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Monte Carlo simulation for the modification of polymer via grafting

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Abstract

Monte Carlo method has been applied to investigate the kinetic of grafting reaction in free radical copolymerization. The simulation is quite in agreement with that of theoretical and experimental results. It proves that the Monte Carlo simulation is an effective method for investigating the grafting reaction of free radical copolymerization. © 2000 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Modification of polymeric materials to improve their performance for specific use has been a fascinating field for research. A great amount of research works have been published in this area [1,2]. Modification of polymers through graft copolymerization offers an effective means for introducing some desirable properties into the polymer without affecting the architecture of the polymer backbone. The functionalized polymers have been extensively used for the compatibilization of immiscible polymer blends as well as the improvement of interfacial adhesion in polymeric composites [3].

Although the free radical graft copolymerization mechanism has been known for some times, relatively few articles described graft copolymerization kinetics. Cameron et al. [4–7] grafted styrene monomer onto polybutadiene in benzene solution at 60°C with benzoyl peroxide as initiator. Chern and Poehlein [8] proposed a detailed mechanism based on Cameron's experimental data. Manaresi et al. [9] grafted styrene onto polybutadiene in bulk at 100°C containing α-dicumyl peroxide as initiator. Sundberg et al. [10–14] grafted styrene onto polybutadiene in emulsion and grafted styrene, acrylate, and methacrylate onto *cis*-polybutadiene in solution.

In the last decades, Monte Carlo simulation was shown to be a powerful method for investigating the kinetics in polymerization [15–19]. With this method, the parameters, such as, number-average degree of polymerization, weight-average degree of polymerization and molecules-weight distribution etc. are able to be monitored at any times in period of polymerization, which are in generally difficult, if not possible, to be obtained experimentally and theoretically. The goal of this study is to apply this stochastic method to the prediction of graft copolymerization characteristics, and

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compare with known theory and experiment to verify the validity of the simulation, so that it can be applied to other new systems, which is in proceeding in our laboratory.

2. Principle of Monte Carlo simulation of copolymerization

The principle for the stochastic simulation of grafting polymerization is based on Gillespie's algorithm [20]. We would like to give a brief description.

Suppose the reaction system is spatially homogeneous and has a volume V. As microscopic elementary reactions occur discretely and stochastically through N reaction channels, the kind of reaction which will happen in a time interval $(t, t+\tau)$ can be determined by a unit-interval uniformly distributed random number, r_1, according to the following relation:

$$\sum_{v=1}^{\mu-1} P_v < r_1 \leq \sum_{v=1}^{\mu} P_v \tag{1}$$

$$P_v = \frac{R_v}{\sum_{v=1}^{N} R_v} \tag{2}$$

where μ is the number of the selected reaction channel;P_v is the reaction probability of reaction v. R_v is the reaction rate of reaction v. N is the total number of reaction channels. Obviously, the probability given in Eq. (2) satisfy the normalization condition,

$$\sum_{v=1}^{N} P_v = 1 \tag{3}$$

If we assume that the reactivities of the chain radicals are independent of the chain length, the reaction rate of reaction v at time t are:

$$R_v = K_q \cdot X_q(t) \quad \text{for first-order reaction} \tag{4}$$

$$R_v = K_{sq} \cdot X_s(t) \cdot X_q(t) \quad \text{for second-order reaction} \tag{5}$$

where K_q, K_{sq} are the reaction rate constants for first- and second-order reactions, respectively. $X_s(t)$, $X_q(t)$ are the number of molecules of species s and q at time t, respectively. The time interval between two successive reaction, τ, is also a stochastic variable which can be determined by another unit-interval uniformly distributed random number, $r_2^{(20)}$.

$$\tau = \frac{1}{\sum_{v=1}^{\mu} R_v} \ln\left(\frac{1}{r_2}\right) \tag{6}$$

The rate constants in Eqs. (1)–(5) are microscopic and stochastic ones. To compare with the experimental results, these rate constants, K^{MC} should be transformed into macroscopic and deterministic rate constants obtained experimentally, $K^{\exp}$, according to the following relations [21,22]:

$$K^{\mathrm{MC}} = K^{\exp} \quad \text{for first-order reaction} \tag{7}$$

$$K^{\mathrm{MC}} = \frac{K^{\exp}}{V \cdot N_{\mathrm{a}}} = \frac{K^{\exp} \cdot [A]_0}{X_A^0} \tag{8}$$

for second-order reaction

Here, $[A]_0$ and X_A^0 are the initial amount concentration and the initial number of molecules of species A. N_{a} is the Avogadro constant and V is the total volume of the system.

