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Study diffusion effects on chain extension reactions based on the reptation theory

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Abstract

The diffusion effects on chain extension reactions, using carboxyl-terminated polyamide12 (PA12, say CA in this paper) as a model reactant with bisoxazolines (OO), were simulated by the stochastic Monte Carlo (MC) method. The chain length dependence and detailed diffusive behavior of each chain were considered based on the reptation theory. It is found that the diffusion effects retard the progress of chain extension reactions and, lead to a lower coupling efficiency and a lower molecular weight. The simulated results indicate that the diffusion effects can make the final molecular weight distribution (MWD) wider. In the presence of diffusion and with the progress of p, peaks in the evolution curves of weight-average molecule weight ($\bar{M}_w$) and valleys in the evolution curves of polydispersity index, d, are observed, respectively, when p is small enough, which is different from those without diffusion effects, and has been analyzed in detail in this paper. The results also show that the effects of reactant degradation make the MWD of the reaction system wider, and weaken the diffusion effects on the coupling reaction.

Keywords: Chain extension reaction; Diffusion effects; Reptation theory

1. Introduction

In any case, a relative high molecular weight and low carboxyl content give polyester and polyamide both improved mechanical and chemical properties, such as toughness and hydrolytic stability [1,2]. But it is difficult to achieve these polymers because further heating during the preparation of the polyester by melt polycondensation process causes an undesirable degradation reaction with a significant increase in carboxyl terminal groups. An efficient approach for these polymers would be chain extension in the melt-phase via the reaction of the hydroxyl, amino or carboxyl terminals with chain extenders. When chain extenders react directly with low molecular weight polymers, they form a linkage between two polymer chains, increasing the molecular weight significantly [3,10]. Recent experimental studies about it mainly focus on the reaction kinetics and the efficiencies of different chain extenders [3]. The modeling of chain extension reaction kinetics has also been paid much attention [4–11]. For example, Chalamet et al. [4,5] proposed a differential equation kinetic model to analyze the effects of experimental condition on the reaction conversion and the structure of the resultant polymers. However, these models are based on the so-called 'equal reactivity assumption', which assumes that all polymer chains of the same functional groups are equally reactive, regardless of their molecular weight or any diffusion limitations that might exist in the system.

There are, however, several situations where the equal reactivity assumption fails [12]. For instance, if the reactive chain ends are far apart, they may explore their own neighborhoods rapidly, but collisions among reactive ends will not begin to occur until the chains diffuse to each other. As the reaction progresses, the concentration of chain ends decreases, comparing to the increasing of coupling resultants. The viscosity of the reaction system will increase considerably with a longer chain length and a higher concentration of coupling resultants due to some effects, such as a stronger entanglement among the longer molecular chains, and so on. In this sticky reaction system, the diffusion of the reactants is confined and diffusion limitations become more important. Eventually, the overall polymerization rate is likely to be affected by diffusion. Moreover, because larger polymer chains have longer diffusion time than their smaller counterparts,

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chain-length dependence of the overall kinetic parameter can be anticipated.

Evidence of diffusion effects on reactivity and polymerization mechanism has been apparent since early experimental studies [13]. It has been recognized that diffusion effects are important in free radical polymerization [14–21]. The impact of diffusion on the termination step is labeled as the Trommsdorff or gel effect, while the effects on propagation and initiation are known as the glass and cage effect, respectively. Different theories for the modeling of such effects have been proposed [22–24]. Diffusion effects on step-growth polymerization have also been investigated [12,25–31]. For example, the effect of diffusion on linear, step-growth polymerizations has been quantified via ‘chain-by-chain’ simulations of the polymerization process [12]. However, diffusion effects on chain extension reactions are understood somewhat less. For instance, Akkapeddi [6] considered the diffusion effects on chain extension reaction of poly(ethylene terephthalate) (PET) and nylons in an extruder. There are few kinetic models including degradation and diffusion effects [7,8]. Moreover, it should be noted that almost all these previous models about diffusion effects are based on the differential equations. In these cases, the chain length dependence and detailed diffusion kinetics of polymer chains are almost omitted. These methods also suffer from the larger calculation, especially in the case of very complex reaction schemes. Therefore, both the accuracy and reaction conversion one can reach are limited by available computer memory and CPU performance [32].

On the other hand, it is known that MC simulation has proved to be a powerful tool in the field of both polymer physics and polymer chemistry. This powerful method has been extensively used to study living free-radical polymerization [32], free-radical polymerization [33a–c], emulsion polymerization [33d,e,34], and so on [35–39]. The stochastic MC method based on the master equations described by Gillespie [40] has also proved to be a useful technique for studying the reaction kinetics [32,35,38]. The kinetic behaviors of chain extension reactions and the change of some parameters, such as MWD and the length of each chain, can be obtained simultaneously by this method. So, it should be a more efficient method to study the diffusion effects.

In this paper, the diffusion effects on chain extension reactions have been simulated by the stochastic MC method. Our main purposes are to exhibit a full view of the diffusion effects on chain extension kinetics, and to gain insight into its mechanism. The chain length dependence and detailed diffusive kinetics of each chain are considered based on the reptation theory [41]. Moreover, the degradation effects of the reactants on the diffusion effects are also discussed.

