

A New Approach for Monte Carlo Simulation of RAFT Polymerization

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ABSTRACT: *In this work, based on experimental observations and exact theoretical predictions, the kinetic scheme of RAFT polymerization is extended to a wider range of reactions such as irreversible intermediate radical terminations and reversible transfer reactions. The reactions which have been labeled as kinetic scheme are the more probable existing reactions as the theoretical point of view. The detailed kinetic scheme is applied to three kinds of RAFT polymerization system by utilizing the Monte Carlo simulation Method. To do this, a new approach of simulation method was used. In this approach, a multi-reaction step was used in each time step. Unknown kinetic rate constants have obtained by curve fitting of the simulation results and theoretical data, applying the least square method; or estimated by considering theoretical facts and experimental findings. The origin of the rate retardation and induction period has been understood by studying the main and pre-equilibrium stages of dithiobenzoate-mediated RAFT homo polymerization. A copolymerization system in the presence of RAFT agent has also been examined to confirm the capability of introduced simulation method in different monomer/RAFT agent systems. The simulation results were in excellent agreement with experimental data, which proves the validity and applicability of the Monte Carlo algorithm.*

KEY WORDS: RAFT polymerization, Monte Carlo method, Mechanism, Kinetics.

INTRODUCTION

Among Controlled /“Living” free Radical Polymerization (CLRP) techniques, Reversible Addition-Fragmentation chain Transfer (RAFT) [1-2] is arguably the most versatile

technique with respect to the types of monomers and reaction conditions. Good control over Molecular Weight Distribution (MWD) and chain microstructure has led to

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employing this technique to access a wide range of polymer architectures and topologies, including block [3], gradient [4], graft, star [5] and hyper branched [6].

Studies over mechanism and kinetics of RAFT have considerably focused on dithiobenzoate-mediated systems [7-9], which show a significant rate retardation and long inhibition period. There are two predominant schools of thought on the origin of this phenomenon: Slow Fragmentation (SF) [7] and irreversible Intermediate Radical Termination (IRT) [8]. In the SF model, intermediate radicals have a very small fragmentation rate constant due to the high stability. Side reactions between intermediate radicals and propagating radicals do not occur meanwhile. On the other hand, IRT model predicts that, the rate retardation is caused by a consequence of irreversible termination of intermediate radicals. This model leads to a small equilibrium constant as a result of fast fragmentation. Both models can predict conversion, molecular weight and PDI data correctly but in some cases their predictions do not match with experimental results. Investigations propose that the origin of rate retardation and induction (inhibition) period may be different [9], and it is crucial to consider different equilibrium constants for pre- and main equilibrium steps. In addition, at the early stages of polymerization (i.e. pre equilibrium reactions are dominant), various radical species go through reversible transfer with different rate constants due to different chemical reactivity toward RAFT agents [10] and the rate constants are more dependent to the length of oligomeric species [11]. These matters emphasize on the fact that individual values must be assumed for equilibrium constants. According to the points mentioned above, one should consider the complex kinetic scheme, contains many side reactions. Recently, *Konkolewicz et al.* [12] have developed a composite model which is in relatively good agreement with the experimental data. Their model cannot be used as a universal kinetic scheme as a result of elimination of many side reactions, which may exist in other systems.

In the literature, Monte Carlo methods [13-15], methods of moments [16] and Ordinary Differential Equations (ODE) [17] have been used to describe the kinetics of polymerization. The statistical nature of chain growth and chain-terminating reactions makes Monte Carlo simulation methods as powerful tools

in this context [18-21]. Because of the ability of storing the whole information of (co)polymerization chains while the reaction proceeds, Monte Carlo simulation methods are able to compute all of the above-mentioned parameters with their distributions as well as their mean values. Furthermore, Monte Carlo methods are capable of considering the composition drift and azeotropic properties of copolymers in good agreement with the experimental and analytical methods [22].

In this paper, we used a kinetic model including reactions that occur probably, based on experimental data. Then, we apply our model to different monomer/RAFT agent systems, both homo- and copolymerization ones. A new approach of Monte Carlo method was used to simulate kinetic model. In this method, a random number was used to determine the number of reactions which can perform at the same time instead of one reaction.

