ELSEVIER

Polymer 41 (2000) 8703–8707

polymer

www.elsevier.nl/locate/polymer

Monte Carlo simulation of gas phase polymerization of 1,3-butadiene Part I. Modeling and programming

Jun Ling, Xufeng Ni, Yifeng Zhang, Zhiquan Shen*

Department of Polymer Science and Engineering, Zhejiang University, Hangzhou 310027, People's Republic of China

Received 13 January 2000; received in revised form 9 March 2000; accepted 21 March 2000

Abstract

Monte Carlo method has been firstly applied to gas phase polymerization system. The kinetics of gas phase polymerization of 1,3-butadiene catalyzed by rare earth complex with trialkyl aluminum is discussed. Both absorption and diffusion of monomer in polymer particles are considered. A model and a computer program to simulate gas phase polymerization system are established. The reaction rate constants are obtained by simulating all the five elemental reactions of the polymerization including propagation. According to the results of Monte Carlo simulation, three reasonable polymerization rate versus time curves coincide with experiments with errors between 0.91 and 5.78%. Two kinds of chain transfer reaction contain similar possibilities but play different roles in polymerization. © 2000 Published by Elsevier Science Ltd.

Keywords: Monte Carlo simulation; Kinetics; Gas phase polymerization

1. Introduction

Monte Carlo methods have been applied for a long time in simulating coupled chemical reactions [1] and polymerization reactions [2] in order to investigate the kinetic behavior at the molecular level. Owing to the speedy development of computer science, recently, Monte Carlo simulation has made a great progress. Platkowski [3] reviewed the concepts and the practices of Monte Carlo simulation methods. Meanwhile, some papers had used a Monte Carlo simulation method for the inverse emulsion polymerization [4], anionic polymerization and copolymerization [5], copolymerization by ester interchange reaction in miscible polyester blends [6]. Tobita [7,8] established a simulation system for the degradation of polymers.

Gas phase polymerization of 1,3-butadiene catalyzed by rare earth complex with trialkyl aluminum has been successfully carried out in our laboratory. This paper reports the first modeling and programming of Monte Carlo simulation of gas phase polymerization of 1,3-butadiene. A set of reaction rate constants in kinetic assumptions was obtained from Monte Carlo simulation, and two kinds of chain transfer reactions are discussed.

2. Kinetics presumption

According to our experiments and the data reported in literature on 1,3-butadiene solution polymerization [9–12], the elemental reactions of gas phase polymerization of 1,3-butadiene are presumed as follows:

initiation k_i: $C + M \rightarrow R_1^*$ Rate $= k_i \cdot [C] \cdot [M]$
propagation k_p: $R_n^* + M \rightarrow R_{n+1}^*$ Rate $= k_p \cdot [R_n^*] \cdot [M]$
deactivation k_d: $R_n^* \rightarrow P_n$ Rate $= k_d \cdot [R_n^*]$
chain transfer to AlR_3
k_{trAl}: $R_n^* + AlR_3 \rightarrow P_n + C$ Rate $= k_{trAl} \cdot [R_n^*] \cdot [AlR_3]$
chain transfer to monomer
k_{trM}: $R_n^* + M \rightarrow P_n + R_1^*$ Rate $= k_{trM} \cdot [R_n^*] \cdot [M]$

where C is the catalytic center and M the monomer.

It was found that 1,3-butadiene cannot be polymerized by trialkyl aluminum alone during gas phase polymerization, which was similar to that in solution polymerization [10,11]. Therefore, in this paper the active site of growing chain (R_n^*) is regarded as rare earth metal–carbon bond and the insertion of monomer to aluminum–carbon bond is neglected.

Polymerization rate versus time curve, shown in Figs. 1–3, reveal a peak that usually appears at 6–10 min after the reaction process begins. The rate of monomer's first insertion into the active site of catalyst is much slower than that of the subsequent propagation. Furthermore, a highly stereoregular polybutadiene with *cis*-1,4 content >97% is

---

* Corresponding author. Tel.: +86-571-795-1059; fax: 86-571-795-1773.
E-mail address: zqshen@163.net (Z. Shen).