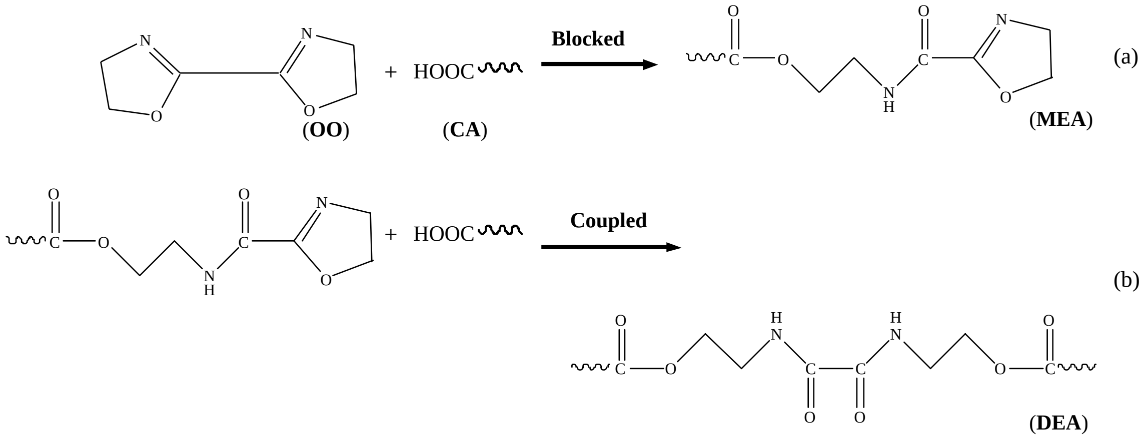
2. Model and Monte Carlo algorithm

2.1. Modeling

The elementary reactions of carboxyl terminated polymers (CA) using bisoxazolines (OO) as coupling agent are given in Scheme 1.

The oxazoline groups can react with the carboxyl terminal groups through addition reactions. These reactions lead first to monoesteramide (MEA) then to diesteramide (DEA). Reaction behavior of carboxyl terminals contained in the initial polymers can be classified into three groups, which are ‘blocked’, ‘coupled’ and ‘unreacted’, respectively. However, these elementary reactions do not include degradation effect which can affect the chain extension efficiency especially under extrusion conditions [4,6,7]. In this simulation, only the degradations of MEA and CA are considered because they have more effects on the diffusion effect of the coupling reaction, i.e. Scheme 1(b). The entire reactions are given in Scheme 2.

In Scheme 2, CA(i) is a CA chain with chain length i, MEA(i) is a monesteramide with chain length i, DEA(i) is a diesteramide with chain length i, and ME(i') is a degradation chain with chain length i'. The addition of CA to the first oxaline function of OO can change the reactivity of the residual oxaline function, leading to different values for the kinetic constant K_B and k_{chem}, where k_{chem}, which is given by the chemistry of the system, is the intrinsic coupling reaction rate and is independent of the chain length involving in the reaction



Scheme 1. The scheme of chain extension reactions using a bisoxazoline coupling agent.

$$\mathrm{OO} + \mathrm{CA}(i) \xrightarrow{K_B} \mathrm{MEA}(i) \qquad i = 1, 2, \ldots, i_{\max} \quad \text{Blocking reaction} \qquad (\mathrm{I})$$

$$\mathrm{MEA}(i) + \mathrm{CA}(j) \xrightarrow{K_{C(i,j)}} \mathrm{DEA}(i+j) \qquad j = 1, 2, \ldots, j_{\max} \quad \text{Coupling reaction} \qquad (\mathrm{II})$$

$$\mathrm{CA}(i) \xrightarrow{K_D} \mathrm{ME}(i') + \mathrm{ME}(j') \qquad \text{Degradation of CA} \qquad (\mathrm{III})$$

$$\mathrm{MEA}(i) \xrightarrow{K_D} \mathrm{ME}(i') + \mathrm{ME}(j') \qquad \text{Degradation of MEA} \qquad (\mathrm{IV})$$

Scheme 2. The entire chain extension concerned in the simulation.

[4]. However, this activity difference should be very small in the presented simulated system [4]. So $K_B = k_{chem}$ is proposed. The same degradation reaction kinetic constant, K_D, is set in Scheme 2(III) and (IV), because CA and MEA has almost the same chemistry structure. For simplicity, the decomposition of these species is randomly selected by mass.

2.2. *Diffusion effects of the coupling reaction*

Chain-length dependence of the kinetic constant is important when the reaction involves two large macromolecules [17]. So, in Scheme 2, only the diffusion effects of the coupling reaction is considered. There are two schools of theories, i.e. the reptation theory [41] and the free volume theory [42], relating the diffusion coefficient to polymer concentration and chain length. In this work, the diffusion process is represented according to the theory of reptation.

The relative contributions of chemical activation and diffusion to their rate constants can be expressed as follow

$$\frac{1}{K_C} = \frac{1}{k_{chem}} + \frac{1}{k_{i,j}} \tag{1}$$

In Eq. (1), $k_{i,j}$ is a 'diffusion' rate constant, i.e. the coupling reaction rate for a system with no chemical barriers where the reaction occurs upon collision of functional groups. Collins and Kimball [43] appear to be the first to give a theoretical justification for Eq. (1). More recent theoretical studies supporting Eq. (1) also exist [12,17,18].

For a bimolecular reaction, $k_{i,j}$ can be expressed in terms of the diffusivities D and trapping radii R of the reactants [44]

$$k_{i,j} \propto (R_i + R_j)(D_i + D_j) \tag{2}$$

Eq. (2) is used here as a first approximation. For linear polymer systems, the implicit assumption is that the overall reaction time is greater than the time required for one chain to disengage from its original tube. Without this simplifying assumption, $k_{i,j}$ would be a function of the reaction time [41]. In Eq. (2), the trapping radius R_i is equal to the gyration radius of a polymer chain with i repeat units [41]. Thus for an ideal coil [45]

$$R_i \propto \sqrt{i} \tag{3}$$

The relation between diffusivity and number of repeat units varies depending on whether the system is entangled or not [41]

$$D_i \begin{cases} i^{-1}, & \text{nonentangled} \\ i^{-2}, & \text{entangled} \end{cases} \tag{4}$$

In 1984, Tirrell [46] showed that the available diffusion data were consistent with the 'inverse square law' indicated by Eq. (4) for entangled, flexible, linear systems. More recent, Lodge's [47] study suggests a slightly different exponent (-2.3 instead of -2).A value of -2 is used in this study.