Kinetic Scheme

Scheme 1 shows the kinetic scheme in which initiation can occur by thermal dissociation of initiator molecules. The initiator fragment radical can react with a monomer molecule to form a primary radical or go through a reversible transfer reaction with different types of RAFT agents. There are three types of RAFT agent in this system based on their leaving groups: initial RAFT (having R as leaving group), RAFTI (having initiator, I, moiety as leaving group) and RAFTP_n (RAFT agent with polymeric leaving group). Primary radicals propagate by reacting with monomer molecules. Another possible reaction of propagating radicals is transfer to RAFT agents. The reversible transfer reactions temporarily deactivate the propagating radical chains and can prohibit them from termination. In addition to RAFT agents, the radical center can transfer to some species (CTA) in the reaction mixture to form a dead polymer and a small radical (denoted as A*). The latter may undergo re-initiation reaction with a monomer molecule. Terminations between radicals can deactivate the radical center and make a radical dead. In addition to common terminations which are present in free radical polymerization systems, we assume the possibility of reaction between intermediate radicals with other types of radicals. Although many of these termination reactions may never occur in a specific reaction system,

considering most of them in the kinetic scheme has the advantage of making the scheme flexible enough to be applied to all RAFT polymerization systems. This type of reaction leads to formation of star like dead polymers. With respect to the number of polymeric arms, we divided star like products into 4-, 3-, 2- and 1-arm star polymers. It is worth noting to mention that star like polymers with less than 3 polymeric arms have no difference with linear polymers.

We extended our scheme to a copolymerization system based on the terminal model. For macro species, the first term of index relates the length (number of monomer units) of chain and the second term shows the monomer type of terminal unit. For small species, the index only relates to the type of monomer.

Monte Carlo Simulation Method

Although by using the Monte Carlo method one can simulate polymerization on a molecular scale, to avoid the huge amount of computation, this method is better to be employed for small amounts of reaction volumes. In other words, the simulation volume has been chosen enough to reduce the simulation time to a reasonable value; however, the reaction volume needs to be large enough to meet the statistical criteria. Therefore, a simulation volume which consists of 10^9 monomer molecules has been employed. Subsequently, the number of other components is calculated based on monomer molecules:

$$V = \frac{N_M}{[M]N_{av}} \quad (1)$$

$$N_X = [X]N_{av}V \quad (2)$$

where, V is simulation volume, N_M denotes the number of monomers, $[M]$ is monomer concentration, N_{av} is Avogadro's number, N_X represents the number of X molecules, and $[X]$ is the concentration of X species. In addition, since the Monte Carlo simulation method deals with a number of molecules (instead of concentration), stochastic reaction rates need to be replaced by the macroscopic ones. Provided that there are L reactions in the simulation, the probability of incidence of reaction (1) P_1 is given by the Eq. (3) [23,24].

$$P_1 = \frac{a_1}{\sum_{i=1}^L a_i} \quad (3)$$

where, a_i is the stochastic reaction rate for a reaction and it is defined by the Eq. (4).

$$a = h \times c \quad (4)$$

In this equation, h represents the number of reactants and c stands for the stochastic rate constants and correlates with ordinary reaction rates:

First-order reactions

$$c = k \quad (5)$$

Second-order reactions

$$c = \frac{k}{VN_{av}} \quad (6)$$

In classic Monte Carlo method, regarding r as a random number which is generated during the simulation, based on the following criteria, a reaction is chosen to happen:

