

Modeling Analysis of Chain Transfer in Reversible Addition-Fragmentation Chain Transfer Polymerization

Xiang Gao,^{1,2} Shiping Zhu²

¹Department of Chemical and Biological Engineering, Zhejiang University, Hangzhou, 310027, China

²Department of Chemical Engineering, McMaster University, Hamilton, Ontario, Canada

Received 8 March 2010; accepted 4 November 2010

DOI 10.1002/app.33708

Published online 27 April 2011 in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: The validity of simplifying the reversible addition-fragmentation chain transfer (RAFT) polymerization as a degenerative chain transfer process was verified in this work. The simplified chain transfer mechanism enabled the direct modeling investigation of chain transfer coefficient in the RAFT polymerization. It also gave the analytical expressions for concentration, chain length, and polydispersity of various chain species. The comparison between the simulations based on chain transfer mechanism and those from general RAFT mechanism showed that this simplified mechanism can accurately predict RAFT polymerization in the absence of side reactions to adduct radicals other than fragmentation. However, significant errors are introduced at high conversion when side

reactions to adduct are present. The chain transfer coefficient of RAFT agent is the key factor in RAFT polymerization. The polydispersity is more sensitive to chain transfer coefficient at low conversion. At high conversion, however, the polydispersity is mainly determined by termination, which can be controlled by RAFT agent concentration and the selection of initiator. At last, an analytical equation is derived to directly estimate chain transfer coefficient of RAFT agent from the experimental data. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 122: 497–508, 2011

Key words: reversible addition-fragmentation chain transfer polymerization; modeling; chain transfer; living polymerization kinetics

INTRODUCTION

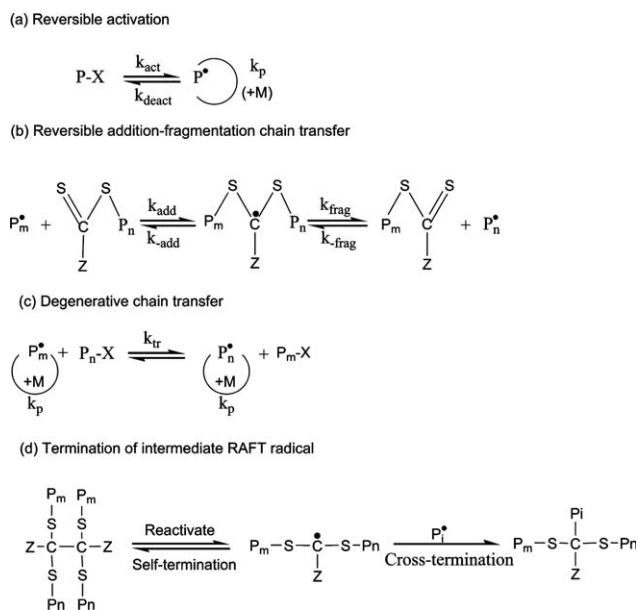
Living radical polymerization techniques, as powerful routes to synthesize well-defined polymer materials with narrow polydispersity or designed structures, attract more and more attention in the recent years. In these polymerization systems, a reversible activation–deactivation process exists and ensures the system living. As shown in Scheme 1(a), the dormant species $P-X$ is activated to generate the reactive radicals P^\bullet , which react with monomers. Propagation continues until the radicals are deactivated by deactivators to form dormant chains. This reversible activation and deactivation process is so fast that only few monomer molecules can be added to polymer chains in a single cycle. As a result, all polymerization chains in the system grow simultaneously during the whole reaction. This accounts for the low polydispersity of polymer chains. Three major capping techniques have been developed to achieve living radical polymerization: Stable free-radical polymerization using nitroxide radical,¹ atom transfer radical polymerization (ATRP) using halogen atom,²

and reversible addition-fragmentation chain transfer (RAFT) polymerization using thiocarbonylthio.^{3,4}

The RAFT polymerization using dithio compounds was discovered by Rizzardo and coworkers⁵ A RAFT [Scheme 1(b)] process serves the activation and deactivation that are required for a living polymerization and the addition of radical P_m^\bullet to the dormant chain TP_n forms the intermediate radicals, which are not stable. Fragmentation occurs and releases either P_m^\bullet or P_n^\bullet . This reversible process can be viewed as a degenerative chain transfer process as shown in Scheme 1(c), where k_{tr} is the rate constant of the exchange reaction. The use of highly reactive thiocarbonylthio RAFT agents with high chain transfer rate is the key to obtain polymers with narrow molecular weight distribution.

Modeling studies on RAFT polymerization have been carried out widely with different methods.^{6–23} Using the method of moment, Wang and Zhu developed a kinetic model for RAFT polymerization predicting the monomer conversion, average molecular weight, and polydispersity of polymer chains.^{20,24} It provided detailed information about the effect of each rate constant and recipe, giving a clear picture of RAFT process. The effects of the diffusion-controlled reactions on RAFT polymerization kinetics and molecular weight development were also investigated through a modeling approach.²¹ Monteiro

Correspondence to: S. Zhu (zhuship@mcmaster.ca).



Scheme 1 Reversible activation and deactivation processes in living polymerization systems.

gave a detailed description of RAFT process in which all possible reactions from initiation to four-arm star formation were included, to provide a comprehensive analysis of influencing factors on the chain growth and polydispersity.^{16,25} Besides the method of moment, a program package PREDICI[®] was also employed for the simulation of RAFT process.^{9,13,17,19,23,26,27} Monte Carlo method, a popular method for polymerization simulation, has also been employed for the modeling research on RAFT polymerization.^{8,11,18}

In all the previous modeling studies, the RAFT polymerization mechanism was described in great details. In this way, RAFT polymerization could be investigated thoroughly. However, it also contained too many differential equations in the models. Sophisticated mathematic tools were always employed to resolve these equations. Therefore, these models have seldom been used by others who are not familiar with these modeling tools to provide guidance for experiment work. Simple solutions, especially analytical equations, are desired for the guidance of experimental work. Therefore, RAFT polymerization is always viewed as a degenerative chain transfer process in experimental studies. A high chain transfer coefficient, C_{tr} ($=k_{\text{tr}}/k_p$), is the key factor for the RAFT polymerization. The corresponding kinetic research is mainly on the chain transfer rate in RAFT system and its effect on polydispersity. The effect of substituents of RAFT agents on their chain transfer coefficient has been investigated comprehensively in many studies.^{28,29} Unfortunately, up to now no modeling supports have been given based on the degenerative chain transfer mechanism in a

RAFT system. As a result, no direct discussion on the effect of chain transfer coefficient, C_{tr} , has been carried out through modeling study. Mueller studied the degenerative chain transfer in general living radical polymerization.^{29–31} As the only modeling support for this degenerative chain transfer mechanism, this model has been used in some RAFT studies to guide the experimental work. However, the equations were derived without the initiator decomposition. The radical termination was neglected as well. As a result, suitable models for RAFT based on the degenerative chain transfer mechanism are desired. The effect of chain transfer coefficient can therefore be better understood.

