

A COMPREHENSIVE MONTE CARLO SIMULATION OF STYRENE ATOM TRANSFER RADICAL POLYMERIZATION

Mohammad Najafi^a, Hossein Roghani-Mamaqani^b, Mehdi Salami-Kalajahi^{a, b} and Vahid Haddadi-Asl^{a, b*}

^a International Affairs, Research Institute of Petroleum Industry (RIPI), 1485733111, Tehran, Iran

^b Polymer Engineering Department, Amirkabir University of Technology, P.O. Box 15875-4413, Tehran, Iran

Abstract An optimized and high-performance Monte Carlo simulation is developed to take thorough account of four different cases of termination in styrene ATRP. According to the simulation results, the bimolecular termination rate constant sharply drops throughout the polymerization when either chain-length dependency of termination rate constant, gel effect, or both together is applied to the simulation. In addition, as expected, the initiator is quickly decomposed at the early stages of the polymerization. The concentration of the catalyst in lower oxidation state decreases at first and then plateaus at higher conversion; furthermore, the steady concentration of M_1^*Y/L in the polymerization is the highest when the chain-length-dependent diffusion-controlled termination rate constant is employed in the simulation. The rates of deactivation and chain end degradation reactions are also smaller in this case. Therefore, the fraction of dormant chains is higher throughout the reaction and consequently the portion of dead polymers decreases. Besides, molecular weight increases linearly with conversion; however, when neither gel effect nor chain-length dependency of termination rate constant is considered, the molecular weight deviates from linearity at the end of the reaction. The peak of chain length distribution shifts toward higher molecular weight too during the reaction. Finally, the molecular weight distribution broadens at higher conversion; however, the chain length distribution of polymers produced under conditions of applying chain-length-dependent diffusion-controlled termination rate constant is narrower.

Keywords: Styrene ATRP; Monte Carlo simulation; Chain length distribution; Gel effect; Chain-length-dependent termination.

INTRODUCTION

Free radical polymerization, because of its robustness and flexibility, has been widely utilized to (co)polymerize a variety of vinyl monomers. However, to produce polymers with highly controlled microstructure and well-defined topology, several attempts have been made to suppress the bimolecular reactions between free radical species in the last few years. In this context, various approaches have been employed and they are mainly referred to as controlled/“living” radical polymerizations^[1, 2] among which nitroxide-mediated polymerization^[3–7], radical polymerization with reversible addition-fragmentation chain transfer (RAFT)^[8–11], and atom transfer radical polymerization (ATRP)^[12–16] have been extensively studied.

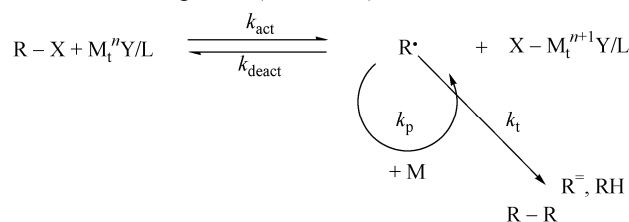
The key kinetic feature of all these methods is the reduction of termination/transfer reactions by switching growing chains between active and dormant states so as to lessen the instantaneous concentration of free radicals and thereby suppressing the bimolecular termination reactions^[17]. Atom transfer radical polymerization, which is based on reversible termination, has attracted more attention due its flexibility and similarity to the conventional

* Corresponding authors: Vahid Haddadi-Asl, E-mail: haddadi@aut.ac.ir; haddadi@ripi.ir

Received April 15, 2009; Revised June 28, 2009; Accepted August 3, 2009

doi: 10.1007/s10118-010-9058-1

free radical polymerization. It employs a transition metal complex as the medium of halogen atom transfer to change a growing radical into an inactive species (Scheme 1)^[18, 19].



Scheme 1 Equilibrium of ATRP reaction

Besides experimental work carried out on the development of atom transfer radical polymerization, several analytical models and mathematical modeling have been introduced to inspect its behavior. For instance, moment equations have been successfully employed to predict the molecular weight averages of living free radical polymerizations^[20–29]. The PREDICI has also been used as a powerful tool to solve a series of differential equations so as to obtain full molecular weight distributions of macromolecules produced by different living free radical polymerizations^[30–35]. However, these tools have some limitations such as being restricted to calculating average values rather than predicting time-related distributions.

On the other hand, Monte Carlo method, owing to the statistical nature of chain growth and chain terminating reactions, is an excellent method widely utilized to simulate conventional free radical (co)polymerization systems^[36–38] as well as controlled free radical reactions^[39–43]. Moreover, Monte Carlo method has some advantages over analytical methods: compared to moment equations, it is not restricted to solving stiff differential equations; nor it is limited to strict assumptions which mainly cause most of analytical methods to lead to approximate results; moreover, it can be easily implemented to different polymerization systems; Monte Carlo method is also capable of calculating chain length distributions in the course of the polymerization since it can store the whole information of each individual polymer chain virtually generated throughout the reaction. Finally, it can visualize the microstructure of the macromolecules. Nonetheless, unfortunately, simulation programs based on Monte Carlo method, if not implemented properly, usually take a long time and a huge amount of memory to complete.

A review of related literature indicates that the Monte Carlo simulations of ATRP — and particularly ATRP of styrene — presented so far^[43–45] have mainly taken account of equilibrium, propagation, termination, and transfer reactions; nevertheless, thermal initiation of styrene and chain end degradation of dormant chains and radicals have not been taken into consideration. Chain end degradation of dormant chains and radicals, by reason of dealing with key elements of the reaction (radicals, dormant chains, and catalyst in higher oxidation state) can greatly influence the living nature of the ATRP, and thereby changing the microstructure of the polymer. Moreover, although the gel effect is considered, most simulations presented have ignored the effect of chain length on termination rate constant; this affects the contribution of termination reaction and accordingly the livingness of the reaction. Additionally, the simultaneous implementation of diffusion-controlled and chain-length-dependent termination to the simulation of styrene ATRP has not been reported so far.

To this end, in this contribution, a Monte Carlo method is developed to simulate the ATRP of styrene by employing a thorough kinetic scheme including chain end degradation and thermal initiation reactions^[46]. Additionally, gel effect is implemented to the simulation; we, also, take account of chain-length-dependent termination reaction; a hybrid model is introduced to the simulation to simultaneously consider diffusion-controlled and chain-length-dependent termination over the course of the polymerization. Conversion; reactant concentration; rate of reactions; molecular weight averages; and molar, weight and z chain length distributions are also considered as the response parameters of the simulation.

SIMULATION DESCRIPTION

The kinetic scheme used in the simulation includes activation, deactivation, thermal initiation, propagation, termination by combination, transfer to monomer, and chain end degradation type A (dormant chain degradation) and chain end degradation type B (radical degradation) reactions^[46]. The elementary reaction steps of styrene ATRP used in the simulation are listed in Eqs. (1) to (9). The kinetic parameters and initial concentrations inputted to the simulation are also given in Table 1.