$$0 < r \leq P_1 \Rightarrow \text{reaction} \quad (7)$$

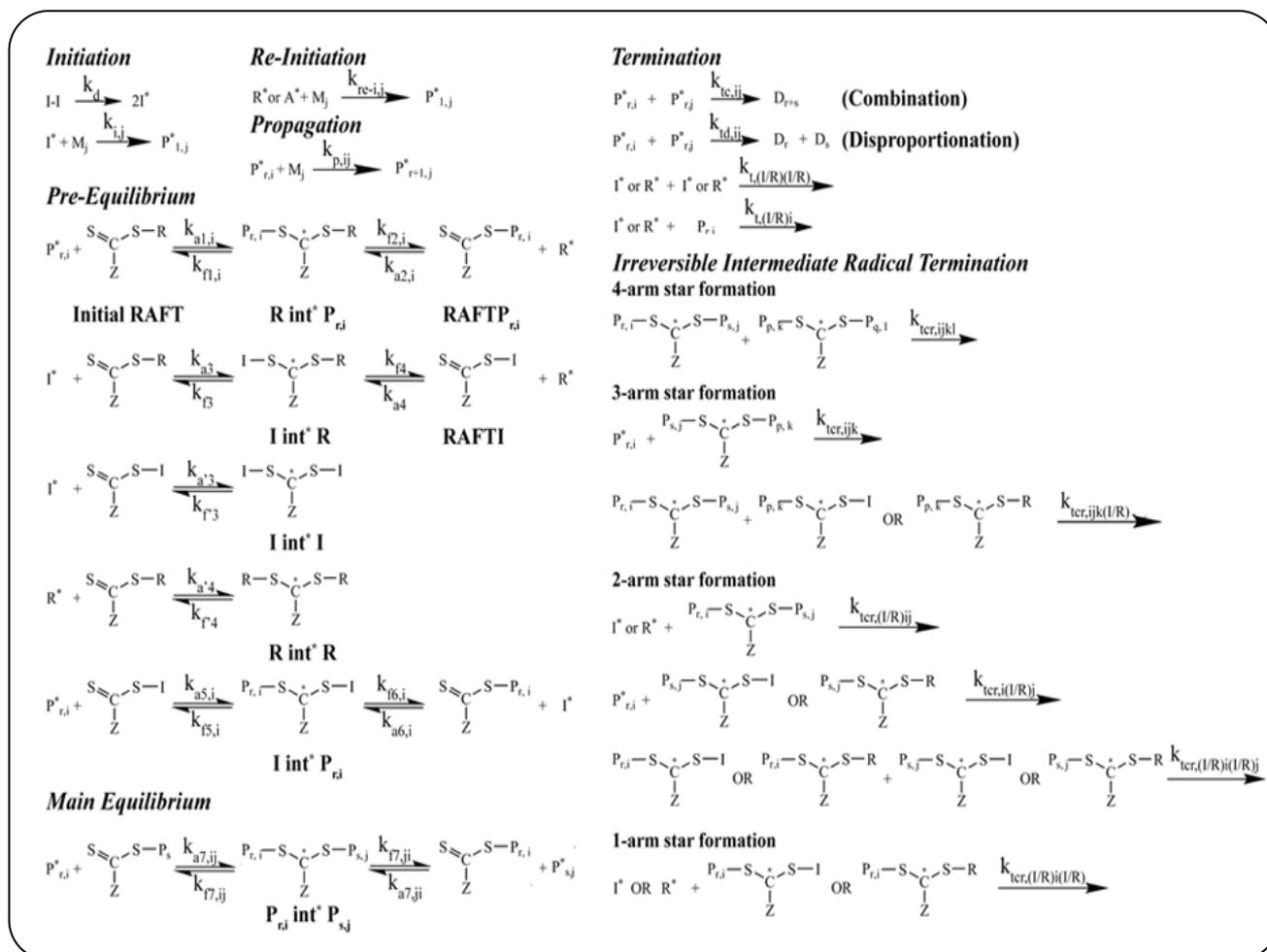
$$P_{1-1} < r \leq P_1 \Rightarrow \text{reaction} \quad (8)$$

In our new method, first a random number is generated during simulation to determine how many reactions can participate in polymerization at the same time step. This will help to program to run fast and make Monte Carlo method more applicable.

In the course of the reaction, to select a polymer chain for reaction, all chains of the same active center are considered as a group at first. Then, the probability of the reaction of this group is calculated by dividing the number of chains in the group by all the chains which is available in the reaction medium. Afterward, the reactions are selected to start randomly. Finally, another random number is generated to compute the reaction time intervals:

$$\tau = \frac{1}{\sum_{i=1}^L a_i} \ln\left(\frac{1}{r}\right) \quad (9)$$

Therefore, improved Mersenne twister random number generator, which had a cycle length of $2^{19937}-1$ and satisfied the tests of uniformity and serial correlation [23-25] have been employed in this work. The simulation program was written in C++ and executed on a four-processor (Pentium Intel Xeon (4×2.3 GHz)) hp server running SuSE Linux as its operating system. Schematic



Scheme 1: RAFT mechanism including probable reactions.

representation of the Monte Carlo method algorithm which is used in the current study is illustrated in Scheme 2.