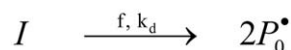
A direct method to estimate the chain transfer coefficient of RAFT agent from experimental data is also expected from the model development. As mentioned above, the chain transfer coefficient is the most important factor in RAFT polymerization. The performance of RAFT agents is evaluated by their chain transfer coefficients. Numerous experimental studies have been carried out on the chain transfer coefficient of various RAFT agents. The Mayo method, a conventional method for estimate of chain transfer rate constant, is employed in the special cases where the consumption of RAFT agent is slow at low conversion.^{28,29} However, when the chain transfer coefficient of RAFT agent is high, this method is not valid. Another method based on the conversion of initial RAFT agents to polymer chains has also been employed.^{28,29} C_{tr} can be estimated from a simplified equation.

$$C_{\text{tr}} \approx \frac{d\ln[CTA]}{d\ln[M]} \quad (1)$$

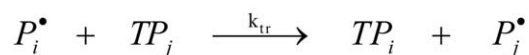
In this method, the concentration of initial RAFT agent must be monitored. However, if the chain transfer coefficient is high (>150), most initial RAFT agents will grow into polymer chains at a very low conversion ($<2\%$), which makes it impossible to measure the concentration of remnant dithioester by NMR even after a very short period of time.^{28,29}

The calculation of C_{tr} from polydispersity data is more accurate considering the polydispersity of polymer chains is more sensitive to C_{tr} than the conversion or chain length. Especially when chain transfer rate is very high, both methods are invalid. Chong et al. employed the equations derived by Mueller to estimate C_{tr} from polydispersity data.²⁹ Since the model by Mueller ignored termination and initiator decomposition, Chong et al. added initiation and radical–radical termination to their calculation. C_{tr} was estimated by fitting the model to experimental data. Due to the complexity of resolving numerous numerical differential equations, this method has not been employed by other researchers to

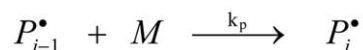
(a) Initiation



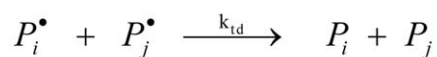
(b) Chain transfer



(c) Propagation



(d) Termination by disproportionation



(e) Termination by combination



Scheme 2 Mechanism of RAFT Polymerization.

estimate C_{tr} from experimental data. As a result, a simpler method to estimate C_{tr} from experimental data is needed, especially by many chemists who work on designing new RAFT agents.

The objective of this work is to investigate the accuracy in treating the complex RAFT polymerization as a simple degenerative chain transfer polymerization. We made an effort to derive analytical equations to calculate the concentration, chain length, and polydispersity of various chain species in RAFT system, and proposed a direct method to estimate chain transfer coefficient of RAFT agent from experimental data. The analytical equations can be used directly by other researchers for a quantitative analysis of experiment data.

MODEL DEVELOPMENT

Polymerization scheme

The model is developed based on the polymerization mechanism as illustrated in Scheme 2. Radicals are generated as in conventional radical polymerization with k_d as the decomposition rate constant and f as the initiator efficiency, respectively. Conventional radical initiators, for example, azo compound or peroxide, are used in RAFT polymerization. One initiator molecule decomposes into two radicals, so a factor of 2 appeared on the right side of Scheme 2(a). Scheme 2(b) is the transfer reaction between living and dormant chains. The subscript i and j stand for

the number of monomeric units incorporated to the polymer chain. The range of i and j is between 0 and infinite. T represents the chain transfer agent in RAFT. TP_i is the dormant chain. When $i = 0$, TP_0 represents initial RAFT transfer agent with its initial concentration shown in Table VI or indicated otherwise. The initial concentrations of radicals (P_0^\bullet) and dead chains (P_0) are both zero. In RAFT polymerization, the reversible chain transfer between active and dormant chains is accomplished through the addition and fragmentation reactions. The overall chain transfer rate constant, k_{tr} , is determined by the rate coefficients in the equilibrium. The efficiency of this step determines living character of the polymerization. As a result, the RAFT process is considered as a chain transfer process, in which the chain transfer coefficient, C_{tr} , has been given great attention. Short radical chains, especially the primary radicals ($i = 0$), may have different chain transfer rate. In this work, however, a single chain transfer reaction rate coefficient is employed to represent the total chain transfer ability of RAFT agent. Scheme 2(c) is the propagation of polymer chains. The bimolecular radical terminations by disproportionation (k_{td}) and combination (k_{tc}) are also taken into consideration in this work [Scheme 2(d,e)].

Derivation

There are three types of chain species involved in RAFT system: propagating radical chains (P_i^\bullet), dormant chains (TP_i), and dead chains (P_i). As shown in Table I, the mass balance equations for these chains, as well as initiator and monomer, are derived

TABLE I
Mass Balance for Various Types of Chain Species,
Initiator, and Monomer

Species	Mass balance equations
Propagating radical chain	$\frac{d[P_i^\bullet]}{dt} = k_p[P_{i-1}^\bullet][M] + k_{tr}[TP_i] \sum_{i=0}^{\infty} [P_i^\bullet] - k_p[P_i^\bullet][M] - k_{tr}[P_i^\bullet] \sum_{i=0}^{\infty} [TP_i] - k_t[P_i^\bullet] \sum_{i=0}^{\infty} [P_i^\bullet] \quad (2)$
Dormant chain	$\frac{d[TP_i]}{dt} = k_{tr}[P_i^\bullet] \sum_{i=0}^{\infty} [TP_i] - k_{tr}[TP_i] \sum_{i=0}^{\infty} [P_i^\bullet] \quad (3)$
Dead chain	$\frac{d[P_i]}{dt} = k_{td}[P_i^\bullet] \sum_{i=0}^{\infty} [P_i^\bullet] + \frac{1}{2}k_{tc} \sum_{j=0}^i [P_j^\bullet][P_{i-j}^\bullet] \quad (4)$
Initiator	$\frac{d[I]}{dt} = -k_d[I] \quad (5)$
Monomer	$\frac{d[M]}{dt} = -k_p \sum_{i=0}^{\infty} [P_i^\bullet][M] \quad (6)$

TABLE II
Definition of Various Chain Moments

Type of chain	Definition of moment
Propagating radical chain	$Q_r^* = \sum_{i=0}^{\infty} i^r [P_i^*]$
Dormant chain	$TQ_r = \sum_{i=0}^{\infty} i^r [TP_i]$
Dead chain	$Q_r = \sum_{i=0}^{\infty} i^r [P_i]$

assuming a batch reactor with negligible volume change. The method of moment is applied to achieve the expressions of molecular weight and molecular weight distribution. The corresponding moments are defined as in Table II. The number-average chain length, weight-average chain length, and polydispersity for the propagating radical chain, dormant chain, and dead chain can be calculated from the previously defined moments according to Table III. Mathematical manipulations yield equations for the zero moments (i.e., molar concentrations of chains), the first moments (i.e., molar concentrations of monomeric units), and the second moments for three types of polymer chains as in Table IV. When $x = 0$, TQ_0 is the concentration of initial RAFT agent. Q_0^* and Q_0 are both zero. All the initial values of upper moments are zero based on their definitions shown in Table II.