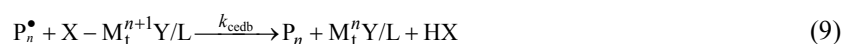
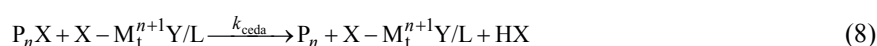
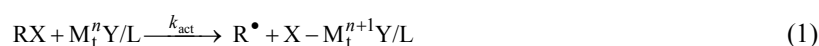


Table 1. Kinetic rate constants and initial concentrations used in simulation of styrene ATRP at 110°C^a

Coefficient/Parameter	Expression/Value	Reference
k_{act} (L·mol ⁻¹ ·s ⁻¹)	0.45	[47, 48]
k_{therm} (L ² ·mol ⁻² ·s ⁻¹)	$2.19 \times 10^5 \exp(-13800/T)$	[49]
k_{deact} (L·mol ⁻¹ ·s ⁻¹)	1.1×10^7	[48]
k_p (L·mol ⁻¹ ·s ⁻¹)	$4.266 \times 10^7 \exp(-3910/T)$	[49]
k_{tc}^0 (L·mol ⁻¹ ·s ⁻¹)	$3.82 \times 10^9 \exp(-958/T)$	[49]
k_{trM} (L·mol ⁻¹ ·s ⁻¹)	$2.31 \times 10^6 \exp(-6377/T)$	[49]
k_{ceda} (L·mol ⁻¹ ·s ⁻¹)	1.0×10^{-4}	[46]
k_{cedb} (L·mol ⁻¹ ·s ⁻¹)	1.63×10^3	[46]
$[M]_0$ (mol·L ⁻¹)	100	This work
$[RX]_0$ (mol·L ⁻¹)	1	This work
$[M_t^n Y/L]_0$ (mol·L ⁻¹)	1	This work

^a T is temperature in Kelvin (K)

As viscosity of the system increased noticeably during the polymerization, a gel effect correlation was implemented to the simulation; the diffusion-controlled rate constant of termination, k_{tc}^{gel} , varies with monomer conversion in the reaction system and the rate coefficient at zero conversion k_{tc}^0 according to Ref. [50]:

$$k_{tc}^{gel} \left(\frac{L}{mol \cdot s} \right) = k_{tc}^0 \times \exp \left[-2(Ax + Bx^2 + Cx^3) \right] \quad (10)$$

where, x is monomer conversion; A , B , and C are correlated to the reaction temperature, T [K], as following:

$$\begin{aligned}
 A &= 2.57 - 5.05 \times 10^{-3} T \\
 B &= 9.56 - 1.76 \times 10^{-2} T \\
 C &= -3.03 + 7.85 \times 10^{-3} T
 \end{aligned}$$

It is well-known that the rate of bimolecular reactions between radicals drastically drops when the length of involving radicals increases. Therefore, a model is needed to calculate the termination rate constant of two radicals with lengths of i and j (where both i and j are larger than unity), *i.e.* $k_{tc}^{i,j}$; such a model is usually developed based on the termination rate constant of two homo-length radicals ($k_{tc}^{i,i}$)^[51–55]. The termination of “short” radicals of the same length happens according to Eq. (11):

$$k_{tc}^{i,i} \left(\frac{L}{\text{mol} \cdot \text{s}} \right) = k_{tc}^0 \times i^{-e_s}, \quad i \leq i_c \quad (11)$$

This k_{tc}^0 is the real rate coefficient for termination between two monomeric free radicals in a system which is not diffusion-controlled. i and i_c are respectively chain length and critical chain length indicating the short length boundary; e_s is also reported to be equal to 0.5^[55].

However, for “long” radicals the following equation is proposed:

$$k_{tc}^{i,i} \left(\frac{L}{\text{mol} \cdot \text{s}} \right) = k_{tc}^0 \times (i_c)^{-e_s + e_L} \times i^{-e_L}, \quad i > i_c \quad (12)$$

where, the $k_{tc}^0 \times (i_c)^{-e_s + e_L}$ term herein gives continuity with Eq. (11) at the “crossover” chain length (i_c); e_L and i_c are equal to 0.16 and 100 respectively^[55]. To summarize, we use the following composite model for a system which is only chain-length dependent and not diffusion-controlled:

$$\begin{aligned}
 k_{tc}^{i,i} \left(\frac{L}{\text{mol} \cdot \text{s}} \right) &= k_{tc}^0 \times i^{-0.5}, \quad i \leq i_c \\
 k_{tc}^{i,i} \left(\frac{L}{\text{mol} \cdot \text{s}} \right) &= k_{tc}^0 \times (i_c)^{-0.34} \times i^{-0.16}, \quad i > i_c
 \end{aligned} \quad (13)$$

Values of the cross-termination rate coefficients ($k_{tc}^{i,j}$), where $i \neq j$, are calculated based on diffusion, harmonic, and geometric means of homo-termination rate constants as summarized below:

$$\begin{aligned}
 k_{tc}^{i,j}(\text{hm}) \left(\frac{L}{\text{mol} \cdot \text{s}} \right) &= k_{tc}^0 \times \left(\frac{2ij}{i+j} \right)^{-0.5}, \quad i \leq i_c \\
 k_{tc}^{i,j}(\text{hm}) \left(\frac{L}{\text{mol} \cdot \text{s}} \right) &= k_{tc}^0 \times (i_c)^{-0.34} \times \left(\frac{2ij}{i+j} \right)^{-0.16}, \quad i > i_c
 \end{aligned} \quad (14)$$

$$k_{tc}^{i,j}(\text{dm}) \left(\frac{L}{\text{mol} \cdot \text{s}} \right) = \frac{1}{2} \times (k_{tc}^{i,i} + k_{tc}^{j,j}) \quad (15)$$

$$k_{tc}^{i,j}(\text{gm}) \left(\frac{L}{\text{mol} \cdot \text{s}} \right) = \sqrt{k_{tc}^{i,i} \times k_{tc}^{j,j}} \quad (16)$$

The overall rate coefficient for termination at any instant of the polymerization is correlated to $k_{tc}^{i,j}$ values (either diffusion, geometric or harmonic mean) by the following form:

$$\overline{k_{tc}} \left(\frac{L}{\text{mol} \cdot \text{s}} \right) = \sum_{i=1}^{\infty} \sum_{j=1}^{\infty} k_{tc}^{i,j} \frac{[R_i] \times [R_j]}{[R] \times [R]} \quad (17)$$

where, $[R_i]$ and $[R_j]$ stand for the concentration of chains with the length of i and j respectively. $[R]$ is also the total concentration of all radical species. As this statement implies, Eq. (17) is not restricted to steady states.

For calculating the simultaneous effect of system viscosity and chain-length dependency of termination rate coefficient, a hybrid model is developed by integrating gel effect (Eq. (10)) into the equations used for calculating chain-length dependency of termination rate constant (Eqs. (11) to (17)). The final form of this relation is given by:

$$\overline{k_{tc}^{gel}} \left(\frac{L}{\text{mol} \cdot s} \right) = \left(\sum_{i=1}^{\infty} \sum_{j=1}^{\infty} k_{tc}^{i,j} \frac{[R_i] \times [R_j]}{[R] \times [R]} \right) \times \exp \left[-2 \{ (2.57 - 5.05 \times 10^{-3} T)x + (9.56 - 1.76 \times 10^{-2} T)x^2 + (-3.03 + 7.85 \times 10^{-3} T)x^3 \} \right] \quad (18)$$

The Monte Carlo methodology employed herein is adopted from the well-known Gillespie's algorithm^[56]. A simulation volume is considered to calculate the number of different reactants based on their concentrations (see Eq. (19)) and to transform the experimental reaction rate constants into stochastic rate constants (Eqs. (20) to (21)) as required in the Gillespie's algorithm.

$$X_M = [M] N_{Av} V \quad (19)$$

where $[M]$ is the monomer molar concentration; N_{Av} and V_s also stand for Avogadro's number and the size of the simulation volume respectively. A similar approach is used to calculate the number of other reactants and/or products generated in the simulation. According to Gillespie's algorithm^[56], the stochastic rate coefficients are transformed from experimental rate constants as reads:

$$k^{MC} = k^{exp}, \text{ for first order reactions} \quad (20)$$

$$k^{MC} = \frac{k^{exp}}{N_{Av} \times V_s}, \text{ for bimolecular reaction between different species} \quad (21)$$

$$k^{MC} = \frac{2k^{exp}}{N_{Av} \times V_s}, \text{ for bimolecular reaction between similar species} \quad (22)$$

It should be noted that since the stochastic rate coefficients (k^{MC}) have units of reciprocal time, experimental rate coefficients (k^{exp}) for bimolecular reactions must be divided by the product $N_{Av} \times V_s$.