RESULTS AND DISCUSSION

Polystyryl Dithiobenzoate-Mediated Polymerization of Styrene

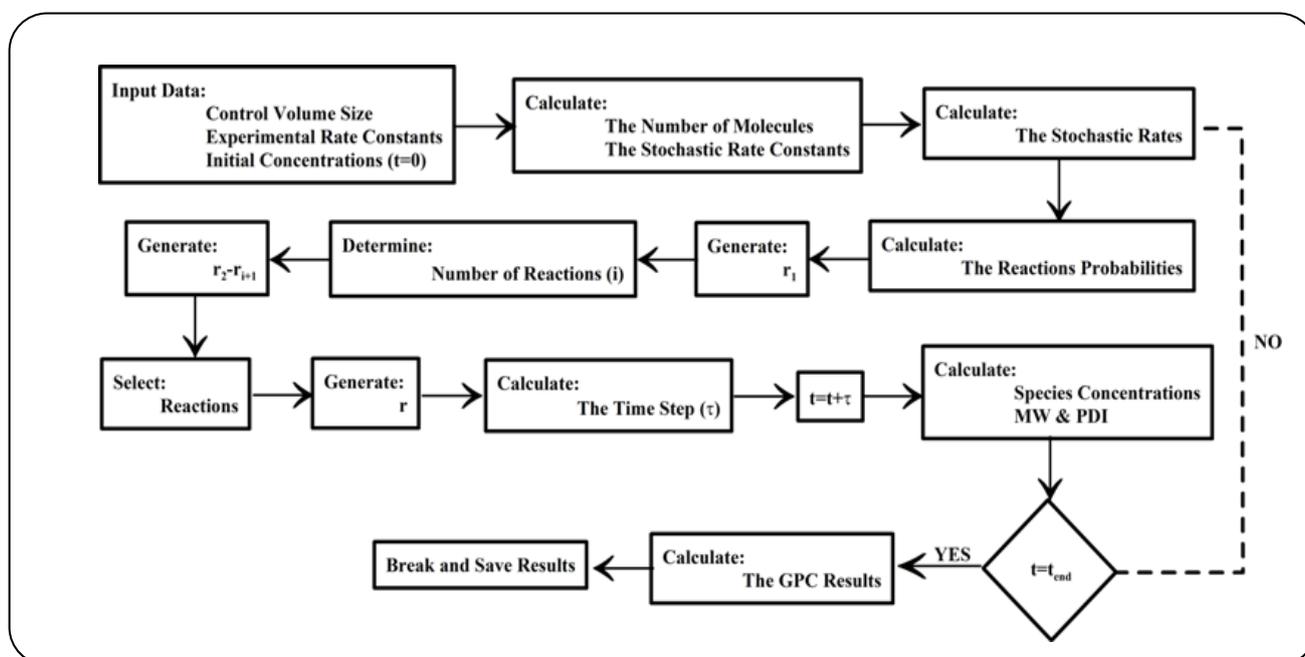
According to literature results [13], the polymerization system reaches the stationary-state in a few seconds by using polymeric RAFT agents. Applying the polymeric RAFT agent eliminates most of pre-equilibrium step's reactions. Both propagating and intermediate radicals reach their equilibrium values in a while, as a result of small value of equilibrium constant for main equilibrium reaction. The obtained data are used for investigation of the main equilibrium in detail. Table 1 shows experimental conditions used by Kwak *et al.* [13] and rate constants used in this work.

Fig. 1-A compares the $\ln([M]_0/[M])$ with time obtained from simulation and experimental data. According to results, conversion increase linear which is the characteristic behavior of RAFT polymerization and no retardation time is seen due to usage of Poly-RAFT (RAFTP) as chain transfer agent. Also, good correlation between simulation and experimental results shows that the used algorithm is appropriate for simulation of such polymerization.