In RAFT system, initiation and radical-radical termination occur as in conventional radical polymerization. The fast build-up of radicals allows the use of stationary state hypothesis (SSH) for radical moments. Applying SSH to eqs (10) and (13), the expressions for the first and second moments of radicals are obtained

TABLE IV
Expressions for Three Types of Moments

Chain species	Zero moments
Propagating radical chain	$\frac{d[Q_0^*]}{dt} = 2fk_d[I] - k_t[Q_0^*][Q_0^*]$ (7)
Dormant chain	$\frac{d[TQ_0]}{dt} = 0$ (8)
Dead chain	$\frac{d[Q_0]}{dt} = k_{td}[Q_0^*][Q_0^*] + \frac{1}{2}k_{tc}[Q_0^*][Q_0^*]$ (9)
First moments	
Propagating radical chain	$\frac{d[Q_1^*]}{dt} = k_p[Q_0^*][M] + k_{tr}[Q_0^*][TQ_1] - k_{tr}[Q_1^*][TQ_0] - k_t[Q_1^*][Q_0^*]$ (10)
Dormant chain	$\frac{d[TQ_1]}{dt} = k_{tr}[Q_1^*][TQ_0] - k_{tr}[Q_0^*][TQ_1]$ (11)
Dead chain	$\frac{d[Q_1]}{dt} = k_t[Q_1^*][Q_0^*]$ (12)
Second moments	
Propagating radical chain	$\frac{d[Q_2^*]}{dt} = k_p[Q_0^*][M] + 2k_p[Q_1^*][M] + k_{tr}[Q_0^*][TQ_2] - k_{tr}[Q_2^*][TQ_0] - k_t[Q_2^*][Q_0^*]$ (13)
Dormant chain	$\frac{d[TQ_2]}{dt} = k_{tr}[Q_2^*][TQ_0] - k_{tr}[Q_0^*][TQ_2]$ (14)
Dead chain	$\frac{d[Q_2]}{dt} = k_t[Q_2^*][Q_0^*] + k_{tc}[Q_1^*][Q_1^*]$ (15)

$$[Q_1^*] = \frac{k_p[M]_0(1-x) + k_{tr}[TQ_1]}{k_{tr}[TQ_0] + k_t[Q_0^*]} [Q_0^*] \quad (16)$$

$$[Q_2^*] = \frac{k_p[Q_0^*][M]_0(1-x) + 2k_p[Q_1^*][M]_0(1-x) + k_{tr}[Q_0^*][TQ_2]}{k_{tr}[TQ_0] + k_t[Q_0^*]} \quad (17)$$

TABLE III
Relationships Between Chain Moments with Number-Average Chain Length, Weight-Average Chain Length, and Polydispersity

Type of chain	Number-average chain length	Weight-average chain length	Polydispersity
Propagating radical chain	$\bar{r}_N = \frac{Q_1^*}{Q_0^*}$	$\bar{r}_W = \frac{Q_2^*}{Q_1^*}$	$PD = \frac{\bar{r}_W}{\bar{r}_N}$
Dormant chain	$\bar{r}_N = \frac{TQ_1}{TQ_0}$	$\bar{r}_W = \frac{TQ_2}{TQ_1}$	$PD = \frac{\bar{r}_W}{\bar{r}_N}$
Dead chain	$\bar{r}_N = \frac{Q_1}{Q_0}$	$\bar{r}_W = \frac{Q_2}{Q_1}$	$PD = \frac{\bar{r}_W}{\bar{r}_N}$
Total chain	$\bar{r}_N = \frac{Q_1^* + TQ_1 + Q_1}{Q_0^* + TQ_0 + Q_0}$	$\bar{r}_W = \frac{Q_2^* + TQ_2 + Q_2}{Q_1^* + TQ_1 + Q_1}$	$PD = \frac{\bar{r}_W}{\bar{r}_N}$

The relationship between conversion and time is as follows:

$$\frac{dx}{dt} = k_p[Q_0^*](1-x) \quad (18)$$

Replacing Q_1^* in eq. (11) by eq. (16) and the time by conversion as a variable based on eq. (18) gives

$$\frac{d[TQ_1]}{dx} = \frac{1-x + C_{tr}[TQ_1]/[M]_0}{\tau + \beta + C_{tr}T_0/[M]_0} \frac{C_{tr}T_0}{1-x} - \frac{C_{tr}[TQ_1]}{1-x} \quad (19)$$

where $\tau = \frac{k_{td}[Q_0^*]}{k_p[M]_0}$, $\beta = \frac{k_{tc}[Q_0^*]}{k_p[M]_0}$, and $T_0 = [CTA]_0$. Solving this differential equation with the initial condition of $[TQ_1] = 0$ at $x = 0$ yields

$$[TQ_1] = \frac{C_{tr}T_0 \left[1-x - (1-x)^{\frac{\tau+\beta}{\tau+\beta+C_{tr}T_0/[M]_0}} \right]}{C_{tr}\tau + C_{tr}\beta - \tau - \beta - C_{tr}T_0/[M]_0} \quad (20)$$

It should be noted that the above integration employed the assumption of constant rate coefficient. Therefore, these equations cannot be applied for the cases where the rate coefficients vary significantly with the conversion, for example, in some cases the termination rate coefficient may be chain-length dependent.³²

In RAFT polymerization, the chain transfer reaction rate is much higher than that of termination, especially when a low polydispersity is targeted:

$$k_t[Q_0^*][Q_0^*] \ll k_{tr}[TQ_0][Q_0^*] \quad (21)$$

Therefore

$$\tau + \beta \ll C_{tr}T_0/[M]_0 \quad (22)$$

This simplification is applied to achieve analytical equations. A comparison of the analytical results based on this simplification to the numerical solution of the differential equations in Table IV shows that the error is smaller than 1% when $C_{tr}T_0/[M]_0 > 0.02$.

The analytical solution for $[TQ_1]$ is then obtained

$$[TQ_1] = \frac{[M]_0 T_0}{B} [1-x - (1-x)^A] \quad (23)$$

where $A = \frac{[M]_0\tau + [M]_0\beta}{T_0}$ and $B = [M]_0\tau + [M]_0\beta - T_0$.

Replacing $[Q_2^*]$ by eq. (17) and solving differential eq. (14) with the initial condition of $[TQ_2]_0 = 0$ at $x = 0$ yield the analytical expression for $[TQ_2]$ as shown in Table V. With the initial conditions of $[Q_0]_0 = 0$, $[Q_1]_0 = 0$, $[Q_2]_0 = 0$ at $x = 0$, the differential equations for dead chains can all be solved and the final analytical expressions are shown in Table V.