The proportionality constants in Eqs. (2)–(4) can be lumped together. Consider the Hatta number (Ha)

$$\mathrm{Ha}(i,j) = \frac{k_{chem}}{k_{i,j}} = \frac{\phi}{(\sqrt{i} + \sqrt{j})(i^{-\theta} + j^{-\theta})} \tag{5}$$

where $\theta = 1$ below entanglement and $\theta = 2$ otherwise. Note that if $i < N_{ent}$ and $i > N_{ent}$, two different values of θ will appear in Eq. (5), where N_{ent} is the critical entanglement chain length. The larger the values of the constant ϕ, the more important diffusion is in the polymerization process. Conversely, $\phi = 0$ corresponds to the case of no diffusion limitations. In terms of the Hatta number, the effective polymerization rate constant is given by

$$K_{C(i,j)} = \frac{k_{chem}}{1 + \mathrm{Ha}(i,j)} \tag{6}$$

With $K_{C(i,j)}$ defined by Eqs. (5) and (6), the diffusion effect of the coupling reaction can be investigated by the following MC method and the differential equation model.

2.3. *Monte Carlo algorithm*

The principle for the simulation of chain extension was based on the Gillespie's algorithm [40]. A small part of the overall reaction volume is picked out to be a suitable simulation space, which provides most of the information. Suppose the volume V contains a spatially homogeneous mixture of N chemical species, which can interact through S specified chemical reaction channels. The kind of reaction μ that will happen in a time interval $(t + \tau \to t + \tau + \Delta t)$ is determined by a unit-interval uniformly distributed random number, r_1, according to the following relation:

$$\sum_{v=1}^{\mu-1} R_v < r_1 \sum_{v=1}^{S} R_v < \sum_{v=1}^{\mu} R_v \tag{7}$$

where R_v is the rate of the vth reaction per molecule in the simulation volume. The time interval between two successive reaction, τ, is a stochastic variable determined by a unit-interval, uniformly distributed random number, r_2,

$$\tau = \frac{1}{\sum_{v=1}^{S} R_v} \ln\left(\frac{1}{r_2}\right) \tag{8}$$

In the present study, the rates from reaction 1 to 4 are listed as follows

$$R_1 = k_{\mathrm{B}}^{\mathrm{MC}}[\mathrm{OO}][\mathrm{CA}]$$

$$R_2 = k_{\mathrm{C}(i,j)}^{\mathrm{MC}}[\mathrm{MEA}]_i[\mathrm{CA}]_j$$

$$R_3 = k_{\mathrm{D}}^{\mathrm{MC}}[\mathrm{CA}]$$

$$R_4 = k_{\mathrm{D}}^{\mathrm{MC}}[\mathrm{MEA}] \tag{9}$$

where [OO], [CA], [MEA] and [DEA] are the concentrations of OO, CA, MEA and DEA, respectively. For simplicity, the normalized concentrations of these species are used in this simulation and they are set $\mathrm{X} = [\mathrm{OO}]_t/[\mathrm{OO}]$ $t = 0$, $\mathrm{A} = [\mathrm{CA}]_t/[\mathrm{CA}]_{t=0}$, $\mathrm{Y} = [\mathrm{MEA}]_t/[\mathrm{CA}]_{t=0}$, $\mathrm{Z} = [\mathrm{DEA}]_t/[\mathrm{CA}]_{t=0}$, $\mathrm{M} = [\mathrm{ME}]_t/[\mathrm{CA}]_{t=0}$, respectively, where t denotes reaction time. The stoichiometric ratio, r, is defined as

$$r = \frac{[\mathrm{O}]_{t=0}}{[\mathrm{CA}]_{t=0}} = \frac{2[\mathrm{OO}]_{t=0}}{[\mathrm{CA}]_{t=0}} \tag{10}$$

where [O] is the concentration of oxazoline groups.

As the microscopic elementary reactions occurred in the simulation, the kind of the reaction that took place in a time interval $(t+\tau \rightarrow t+\tau+\Delta\tau)$ could be determined by the probability of each reaction. The following relationship can be obtained:

$$P_v = \frac{R_v}{\sum_{v=1}^{S} R_v} \tag{11}$$

and it satisfies the relation

$$\sum_{v=1}^{S} P_v = 1 \tag{12}$$

The MC rate constant, k^{MC}, is microscopic and can be transformed into the macroscopic experimental constant, k^{exp}, according to the following relationships:

$$k^{\mathrm{MC}} = k^{\mathrm{exp}} \quad (\text{for first} - \text{order reactions}) \tag{13}$$

$$k^{\mathrm{MC}} = \frac{k^{\mathrm{exp}}}{VN_{\mathrm{A}}} \quad (\text{for second} - \text{order reactions}) \tag{14}$$

where N_{A} is the Avogadro's constant and V is the total volume of the system. v Can be eliminated by the initial molar concentration of one kind of reactant, e.g. $[\mathrm{B}]_0$, through the definition of molar concentration, $VN_{\mathrm{A}} = \mathrm{X}_{\mathrm{B}}^0/[\mathrm{B}]_0$, with $\mathrm{X}_{\mathrm{B}}^0$ as the initial number of molecules of species B used in MC simulation [32,48,49]. Using the above process, the simulated results are given in real time scale and can be directly compared with the experimental results.