Figure 1-B shows the concentration of free radicals with time. As seen from simulation results, at first the concentration starts from zero and suddenly increases to a higher value and then increases gradually. It is ascribed to less termination reactions with respect to initiation reactions which is characteristic of RAFT Polymerization.

Table 1: Experimental Conditions and rate constants of polystyryl dithiobenzoate-mediated styrene polymerization at 60°C.

Parameter	Value	Ref.	Unit
[AIBN] ₀	0.3	13	mol/L
[RAFT] ₀	0.1	13	mol/L
[styrene] ₀	8.74	13	mol/L
$f \times k_d$	$8.256 \times 10^{14} \exp(-127600/RT)$	23	1/s
k_i, k_{re-i}	$3.2 \times 10^7 \exp(-24300/RT)$	24	L/(mol s)
k_p	$4.2 \times 10^7 \exp(-32500/RT)$	23	L/(mol s)
k_{tc}	$3.904 \times 10^8 L^{-0.16a}$	25	L/(mol s)
k_{a5}, k_{a6} and k_{a7}	1×10^6	11	L/(mol s)
k_{f5}	0.5	-----	1/s
k_{f6}	1×10^5	11	1/s
k_{f7}	1.67×10^4	26	1/s
k_{ti}	$0.5 \times (k_{tc}(1) + k_{tc}(L))$	25	L/(mol s)
$k_{ter,111}$	$0.6 \times k_{tc}(L)$	27	L/(mol s)
$k_{ter,i11}$	$0.5 \times (k_{tc}(1) + k_{ter,111})$	25	L/(mol s)
$k_{ter,i11}, k_{ter,i1i}$ and $k_{ter,1i1}$	$k_{tc}(L)$	25	L/(mol s)
$k_{ter,i111}$	$k_{ter,111}$	25	L/(mol s)
$k_{ter,1111}$	$0.08 \times k_{ter,111}$	-----	L/(mol s)



Scheme 2: Used algorithm for Monte Carlo simulation method applied for RAFT polymerization.

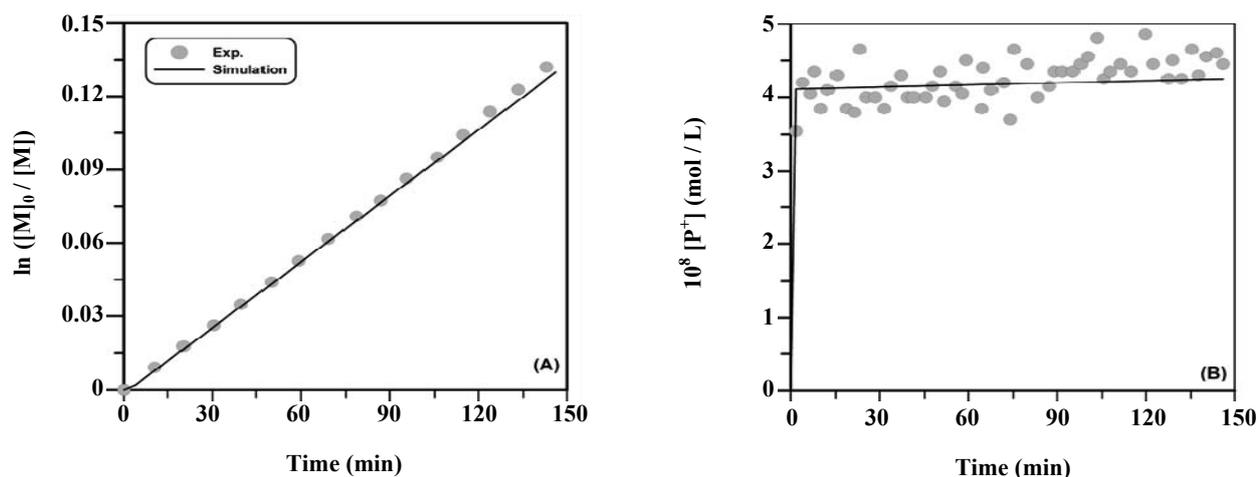


Fig.1: Logarithmic monomer conversion and propagating radical concentration in polystyryl dithiobenzoate-mediated styrene polymerization at 60°C.

