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Universal Kinetic Modeling of RAFT Polymerization using Moment Equations

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Abstract**—**In the following text, we show that by introducing universal kinetic scheme, the origin of rate retardation and inhibition period which observed in dithiobenzoate-mediated RAFT polymerization can be described properly. We develop our model by utilizing the method of moments, then we apply our model to different monomer/RAFT agent systems, both homo- and copolymerization. The modeling results are in an excellent agreement with experiments and imply the validity of universal kinetic scheme, not only for dithiobenzoate-mediated systems, but also for different types of monomer/RAFT agent ones.

Keywords**—**RAFT Polymerization, Mechanism, Kinetics, Moment Equations, Modeling.

I. 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 employing this technique to access a wide range of polymer architectures and topologies, including block [3-5], gradient [6], graft, star [7] and hyper branched [8-12]. Studies over mechanism and kinetics of RAFT have considerably focused on dithiobenzoate-mediated systems [13-27], 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) [15-16, 34-35, 37-44] and irreversible intermediate radical termination (IRT) [5, 14, 17-18, 24-25, 32, 36, 45-54]. In the SF model, intermediate radicals have a very small fragmentation rate constant due to the high stability, so the equilibrium constant is rather large (10^4-10^7) and the system spends a long time-span in the non-stationary state until large amounts of intermediate radicals accumulate. 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 (10^1-10^2) as a result of fast fragmentation. In this model, all of the reversible reactions are in equilibrium, and the system is in a stationary state. Both models can predict conversion, molecular weight and PDI data correctly but in some cases their predictions do not match with experimental results. ESR (Electron Spin Resonance) tests [2-3, 32, 48, 53, and 55] demonstrate that intermediate radical concentration is about 10^{-7}-10^{-5}, which is orders of magnitude smaller than SF model's prediction but consistent with that of IRT Model.

On the other side, IRT model predicts a great amount of 3-arm and in some cases 4-arm star-shaped dead polymers which have not been detected yet. However, SF model can predict molecular weight distribution (MWD) agrees with the experimental results consistently. Investigations propose that the origin of rate retardation and induction (inhibition) period may be different [13, 56-57], 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 [38, 58-60] and the rate constants are more dependent to the length of oligomeric species [27-29, 47]. These matters emphasize on the fact that individual values must be assumed for equilibrium constants. According to the points mentioned, one should consider the complex kinetic scheme, contains many side reactions. The presence of each reaction varies by changing the type of both monomer and RAFT agent. Mcleary et al. [58-59] showed the effect of monomer/RAFT agent on mechanism and kinetics of the RAFT polymerization.

In the literature, Monte Carlo methods [18, 22-23, 61-62], methods of moments [24-25] and ordinary differential equations (ODE) [15-16, 21, 31, and 63] have been used to describe the kinetics of RAFT polymerization. Recently, Konkolewicz et al. [63] 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 this paper, we develop a universal 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. Our aim is to show that these

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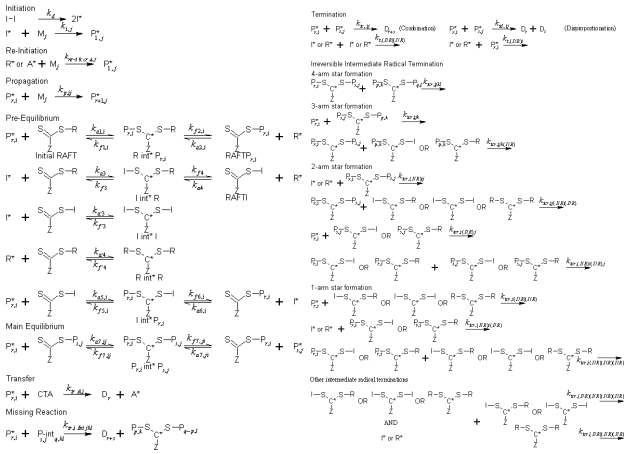
confusing observations (sometimes conflicting) look like puzzle pieces which can be reordered by introducing the universal kinetic scheme. This work does not intend to solve this puzzle, but may be the first attempt to find out the correlation of these pieces.