PII: S0032-3861(00)00271-8

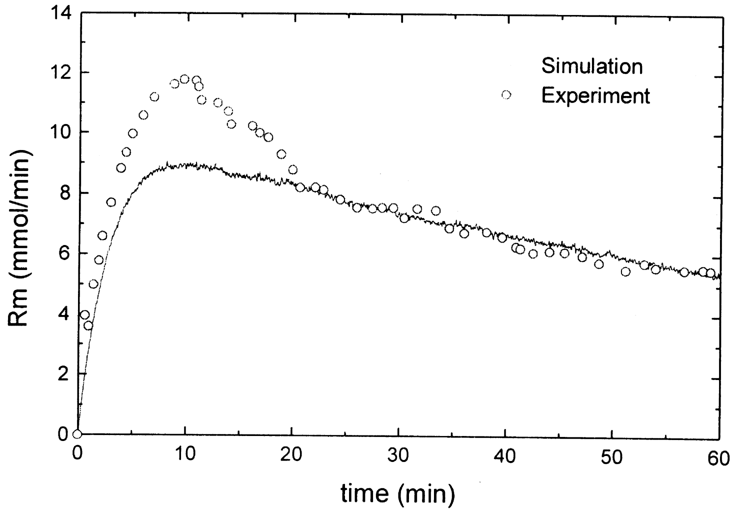

Fig. 1. Comparison of the polymerization rate–time curve of simulation and experiment. Run 1: [Cat] = 4.87×10^{-5} mol/l; monomer = 0.201 MPa; $T = 40$°C; error% = 5.78.

obtained from gas phase polymerization. According to Furukawa's "back-biting" mechanism [13], *cis*-1,4 chain structure accelerates the propagation. Therefore, "slow initiation, fast propagation" is presumed, i.e. $k_i < k_p$.

Besides initiation, propagation and deactivation, two types of chain transfer reactions in polymerization are taken into account: transfer to the trialkyl aluminum and transfer to the monomer.

3. Modeling and simulation

Gas phase polymerization was performed in a stainless steel reactor with a stirrer under constant temperature (T) and pressure (P). The apparent polymerization rate is defined as the consumption of 1,3-butadiene: $R_m = \delta n/\delta t$, where δn is the amount of consumed monomer during the measured time (δt) which is correlated to the decreased pressure (δp) in the reactor. As the polymer absorbs the monomer, the amount of the consumed monomer (δn) equals the sum of both the part that is correlated to apparent pressure decrease (δn_p) and the part that is released from the polymer (δn_S): $\delta n = \delta n_p + \delta n_S$. The function $\delta n_p = f(\delta p)$ is derived from Peng's equation [14]:

$$P = \frac{\mathrm{R}T}{V_m - b} - \frac{a(T)}{V_m(V_m + b) + b(V_m - b)}$$

which was used to replace the ideal gas equation for calculating monomer concentration of the bulk gas phase.

Absorption factor, $S_{T,P}$, is defined as the amount of 1,3-butadiene absorbed by polybutadiene under established temperature (T) and pressure (P). $S_{T,P}$ is presumed to be independent of the size of the polymer particles and of the

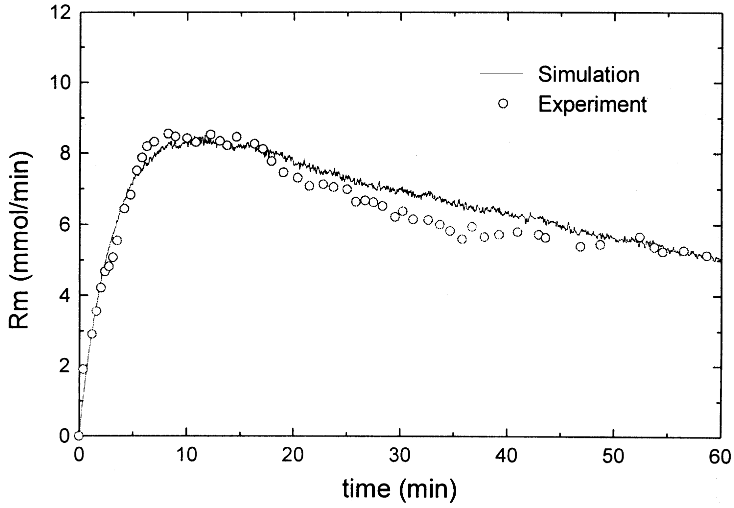

Fig. 2. Comparison of the polymerization rate–time curve of simulation and experiment. Run 2: [Cat] = 5.05×10^{-5} mol/l; monomer = 0.176 MPa; $T = 40$°C; error% = 3.07.