Cyanoisopropyl Dithiobenzoate-mediated polymerization of Styrene

As mentioned before, dithiobenzoate-mediated RAFT polymerizations show significant rate retardation and long inhibition period (induction time). Investigations reveal that the origins of these phenomena are different. By using a polymeric RAFT agent, the inhibition does not occur (Figure 1-A), which proves that the reason of rate retardation is different from inhibition. Inhibition period has been observed at the early stage of RAFT polymerization which is controlled by non-polymeric RAFT agents such as cyanoisopropyl dithiobenzoate and cumyl dithiobenzoate. Almost all of the pre-equilibrium reactions occur at this stage of the polymerization reaction. With the application of a relatively large amount of RAFT agent, the induction period extends and its kinetic effects can clearly be observed. To validate our model and algorithm, a comparison of simulation results with experimental data has been done. Table 2 lists the reaction conditions and kinetic parameters. The details of the experiments can be read in *Mcleary's* work [10].

In Figure 2-A, the logarithmic monomer conversion data [10] have been compared with the simulation results. The slope of the curve is proportional to the rate of the monomer consumption. Most of monomer is consumed in propagation reaction. Therefore, the slope is determined by the product of propagation rate constant (k_p) and the total concentration of propagating radicals. The change in the slope is a result of variation in the radical concentration profiles, which are not in stationary state.

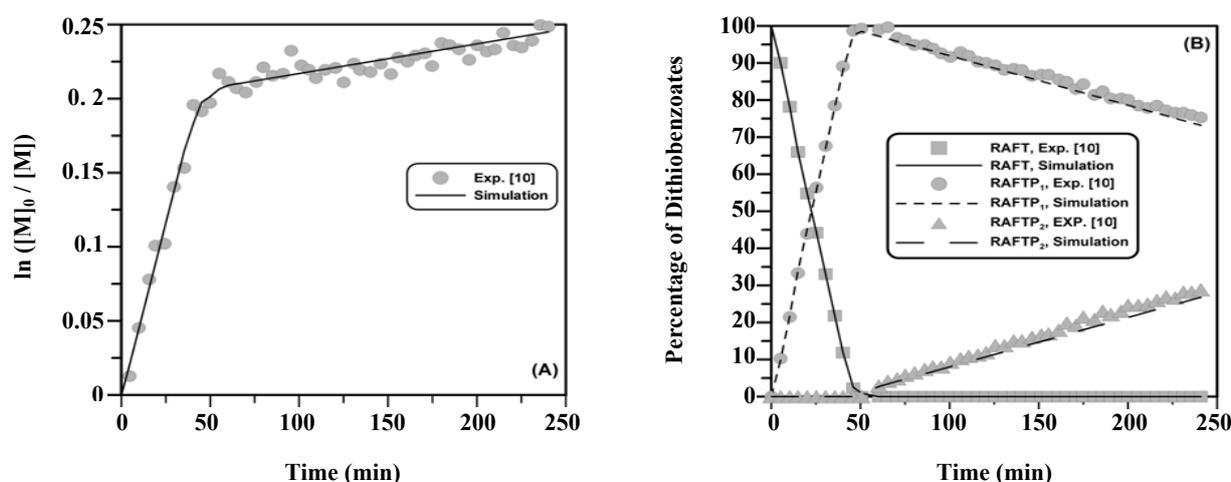
Moreover, when the entire initial RAFT agents are consumed (i.e. about 50 minutes after the reaction initiates (Fig. 2-B)), the slope of the curve diminishes dramatically, which implies that the equilibrium is moving toward the formation of mono-adduct species; in other words, the propagating radicals undergo transfer reactions and change into dormant species. Fig. 2-B shows the experimental and simulation results for the percentage of different dithiobenzoate compounds comprising RAFT agent, RAFTP₁ (Poly-RAFT with one styrene monomer) and RAFTP₂ (Poly-RAFT with two styrene monomer). As it can be seen from results, RAFT agent is consumed totally at about 50 minutes and converted to RAFTP₁. After reaching a maximum value, the percentage of RAFTP₁ decreases and it is converted to RAFTP₂. Also, simulation results are in good agreement with experimental data. This is the advantage of Monte Carlo simulation method to predict the concentration of different compound with different chain length while other modeling methods such as Moment Equations method cannot do that.