From eqs. (5), (7), and (18), the expression of $[Q_0^*]$ as a function of conversion is obtained

$$[Q_0^*] = \sqrt{\frac{2fk_d I_0}{k_t}} + \frac{k_d}{2k_p} \ln(1-x) \quad (24)$$

The analytical expressions for the three types of moments shown in Table V are obtained. The number-average chain length, weight-average chain length, and polydispersity for the propagating radical chains, dormant chains, and dead chains can all be calculated from these expressions.

RESULTS AND DISCUSSION

Model parameters

In this work, the kinetic parameters employed in our previous studies, as shown in Table VI, were selected for simulation.^{10,20,22} Some parameters are varied to investigate their effect on the RAFT polymerization while all the others remain unchanged.

Difference between two mechanisms

Although the addition-fragmentation reaction has been always viewed as an exchanging or degenerative chain transfer process, no investigation has been given to examine the possible difference caused by this simplification. To examine the validity of this simplification, our previous modeling work of RAFT polymerization, in which the general RAFT mechanism including addition and fragmentation reactions was studied, is selected to make the comparison.²⁰

When the chain transfer mechanism is applied to study the RAFT process, an overall chain transfer rate constant k_{tr} is employed. It is given by the following expression,^{33,34}

$$k_{tr} = k_{add} \times \frac{k_{frag}}{k_{-add} + k_{frag}} \quad (25)$$

where $k_{frag}/(k_{-add} + k_{frag})$ represents the probability for the intermediate in Scheme 1(b) to be fragmented into P_n^* and TP_m . Since P_m and P_n are both polymer chains, the probability to become P_n^* or P_m^* is assumed to be the same, which gives the equation of

$$k_{tr} = 0.5k_{add} \quad (26)$$

The relationship between k_{tr} and k_{add} , as shown in eq. (26), was verified in this work through comparing the analytical solutions based on the chain transfer mechanism and numerical results from the general RAFT mechanism.²⁰ Same kinetic parameters are used in both calculations. The cross-termination rate constant, k_{ctv} is set zero because it is assumed that no other reactions happening to adduct radicals other than fragmentation.

From Figure 1, it can be seen that when $k_{tr} = 0.5 k_{add}$, the analytical results from chain transfer

TABLE V
Analytical Expressions for Three Types of Moments

Chain species	Zero moments
Propagating radical chain	$[Q_0^\bullet] = \sqrt{\frac{2fk_d I_0}{k_t}} + \frac{k_d}{2k_p} \ln(1-x)$
Dormant chain	$[TQ_0] = T_0$
Dead chain	$[Q]_0 = -\ln(1-x)\tau[M]_0 - \frac{1}{2}\ln(1-x)\beta[M]_0$
First moments	
Propagating radical chain	$[Q_1^\bullet] = \frac{k_p[M]_0(1-x) + k_{tr}[TQ_1]}{k_{tr}T_0 + k_t[Q_0^\bullet]} [Q_0^\bullet]$
Dormant chain	$[TQ_1] = \frac{[M]_0 T_0}{B} [1-x - (1-x)^A]$
Dead chain	$[Q_1] = [M]_0 \frac{T_0}{B} (1-x)^A + (\tau + \beta)(C_{tr} - 1) \frac{[M]_0^2}{C_{tr}B} x - \frac{[M]_0 T_0}{B}$
Second moments	
Propagating radical chain	$[Q_2^\bullet] = \frac{k_p[Q_0^\bullet][M]_0(1-x) + 2k_p[Q_1^\bullet][M]_0(1-x) + k_{tr}[Q_0^\bullet][TQ_2]}{k_{tr}T_0 - k_t[Q_0^\bullet]}$
Dormant chain	$[TQ_2] = \left(\frac{2[M]_0^2 C_{tr}T_0 + B}{2-A} \frac{1}{C_{tr}T_0B} + \frac{[M]_0}{1-A} - \frac{2[M]_0^2}{B} x \right) (1-x)^A + \frac{2[M]_0^2 C_{tr}T_0 + B}{A-2} \frac{1}{C_{tr}T_0B} (1-x)^2 - \frac{[M]_0}{1-A} (1-x)$
Dead chain	$[Q_2] = \frac{2[M]_0^2 A}{C_{tr}T_0B} \left(\frac{B}{C_{tr}} + T_0 + \frac{B + C_{tr}T_0}{A-2} + \frac{(B + C_{tr}T_0)^2 \beta[M]_0}{C_{tr}T_0B} \frac{1}{2A} \right) \left(x - \frac{1}{2}x^2 \right) + \frac{1-A - [M]_0}{1-A} Ax + \frac{2[M]_0^2 (ABT_0 + \beta C_{tr}[M]_0 T_0 + \beta[M]_0 B)}{C_{tr}T_0B^2(A+1)} (1-x)^{A+1} + \left(\frac{2(Ax+1)[M]_0^2}{B(A+1)} - \frac{2[M]_0^2 B + C_{tr}T_0}{2-A} \frac{1}{C_{tr}T_0B} - \frac{[M]_0}{1-A} \right) (1-x)^A - \frac{[M]_0^3 \beta}{2AB^2} (1-x)^{2A} - \left[\frac{2[M]_0^2}{(A+1)B} \frac{ABT_0 + B\beta[M]_0 + C_{tr}\beta[M]_0 T_0 + BC_{tr}T_0}{BC_{tr}T_0} - \frac{2[M]_0^2 B + C_{tr}T_0}{2-A} \frac{1}{C_{tr}T_0B} - \frac{[M]_0}{1-A} - \frac{[M]_0^3 \beta}{2AB^2} \right]$

mechanism are close to the numerical solutions from general RAFT process. It proves the validity of the assumption concerning the relationship between k_{add} and k_{tr} [eq. (26)]. The effect of the fragmentation reaction needs to be investigated, because it is ignored in the chain transfer mechanism. The comparison between the analytical calculations based on chain transfer mechanism and the numerical results from general RAFT process with different values of k_{frag} is given in Figure 2.

It can be seen that the fragmentation rate has no effect on chain length and polydispersity when side reactions of adduct are neglected. In RAFT polymerization, although the fragmentation rate determines the concentration of adduct radicals in the system and affects the polymerization rate, the chain transfer equilibrium [Scheme 1(b)] is established quickly and the concentration of adduct radicals varies little. The neglect

of k_{frag} in the chain transfer mechanism does not affect its validity for representing general RAFT process.