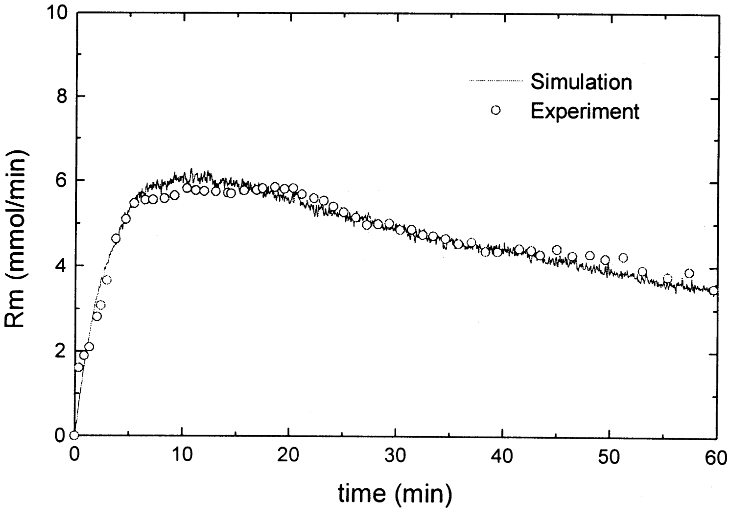

Fig. 3. Comparison of the polymerization rate–time curve of simulation and experiment. Run 3: [Cat] = 3.03×10^{-5} mol/l; monomer = 0.201 MPa; $T = 40$°C; error% = 0.91.

structure mode of accumulation. Thus the decreased pressure (δp) correlates with the amount of absorption (δS): $\delta n_S = N_{PBd} \cdot \delta S$. δS is measured by collecting the 1,3-butadiene gas released from polybutadiene. However, the measurement of δS is not very precise. The value of δS has also been calculated theoretically which will be discussed later. According to the measurement, monomer concentration in the polymer is about 1.6 mol/l at 40°C and 0.2 MPa.

Diffusion of the monomer in polymer particle is considered in the study. The monomer is absorbed at the surface of the polymer particles as it enters them. During the polymerization, growing centers are wrapped in polymer particles. Because of the diffusion resistance in particles, radial distribution of monomer concentration develops along the particle diameter coinciding with Sun's model [15]. In order to simplify the modeling, only gas phase 1,3-butadiene concentration is used in the Monte Carlo simulation. Therefore, k_i, k_p and k_{trM} obtained from simulation contain a factor K given by $K = [M]^0/[M]$ (where $[M]^0$ denotes the real monomer concentration), and real rate constants ($k^0_{i,p,trM}$) are described as $k_{i,p,trM} = K \cdot k^0_{i,p,trM}$.

Based on the above assumptions, polymerization rate obtained from experiments (R_m) and the amount of polybutadiene calculated by integral method are iterated from the following equation:

$$R_m = [f(\delta p) + N_{PBd}\delta S] \cdot \frac{1}{\delta t}$$

until an error of 0.01% is reached. Meanwhile, δS is obtained by comparing N_{PBd} with the quantity of the product obtained from experiment. The comparison of the iteration curve and experiment results is shown in Fig. 4.

Monte Carlo method used for programming in this paper

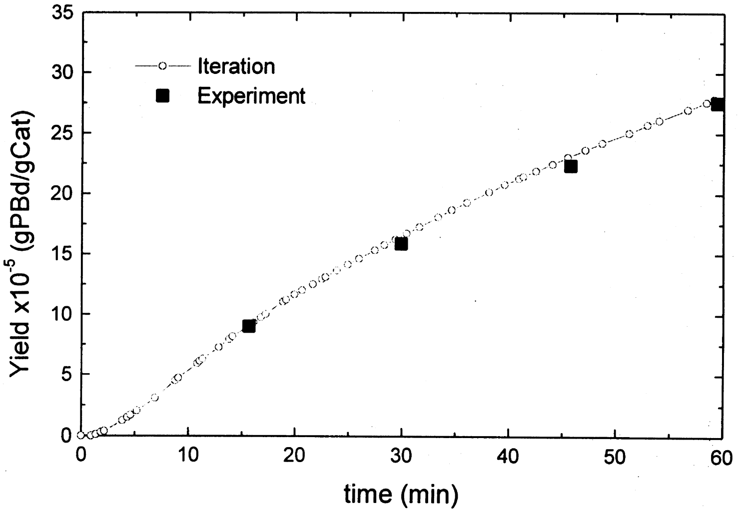

Fig. 4. Iterated yield of the polymer by δS adjustment.