Benzyl Dithioisobutyrate-mediated Copolymerization of Styrene and Butyl Acrylate

It is well known that copolymerization systems are more practical for obtaining desired architectures. *Sun et al.* [4] have been done some experiments on St/BA systems both in batch and semi-batch reactors. Our aim is not to synthesize different copolymer architectures, but we intend to investigate the kinetics of RAFT

Table 2: Experimental conditions and rate constants of cyanoisopropyl dithiobenzoate-mediated styrene polymerization at 70°C.

Parameter	Value	Ref.	Unit
[AIBN] ₀	0.1	10	mol/ L
[RAFT] ₀	0.736	10	mol/ L
[styrene] ₀	3.65	10	mol/ L
[C ₆ D ₆] ₀	5.4	10	mol/ L
f×k _d	8.256×10 ¹⁴ exp(-127600/RT)	23	1/s
k _i , k _{re-i}	3.2×10 ⁷ exp(-24300/RT)	23	L/(mol s)
k _p	4.2×10 ⁷ exp(-32500/RT)	23	L/(mol s)
k _{tc}	5×10 ⁸ L ^{-0.16}	25	L/(mol s)
k _{a1-7}	1.2×10 ⁶	12	L/(mol s)
k _{f1} , k _{f5}	L=1: 0.3077 L>1: 0.0012	----	1/s
k _{f2} , k _{f6}	1×10 ⁵	12	1/s
k _{f3} , k _{f4} , k _{f3} ' and k _{f4} '	4	----	1/s
k _{f7}	L=1: 74 L>2: 0.11	----	1/s
k _{ti}	0.5 × (k _{tc} (1)+k _{tc} (L))	25	L/(mol s)

**Fig. 2: Logarithmic monomer conversion and percentage of different dithiobenzoates compounds in cyanoisopropyl dithiobenzoate-mediated styrene polymerization at 70°C.**

polymerization from a different point of view. The details of each experiment given in Table 3 can be found in the original work [4]. Once again, unknown parameters were also calculated by using conversion data and applying the least square method to obtain the best fit.

The conversion data and simulation results are illustrated in Fig. 3-A. As expected, an increment of the initial molar fraction of BA increases monomer

consumption due to a higher propagation rate. As a consequence of the presence of solvent, gel effect does not play a significant role in the polymerization rate, and the slope of all curves (i.e. rate of monomer consumption) does not increase during the course of the polymerization. Also, a good correlation can be observed between experimental and simulation results.

Fig. 3-B shows the cumulative copolymer composition.

Table 3: Experimental conditions and rate constants for benzyl dithioisobutyrate-mediated copolymerization of Styrene and Butyl Acrylate at 70°C.

Parameter	Value					Ref.	Unit
	2b	3d	4c	5c	6c		
[AIBN] ₀	0.007	0.007	0.007	0.007	0.007	4	mol/ L
[RAFT] ₀	0.02082	0.01672	0.01760	0.01860	0.01962	4	mol/ L
[styrene] ₀	4.2607	0	0.9002	1.9006	3.0139	4	mol/ L
[BA] ₀	0	3.4261	2.7011	1.8978	1.0026	4	mol/ L
[Toluene] ₀	4.8234	4.7731	4.7853	4.7955	4.8087	4	mol/ L
$f \times k_d$	$8.256 \times 10^{14} \exp(-127600/RT)$					23	1/s
k_{ij}, k_{re-ij}	$3.2 \times 10^7 \exp(-24300/RT)$					24	L/(mol s)
k_{p11}	$4.2 \times 10^7 \exp(-32500/RT)$					23	L/(mol s)
k_{p22}	$10^{\exp(6.0123-784.4/RT)}$					23	L/(mol s)
k_{tc11}	$5 \times 10^8 L^{-0.16}$					25	L/(mol s)
k_{tc22}	$L \leq 40: 1 \times 10^9 L^{-0.2}$ $L > 40: 2.217 \times 10^{10} L^{-1.04}$					25	L/(mol s)
k_{tc12} or k_{tc21}	$(k_{tc11} \times k_{tc22})^{0.5}$					25	L/(mol s)
k_{a1-7}	4×10^6					-----	L/(mol s)
k_{f1-7}	1×10^4					-----	1/s
$C_{tr,m11}$	1.3×10^{-4}					23	-
$C_{tr,m22}$	1.05×10^{-4}					23	-
k_{tir}	5×10^8					23	1/s
k_{ti}	$0.5 \times (k_{tc1}(1) + k_{tc1}(L))$					23	L/(mol s)
k_{tc1ijk}	$\langle k_t \rangle^a \times 10^{-3} \times \exp(-f_{st}/0.02)$					4	L/(mol s)
r_{st}	0.723					4	-
r_{BA}	0.189					4	-