TABLE VI
Reactant Concentrations and Rate Constants Employed in the Simulation

Reactant	Reactant concentration
Monomer	$[M]_0 = 5 \text{ mol L}^{-1}$
Initiator	$[I]_0 = 5 \times 10^{-3} \text{ mol L}^{-1}$
RAFT agent	$[CTA]_0 = 10^{-2} \text{ mol L}^{-1}$
Rate	Rate constant
Initiator decomposition	$k_d = 10^{-5} \text{ s}^{-1}$
Initiator efficiency	$f = 0.5$
Propagation	$k_p = 10^3 \text{ mol L}^{-1} \text{ s}^{-1}$
Termination	$k_{td} = k_{tc} = 10^7 \text{ mol L}^{-1} \text{ s}^{-1}$
Chain transfer	$k_{tr} = 5 \times 10^5 \text{ mol L}^{-1} \text{ s}^{-1}$
Addition	$k_{add} = 10^6 \text{ mol L}^{-1} \text{ s}^{-1}$
Fragmentation	$k_{frag} = k_{-add} = 10^4 \text{ mol L}^{-1} \text{ s}^{-1}$

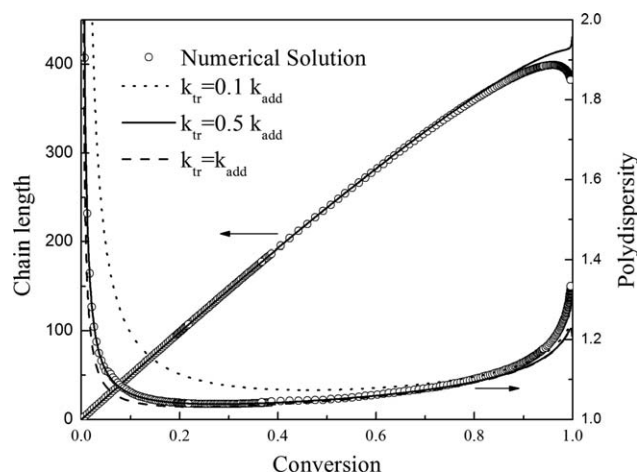


Figure 1 The relationship between k_{tr} and k_{add} .

In the calculations, it was assumed that no side reactions other than fragmentation happening to adduct radicals. However, side reactions to the adduct radicals including cross-termination between adduct and propagating radicals may exist as shown in Scheme 1(d). Possible errors caused by neglecting adduct termination in the chain transfer mechanism are shown in Figure 3.

It can be seen that significant adduct termination can cause big errors at high conversion. However, the errors are small at most of the time, especially at the beginning, which is the most important stage for investigating C_{tr} because polydispersity is most sensitive to the parameter in the early stage. Furthermore, since the termination rate of adduct radicals is normally smaller than that of propagating radicals, the influence of adduct radical termination is minor in most cases.

If the adduct termination rate is large, however, the simplification of general RAFT process to chain

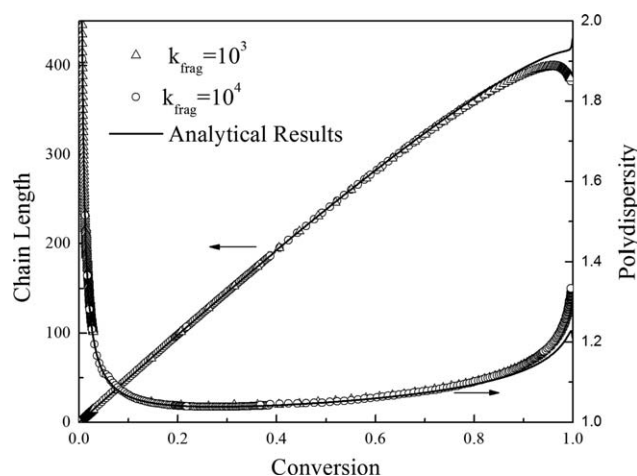


Figure 2 Effect of the fragmentation on the chain length and polydispersity with $k_{frag} = 10^3$ and 10^4 mol L⁻¹ s⁻¹. Other parameters are given in Table 6.

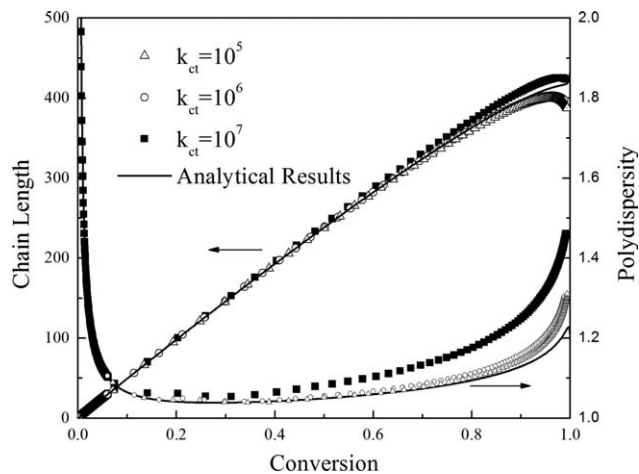


Figure 3 Effect of the adduct termination on the chain length and polydispersity with $k_{ct} = 10^5$, 10^6 , and 10^7 mol L⁻¹ s⁻¹. Other parameters are given in Table 6.

transfer mechanism will be invalid. It has been claimed that slow fragmentation or significant adduct termination exist in many RAFT reactions.^{35,36} The debate on the fate of the RAFT adduct radicals is still not settled. This model is limited to RAFT polymerizations with fast fragmentation rate and negligible side reactions to the intermediate radicals. In practical view only these RAFT polymerization processes are desired to achieve fast polymerization rate and good control.

Kinetic study of RAFT polymerization

The kinetics of RAFT polymerization is studied based on the chain transfer mechanism in this work. The zero, first, and second moments from the analytical solution are developed first.

The zero moments, shown in Figure 4(a), represent the concentration of three types of polymer chains. The dormant chains are the majority in the system. The concentration of propagating radical chains is $\sim 10^{-8}$ – 10^{-7} mol/L. The concentration of dead chains increases with conversion because of radical termination in RAFT polymerization. This indicates that in RAFT polymerization the termination must be taken into consideration in the model development. The concentrations of monomeric units for the three types of polymer chains are approximately two orders of magnitude higher than those of polymer chains. The concentrations of the second moments are also about two orders of magnitude higher than those of the first moments.

Figure 4(b) gives the number-average chain lengths of the polymer chains. The chain lengths of dormant, propagating, and total chains are almost the same during the whole polymerization, which indicates sufficient chain transfer reaction. The dead chains are shorter, because they do not participate in