II. Kinetic Scheme

Scheme 1 shows the universal 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. Termination can occur irreversibly which is closer to experimental observations [45]. 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.

Buback and coworkers have proposed a new reaction called 'missing reaction step' [19-20]. This step can be dominated for highly reactive radical chains such as acrylates. Due to the scarcity in theoretical researches on this topic, we assume that only three-arm star polymers can participate in this reaction.

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. By using this kinetic scheme, the mass balance of different species, can be obtained. For simplicity and reducing the number of unknown parameters, terminal model has been applied in the case of copolymerization. As we see later, this assumption does not have any significant effect on the results.



Scheme 1. Universal RAFT mechanism including probable side reactions

The reactions between macro species are chain length dependent and controlled by diffusion limitations. In this work only a single power law is used for the chain length dependency of termination reactions. Geometric mean and diffusive mean have been used for long-long terminations and short-long terminations respectively [64].

III. Results and Discussion

A. Homopolymerization

1. Investigation of rate retardation in main equilibrium

Based on the ESR findings [32], the polymerization system reaches the stationary-state in a few seconds by using polymeric RAFT agents. Exercising the polymeric Raft agent make the main equilibrium dominant and pre-equilibrium step is limited to only one reaction. Both propagating and intermediate radicals reach their equilibrium value in a while implying small value for main equilibrium reaction. We used the obtained data for a closer investigation of the main equilibrium. Table I lists experimental conditions used by Kwak [32] et al. and rate constants used in this work. For getting a better view to the reader, we compared our results with SF [15] (K_{eq} = 1.6×10^7, no intermediate radicals termination) and IRT [45] (K_{eq} = 55, $k_{tcross} \approx 0.5\times k_t$, only three-arm star-shaped products considered) models. Unknown parameters are obtained by fitting the modeling results and experimental data.

Figures 1 shows the concentration profiles of macro-intermediate radicals (A) and propagating radicals (B). It is crystal clear that the SF model fails to predict the radical species concentrations as a result of assuming high equilibrium constant. Both our model and the IRT model predictions are in a good agreement with the experimental data, which indicates that the system reaches equilibrium in a

while and the fragmentation of polymeric intermediate radical species is fast.

TABLE I
EXPERIMENTAL CONDITIONS AND RATE CONSTANTS OF POLYSTYRYL DITHIOBENZOATE-MEDIATED STYRENE POLYMERIZATION AT 60°C [a]

Parameter	Value	Ref.	Unit
$[AIBN]_0$	0.3	32	mol/lit
[RAFT]0	0.1	32	mol/lit
[styrene]0	8.74	32	mol/lit
fb×kd	8.256×1014exp(-127600/RT)	65	1/sec
ki , kre-i	3.2×107 exp(-243000/RT)	66	lit/(mol sec)
kp	4.2×107 exp(-325000/RT)	65	lit/(mol sec)
ktc	3.904×108L-0.16c	64	lit/(mol sec)
ka5	106	This Work	lit/(mol sec)
ka6	106	This Work	lit/(mol sec)
ka7	106	This Work	lit/(mol sec)
kf5	0.5	This Work	1/sec
kf6	105	This Work	1/sec
kf7	1.67×104	This Work	1/sec
kti	0.5 × (ktc(1)+ktc(L))	This Work	lit/(mol sec)
ktcr,111	0.6 × ktc(L)	This Work	lit/(mol sec)
ktcr,i11	0.5 × (ktc(1)+ktcr,111)	This Work	lit/(mol sec)
ktcr,i1i1	ktc(L)	This Work	lit/(mol sec)
ktcr,i1i	ktc(L)	This Work	lit/(mol sec)
ktcr,1i1	ktc(L)	This Work	lit/(mol sec)
ktcr,i111	ktcr,111	This Work	lit/(mol sec)
ktcr,1111	0.8 × ktcr,111	This Work	lit/(mol sec)

[a] Other coefficients have supposed to be zero
[b] Initiator efficiency (0.64)
[c] Number-average chain length