3. Results and discussion

Manaresi et al. [9] grafted styrene onto the *cis*-1,4-polybutadiene in bulk at 100°C with α-dicumyl peroxide as initiator. According to the view of the Manaresi et al., the mechanism proposed for low extents of reaction and low rubber concentration is:

(1) $\mathrm{I} \xrightarrow{K_{\mathrm{d}}} 2\mathrm{I}^{\cdot}$ decomposition of initiator
(2) $\mathrm{I}^{\cdot} + \mathrm{M} \xrightarrow{K_{\mathrm{i1}}} \mathrm{M}_1^{\cdot}$ initiation
(3) $2\mathrm{M} \xrightarrow{K_{\mathrm{th}}} 2\mathrm{M}_1^{\cdot}$ thermal initiation
(4) $\mathrm{I}^{\cdot} + \mathrm{RH} \xrightarrow{K_{\mathrm{i2}}} \mathrm{IH} + \mathrm{R}^{\cdot}$ attacking rubber
(5) $\mathrm{R}^{\cdot} + \mathrm{M} \xrightarrow{K_{\mathrm{i3}}} \mathrm{RM}_1^{\cdot}$ re-initiation
(6) $\mathrm{M}_n^{\cdot} + \mathrm{M} \xrightarrow{K_{\mathrm{p}}} \mathrm{M}_{n+1}^{\cdot}$ propagation of homopolymerization
(7) $\mathrm{RM}_n^{\cdot} + \mathrm{M} \xrightarrow{K_{\mathrm{p}}} \mathrm{RM}_{n+1}^{\cdot}$ propagation of graft polymerization
(8) $\mathrm{M}_n^{\cdot} + \mathrm{M} \xrightarrow{K_{\mathrm{tM}}} \mathrm{M}_n + \mathrm{M}_1^{\cdot}$ chain transfers to monomer
(9) $\mathrm{RM}_n^{\cdot} + \mathrm{M} \xrightarrow{K_{\mathrm{tM}}} \mathrm{RM}_n + \mathrm{M}_1^{\cdot}$ chain transfers to monomer
(10) $\mathrm{M}_n^{\cdot} + \mathrm{RH} \xrightarrow{K_{\mathrm{tR}}} \mathrm{M}_n\mathrm{H} + \mathrm{R}^{\cdot}$ chain transfers to rubber
(11) $\mathrm{RM}_n^{\cdot} + \mathrm{RH} \xrightarrow{K_{\mathrm{tR}}} \mathrm{RM}_n\mathrm{H} + \mathrm{R}^{\cdot}$ chain transfers to rubber
(12) $\mathrm{M}_n^{\cdot} + \mathrm{M}_m^{\cdot} \xrightarrow{K_{\mathrm{t1}}} \mathrm{M}_{n+m}$ termination
(13) $\mathrm{RM}_n^{\cdot} + \mathrm{RM}_m^{\cdot} \xrightarrow{K_{\mathrm{t1}}} \mathrm{RM}_{n+m}\mathrm{R}$ termination
(14) $\mathrm{RM}_n^{\cdot} + \mathrm{M}_m^{\cdot} \xrightarrow{K_{\mathrm{t1}}} \mathrm{RM}_{n+m}$ termination
(15) $\mathrm{R}^{\cdot} + \mathrm{R}^{\cdot} \xrightarrow{K_{\mathrm{t3}}} \mathrm{RR}$ termination
(16) $\mathrm{R}^{\cdot} + \mathrm{RM}_n^{\cdot} \xrightarrow{K_{\mathrm{t2}}} \mathrm{RM}_n\mathrm{R}$ termination
(17) $\mathrm{R}^{\cdot} + \mathrm{M}_n^{\cdot} \xrightarrow{K_{\mathrm{t2}}} \mathrm{RM}_n$ termination

where I the peroxide, M is the monomer, RH is the polybutadiene, $\mathrm{M}_n^{\cdot}$ is the free styrene chain radical with chain length n, $R_n^{\cdot}$ is the grafted styrene chain radical with chain length n, $R^{\cdot}$ is the radical on the polybutadiene chain, K_d, K_{th}, K_{i1}, K_{i2}, K_{i3}, K_p, K_{tM}, K_{tR}, K_{t1}, K_{t2}, K_{t3} are the rate constants for the 17 reaction channels.