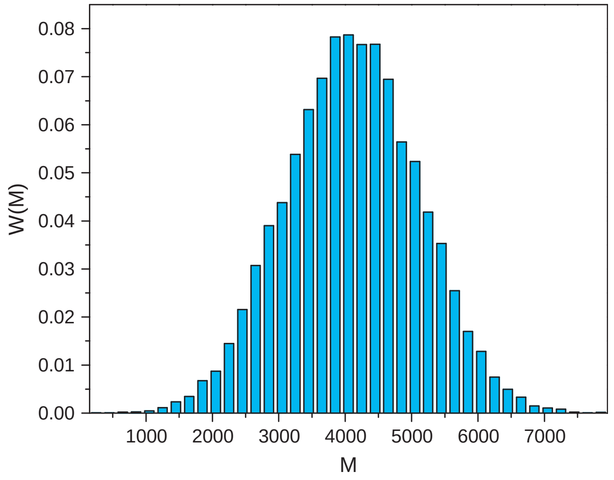


Fig. 1. MWDs of initial 20,000 CA chains.

This study primarily concerns the use of carboxyl-terminated polyamide12 (PA12, say CA in this paper) as a model reactant with OO. It should be noted that all the MC simulations in this paper are really in the space of molecular weight and not in the real space of entangled chains. In fact, whether the chain is entangled or not is judged on the basis of its molecular weight according to Eqs. (3)–(5) during each simulation. A total of 20,000 CA chains were initially generated in this simulation. The MWD of these chains is shown in Fig. 1. The average chain length is about 20. The main simulated reaction temperature was 200 °C. The kinetic constant K_{B} was obtained from the calculation based on the corresponding rate constant at lower temperature and activation energies. For K_{B}, a value of 2×10^{-4} kg mol^{-1} s^{-1} at 120 °C with the activation 79.5 kJ mol^{-1} was reported in Ref. [4]. Using the Arrhenius equation, a value of 1.03×10^{-2} kg mol^{-1} s^{-1} was obtained. Based on the value of K_{B}, different values of K_{D} were used to investigate the effect of reactant degradation. The initial concentration of carboxyl group, $[\mathrm{COOH}]_0$, was set 1 mmol g^{-1}. The critical entanglement chain length, N_{ent}, was set 10 unless otherwise indicated. The reaction is considered to be completed when the conversions of all species are almost unchangeable. In the following section, it can be found that those values result in a good agreement with the experimental data.

3. Results and discussions

3.1. Diffusion effects on chain extension reaction kinetics

We would first like to compare the simulated results with those obtained from the experiments. Douhi et al. [3e] reported the studies of chain extension reaction between OO and carboxyl-terminated polymers. The molar ratio of oxazoline groups to carboxyl acid groups, r, is 1. The reaction temperature is 200 °C. The same initial conditions are set in the MC simulation. In this simulation $\phi = 0.01$ is selected. A logarithm time axis is selected in the figure in order to make the most important region, where time is smaller than 50 min and

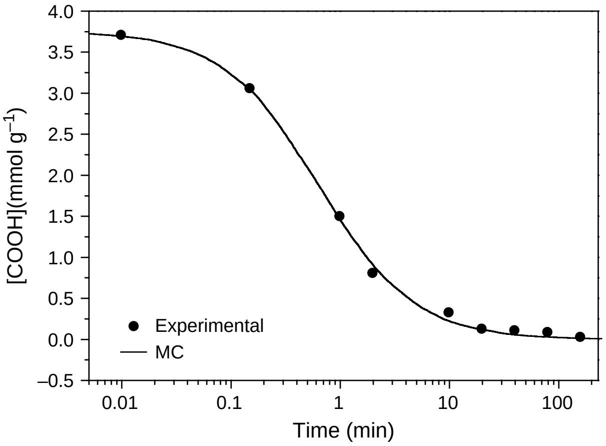


Fig. 2. Dependence of the concentration of carboxyl groups [COOH] vs reaction time for the chain extension between bisoxazolines and carboxyl-terminated polymers at 200 °C. Parameters used in the simulation are $k_1=k_2=1.03\times10^{-2}$ kg mol^{-1} s^{-1}, $k_3=k_4=0$, $r=1$ and $\phi=0.01$.

almost all reactions occur, clear. It can be found from Fig. 2 that the simulated result is in a good agreement with the experimental result, which implies that the kinetic constant values used in the study are reasonable.

If the degradation effects are not considered, in accordance with Scheme 2, the 'chain-by-chain' differential equation model can be deduces as follows

$$\frac{dA_i}{dt} = -2K_1X\sum_{i=1}^{\infty}A_i - A_i\sum_{j=1}^{\infty}K_{2(i,j)}Y_j \tag{15}$$

$$\frac{dY_i}{dt} = 2K_1X\sum_{i=1}^{\infty}A_i - Y_i\sum_{j=1}^{\infty}K_{2(i,j)}A_j \tag{16}$$

$$\frac{dZ_i}{dt} = \sum_{j=1}^{i-1}K_{2(i-j,j)}A_{i-j}Y_j \tag{17}$$

where $K_1=K_B[CA]_{t=0}$ and $K_{2(i,j)}=K_{C(i,j)}[CA]_{t=0}$. Details concerning the derivation of Eqs. (15)–(17) can be found elsewhere [9,11,50]. Fig. 3 shows the plots of the normalized concentrations of different reactants and resultants against reaction time. A close relation between the data calculated by the differential equation kinetic model and that by the MC simulation is observed. This is a direct proof that the method used to deal with the system is reasonable. The initial reactants vary considerably with the increasing reaction time up to about 10 min. Thereafter, it slightly varies with the increasing reaction time. Those changes are basically consistent with the experimental observation [3,6].