The probability of any reaction (p_k) happening at a particular time is calculated by Eq. (23), and a condition in the standard form of Eq. (24) is used to decide which reaction type would occur:

$$p_k = \frac{a_k}{\sum_{k=1}^N a_k} \quad (23)$$

$$\sum_{k=1}^{n-1} p_k < r_1 \leq \sum_{k=1}^n p_k \quad (24)$$

where a_k is the reaction rate of k^{th} reaction; N is the total number of reaction types available in the system; n is the number of reaction type selected to proceed and r_1 is a random number distributed uniformly in the interval (0, 1).

To determine the time interval (τ) between two successive reactions, the following relation is used:

$$\tau = \frac{1}{\sum_{k=1}^N a_k} \ln \left(\frac{1}{r_2} \right) \quad (25)$$

where, r_2 is another random number generated by the same subroutine.

A subroutine on the base of improved Mersenne Twister algorithm is used in the simulation to produce random numbers with long period lengths; this condition should be met to avoid the repetition of random numbers in polymerization reactions^[57]. A suitable and optimized program is written in C++ language and compiled on a 64-bit openSuSE Linux operating system to manage the huge amount of memory requested by the program. The average run time of the program for a simulation volume of 1×10^{-14} on a computer equipped with two 2.0 GHz CPU's and 4 GB memory is approximately 3 h.

RESULTS AND DISCUSSION

It is obvious that in controlled/"living" radical polymerizations the molecular weight of chains increases throughout the reaction and consequently raises the viscosity of system. On the other hand, as macromolecules become longer, their hindrance effect and lower mobility reduce the reaction rates of bimolecular termination. In detail, the reaction rates of bimolecular termination between long chains are almost an order of magnitude smaller than those of monomeric species. Gel effect reduces the termination even more too. Therefore, to consider these phenomena, we apply a composite model to our Monte Carlo simulation method to take account of both gel effect and chain-length dependency of termination reactions. In the latter case, a critical chain length, around which the dependency of termination rate constant on chain length is calculated by using two different equations, is defined. In addition, gel effect and chain-length dependency of termination are simultaneously calculated through a hybrid model implemented to the simulation. It should also be noted that the legends of different cases used henceforth are defined as following:

"None": neither chain-length dependency nor gel effect is implemented to the simulation;

"CLD": only chain-length dependency is included in the simulation;

"Gel": only gel effect is applied to the simulation;

"Gel & CLD": both gel effect and chain-length dependency are implemented to the simulation.

Simulating Bimolecular Termination Rate Constant

According to Fig. 1, it is evident that $k_{tc}^{i,j}$ decreases as the chain length rises and finally plateaus; therefore, it can be inferred that the dependency of bimolecular termination rate constants on chain length is mainly controlled by a certain chain length beyond which the mobility and consequently reactivity of radical chains remain constant, and thus no more decrease in the reaction rate constants is seen. However, $k_{tc}^{100,j}$ is smaller than $k_{tc}^{1,j}$ in the steady regime; this demonstrates that when one of the species in bimolecular terminations is a monomeric species, the termination rate coefficient is higher than when both species are large macromolecules. In addition, when $i = 1$, $k_{tc}^{1,j}(hm) > k_{tc}^{1,j}(dm) > k_{tc}^{1,j}(gm)$, while when $i = 100$, all the three mean values nearly yield the same result.

Figure 2 illustrates the dependence of average termination rate constant on monomer conversion for systems with only chain-length-dependent termination, *i.e.* "CLD" case. The variation of average chain-length-dependent and diffusion-controlled termination rate constant in the course of the polymerization is also very similar to that given in Fig. 2. The average termination rate decreases as the polymerization proceeds in both cases. Diffusion, geometric, and harmonic means all lead to similar results; therefore, to avoid extra computation, only the module which calculates the geometric mean is hereafter invoked in the simulation program.

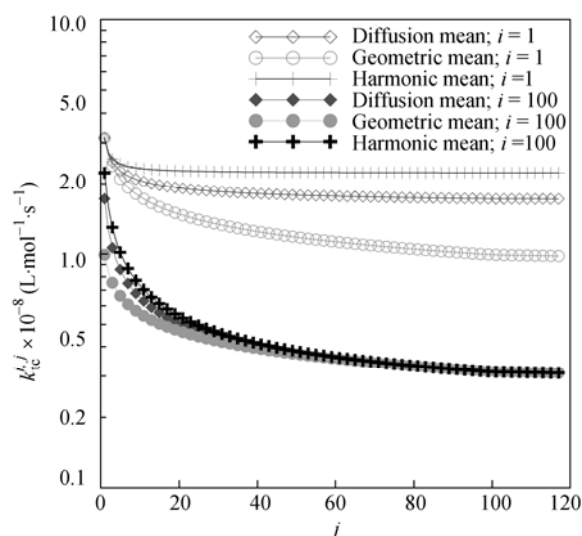


Fig. 1 Cross-termination rate coefficients as a function of chain length j

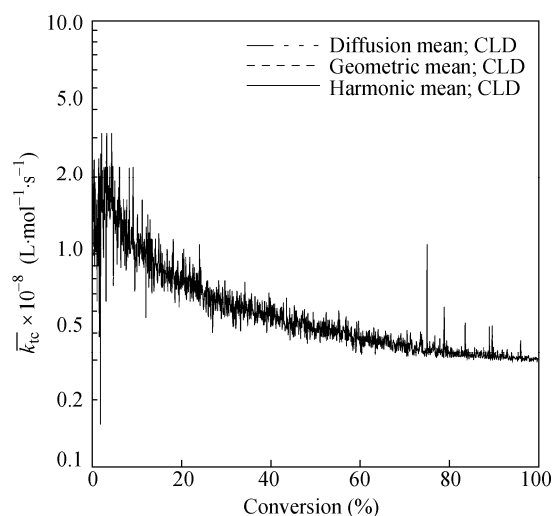


Fig. 2 $\bar{k}_{tc}$ as a function of monomer conversion for “CLD” case

Simulating Change in Reactant Concentration

In accordance with the results (Fig. 3), $\ln\left(\frac{M_0}{M}\right)$ grows linearly at the initial stages of the reaction; however, due to termination reactions, at the final stages of the polymerization the $\ln\left(\frac{M_0}{M}\right)$ curves — particularly in “None” case — start leveling off and deviating from linearity. Moreover, the effects including gel effect and/or chain-length dependency of termination reaction rate in the simulation, as represented by “Gel”, “CLD”, and “Gel & CLD” cases, change the trend of monomer conversion and result in a more linear trend; actually, owing to a smaller termination rate constant, the reaction proceeds to higher conversion when bimolecular termination reaction rates are computed by diffusion-controlled and/or chain-length-dependent termination rate coefficients. As the amount of bimolecular termination reactions decreases, the polymer radicals can further maintain their livingness during the reaction. In addition, the highest conversion can be reached in the “Gel & CLD” case, in which the termination reactions have been minimized. Additionally, in this case the $\ln\left(\frac{M_0}{M}\right)$ curve is entirely linear throughout the reaction.