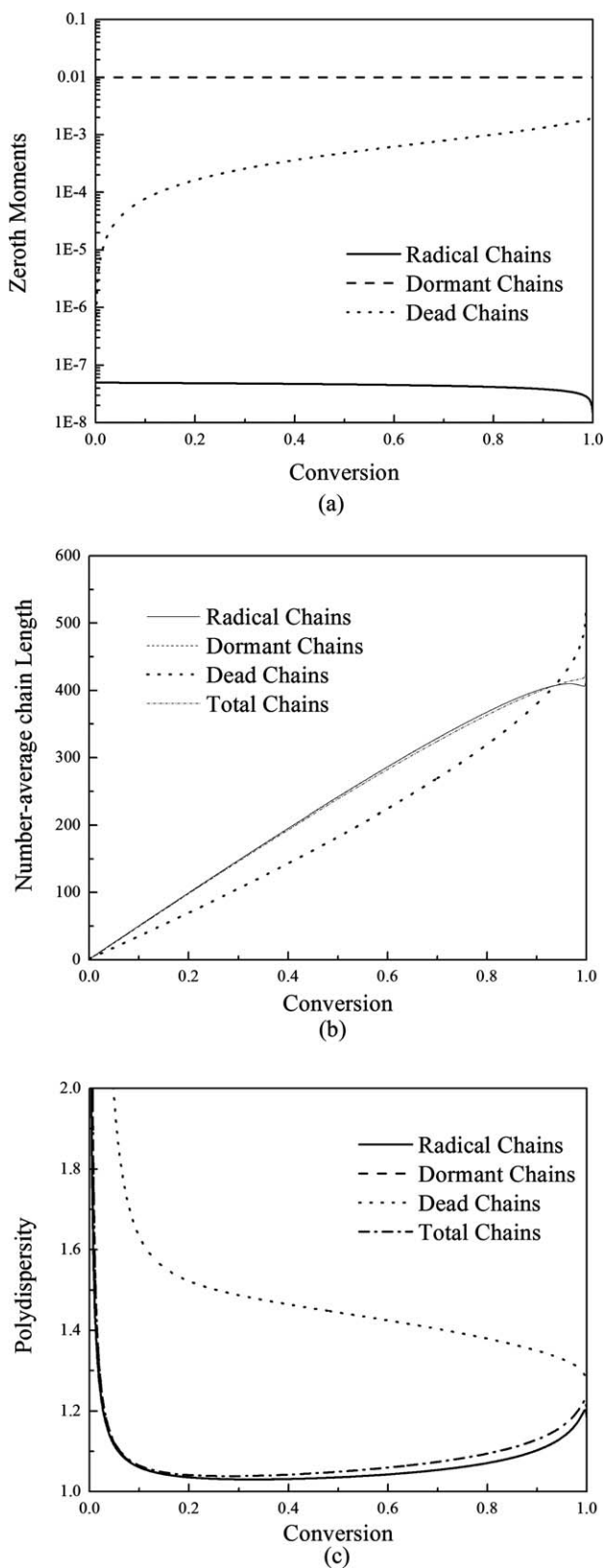


Figure 4 Development of (a) zero moments, (b) chain length and (c) polydispersity of various types of chains in RAFT system. The parameters are $[M]_0 = 5 \text{ mol L}^{-1}$, $[I]_0 = 5 \times 10^{-3} \text{ mol L}^{-1}$, $[CTA]_0 = 10^{-2} \text{ mol L}^{-1}$, $k_{td} = 10^{-5} \text{ s}^{-1}$, $f = 0.5$, $k_p = 10^3 \text{ mol L}^{-1} \text{ s}^{-1}$, $k_{td} = k_{tc} = 10^7 \text{ mol L}^{-1} \text{ s}^{-1}$ and $k_{tr} = 5 \times 10^5 \text{ mol L}^{-1} \text{ s}^{-1}$.

further propagation. At high conversion, however, their chain length becomes longer than that of total chains. It is because at high conversion the propagating rate decreases due to monomer depletion while the termination rate is little influenced. The dead polymer chains formed by combination have chain lengths doubled. At the end of reaction, the total chain length reaches 430, smaller than the theoretical value, 500, from the recipe. It is caused by significant radical termination in RAFT polymerization, which also demonstrates the importance of the radical termination in RAFT process.

Figure 4(c) gives the polydispersity indexes of various types of polymer chains. The curves for propagating radicals and dormant chains overlap. This suggests sufficient chain transfer between propagating radicals and dormant chains, which enables all the chains have equal opportunity to grow. The polydispersity of total chains is close to that of dormant chains, because most of the chains in the system are dormant, especially at the beginning. However, the polydispersity of dead chains is much higher than others. It decreases with the conversion despite of the fact that the chain length of dead chains increases with the conversion. As shown in Figure 4(a), the concentration of dead chains increases by orders of magnitude with the conversion. As a result, the dead chains generated at low conversion contribute little to the cumulative polydispersity value due to their small population. Therefore, the cumulative polydispersity of dead chains has the same trend as that of dormant chains, decreasing with the conversion.

The most important kinetic parameter in RAFT polymerization is C_{tr} . RAFT agent with high C_{tr} is believed to be the key to obtain polymers with low polydispersity. Figure 5 shows the effect of C_{tr} on chain length development and polydispersity.

From Figure 5(a), it can be seen that C_{tr} has no effect on molecular weight development. It is because the radicals are neither formed nor destroyed in the chain transfer process. However, C_{tr} influences the polydispersity of polymer chains significantly as shown in Figure 5(b). When C_{tr} is adequately high (>500), the polydispersity of polymer chains reaches a low level at low conversion because of a fast chain transfer between propagating radical and dormant chains. In contrast, if the chain transfer rate is low, it costs longer time for all the initial RAFT agents to undergo chain transfer reaction and grow into polymer chains. Therefore, the polydispersity of polymer chains decreases in a slower manner when C_{tr} is smaller, as shown in Figure 5(b). The result in Figure 5 shows that the polydispersity is more sensitive to C_{tr} at low conversion, which may help to determine C_{tr} more accurately from experimental data in this area. When the chain

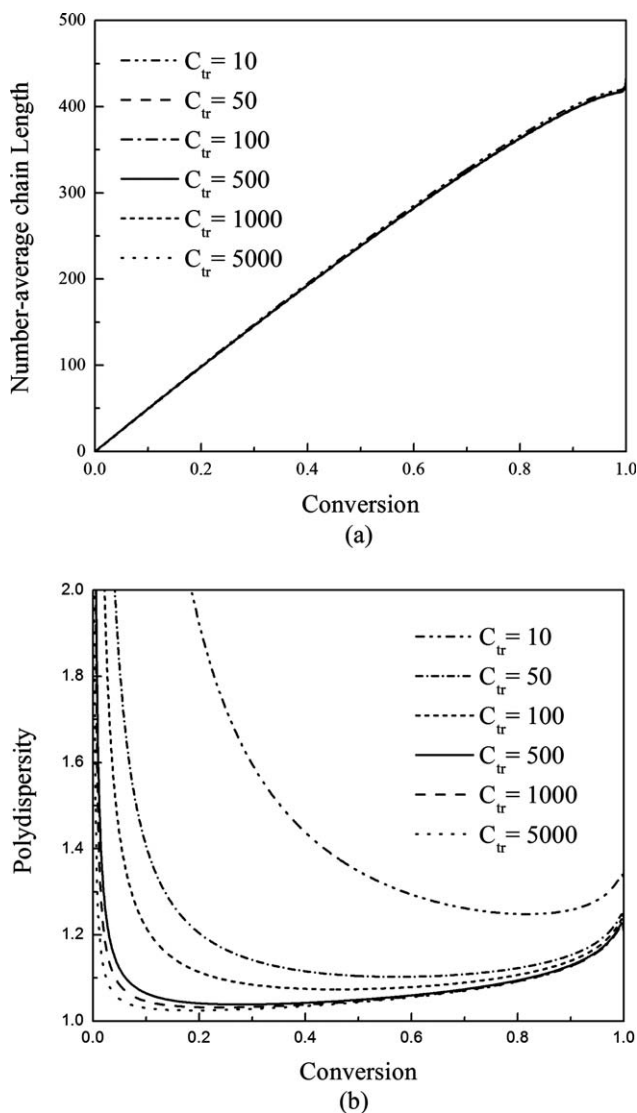


Figure 5 Effect of the transfer coefficient on (a) the chain length and (b) polydispersity with $C_{tr} = 10, 50, 100, 500, 1000,$ and 5000 . Other parameters are given in Table 6.