Table 1
Optimal reaction constants (l mol^{-1} min^{-1}; k_d, min^{-1})

k_i	k_p	k_{trAl}	k_{trM}	k_d
3.6 ± 0.2	19 000 ± 1000	40 ± 5	1.0 ± 0.1	0.0140 ± 0.0005

is based mainly on the literature with a few modifications [2,3]. All five elemental reactions of polymerization including propagation are involved in simulation. As far as the ith reaction is concerned, its possibility is $a_i = \pi_i \cdot \prod_j X_{i,j}$ at time t, where $X_{i,j}$ is the number of the jth kind of molecules. After normalization, above equations become $a_i^0 = a_i / \sum_i a_i$. Accumulated possibilities are shown as $P_i = \sum_1^i a_i^0$. Then the kind of reaction is determined by drawing a random number r_1 from P_i. The time increment is determined by Gillespie's method [1]

$$\tau = \frac{\ln(1/r_2)}{\sum_i a_i}$$

where r_2 is another random number.

It is well known that the major problem in programming Monte Carlo method is the huge amount of calculation needed and the limited memory capacity of the computer. The program in our study is designed in the C++ language. Random numbers are obtained from the generator of C++ compiler. The time in computer serves as the seeds in initiating random numbers, and reset the generator several times with the help of random number r_3 during the program running to guarantee that the random numbers had a long period. Huge arrays are established for recording 120,000 units per chain, which give the macromolecules with a molecular weight over six million. Because the possibility of propagation is much larger than other reactions, Tong's method [16] is applied for the small possibility events

$$a_S' = n \cdot a_S, \qquad \mathrm{WF} = \frac{n \cdot a_S}{a_L}$$

where the factor WF is predetermined as 0.001. Because of the limit of the computer's memory, the number of monomer molecules in the simulations are fixed as 1×10^8 which occupy simulation volumes between 10^{-15} and 10^{-14} l under various experimental conditions. Thus, the average time increment was about 10^{-3} ms in all the reactions except propagation. It costs 20 min to finish a 60 min polymerization on a Pentium II 350 MHz computer.

Table 3
Monte Carlo simulation results of chain transfer reaction in polymerization (polymerization conditions are same as Table 2)

Run	CTR-Al	CTR-M	CTR total	CTR-Al/CTR-M
1	3.0	3.1	6.1	0.97
2	3.4	2.6	6.0	1.31
3	2.0	3.3	5.3	0.61

Monte Carlo simulation program builds a Rm–time curve with given rate constants. The optimal constants are obtained when the minimum difference between the experimental and simulation results is reached. The confidence intervals of every constant are defined as their adjustment values in the simulation. To examine the quality of simulation, average error is calculated as

$$\mathrm{error\%} = \frac{1}{N} \sum \frac{|\mathrm{Rm}^{\mathrm{Sim}} - \mathrm{Rm}^{\mathrm{Exp}}|}{\mathrm{Rm}^{\mathrm{Exp}}}$$

where $\mathrm{Rm}^{\mathrm{Sim}}$ and $\mathrm{Rm}^{\mathrm{Exp}}$ are Rm values of simulation and experiment, respectively, and N is the number of experimental data.

Tables 1–3 and Figs. 1–5 summarize the results of the Monte Carlo simulations.

4. Results and discussion

In order to examine the absorption mentioned above, the iteration curve of polymerization yield versus time in a single experiment according to δS modification has been made. Fig. 4 shows the remarkable agreement of the four experimental results with iterations and proves that the assumption of monomer absorption in polymer particles is correct, and δS varies from 0.0015 to 0.0025 under various polymerization conditions.

Rm–time curves of Monte Carlo simulation correspond to experiments as shown in Figs. 1–3 with average errors between 0.91 and 5.78% by using the rate constants in Table 1. Errors in Figs. 2 and 3 are very little. The large difference between the experimental and simulation results in Fig. 1, occurring at the beginning of polymerization, may be caused by larger amount of catalyst, higher monomer pressure and the poor transfer of reaction heat to the outside.

Table 2
Molecular weights from Monte Carlo simulations and experiments (polymerization conditions: 40°C, 60 min; catalyst contains a fixed ratio of trialkyl aluminum)

Run	[Catalyst] × 10^{-5} (mol/l)	Pressure (MPa)	M_n[a] × 10^{-4}	M_n[b] × 10^{-4}	M_w[a] × 10^{-4}	MWD[a]
1	4.87	0.201	43.5	43.9	85.1	1.95
2	5.05	0.176	38.9	42.5	75.6	1.94
3	3.03	0.201	52.3	44.9	100.6	1.92

[a] Obtained from Monte Carlo simulations.
[b] Measured by viscosity in toluene at 30°C.