The change in the concentration of initiator over the course of the polymerization reaction is delineated in Fig. 4. Thanks to fast initiation, initiator is entirely decomposed at the very early stages of the polymerization. It is also clear that the same results are obtained for all cases since initiator is completely consumed in the activation process without being affected by termination or transfer reactions.

Figures 5 and 6 show the dependence of catalyst concentration in lower oxidation state, namely $M_t^n Y/L$, and in higher oxidation state, that is $X-M_t^{n+1}Y/L$, respectively. According to Fig. 5, the concentration of $M_t^n Y/L$ decreases as the reaction progresses; nevertheless, it reaches a plateau in “Gel” and “Gel & CLD” cases. Since the progress of the polymerization gives rise to radical termination, albeit so small in ATRP, the concentration of growing radicals lessens, which correspondingly shifts the equilibrium toward the formation of new growing radicals and thereby consuming more of $M_t^n Y/L$. Besides, the concentration of $M_t^n Y/L$ takes the lowest quantity in “None” case and the highest quantity in “Gel & CLD” case, which, in the latter case, is mainly because of less termination reactions. In fact, because of the smaller bimolecular termination rate constant used in this case, less bimolecular termination happens and consequently the concentration of growing

radicals decreases much less. Therefore, a smaller amount of $M_t^n Y/L$ is used before it reaches a steady regime. It is also evident that the control over the polymerization begins at the initial stages of the reaction in “CLD” and “Gel & CLD” cases. However, gel effect influences the polymerization at the later stages (or rather at the final stages) of the reaction and starts the steady regime at higher conversion.

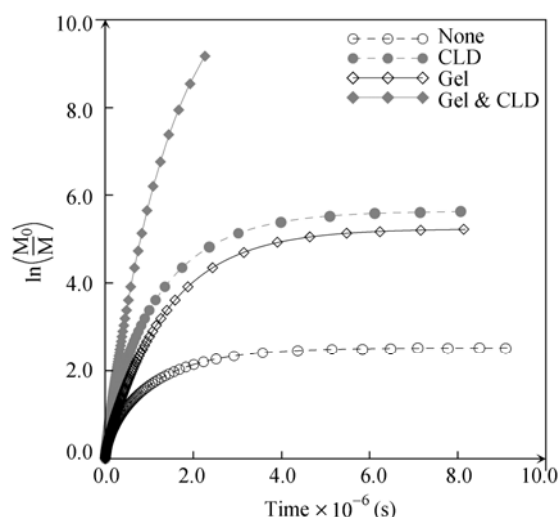


Fig. 3 Illustration of the dependence of $\ln\left(\frac{M_0}{M}\right)$ on reaction time

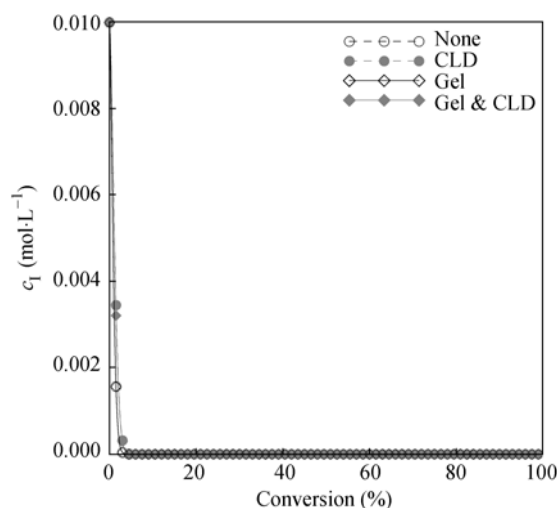


Fig. 4 Change in initiator concentration

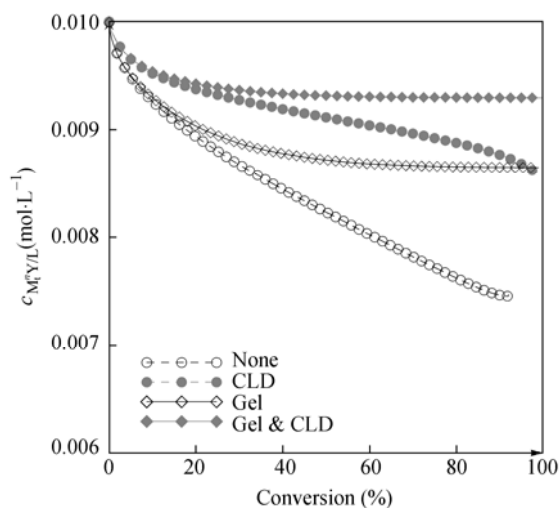


Fig. 5 Change in $M_t^n Y/L$ concentration

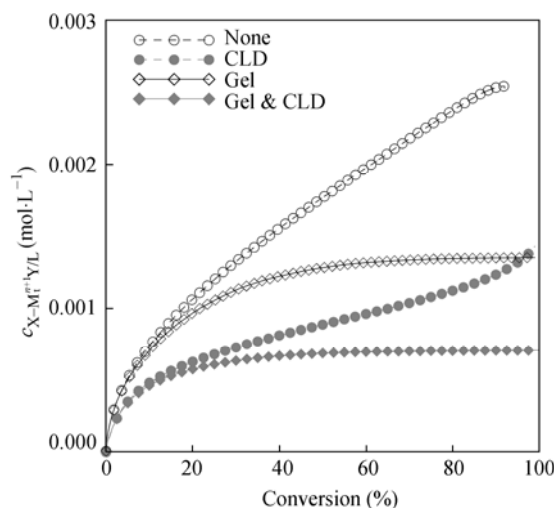


Fig. 6 Change in $X-M_t^{n+1} Y/L$ concentration

On the other hand, the concentration of $X-M_t^{n+1} Y/L$ increases as the polymerization reaction progresses; nonetheless, it levels off in “Gel” and “Gel & CLD” cases. By reason of irreversible termination of growing radicals, the equilibrium reaction in ATRP tends to move toward the activation of dormant chains and the production of new radicals; hence, contrary to $M_t^n Y/L$, the concentration of $X-M_t^{n+1} Y/L$ increases. Moreover, the concentration of $X-M_t^{n+1} Y/L$ is the highest in “None” case and the lowest in “Gel & CLD” case, which represents less accumulation of catalyst in higher oxidation state in the latter. Indeed, as a result of the smaller

termination rate constant obtained in “Gel & CLD” case, less growing radicals terminate, and therefore less $X-M_t^{n+1}Y/L$ is built up.

Figure 7 portrays the dependence of concentration of dormant chains on monomer conversion. Dormant chains are quickly initiated at the very early stages of the polymerization and their concentration decreases throughout the reaction. It is also clear that dormant chain concentration is the lowest in “None” case and the highest in “Gel & CLD” case. In other words, when both gel effect and chain-length dependency of termination rate constant are taken into account, the livingness of ATRP, due less termination, increases and dormant chain concentration remains high (about 80% of the whole chains) up to very high conversion.

The concentration of initiated chains drastically increases and reaches the initiator concentration, that is to say $0.01 \text{ (mol}\cdot\text{L}^{-1}\text{)}$, at the initial stages of the polymerization (Fig. 8). This means that the initiator is completely decomposed at the beginning of the reaction. However, the concentration of dead polymers gradually increases during the reaction and, it reaches not more than about 80% of the initiated chains. Some chains remain alive even at the end of the polymerization. Moreover, due to the least termination, about 60% of chains remain alive at the end of the reaction in “Gel & CLD” case, while a greater majority of chains irreversibly terminate before the polymerization finishes in “None” case. Finally, the effect of chain-length dependent termination is stronger than gel effect as mentioned beforehand.