transfer becomes sufficient, the difference between the polydispersity curves with different C_{tr} values becomes smaller. When C_{tr} is adequately high, the curves overlap at high conversion. For a targeted polydispersity at high conversion, there exists a certain C_{tr} value. RAFT agent with higher chain transfer gives little further advantage. The polydispersity of polymer chains at high conversion is mainly determined by termination, which can be controlled by selection of proper initiator. If a low polydispersity of polymer chains (<2) is targeted, a RAFT agent with the chain transfer coefficient larger than 50 must be selected.

In addition to C_{tr} , radical termination is another important factor, which determines the polydispersity at high conversion. The initiator concentration and decomposition rate determine the concentration of radicals, which affect the propagating and termi-

nation rate. Figure 6 gives three RAFT systems with different initiator concentrations.

It can be seen the concentration of initiator influences both chain length and polydispersity significantly, especially at high conversion. When the initiator concentration increases, there are more propagating radicals in the RAFT system. As a result, the termination reaction becomes significant, which causes a loss of control over the RAFT process. From Figure 6, it can be seen when the concentration of initiator is high (0.05 mol/L), the chain length development deviates from the theoretical linear growth in living polymerization. Large amount of propagating radicals terminate before undergoing many chain transfer and propagating circles, which gives small chain length leading to the deviation. These dead chains also cause the increase of polydispersity as shown in Figure 6. A low initiator concentration can decrease the concentration of radicals and avoid radical termination. When the initiator concentration is 0.0005 mol/L, the termination is very low and the polydispersity remains low up to high conversion. However, low radical concentration also means low polymerization rate. As a result, an appropriate initiator concentration is important in the RAFT system. High initiator concentration, which gives high polydispersity, should be avoided.

It is noticed that the termination mainly influences the polydispersity at high conversions. At low conversion, the curves of polydispersity from different initiator concentrations overlap because in this area the influence of termination is not significant. The main influencing factor is C_{tr} as discussed above. At high conversion, however, the effect of C_{tr} becomes minor and the termination dominates. Comparison between Figure 5 and 6 shows that the selection of initiator is as important as the selection of RAFT agent with high chain transfer coefficient.

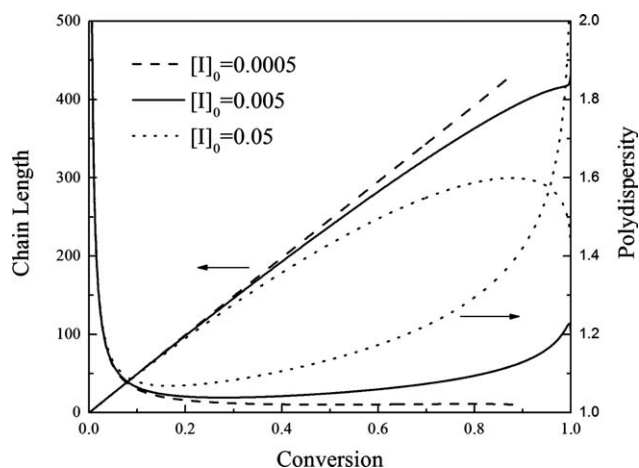


Figure 6 Effect of the initiator concentration on the chain length and polydispersity with $[I]_0 = 0.0005, 0.005,$ and 0.05 mol L^{-1} . Other parameters are given in Table 6.

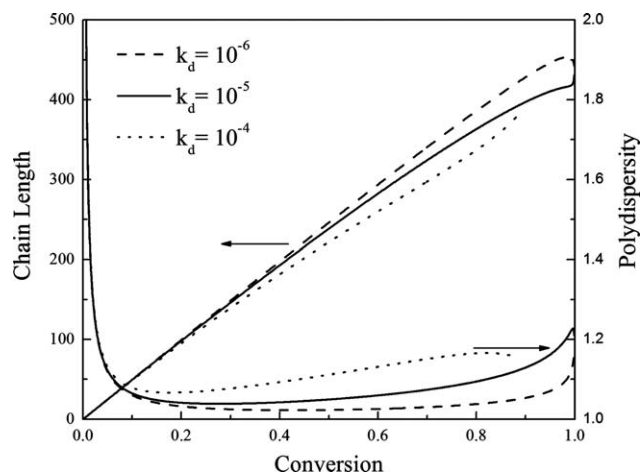


Figure 7 Effect of the initiator decomposition rate constant on the chain length and polydispersity with $k_d = 10^{-6}$, 10^{-5} , and 10^{-4} s^{-1} . Other parameters are given in Table 6.

Figure 7 shows the effect of decomposition rate constant, k_d , on chain length development and polydispersity. Similar to the effect of initiator concentration, increasing initiator decomposition rate increases the concentration of radicals. As a result, the increasing termination rate makes the molecular weight development less controlled, with the final molecular weight deviating from the theoretical value. Similar effect also happens to the polydispersity of polymer chains as shown in Figure 7.

Figure 8 gives the influence of RAFT agent concentration on chain length development and polydispersity. RAFT agent concentration is the determining factor for chain length. A higher RAFT agent concentration gives a lower molecular weight with the theoretical value of $[M]_0/[CTA]_0$. The effect of RAFT agent concentration on polydispersity varies at different stages of polymerization. At low conversion, a higher RAFT agent concentration leads to a higher polydispersity because it costs longer time for all the RAFT agent molecules to complete chain transfer with radicals. This is similar to the system in which the RAFT agent has a low chain transfer rate. At high conversion, however, a higher RAFT agent concentration decreases polydispersity greatly due to the good control of termination. A high concentration of RAFT agent increases the concentration of dormant chains and decreases radical termination at the same time.

Analytical solutions of the moment equations

Analytical solutions are always desired by researchers for the quantitative analysis of experimental data. In the RAFT system, the majority of chains are dormant, as shown in Figure 4(a). The chain length is mainly determined by that of dormant chains,

which was also demonstrated in the above simulation. From Figure 4(c), it can be seen that the polydispersity of total chains is very close to that of dormant chains. It is therefore reasonable to use chain length and polydispersity of the dormant chains to represent those of total chains. Based on this simplification, analytical equations to estimate number-average chain length and polydispersity can be derived as in Table VII. Please note all these equations are only valid to RAFT polymerizations with fast fragmentation rate and negligible side reactions to the intermediate radicals.