^a $\langle k_t \rangle = P_1^2 k_{t,11} + 2P_1 P_2 k_{t,12} + P_2^2 k_{t,22}$, where P_i is the relative concentration of the terminal radical i

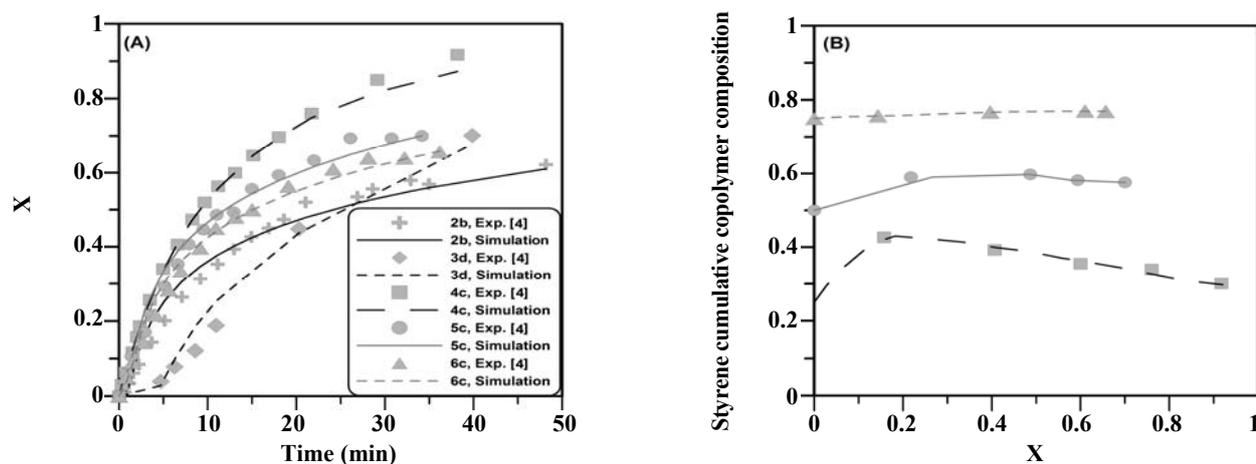


Fig. 3: Comparing conversion data and cumulative styrene copolymer composition with the simulation data in the copolymerization of styrene and butyl acrylate mediated by Benzyl dithioisobutyrate at 70°C.

Based on Feldermann's results, RAFT agent does not cause a significant change in monomer reactivity ratios [28]. By using the Lewis-Mayo copolymerization equation, the azeotrope point ($F_1 = f_1$) of the system can be calculated as follows:

$$f_1 = F_1 = \frac{1-r_2}{2-r_1-r_2} \quad (10)$$

By substituting the values of r_1 (styrene reactivity ratio) and r_2 (butyl acrylate reactivity ratio), the azeotrope point is equal to 0.7454. The cumulative copolymer composition close to this value is quite constant during the polymerization, but varies by changing the initial molar fraction of the monomers. The simulation prediction agreed well with the experimental data for the three different $f_{St,0}$ values. It becomes clear that the simulation is predictive not only for the polymerization rate but also for the copolymer composition.

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