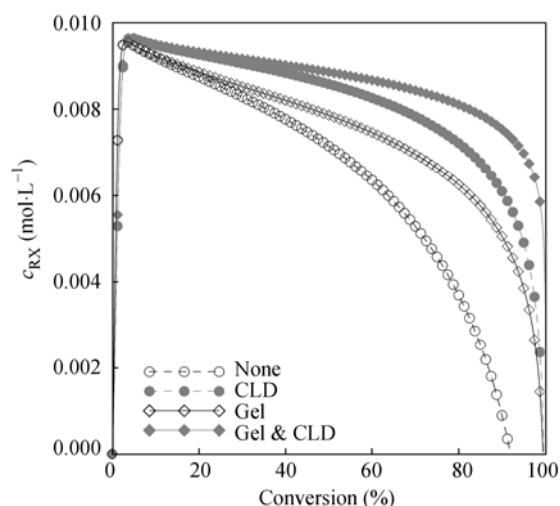


Fig. 7 Change in concentration of dormant chains

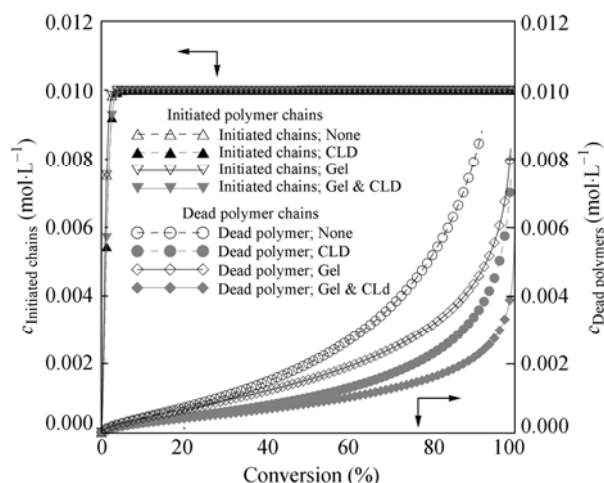


Fig. 8 Dependence of concentration of initiated chains and dead polymers on monomer conversion

Simulating Dependence of Reaction Rates on Monomer Conversion

The rate of dormant chain activation decreases nearly the same as the concentration of dormant chains (Fig. 9). The activation process deteriorates as the polymerization proceeds; it is also obvious that the rate of dormant chain activation remains high enough even at the final stages of the polymerization when the system is simultaneously diffusion-controlled and chain-length dependent; this is ascribed to less irreversible termination of radicals as a result of smaller termination rate constant. Furthermore, the chain-length dependency of termination rate constant, when applied to the simulation, maintains the rate of dormant chain activation higher than what is obtained in the presence of gel effect. According to Fig. 10, the rate of radical deactivation rises; however, it plateaus in “Gel” and “Gel & CLD” cases. Since the concentration of radicals is approximately constant during the polymerization, the rate of radical deactivation varies similar to the variation of concentration of catalyst in higher oxidation state. It can also be deduced that the diffusion-controlled termination, contrary to the chain-length-dependent one, affects the rate of deactivation process at the later stages of the polymerization. In addition, the smallest rate of radical deactivation is obtained in “Gel & CLD” case.

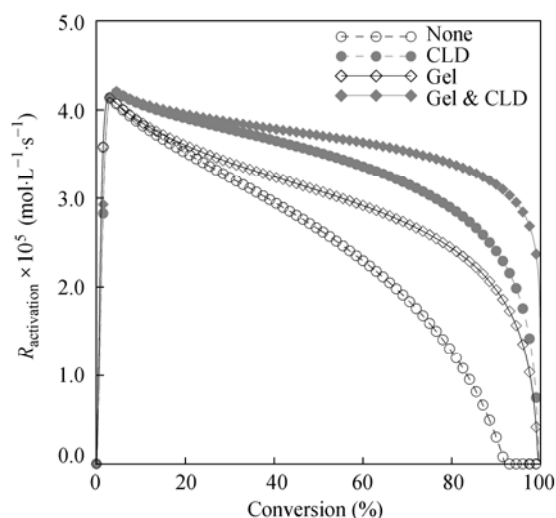


Fig. 9 Dependence of rate of dormant chain activation on monomer conversion

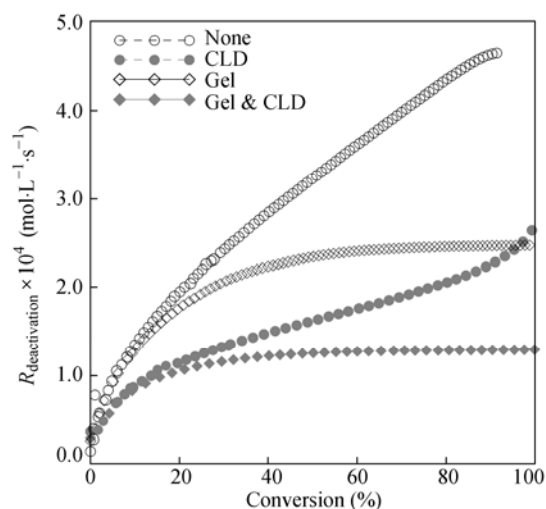


Fig. 10 Dependence of rate of radical deactivation on monomer conversion

Since the termination rate is entirely dependent on the radical concentration, when neither gel effect nor chain-length dependency of termination rate constant, namely “None” case, is taken into account, the rate of termination by combination remains intact and high during the reaction (Fig. 11). Nonetheless, when gel effect is added to the simulation, the rate of termination by combination gradually drops as the polymerization progresses. On the other hand, in “CLD” and “Gel & CLD” cases the termination reaction rate sharply decreases at the initial stages of the polymerization and remains low throughout the reaction. Moreover, it is nearly equal to zero after 50% conversion in “Gel & CLD” case.

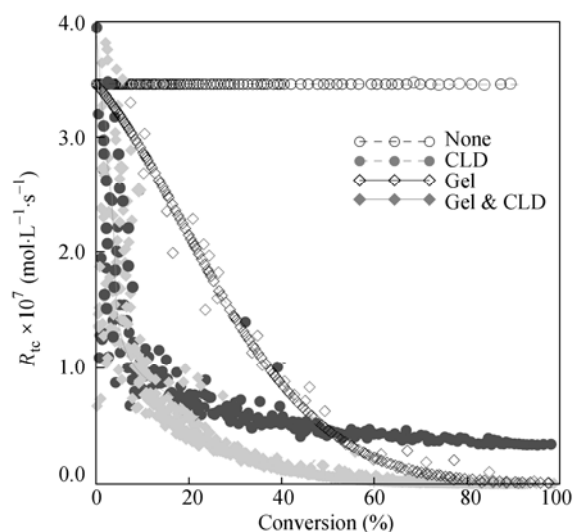


Fig. 11 Dependence of rate of termination by combination on monomer conversion

The rate of chain end degradation type A goes through a maximum as the reaction proceeds (see Fig. 12). It is seen that in “CLD” case, and more noticeably in “Gel & CLD” case, its curve flattens; this means that the rate of chain end degradation type A decreases to a greater extent and, apart from the beginning and the late stages of the polymerization, remains leveled during the reaction. The smallest rate of chain end degradation type A is found in “Gel & CLD” case, which consequently leads to less dormant chain termination and thereby a higher

degree of livingness.