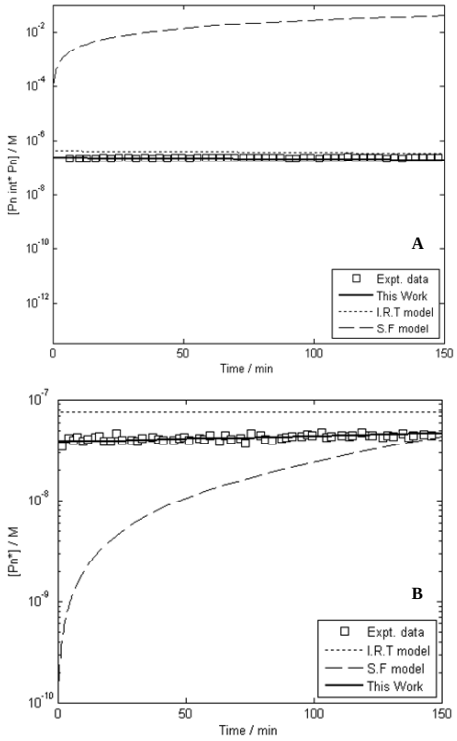


Fig. 1. Macro-intermediate (A) and propagating radical concentration in polystyryl dithiobenzoate-mediated styrene polymerization at 60°C (experimental data were taken from ref. 32)

The monomer conversion profile can be seen in Figure 2. Although, IRT model predicts the concentration profile of radicals properly, because of ignoring some side reactions, its prediction is not in line with the experimental monomer conversion data. The difference between our model and the IRT model is not only a minor difference between the value of equilibrium constants, but also the extended kinetic scheme based on more termination reactions between intermediate radicals. Ignoring some termination reactions leads to faster monomer consumption. This matter is clearly shown in Figure 2 for the IRT model. Again the SF model predicts values which are not in agreement with the experiments. In the SF model, as a fact of assumption of high stability for intermediate radicals, the concentration of propagating radicals is too low, until the equilibrium is reached (Figure 1 (B)). Therefore, the rate of monomer consumption is too small in the non-stationary state.

These evidences suggest a kinetic scheme based on a stationary-state model in main equilibrium, considering more reactions as mentioned before. This statement is verifiable at least for this type of system.

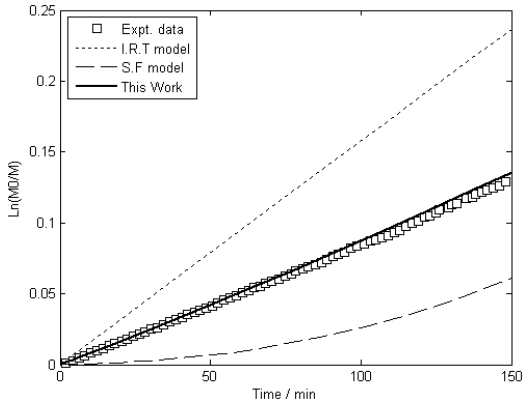


Fig. 2. Monomer consumption vs time in polystyryl dithiobenzoate-mediated styrene polymerization at 60°C (experimental data were taken from ref. 32)

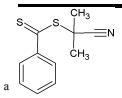
2. Investigation of Inhibition Period in Pre-Equilibrium

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 2), which proves that the reason of rate retardation is different from inhibition. Inhibition period has been observed at the early stages 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 moment of the polymerization reaction. With the application of a relatively large amount of RAFT agent, the induction period extends and its kinetic effects can be observed clearly. At this level, some facts have been ratified: (i) radical storage experiments [37, 42] have revealed the stability of some species in reaction mixture, which retards monomer to polymer conversion; however, it is not clear whether those species are radicals or not; (ii) Besides, in situ NMR investigations [13] imply that there is a high selectivity toward formation of mono-adduct species. The results are quite the same for both styrene and acrylate systems using dithiobenzoate as a RAFT agent; ESR detections also support the above results [13]; (iii) On the other hand, quantum calculations [27-29] have shown that the equilibrium constants are chain length dependent. We developed our model based on these findings. Validation of our model has been done by comparing modeling results and experimental data. Table II lists the reaction conditions and kinetic parameters. The details of the experiments can be read in Mcleary's work [59].