In this kinetic treatment, Manaresi et al. [9] considered the free and grafted polystyrene radicals to be equally reactive. The peroxide efficiency was considered to be constant and was included in the constant K_d. The thermal initiation is second order. Assuming that a stationary state exists for all radicals, Manaresi et al. developed a rigorous mathematical model of the reaction. According to this model, they estimated the following values of kinetic constants:

$$K_d = 2.26 \times 10^{-6}, K_p = 1.67 \times 10^3, K_{t1} = 1.88 \times 10^8, K_{th} = 5.264 \times 10^{-11},$$

$$K_{tm} = 0.3384, K_{tR} = 1.88, \frac{K_{i3}}{K_{t2}} = 3.0 \times 10^{-9}, \frac{K_{i2}}{K_{i1}} = 2, \theta = \frac{K_{t1} \cdot K_{t3}}{K_{t2}^2} = 0.0005 \sim 0.01$$

By using above values of kinetic constants, we performed the Monte Carlo simulation for grafting polymerization of styrene on *cis*-1,4-polybutadiene. The Monte Carlo performance of grafting mechanism proposed by Manaresi et al. can be described in detail as follows:

1. Separate a small volume from reaction system, in which it contains 7.866×10^{10} styrene monomers, the amount of butadiene segments (these butadiene segments exist in *cis*-1,4-polybutadiene chains style) and α-dicumyl peroxide molecules varied depend on the simulation conditions. In this simulation, we supposed 10^{10} molecules as 1 mol/l.
2. Calculate the reaction probability of 17 reaction channels, $P_1, P_2, \ldots, P_{17}$, by using a combination of Eqs. (2), (4), (5), (7) and (8) and the value of kinetics constants given above.
3. Arrange $P_1, P_2, \ldots, P_{17}$ in a confirmed sequence.
4. Produce a random number $R \in [0, 1)$, if $R < P_1$, the first reaction won, if $\sum_{i=1}^{x} P_i < R < \sum_{i=1}^{x+1} P_i$, the $(X + 1)$ reaction won, $x = 1, 2, \ldots, 16$.

The program was written in Fortran language, debugged and executed at Pentium 166 Hz Personal Computer. Fig. 1 shows that the total amount of radicals in the system increase as times in the period of 0–3 s, and reach its maximum value and remain unchanged after ~3 s, which is short enough in comparison with the whole reaction times of reaching high conversion (generally several hours), so the stationary state assumptions used by Manaresi et al. [9] in their mathematical model of reaction are proved to be correct. Figs. 2 and 3 show the agreement among the

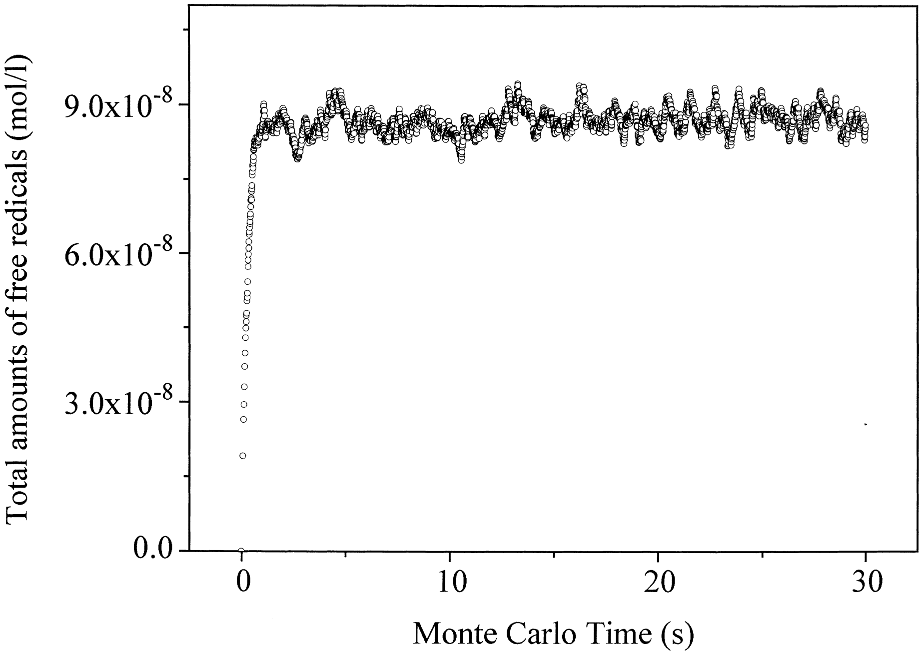

Fig. 1. Simulation of the total amount of free radical in the reaction system at time t.