Chain end degradation type B shows a variation similar to deactivation reaction since the same species are involved in both reactions (Fig. 13). It increases as the polymerization progresses although it finally levels off in “Gel” and “Gel & CLD” cases. Besides, it is evident that this type of degradation remains very low in intensity when the termination reaction rate coefficient is diffusion-controlled and/or chain-length dependent. This is mainly because of a reduction in the termination rate, which consequently results in a smaller amount of catalyst in higher oxidation state; the concentration of catalyst in higher oxidation state can influentially impact upon the rate of chain end degradation type B.

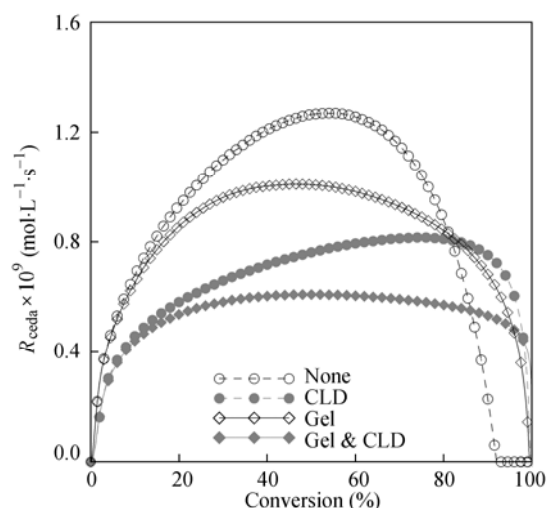


Fig. 12 Dependence of rate of chain end degradation type A on monomer conversion

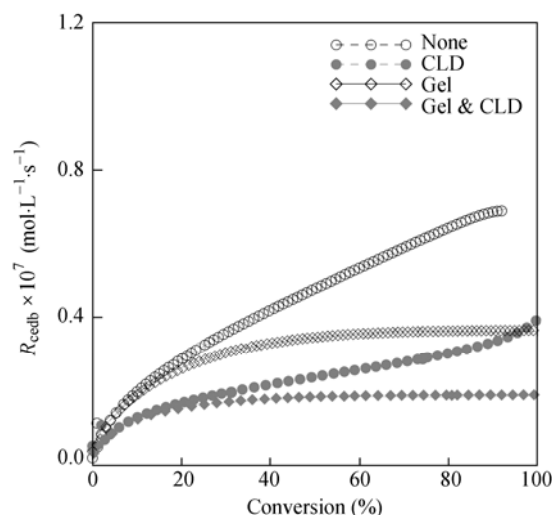


Fig. 13 Dependence of rate of chain end degradation type B on monomer conversion

Simulating Dependence of Molecular Weight and Polydispersity Index on Monomer Conversion

Weight-average molecular weight increases over the course of the polymerization approximately linearly (Fig. 14). However, there is an increase in molecular weight particularly in “None” case, at the final stages of the polymerization; this deviation from linearity is referred to coupling termination reactions and is more remarkable in the absence of gel effect and/or chain-length-dependent termination reactions. However, due to the reduction of termination reactions in “Gel & CLD” case, less chain coupling happens at the end of the reaction, and molecular weight curve keeps its linearity up to high conversion. The same trend can also be seen for number- and z-average molecular weights. It is obvious that the deviation from linearity is higher in weight- and z-average molecular weights; however, in “Gel & CLD” case both weight- and z-average molecular weights rise linearly up to the end of the polymerization. Therefore, the real kinetics of ATRP can precisely be predicted when diffusion-controlled and chain-length-dependent termination rate coefficients are taken into consideration.

As it is shown in Fig. 15, polydispersity index of polymer produced in ATRP greatly drops over the course of the polymerization. In fact, as the reaction proceeds, chains become more similar in length. This decrease in polydispersity index continues to the very end of the polymerization. Moreover, it is shown that the polydispersity index of polymers simulated by using “None” case is slightly higher. This is mainly because of more coupling reactions at the final stages of the polymerization in this case, which greatly raises PDI. However, in “Gel & CLD” case, upon the progress of the reaction up to very high conversion PDI significantly falls and almost amounts to unity.

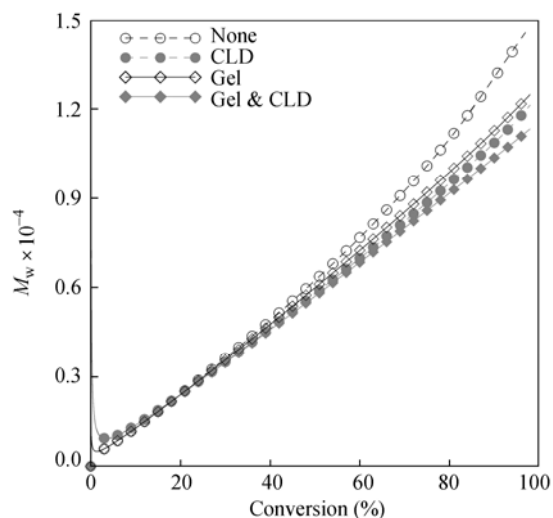


Fig. 14 Illustration of the dependence of weight-average molecular weight on monomer conversion

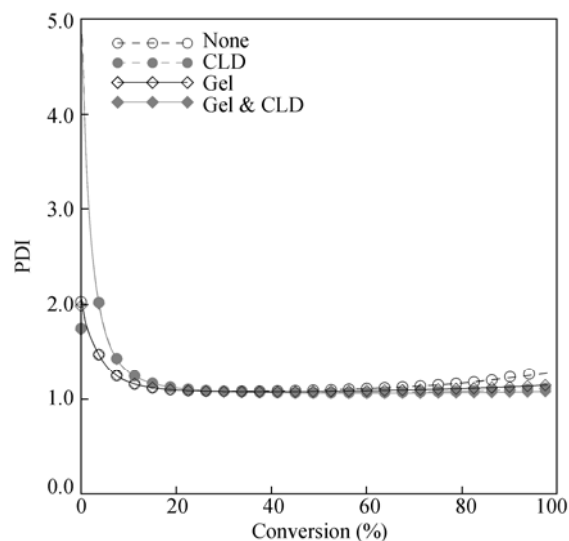


Fig. 15 Illustration of the dependence of polydispersity index on monomer conversion

Simulating Complete Molecular Weight Distribution throughout Polymerization

Monte Carlo method, contrary to many analytical models, is able to easily calculate the molecular weight distributions during the polymerization as it is not dependent on solving some stiff, time-related differential equations. As mentioned above, the number, weight, and z distributions of polymer chains can all be computed by Monte Carlo methods. The weight molecular weight distributions in different cases, *i.e.* “None”, “CLD”, “Gel”, and “Gel & CLD” are plotted as a function of polymerization conversion (see Fig. 16) as an instance. It can be noticed as follows:

(1) The location of the peaks of number, weight, and z distributions shifts to higher molecular weight while the polymerization proceeds; in fact, this additionally affirms the feature of controlled/“living” radical polymerization, by which molecular weight linearly increases throughout the polymerization.

(2) The molecular weight distributions broaden at higher monomer conversion because of the accumulation of dead chains in the reactor; this can remarkably be seen in “None” case.

(3) The molecular weight distributions of chains generated by using simultaneously diffusion-controlled and chain-length-dependent termination reactions are narrower at the final stages of the polymerization where coupling termination reactions mostly widen the molecular weight distributions.