The coupling efficiency, p, of the initial carboxyl groups is defined as

$$p = 2\frac{[DEA]_t}{[CA]_{t=0}} \tag{18}$$

Fig. 4 shows the temporal variation of p with the change of ϕ. One can find that p decreases comparing to the increasing ϕ at the same time, which demonstrates that the diffusion effects can retard the progress of chain extension reactions.

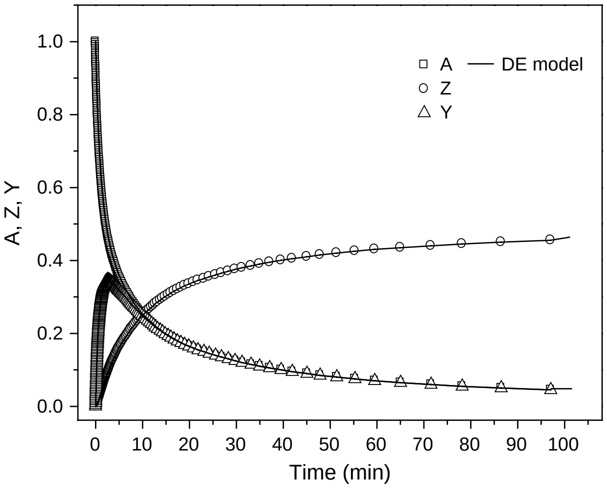


Fig. 3. Plots of the normalized concentrations of different reactants and resultants against reaction time for the chain extension between OO and CA. The dots are the data simulated by MC and solid lines are relative data calculated by the differential equation model. Parameters used in the simulation are $K_B=1.03\times10^{-2}$ kg mol^{-1} s^{-1}, $K_D=0$, $r=1$ and $\phi=0.1$.

Besides coupling efficiency and MWD, the average molecular weight is an important characteristic of resultant polymers. Fig. 5 shows the temporal variation of number average molecular weight ($\bar{M}_n$) with different values of ϕ. It is clear that $\bar{M}_n$ decreases with the increasing ϕ, demonstrating that the stronger diffusion effects lead to the lower average molecular weight and retard the change of average molecular weight. The change of $\bar{M}_n$ is basically consistent with that of coupled efficiency.

Consider the relationships [7,8,10,11]

$$\frac{M_{n,t}}{M_{n,0}} = \frac{1+r}{1+r(1-p)} \tag{19}$$

$$\frac{d}{d_0} = \frac{(1+r+2rp)(1+r-rp)}{(1+r)^2} \tag{20}$$

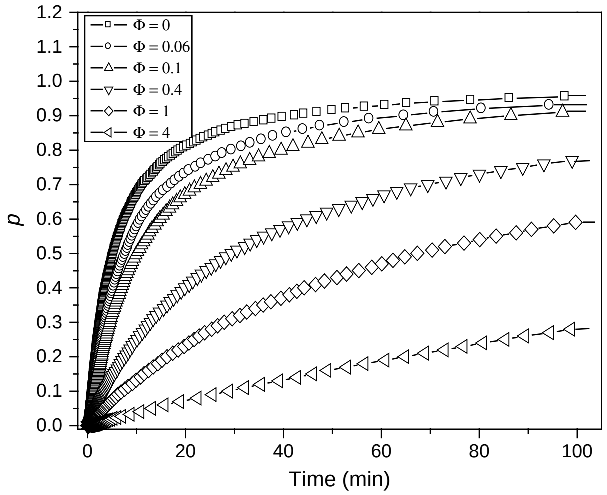


Fig. 4. The plots of coupling efficiency p against reaction time with different values of ϕ. Parameters used in the simulation are $K_B=1.03\times10^{-2}$ kg mol^{-1} s^{-1}, $K_D=0$ and $r=1$.

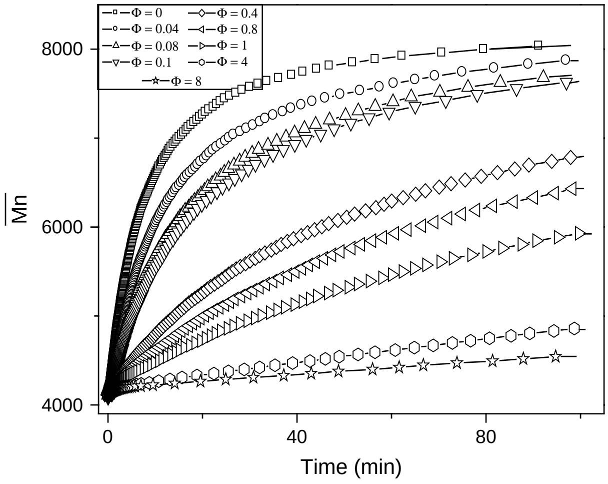


Fig. 5. Plots of number average molecular weight, $\bar{M}_n$, against reaction time with different values of ϕ. Parameters used in the simulation are $K_B = 1.03 \times 10^{-2}$ kg mol^{-1} s^{-1}, $K_D = 0$ and $r = 1$.