Some of the kinetic rate constants were determined by fitting the model results and experiment findings. A more careful study of the equilibrium constants points out the asymmetric fragmentation of intermediate radicals and slower fragmentation compare to intermediate radicals which are present in main equilibrium (i.e. Pn int* Pn).

TABLE II
EXPERIMENTAL CONDITIONS AND RATE CONSTANTS OF CYANOISOPROPYL DITHIOBENZOATE[A]-MEDIATED STYRENE POLYMERIZATION AT 70°C [b]

Parameter	Value	Ref.	Unit
[AIBN]0	0.1	59	mol/lit
[RAFT]0	0.736	59	mol/lit
[styrene]0	3.65	59	mol/lit
[C6D6]0	5.4	59	mol/lit
fc×kd	8.256×1014exp(-127600/RT)	65	1/sec
ki , kre-i	3.2×107exp(-243000/RT)	66	lit/(mol sec)
kp	4.2×107exp(-325000/RT)	65	lit/(mol sec)
ktc	5×108L-0.16	64	lit/(mol sec)
ka1, ka5	1.2×106	This Work	lit/(mol sec)
ka2, ka6	1.2×106	This Work	lit/(mol sec)
ka3, ka4	1.2×106	This Work	lit/(mol sec)
ka'3, ka'4	1.2×106	This Work	lit/(mol sec)
ka7	1.2×106	This Work	lit/(mol sec)
kf1, kf5	L=1: 0.3077 L>1: 0.0012	This Work	1/sec
kf2, kf6	1×103	This Work	1/sec
kf3, kf4	4	This Work	1/sec
kf'3, kf'4	4	This Work	1/sec
kf7	L=1: 74 L>2: 0.11	This Work	1/sec
kti	0.5 × (ktc(1)+ktc(L))	This Work	lit/(mol sec)



[a]

[b] Other coefficients have supposed to be zero
[c] Initiator efficiency (0.64)

Figure 3 shows the concentrations of RAFT and polyRAFT versus polymerization time. The average chain length of polyRAFT at this level of the reaction is less than two (calculated by moment equations), which indicates that mono-adduct species are in the majority. Having consumed RAFT agent, the other dormant species (i.e. PolyRAFT) are produced. The modeling results are in acceptable accordance with experiments. Both the SF and IRT models fail to predict concentration profiles. The SF model assumes a very high stability for intermediate radicals, while the IRT model supposes a fast fragmentation. Both of the models use the same value for pre-equilibrium and main equilibrium constants and disregard the differences of chemical species, length of each reactant and asymmetric equilibrium, which leads to poor agreement with the experimental data. The total concentrations of polymeric RAFT agents are equal to primary RAFT agent, implying that the cross terminations have not occurred.

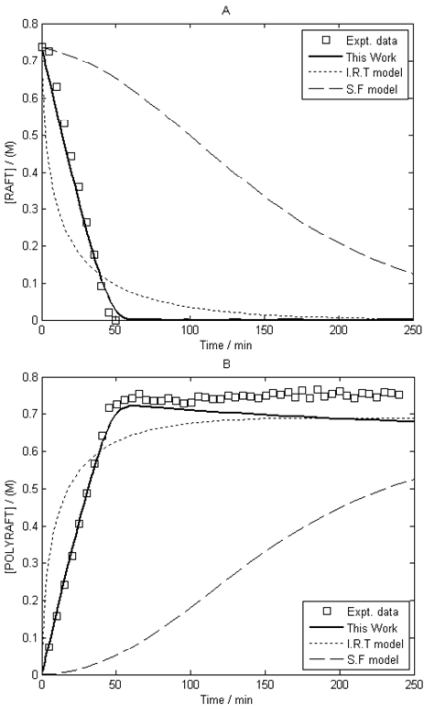


Fig. 3. Comparing experimentally determined (A) RAFT and (B) PolyRAFT concentration and theoretical results in cyanoisopropyl dithiobenzoate-mediated styrene polymerization at 70°C (experimental data were taken from ref. 59)

In Figure 4, the monomer conversion data have been compared with the modeling results. The slope of the curve is proportional to the rate of the monomer consumption. Based on the mass balance equation for monomer (See Appendix), most of the monomers are 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 an outcome of change in the radical concentration profiles, which are not in stationary state. Moreover, when all the initial RAFT agents are consumed, 50 minutes after the beginning of the reaction (Figure 3), the slope of the curve diminish dramatically, implying that the equilibrium is toward the formation of mono-adduct species; in the other words, the propagating radicals undergo transfer reactions and change into dormant species.