It is also inferred that gel effect and chain-length-dependent termination reactions influence the molecular weight distributions mainly at high conversion; in addition, chain-length-dependent termination reactions affect the molecular weight distributions more strongly than diffusion-controlled termination reactions. Moreover, the peaks of molecular weight distributions (especially at high conversion) are located at higher molecular weights in “None” case, where termination reactions are more influential. Finally, there is a noticeable portion of chains with very low or very high molecular weight at high conversion in “None” case; this can be inferred from the tails of molecular weight distribution at both sides. This is attributed to either premature termination of chains at the early stages of the polymerization (which produces low-molecular-weight tail) or coupling termination at the final stages of the reaction (which produces high-molecular-weight tail).

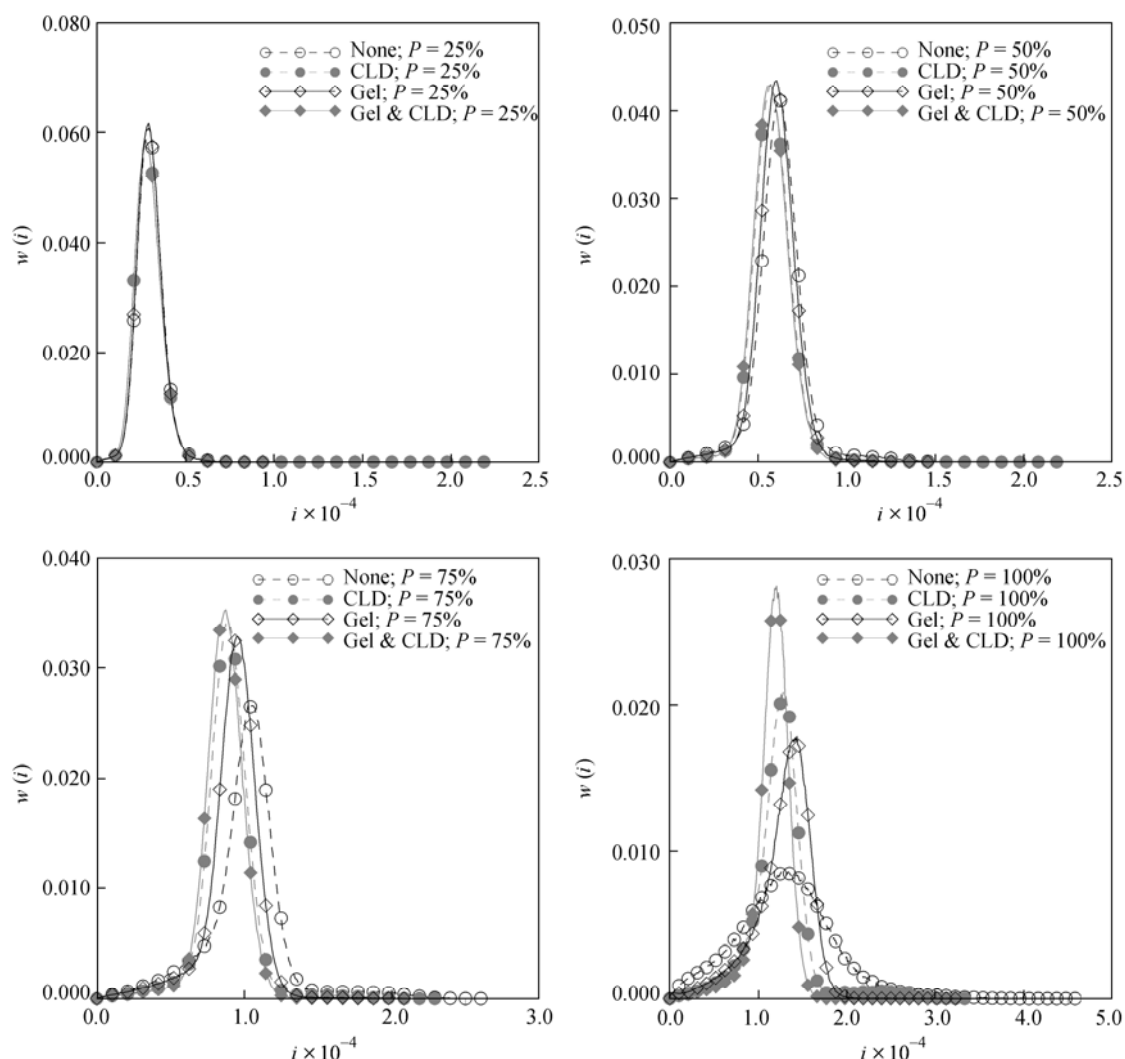


Fig. 16 Evolution of weight distribution throughout polymerization reaction

CONCLUSIONS

An optimized and high-performance Monte Carlo simulation is developed to thoroughly simulate the effect of diffusion-controlled and chain-length-dependent bimolecular termination reactions on the polymer microstructure in controlled/“living” radical polymerization of styrene. It is found out that as the chain length of radicals increases the termination rate constant drops and finally levels off beyond a certain chain length. In addition, simulation results show that termination rate constant greatly decreases over the course of the polymerization when it is diffusion-controlled. The linear plot of $\ln\left(\frac{M_0}{M}\right)$ against reaction time proves that the

degree of livingness of the polymerization varies when termination reactions become diffusion-controlled and/or chain-length-dependent; the reaction also proceeds to high conversion in such conditions. In addition, the initiator is completely decomposed at the early stages of the polymerization. The concentration of catalyst in higher oxidation state rises at first and then levels off; the amount of $X-M_t^{n+1}Y/L$ generated in the polymerization has the lowest value in “Gel & CLD” case too. Catalyst in lower oxidation state approximately shows a reverse trend. It decreases at first, and levels off in the end. The rate of deactivation and chain end

degradation reactions are smaller when diffusion-controlled chain-length-dependent termination is used. Therefore, the fraction of dormant chains is higher throughout the reaction and consequently the portion of dead polymers decreases. The rate of termination by combination is constant in “None” case, while it sharply lessens throughout the reaction when diffusion-controlled and/or chain-length-dependent termination is used in the model. Besides, molecular weight linearly increases with conversion; however, when neither gel effect nor chain-length dependency of termination rate constant is considered, the molecular weights (especially M_w and M_z) deviate from linearity at the end of the reaction. Furthermore, polymers produced through termination reactions with no chain-length dependency have higher molecular weight. In addition, the peaks of molecular weight distributions shift toward higher molecular weight throughout the polymerization. Finally, the molecular weight distributions become wider at the end of the polymerization. However, as expected, diffusion-controlled and chain-length-dependent termination reactions result in narrower molecular weight distributions; this is mainly imputed to a reduction in the accumulation of dead chains in the reactor.

ACKNOWLEDGEMENTS We wish to thank Ms. Ghazal Assadi-pour for her invaluable cooperation in the optimization of the simulation program. Also, the support of Research Institute of Petroleum Industry is highly appreciated.