which have been proved to be valid in the absence of diffusion effects. Fig. 6 shows the evolution of the normalized $\bar{M}_w$ and polydispersity index, d, with the increasing coupling efficiency p. It is seen that the simulated results are very similar to those calculated by above models. The discrimination between the simulated and calculated results when p is larger is due to the fact that the models do not consider the MWD [10]. The figure indicates that, with increasing p, there is a peak in the curve of the polydispersity index, demonstrating that the MWD in the middle stage is wider than those in the initial and last stages. In the presence of diffusion, however, peaks in the evolution curves of $\bar{M}_w$ but valleys in the evolution curves of d are observed when p is small enough (see inset in Fig. 6). And the peak increases for higher ϕ, comparing to the decreasing d. These phenomena have also been observed in the same simulation by the diffusion theory of polydisperse reacting polymer systems [11]. To explain these phenomena, the dependence of the normalized kinetic constant of the coupling reaction, $K_{C(i,j)}/k_{chem}$, on the chain length of reactants is calculated and shown in Fig. 7. It can be found that the reaction rate constants of short chains are much larger than those of long chains. Therefore, the reaction of short chains is favored while the formation of long chains is hindered. In this case, d decreases considerably and $\bar{M}_w$ becomes bigger [12]. These phenomena are more clear for higher ϕ. However, narrowing of the distribution does not continue indefinitely. As the MWD is narrowing, the concentration of chains of average length is maximized. There is a point where concentration effects outweigh diffusion phenomena. Then chains of average length react preferentially to those with higher molecular weights.

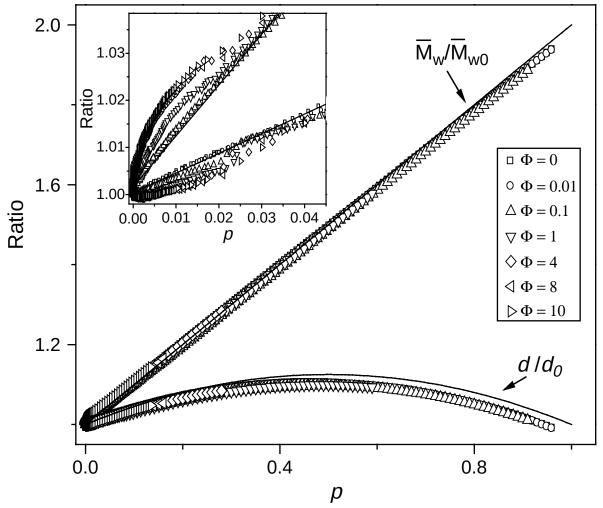


Fig. 6. Plots of normalized $\bar{M}_w$ and normalized polydispersity index, d, against the coupling efficiency, p, with different values of ϕ. The inset indicates the data with small p. The dots are the data simulated by MC and solid lines are the corresponding data calculated by the differential equation model (Eqs. (19) and (20)). Parameters used in the simulation are $K_B = 1.03 \times 10^{-2}$ kg mol^{-1} s^{-1}, $K_D = 0$ and $r = 1$.

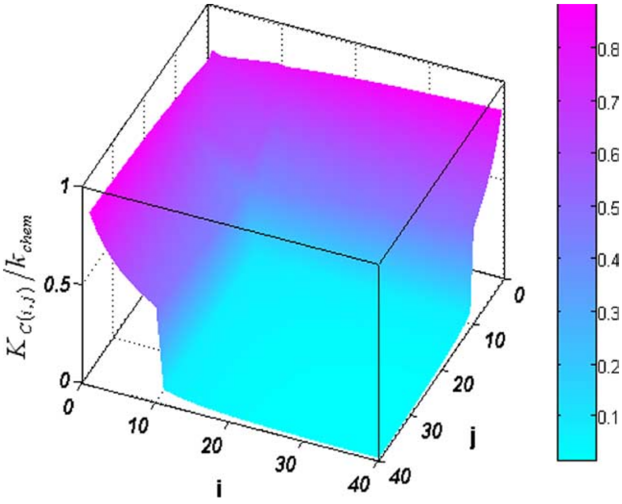


Fig. 7. The dependence of the normalized kinetic constant of the coupling reaction, $K_{C(i,j)}/k_{chem}$, on the chain length of reactants. Parameters used in the simulation are $K_B = 1.03 \times 10^{-2}$ kg mol^{-1} s^{-1}, $K_D = 0$ and $r = 1$.

Fig. 8 exhibits plots of the final MWD with the change of ϕ. The reactions have adequately progressed in this simulation. There are two peaks in the MWD curve of the total chains,

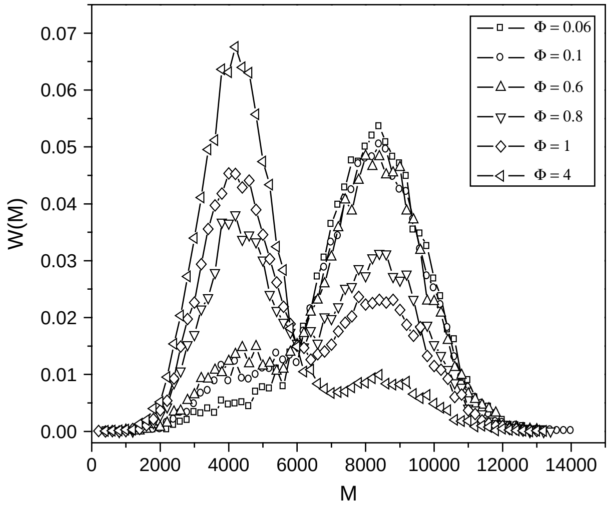


Fig. 8. Plots of the MWD with different values of ϕ. Parameters used in the simulation are $K_B = 1.03 \times 10^{-2}$ kg mol^{-1} s^{-1}, $K_D = 0$ and $r = 1$.