Although the model can describe details of RAFT polymerization process both in pre- and main equilibrium stages properly, but it is difficult to describe how these apparently contradictory rate constants in pre- and main equilibrium can be related.

B. Copolymerization: Applying universal kinetic scheme to other RAFT agent-mediated polymerization system

It is well known that copolymerization systems are more practical for obtaining desired architectures. Sun and coworkers [6] have been done some experiments on the St/BA system both in batch and semi-batch reactors. By the support of mathematical modeling, they synthesized uniform and linear gradient copolymers.

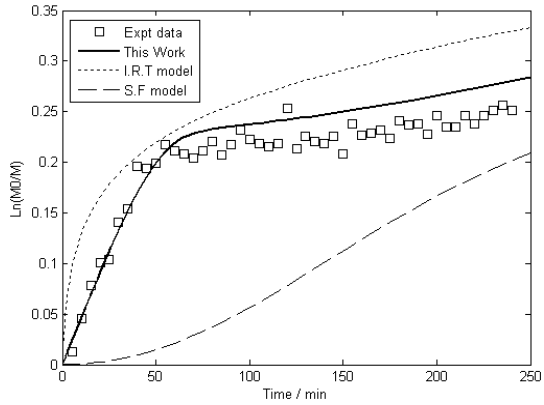
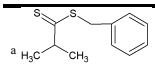


Fig. 4. Comparing between model predictions and experimental conversion data in cyanoisopropyl dithiobenzoate-mediated styrene polymerization at 70°C (experimental data were taken from ref. 59)

TABLE III
EXPERIMENTAL CONDITIONS AND RATE CONSTANTS OF COPOLYMERIZATION OF STYRENE AND BUTYL ACRYLATE MEDIATED BY BENZYL DITHIOISOBUTYRAT[A] AT 70°C[b]

Parameter	Value					Ref.
	2b	3d	4c	5c	6c	
$[AIBN]_0$	0.007	0.007	0.007	0.007	0.007	6
$[RAFT]_0$	0.02082	0.01672	0.01760	0.01860	0.01962	6
$[styrene]_0$	4.2607	0	0.9002	1.9006	3.0139	6
$[BA]_0$	0	3.4261	2.7011	1.8978	1.0026	6
$[Toluene]_0$	4.8234	4.7731	4.7853	4.7955	4.8087	6
fc×kd	8.256×1014exp(-127600/RT)					65
kij , kre-ij	3.2×107exp(-243000/RT)					66
kp11	4.2×107exp(-325000/RT)					65
kp22	10exp(6.0123-784.4/RT)					65
ktc11	5×108L-0.16d					64
ktc22	L≤40: 1×109L-0.2 L>40: 2.217×1010L-1.04					64
ktc12 or ktc21	(ktc11×ktc22)0.5					
ka1-7	4×106					
kf1-7	1×104					
Ctr,m11	1.3×10-4					
Ctr,m22	1.05×10-4					
ktir	5×108					
kti	0.5 × (ktci(1)+ktci(L))					
ktcrijk	<kt>e×10-3×exp(-fstf/0.02)					6
rst	0.723					6
rBA	0.189					6



[a] H_3C CH_3

[b] Other coefficients have supposed to be zero

[c] Initiator efficiency (0.64)

[d] Number-average chain length

[e] $\langle k_t \rangle = P_1^2 k_{t,11} + 2P_1P_2k_{t,12} + P_2^2 k_{t,22}$, where P_i is the relative concentration of the terminal radical i

[f] Styrene molar fraction

Our aim is not to synthesize different copolymer architectures, but we intend to investigate the kinetics of RAFT polymerization from a different point of view. The details of each experiment given in Table III can be found in the original article [6]. Unknown parameters were also

calculated by fitting the modeling results and experimental data.