REFERENCES

- 1 Matyjaszewski, K., “Controlled radical polymerization” (ACS Symposium Series 685), American Chemical Society, Washington, DC, 1998
- 2 Matyjaszewski, K., “Controlled/living radical polymerization. Progress in ATRP, NMP, and RAFT” (ACS Symposium Series 768), American Chemical Society, Washington, DC, 2000
- 3 Georges, M.K., Veregin, R.P.N., Kazmaier, P.M. and Hamer, G.K., *Macromolecules*, 1993, 26: 2987
- 4 Solomon, D.H., Rizzardo, E. and Cacioli, P., 1986, U.S. Pat., 4581429
- 5 Greszta, D. and Matyjaszewski, K., *Macromolecules*, 1996, 29: 7661
- 6 Benoit, D., Chaplinski, V., Braslau, R. and Hawker, C.J., *J. Am. Chem. Soc.*, 1999, 121: 3904
- 7 Le Mercier, C., Lutz, J.F., Marque, S., Le Moigne, F., Tordo, P., Lacroix-Desmazes, P., Boutevin, B., Couturier, J.L., Guerret, O., Martschke, R., Sobek, J. and Fischer, H., “Controlled/living radical polymerization” (ACS Symposium Series 768), ed. by Matyjaszewski, K., American Chemical Society, Washington, DC, 2000, p.108
- 8 Chiefari, J., Chong, Y.K., Ercole, F., Krstina, J., Jeffery, J., Le, T.P.T., Mayadunne, R.T.A., Meijs, G.F., Moad, C.L., Moad, G., Rizzardo, E. and Thang, S.H., *Macromolecules*, 1998, 31: 5559
- 9 Chong, Y.K., Le, T.P.T., Moad, G., Rizzardo, E. and Thang, S.H., *Macromolecules*, 1999, 32: 2071
- 10 Moad, G., Chiefari, J., Chong, Y.K., Krstina, J., Mayadunne, R.T.A., Postma, A., Rizzardo, E. and Thang, S.H., *Polym. Int.*, 2000, 49: 993
- 11 Rizzardo, E., Chiefari, J., Mayadunne, R.T.A., Moad, G. and Thang, S.H., “Controlled/living radical polymerization” (ACS Symposium Series 768), ed. by Matyjaszewski, K., American Chemical Society, Washington, DC, 2000, p.278
- 12 Wang, J.S. and Matyjaszewski, K., *J. Am. Chem. Soc.*, 1995, 117: 5614
- 13 Matyjaszewski, K., Gaynor, S. and Wang, J.S., *Macromolecules*, 1995, 28: 2093
- 14 Kato, M., Kamigaito, M., Sawamoto, M. and Higashimura, T., *Macromolecules*, 1995, 28: 1721
- 15 Patten, T.E. and Matyjaszewski, K. *Adv. Mater.*, 1998, 10: 901
- 16 Matyjaszewski, K., *Chem. Eur. J.*, 1999, 5: 3095
- 17 Fischer, H., *J. Am. Chem. Soc.*, 1986, 108: 3925
- 18 Matyjaszewski, K. and Xia, J., *Chem. Rev.*, 2001, 101: 2921
- 19 Kamigaito, M., Ando, T., and Sawamoto, M., *Chem. Rev.*, 2001, 101: 3689
- 20 Zhu, S., *J. Polym. Sci., Part B: Polym. Phys.*, 1999, 37: 2692
- 21 Zhu, S., *Macromol. Theory Simul.*, 1999, 8: 29
- 22 Delgadillo-Velazquez, O., Vivaldo-Lima, E., Quintero-Ortega, I. and Zhu, S., *AIChE J.*, 2002, 48: 2597

- 23 Fu, Y., Mirzaei, A., Cunningham, M.F. and Hutchinson, R.A., *Macromol. React. Eng.*, 2007, 1: 425
- 24 Al-Harhi, M., Soares, J.B.P. and Simon, L., *Macromol. Chem. Phys.*, 2006, 207: 469
- 25 Schork, F. J. and Smulders, W., *J. Appl. Polym. Sci.*, 2004, 92: 539
- 26 Wang, A. and Zhu, S., *J. Polym. Sci., Part A: Polym. Chem.*, 2003, 41: 1553
- 27 Zhang, M. and Ray, H., *J. Appl. Polym. Sci.*, 2002, 86: 1630
- 28 Zhang, M. and Ray, H., *J. Appl. Polym. Sci.*, 2002, 86: 1047
- 29 Zhang, M. and Ray, H., *Ind. Eng. Chem. Res.*, 2001, 40: 4336
- 30 Bonilla, J., Saldivar, E., Flores-Tlacuahuac, A., Vivaldo-Lima, E., Greszta, D., and Matyjaszewski, K., *Macromolecules*, 1996, 29: 7661
- 31 Shipp, A. and Matyjaszewski, K., *Macromolecules*, 1999, 32: 2948
- 32 Shipp, A. and Matyjaszewski, K., *Macromolecules*, 2000, 33: 1553
- 33 Lutz, J. and Matyjaszewski, K., *Macromol. Chem. Phys.*, 2002, 203: 1385
- 34 Barner-Kowollik, C., Quinn, J.F., Morsley, D.R. and Davis, T.P., *J. Polym. Sci., Polym. Chem. Ed.*, 2001, 39: 1353
- 35 Chaffey-Millar, H., Busch, M., Davis, T.P., Stenzel, M.H. and Barner-Kowollik, C., *Macromol. Theory Simul.*, 2005, 14: 143
- 36 Mohammadi, Y., Najafi, M. and Haddadi-Asl, V., *Macromol. Theory Simul.*, 2005, 14: 325
- 37 Najafi, M., Haddadi-Asl, V., and Mohammadi, Y., *J. Appl. Polym. Sci.*, 2007, 106: 4138
- 38 He, J., Zhang, H.D. and Yang, Y., *Macromol. Theory Simul.*, 1995, 4: 811
- 39 Tobita, H., *Macromol. Theory Simul.*, 2003, 12: 32
- 40 He, J., Zhang, H. and Yang, Y., *Macromol. Theory Simul.*, 1993, 2: 747
- 41 He, J., Li, L. and Yang, Y., *Macromol. Theory Simul.*, 2000, 9: 463
- 42 Tobita, H., *Macromol. Theory Simul.*, 2006, 15: 23
- 43 He, J., Zhang, H., Chen, J. and Yang, Y., *Macromolecules*, 1997, 30: 8010
- 44 Al-Harhi, M., Soares, J.B.P. and Simon, L.C., *Macromol. React. Eng.*, 2007, 1: 468
- 45 Al-Harhi, M., Soares, J.B.P. and Simon, L.C., *Macromol. React. Eng.*, 2007, 1: 95
- 46 Kwark, Y.J. and Novak, B.M., *Macromolecules*, 2004, 37: 9395
- 47 Queffelec, J., Gaynor, S. G. and Matyjaszewski, K., *Macromolecules*, 2000, 33: 8629
- 48 Ohno, K., Goto, A., Fukuda, T., Xia, J. and Matyjaszewski, K., *Macromolecules*, 1998, 31: 2699
- 49 Fu, Y., Hutchinson, R. A. and Cunningham, M.F., *Macromol. React. Eng.*, 2007, 1: 243
- 50 Hui, A. and Hamielec, E., *J. Appl. Polym. Sci.*, 1972, 16: 749
- 51 Olaj, O.F. and Vana, P., *Macromol. Rapid Commun.*, 1998, 19: 433
- 52 Olaj, O.F. and Vana, P., *Macromol. Rapid Commun.*, 1998, 19: 533
- 53 Olaj, O.F., Vana, P., Kornherr, A. and Zifferer, G., *Macromol. Chem. Phys.*, 1999, 200: 2031
- 54 Buback, M., Egorov, M., Junkers, T. and Panchenko, E., *Macromol. Rapid Commun.*, 2004, 25: 1004
- 55 Smith, G.B., Russell, G.T. and Heuts, J.P.A., *Macromol. Theory Simul.*, 2003, 12: 299
- 56 Gillespie, D., *J. Phys. Chem.*, 1977, 81: 2340
- 57 Matsumoto, M. and Nishimura, T., *ACM Trans. Model. Comput. Simul.*, 1998, 8: 3