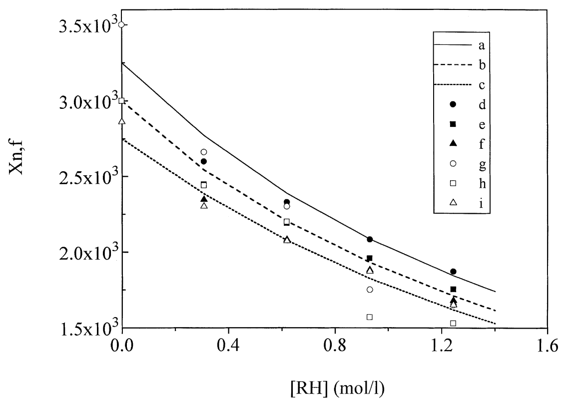

Fig. 2. Simulation data (solid), calculated curves (lines) and experimental data (open) for the number-average degree of polymerization of free polystyrene. (a), (d), (g) 0.00310; (b), (e), (h) 0.00620; (c), (f), (i) 0.00930 mol/l peroxide.

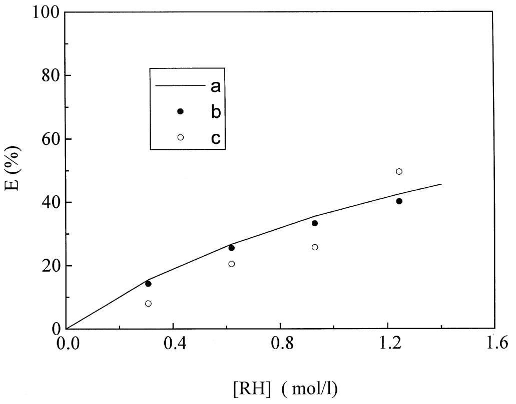

Fig. 4. Simulation data (solid), calculated curve (line) and experimental data (open) for the grafting efficiency at 0.00310 mol/l peroxide.

simulation, theoretical and experimental data of the number-average degree of polymerization of free and grafted polystyrene $\bar{X}_{n,\mathrm{f}}$, $\bar{X}_{n,\mathrm{g}}$, the theoretical and experimental data are from Manaresi et al. [9]. Fig. 4 shows that the simulation data of grafting efficiency is in agreement with that of the theoretical analysis. However, in Figs. 2–4, it is clear that there exists small differences between simulated and calculated results, this is due to the influence of the system size. The maximum monomer numbers in our simulation system is $\sim 10^{10}$, further increasing the monomer numbers will result in an unbearable long calculation time in present calculation system. However, 10^{10} monomers is far from the molecule numbers contained in the true reaction system ($\sim 10^{23}$). Further decreasing the concentration of monomer will make the difference between the simulation and theoretical results as shown in Fig. 2, when concentration of butadiene is lower than 0.4 mol/l, i.e. less than 4×10^9 butadiene units in the system, the bigger difference appears. From Fig. 3, when concentration of butadiene is lower than 0.5 mol/l, and lower initiator concentration (0.00310 mol/l), bigger difference also appears. So, it is believable that the difference can be avoided by increasing the monomer numbers with high performance calculation system.

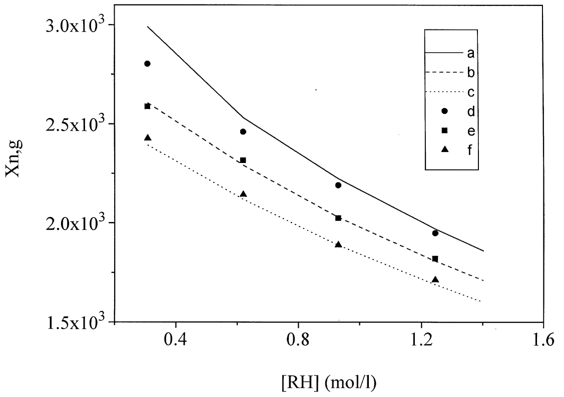

Fig. 3. Simulation data (solid), calculated curves (lines) for the number-average degree of polymerization of grafted polystyrene. (a), (d) 0.00310; (b), (e) 0.00620; (c), (f) 0.00930 mol/l peroxide.

4. Conclusions

Based on the mechanism proposed by Manaresi et al. in investigating the kinetics of the grafting styrene onto the *cis*-1,4-polybutadiene, Monte Carlo method has been proved to be an effective method for investigating the kinetic of grafting reactions in free radical copolymerization. Not like the analytical method used by Manaresi et al., we need not assume a stationary state for all radicals. Therefore, this method can be applied to any other grafting copolymerization reaction system which is proceeding in our laboratory.

Acknowledgements

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