Figure 9 gives the comparison between the simulation results from these analytical equations and the results obtained by Wang and Zhu based on the general RAFT mechanism.²⁰ It can be seen that these analytical equations provide a simple and accurate way

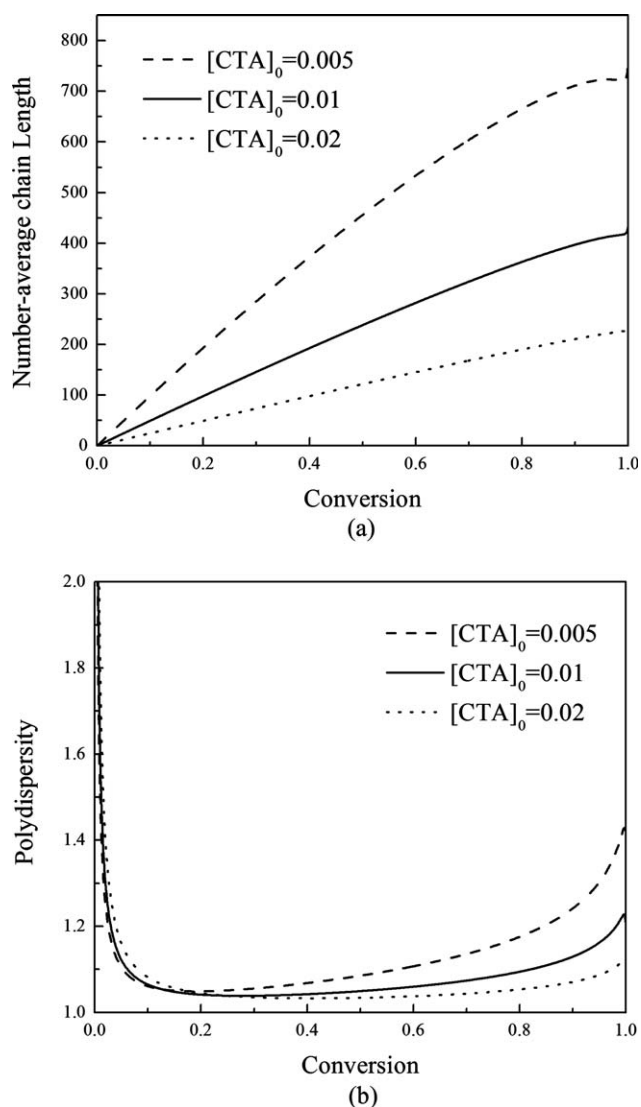


Figure 8 Effect of the RAFT agent concentration on (a) the chain length and (b) polydispersity with $[CTA]_0 = 0.05$, 0.01 and 0.02 mol L^{-1} . Other parameters are given in Table 6.

TABLE VII
Simple Equations to Guide Experimental Work and Calculate C_{tr} from Polydispersity Data

Chain length:

$$\bar{r}_N = \frac{[M]_0}{B} [1 - x - (1 - x)^A] \quad (27)$$

Polydispersity:

$$PD = \frac{\frac{2B}{A-2} \frac{C_{tr} T_0 + B}{C_{tr} T_0^2} [(1-x)^2 - (1-x)^A] + \frac{B^2}{(A-1)T_0[M]_0} [(1-x) - (1-x)^A] - \frac{2B}{T_0} x(1-x)^A}{[(1-x) - (1-x)^A]^2} \quad (28)$$

Transfer coefficient:

$$C_{tr} = \frac{2B^2[(1-x)^2 - (1-x)^A]}{(A-2)T_0^2 PD [(1-x) - (1-x)^A]^2 + 2B(A-2)T_0 x(1-x)^A - \frac{(A-2)T_0 B^2}{(A-1)[M]_0} [(1-x) - (1-x)^A] - 2BT_0 [(1-x)^2 - (1-x)^A]} \quad (29)$$

for the calculation of chain length and polydispersity in the RAFT system, especially at low conversion.

Equation 28 also makes it possible to obtain a direct method to estimate C_{tr} from experimental data. The equation is derived and shown in Table VII. This equation allows one to calculate C_{tr} from polydispersity data. The use of polydispersity data is more accurate in the estimate of C_{tr} . It is a much simpler method considering that there is no numerical fitting and no need to measure the concentration of RAFT agent. However, it should be noted the polydispersity measurement of polymer chains with low molecular weight requires appropriate GPC column set.

In RAFT polymerization, the initiator decomposition, radical termination, and chain propagation are the same as those in conventional radical polymerization. The kinetic parameters required in eq. 29 to estimate C_{tr} are readily obtained. The experimental data at low conversion are recommended for the estimate of C_{tr} . As discussed above, the polydispersity is very sensitive to C_{tr} at low conversion, while other factors have little effect on polydispersity in this area.

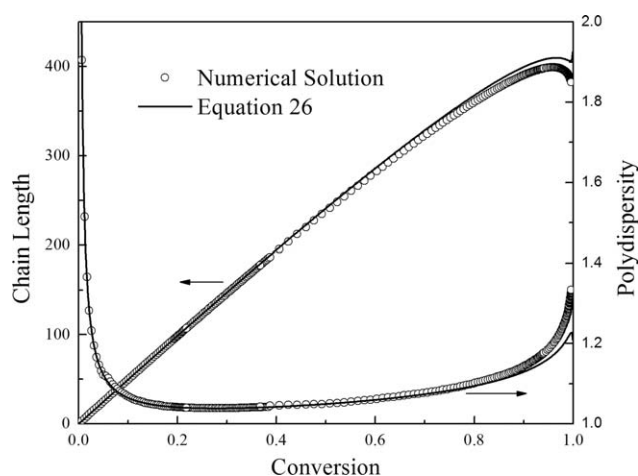


Figure 9 The accuracy of equation 27 and 28 for the calculating of chain length and polydispersity in general RAFT system. The parameters are given in Table 6.

CONCLUSIONS

Based on the chain transfer mechanism, analytical expressions for concentration, chain length, and polydispersity of various types of chain species in RAFT polymerization were derived. The comparison between the simulation results from these analytical equations and those from the model based on general RAFT mechanism demonstrated the validity of applying degenerative chain transfer mechanism to RAFT polymerization. The fragmentation rate of adduct radicals has little influence on chain length development and polydispersity in the absence of side reactions. However, large errors emerge at high conversions when side reactions are significant. Simulation based on chain transfer mechanism enabled the discussion about the effect of C_{tr} on RAFT polymerization. The kinetic analysis showed that the chain transfer coefficient is the key factor in RAFT polymerization. The polydispersity is most sensitive to C_{tr} at low conversion. C_{tr} should be larger than 50 for a low polydispersity. At high conversion, however, the polydispersity is mainly determined by termination, which can be controlled by RAFT agent concentration and the selection of initiator. The accuracy of the simple equations to estimate chain length and polydispersity were confirmed. When the direct method derived in this work is employed to estimate C_{tr} from experimental data, the selection of polydispersity data at low conversion is recommended.

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