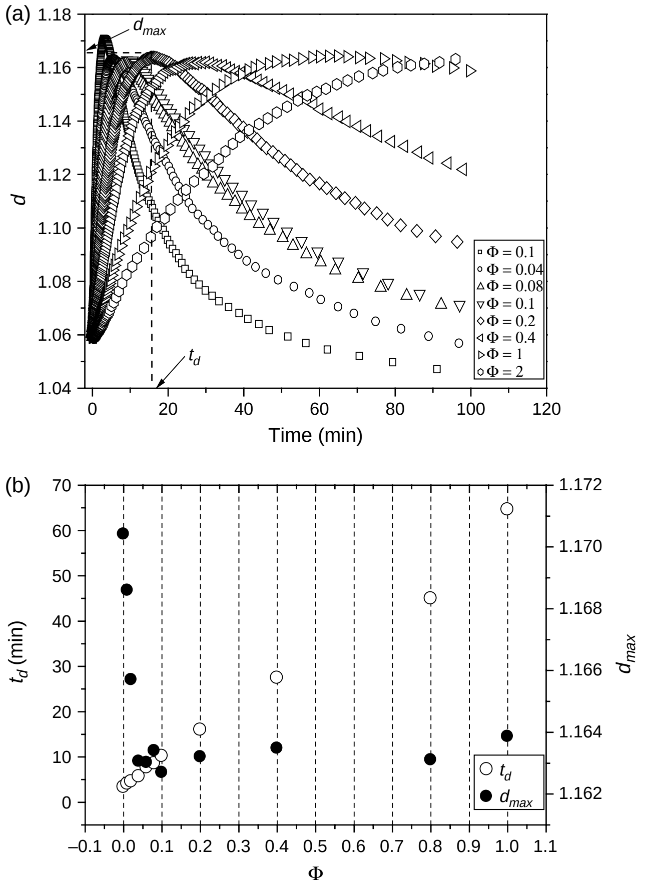


Fig. 9. (a) Plots of polydispersity index, d, against reaction time with different values of ϕ. (b) Relation among delay time t_d, maximal polydispersity, d_{max}, and ϕ. Parameters used in the simulation are $K_B = 1.03 \times 10^{-2}$ kg mol^{-1} s^{-1}, $K_D = 0$ and $r = 1$.

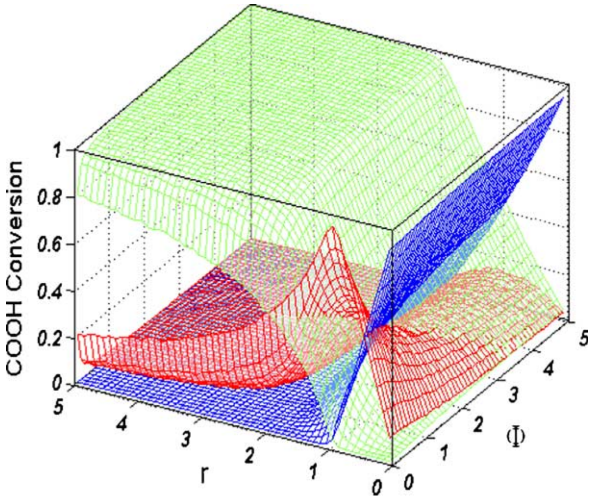


Fig. 10. The relationship among three group polymers, r and ϕ. Parameters used in the simulation are $K_B = 1.03 \times 10^{-2}$ kg mol^{-1} s^{-1}, $K_D = 0$. (🟦) Unreacted group. (🟥) Coupled group. (🟩) Blocked group.

corresponding to the superposition of MEA and residual CA chains, and DEA chains, respectively [9,10]. In the presence of diffusion effects, the peak in high molecular weight becomes lower with increasing ϕ, demonstrating that the coupling resultant, i.e. DEA, decreases with more serious diffusion effects. The variation of these two peaks corresponds to different polydispersities of MWD [9,10]. Therefore, the diffusion effects have a considerable effect on the spread of MWD of the reaction system.

The polydispersity index, d, is calculated in order to consider the polydispersity of MWD under the effects of diffusion. Fig. 9(a) plots d against reaction time with different values of ϕ. Because the peak in high molecular weight appears and becomes higher, the polydispersity indexes increase sharply at the initial stage and a peak appears in each curve of d when ϕ is not more than 1 [9,10]. Then, d decreases with the progress of the reaction as the peak in low molecular disappears gradually. The polydispersity indices at the later stage become smaller with increasing ϕ, demonstrating that the diffusion effects can make the final MWD wider. The maximal value of d and its appearance time are defined as d_{max} and t_d, respectively, in this study. t_d denotes the delay time for the appearance of the peak due to the diffusion effects. Fig. 9(b) reflects the change of d_{max} and t_d against ϕ. Only the region within about $\phi \leq 1$ is considered because d is so large that the peak almost disappears in the later stage. It can be seen that d_{max} decreases sharply with smaller values of ϕ. However, d_{max} has little change when ϕ is bigger than 0.1. The delay time, t_d, always increases considerably, indicating that the diffusion effects can retard the variation of MWD.

