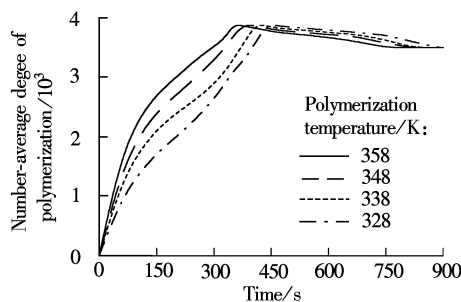


Fig. 3 Number-average degree of polymerization vs. time at different temperatures

It is shown from all the curves in Fig. 3 that the number-average degree of polymerization increases as the polymerization time increases until about 400 s. The number-average degree of polymerization increases up to its maximum and then decreases a little bit to become constant. From Fig. 3, we also notice that the maximum values of the number-average degree of polymerization are constant and their positions are different at different temperatures. The peak appears earlier with the higher temperature. It means that the time from the minimum value to the maximum value decreases with the increase of polymerization temperature. According to $k = k_0 \exp(-E_0/RT)$, we can obtain that the values of the kinetic rate constants increase with the increase of polymerization temperature. However, the value of k_p increases faster than that of other constants listed in Tab. 1, where the value of k_{p0} is greater than the other k_0 . Therefore, the rate of propylene propagation increases faster comparatively, and the peak appears earlier with the increase of polymerization temperature.

To indicate the effects of the polymerization temperature on the molecular weight in detail, we obtained the molecular weight distribution data at different temperatures via the Monte Carlo simulation. According to Fig. 3, we chose 500 s as the simulation time when the number-average degree of the simulated system is closer to that of a factory in industry. The simulated average molecular weights and their polydispersity indices at different temperatures are listed in Tab. 2. The corresponding molecular weight distribution curves at different temperatures are shown in Fig. 4.

Tab. 2 Molecular weight and its polydispersity index at different temperatures

Temperature/K	Number-average molecular weight/ 10^5	Weight-average molecular weight/ 10^5	Polydispersity index
328	1.646 40	3.407 88	2.069 9
338	1.630 46	3.393 80	2.081 5
348	1.605 66	3.357 76	2.091 2
358	1.587 53	3.333 97	2.100 1

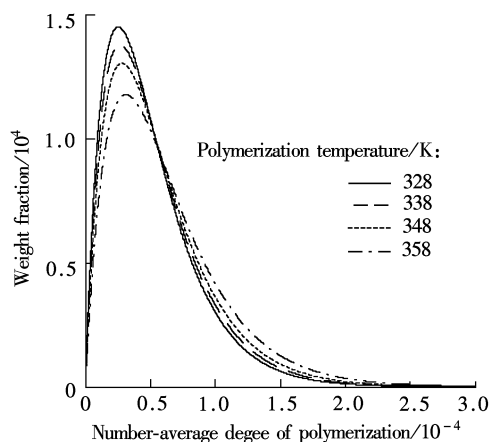


Fig. 4 Weight fraction vs. number degree of polymerization at different temperatures

Tab. 2 shows that the average molecular weight (the number-average molecular weight and the weight-average molecular weight) decreases a little when the polymerization time is 500 s, but the polydispersity index increases a little as the polymerization temperature increases. From Fig. 4, we can obtain that the higher the temperature, the less the peak's value. It means that the curve changes more evenly and its width changes more greatly with the increase of polymerization temperature. So, we can determine that the molecular weight distribution shifts to wider distribution with the increase of polymerization temperature, namely, the polymers with the higher molecular weight and narrower molecular weight distribution can be obtained at a lower polymerization temperature. This result is similar to that obtained by Choi et al.^[10] and is attributed to Ziegler-Natta catalyst with multi-active sites. In fact, the multi-active sites lead to the wide molecular weight distribution. Moreover, with the increase of polymerization temperature, the consumption rate of the propylene increases. Accordingly, the concentration of the propylene near the active sites decreases with the increase of polymerization temperature. According to Ref. [10], lower concentration of the propylene leads to wider molecular weight distribution. In short, the Monte Carlo simulation shows that the average molecular weight decreases, yet the molecular weight distribution changes more broadly with the increase of polymerization temperature.

3 Conclusion

The Monte Carlo simulation was used to study the validity of the stationary state assumption and the effects of the polymerization temperature on the polymerization. The simulated results show that the stationary state assumption used in the system of the propylene polymerization is valid. For simulated polymerization time, the consumption rate of propylene increases with the increase of polymerization temperature. The maximum values of the number-average degree of polymerization are constant at different polymerization temperatures; however, the peak appears earlier with the higher temperature, and as the polymerization temperature increases, the average molecular weight decreases and the molecular weight distribution changes greatly. Further study on propylene polymerization systems via the Monte Carlo simulation is in progress.

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基于蒙特卡罗模拟的不同聚合温度下的丙烯聚合动力学研究

罗正鸿¹ 黄 凯² 曹志凯¹

(¹ 厦门大学化学工程与生物工程系, 厦门 361005)

(² 东南大学化学化工系, 南京 210096)

摘要:在不考虑其他杂质参与聚合反应的情况下,并基于已有对丙烯聚合反应过程的普适化认识,提出了一个普适的丙烯聚合反应机理(基元反应).在已有的丙烯聚合反应机理基础上,为了证实该聚合反应过程总活性基是否满足“稳态假定”以及考察聚合反应温度对聚合过程的影响,采用蒙特卡罗模拟方法研究了传统 Ziegler-Natta 催化剂催化下的丙烯聚合动力学.模拟得到的总活性基数目在丙烯聚合初期快速增加到峰值,然后随聚合反应的进行保持恒定,证实了丙烯聚合过程中总活性基符合稳态假定.同时,模拟得到了聚合温度对丙烯聚合过程的转化率、分子量的影响.模拟结果表明:在聚合过程中,丙烯单体的消耗速率随聚合温度升高而增加;不同聚合温度下的数均聚合度峰值相同,但随温度增加,数均聚合度峰值来得早;随聚合温度增加,数均分子量减少,分子量分布变宽.

关键词:蒙特卡罗模拟;丙烯聚合;动力学;聚合温度

中图分类号:TQ316.3