The conversion data and model results are illustrated in Figure 5. As expected, increment of the initial molar fraction of BA increases monomer consumption due to a higher propagation rate. As a sequence 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.

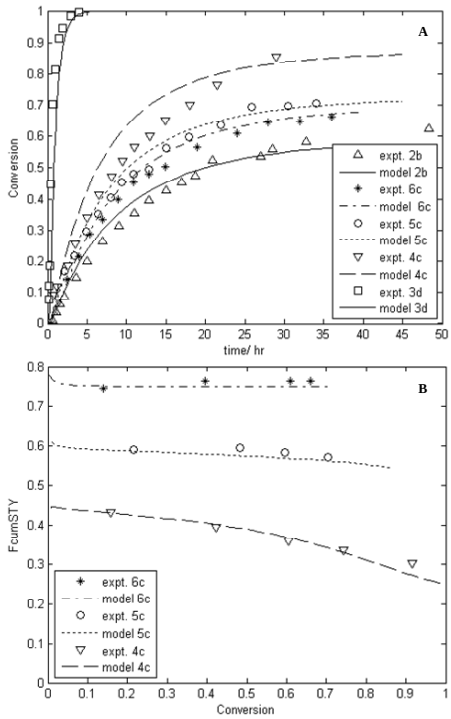


Fig. 5. Comparing conversion data (A) and cumulative styrene copolymer composition (B) with modeling data in copolymerization of Styrene and Butyl Acrylate Mediated by Benzyl Dithioisobutyrat at 70°C (experimental data were taken form ref. 6)

Figure 5B shows the cumulative copolymer composition. Based on Feldermann's results, RAFT agent does not cause a significant change in monomers reactivity ratios [67]. By using the Lewis-Mayo copolymerization equation, the azeotrope point ($F_1 = f_1$) of the system can be calculated as follows:

$$f_1 = F_1 = \frac{1 - r_2}{2 - r_1 - r_2} \tag{1}$$

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 near this value is quite constant during the polymerization, but varies by changing the initial molar fraction of the monomers.

Figure 6 shows that the initial molar fraction of monomers can affect the fraction of living chains. By increasing the initial molar fraction of styrene, the termination rate increases ($k_{t,st}/k_{t,BA} \approx 2$). Therefore, for a specific radical chain, the probability of termination reactions raises which results the reduction in the amount of living species.

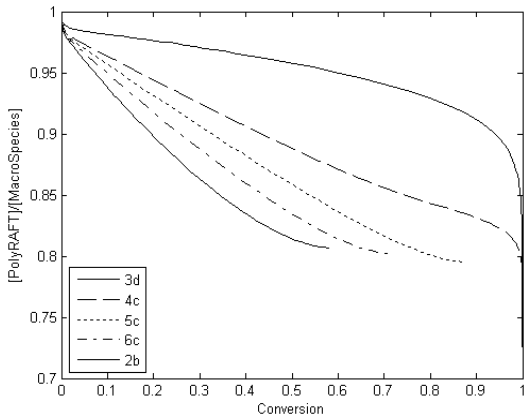


Fig. 6. The molar fraction of living polymer chains among macro species during copolymerization of Styrene and Butyl Acrylate Mediated by Benzyl Dithioisobutyrat at 70°C

C. Conclusion

Different RAFT polymerization systems were examined by using a universal kinetic scheme. The results revealed some important points: (i) the weakness and strength of each reaction differs by changing monomer type and RAFT agent; (ii) the origin of induction time and rate retardation is different; (iii) equilibrium constants for macro species are chain length dependent specially at the early stages of the reaction; (iv) there is a high selectivity toward mono-adduct species formation; (v) like free radical polymerizations, copolymer composition in controlled free radical polymerization batch systems is determined by reactivity ratios of the monomers. Nevertheless, correlating all these findings to solve RAFT mechanism puzzle is still a big deal.

The results show the validity of universal kinetic scheme for RAFT agents other than dithiobenozate.

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