In the chain extension reaction by OO, reaction behavior of carboxyl terminals contained in the initial polymer can be classified into three groups, i.e. 'coupled', 'blocked' and 'unreacted' as shown in Scheme 1. Fig. 10 is a three-dimensional diagram showing the variations of these three group polymers with the changes of r and ϕ. All reactions have been completed in this simulation. The results in Fig. 10 demonstrate that, with the increasing ϕ, the coupled group decreases comparing to the increasing of the blocked group, which indicates that a stronger diffusion effect leads to a lower coupling efficiency, corresponding to Fig. 4. The figure also reproduces our previous simulated results [9,10]. A peak appears at the surface of the coupled group with $r = 1$, demonstrating that the coupling efficiency is the highest when the initial concentrations of carboxyl and oxazoline groups are equal. However, the peak declines for larger ϕ. It can be found that the effect of diffusion on the change of these groups is very slight beyond the point with value about $\phi = 3$. These results imply that the diffusion effects of the reactants can change the ratio between the coupled and the blocked groups markedly. However, the unreacted group remains almost unchangeable with the increasing ϕ.

3.2. Effects of reactant degradation on diffusion

The results presented here describe the effect of reactant degradation, which can affect the chain extension kinetics especially under extrusion conditions and, on the diffusion limitations [4,6,7]. Scheme 2(III) and (IV) account for this effect.

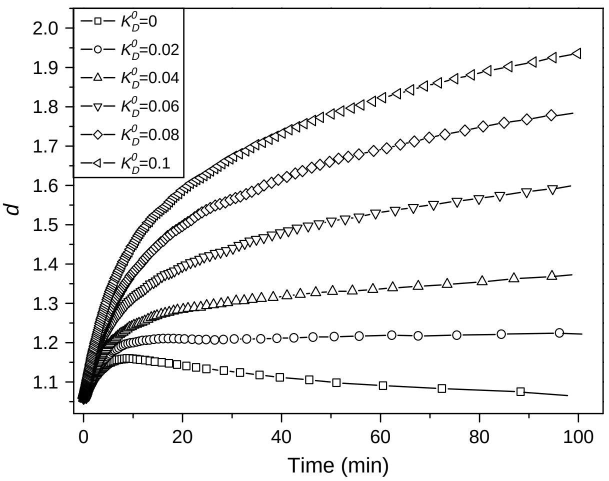


Fig. 11. Plots of polydispersity index d against reaction time with different values of K_D^0. Parameters used in the simulation are $K_B=1.03\times10^{-2}$ kg mol^{-1} s^{-1}, $r=1$, and $\phi=0.1$.

Fig. 11 shows the evolution of polydispersity index, d, against reaction time with different K_D^0, i.e. K_D/K_B. Values of K_D^0 indicate the importance of degradation. As K_D^0 becomes bigger, d increases considerably. And there is no peak appearing on the plots when the value of K_D^0 is higher than 0.2. The figure reflects that the effect of reactant degradation makes the MWD of the reaction system wider and leads to shorter chain lengths. In this case, the diffusion effects of the coupling reaction may be weakened.

Fig. 12 is a three-dimensional diagram showing the relationship among $\bar{M}_n$, ϕ and K_D^0. As known, $\bar{M}_n$ decreases for higher ϕ and, a larger diffusion effect leads to a lower average molecular weight. From Fig. 12, the results imply that the degradation of reactants, i.e. CA and MEA, is also a key factor that affects the $\bar{M}_n$ of the system. It can be found that the change range of $\bar{M}_n$ becomes smaller with the increasing K_D^0, which proves directly that the degradation of reactants can weaken the diffusion effects of the coupling reaction.

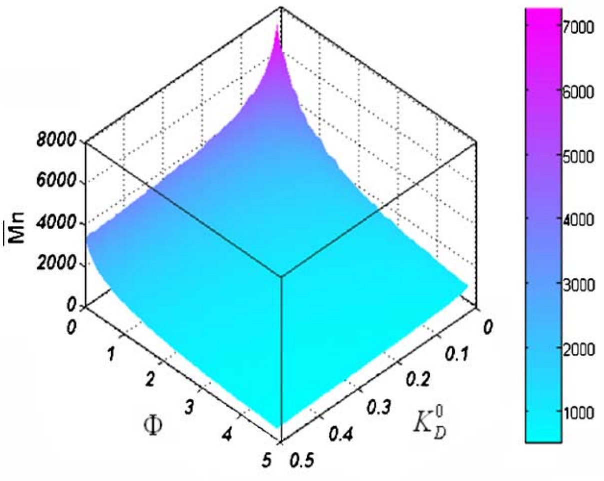


Fig. 12. Three-dimensional diagram showing the relationship among number average molecular weight, ϕ and K_D^0. Parameters used in the simulation are $K_B=1.03\times10^{-2}$ kg mol^{-1} s^{-1} and $r=1$.

4. Conclusions

The stochastic MC method based on the master equations is successfully used to investigate the diffusion effects on chain extension reactions. Thus, the reaction kinetics and the changes of some parameters, such as chain length, MWD and so on, can be obtained simultaneously. Moreover, the chain length dependence and detail diffusive behavior of each chain are considered based on the reptation theory.

The results show that the diffusion effects can retard the progress of chain extension reactions. A stronger diffusion effect corresponds to a lower coupling efficiency, p. It can be found that the diffusion effects of the reactants can change the ratio between the coupled and the blocked groups markedly. The simulated results indicate that the diffusion effects make the final MWD wider, and lead to a lower average molecular weight than the reaction controlled by other effects. In the presence of diffusion and with the progress of p, peaks in the evolution curve of weight-average molecule weight ($\bar{M}_w$) but valleys in the evolution curve of polydispersity index, d, are observed, respectively, when p is small enough. These phenomena are different from those without diffusion and, have been analyzed in detail in this paper. The results also show that the effect of resultants degradation can make the MWD of the reaction system wider, and can weaken the diffusion effects on the coupling reaction.

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