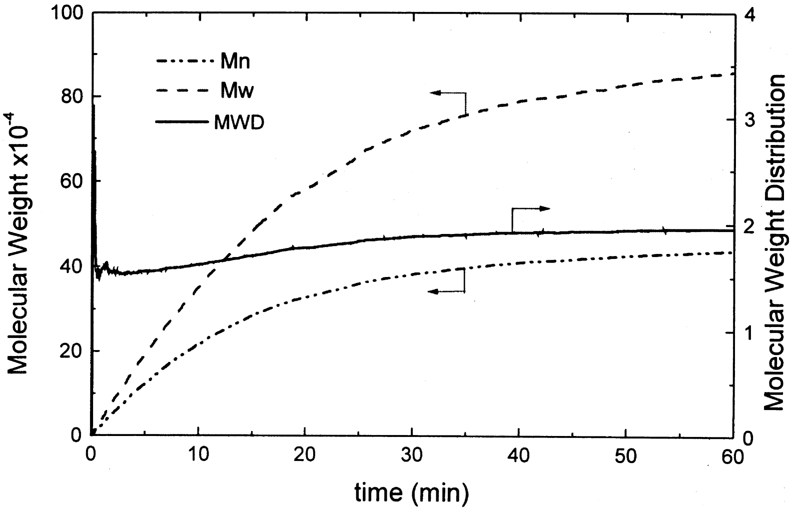

Fig. 5. Simulated molecular weight and its distribution of Run 1.

After 20 min, polymerization reached a "pseudo-stability" due to the small deactivation constant and the balance maintained between the concentrations of the active center and the catalyst.

Molecular weights obtained from simulations and experiments are listed in Table 2. Number average molecular weights are measured by viscosity and calculated according to the equation [17] $[\eta] = 3.05 \times 10^{-4} M_n^{0.725}$. As shown in Fig. 5, molecular weights and molecular weight distribution increase along with the reaction time approaching their maximum values.

Two kinds of chain transfer reactions: CTR-Al and CTR-M are affected by the catalyst amount and monomer pressure as shown in Table 3. On average a growing chain involves about six times of transfer reactions. In gas phase polymerization, trialkyl aluminum concentration is less than the monomer concentration. Moreover, trialkyl aluminum is supported on a carrier with a lower diffusion velocity than that of the monomer. Despite the fact that the trialkyl aluminum transfer constant is higher than that of the monomer ($k_{trAl}/k_{trM} = 40$), the two reactions occur at the same level.

5. Conclusions

Monte Carlo simulation has been applied to a gas phase polymerization system. 1,3-butadiene acts as an example to verify the modeling method and the program. Coinciding with experimental results, the Monte Carlo simulation gives a set of reaction rate constants and three reasonable polymerization rate versus time curves with errors between 0.91 and 5.78%. Two kinds of chain transfer reaction containing similar possibilities are derived. Further studies on gas phase polymerization systems by Monte Carlo simulation are in progress.

Acknowledgements

The authors are grateful to the financial supports of National Natural Science Foundation of China (No. 29734130 and 29974024), The Ministry of Education of China (G98402), and Zhejiang Provincial Commission of Science and Technology.

References

[1] Gillespie DT. J Phys Chem 1977;81(25):2340.
[2] Yang YL, Zhang HD. Monte Carlo method in polymer science. Shanghai: Fudan University Press, 1993 (chap. 7, p. 237).
[3] Platkowski K, Reichert K-H. Polymer 1999;40:1057.
[4] Platkowski K, Pross A, Reichert K-H. Polym Int 1998;45:229.
[5] Hamaide T. Actual Chim 1997;10:26 (Chem Abstr 128:74904f).
[6] Jang SS, Ha WS, Jo WH, Youk JH, Kim JH, Park CR. J Polym Sci: Polym Phys Ed 1998;36:1637.
[7] Tobita H. Macromolecules 1996;29:3000.
[8] Tobita H. Macromolecules 1996;29:3010.
[9] Iovu H, Hubca G, Racoti D, Hurst JS. Eur Polym J 1999;35:335.
[10] Pan E, Zhong CQ, Xie DM, Ouyang J. Acta Chim Sinica 1982;40(4):301.
[11] Pan E, Zhong CQ, Xie DM, Ouyang J. Acta Chim Sinica 1982;40(5):395.
[12] Ji XZ, Feng SF, Li YL, Ouyang J. Chin J Appl Chem 1985;2(4):16.
[13] Furukawa J. Pure Appl Chem 1975;42(4):495.
[14] Peng DY, Robinson DB. Ind Engng Chem Fundam 1976;15(1):59.
[15] Sun JZ, Eberstein C, Reichert KH. J Appl Polym Sci 1997;64:203.
[16] Tong WD, Lu JM, Sun M, Yang YL. Chem J Chin Univ 1997;12:979.
[17] Danusso F, Moraglio G, Gianotti G. J Polym Sci 1961;51:475.