Iranian Polymer Journal
20 (6), 2011, 459-478

Available online at: http://journal.ippi.ac.ir

Dithioester-mediated RAFT Polymerization: A Kinetic Study by Mathematical Modelling

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Received 30 August 2010; accepted 28 February 2011

ABSTRACT

Although reversible addition-fragmentation chain transfer (RAFT) polymerization has attracted great attention of many researchers over recent years, outstanding questions on the mechanism and kinetics of dithioester-mediated RAFT polymerization (especially dithiobenzoates) still have remained unsolved. In this work, based on experimental observations and exact theoretical predictions, the kinetic schemes of RAFT polymerization are 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 schemes are theoretically the most probable existing reactions and are used for mathematical modelling. The detailed kinetic scheme is applied to three kinds of RAFT polymerization systems by utilizing the method of moments. Unknown kinetic rate constants are obtained by curve fitting of the modelling results and theoretical data, and applying the least square method; or estimation by considering the theoretical facts and experimental findings. The origin of the rate retardation and induction periods has been understood by studying the main and pre-equilibrium stages of dithiobenzoate-mediated RAFT homopolymerization. A copolymerization system in the presence of RAFT agent has also been examined to confirm the capability of introduced kinetic scheme in different monomer/RAFT agent systems. Although unknown parameters were obtained theoretically, their consistency with other researchers' works shows the accuracy of the modelling procedure. The modelling results are in excellent agreement with experimental data which proves the validity and applicability of the detailed kinetic scheme. The results have shown that some reactions may not occur in many RAFT polymerization systems and can be eliminated and therefore more kinetic and mechanistic studies are required.

Key Words:

RAFT polymerization;
moment equations;
copolymerization;
mechanism;
kinetics.

INTRODUCTION

Among "controlled/living" radical polymerization (CLRP) techniques, reversible addition-fragmentation chain transfer (RAFT) [1,2] is arguably the most versatile method with respect to the types of monomers and reaction conditions. The necessity for good control over molecular weight distribution (MWD) and chain length has led to adoption of this technique to access a wide range of polymer architectures and topologies including block [3,5], gradient [6], graft, star [7.8], and hyperbranched structures [9-12].

The studies over the mechanism and kinetics of RAFT have been mainly limited to dithiobenzoate-mediated systems [13-16] which

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show a significant rate retardation and long inhibition period. In this regard, there are two predominant schools of thought on the origin of this phenomenon: slow fragmentation (SF) [15, 17-19] and irreversible intermediate radical termination (IRT) [16, 20-22].

In "slow fragmentation" model, intermediate radicals due to their high stability have a very small fragmentation rate constant. Thus, the equilibrium constant is rather large (10^4-10^7) and the system spends a long time in non-stationary state until large amounts of intermediate radicals accumulate while, there are no side reactions between the intermediate and propagating radicals.

In contrast, the "intermediate radical termination" model predicts that the rate retardation is caused as a consequence of irreversible termination of intermediate radicals. This model results in a small equilibrium constant (10-100) as a result of fast fragmentation. In this model, all reversible reactions are at equilibrium while the system is in the stationary state.

Both models can predict conversion, molecular weight, and PDI data correctly, but in some cases their predictions do not match the experimental results. Electron spin resonance (ESR) tests [2,21,23,24] demonstrate that intermediate radical concentration is about 10^{-7}-10^{-5}, which is consistent with the data obtained by the latter model, though by some orders of magnitude it is smaller than predicted results of the former model.

In opposite, the "intermediate radical termination" model, predicts a great amount of three-arm and in some cases four-arm star-shaped dead polymers which have not been detected yet. However, "slow fragmentation" model can predict molecular weight distribution (MWD) which is consistent with the experimental results.

Some investigations propose that the origin of rate retardation and induction (inhibition) periods may be different [13,25], and it is crucial to consider different equilibrium constants for the pre- and main-equilibrium steps. In addition, at the early stages of polymerization (i.e., when pre-equilibrium reactions are dominant) various radical species go through reversible transfer with different rate constants due to different chemical reactivities towards RAFT agents [26-29]. Also, the rate constants are more dependent on the length of oligomeric species [30-32]. These findings emphasize that individual value must be assumed for each equilibrium constant.

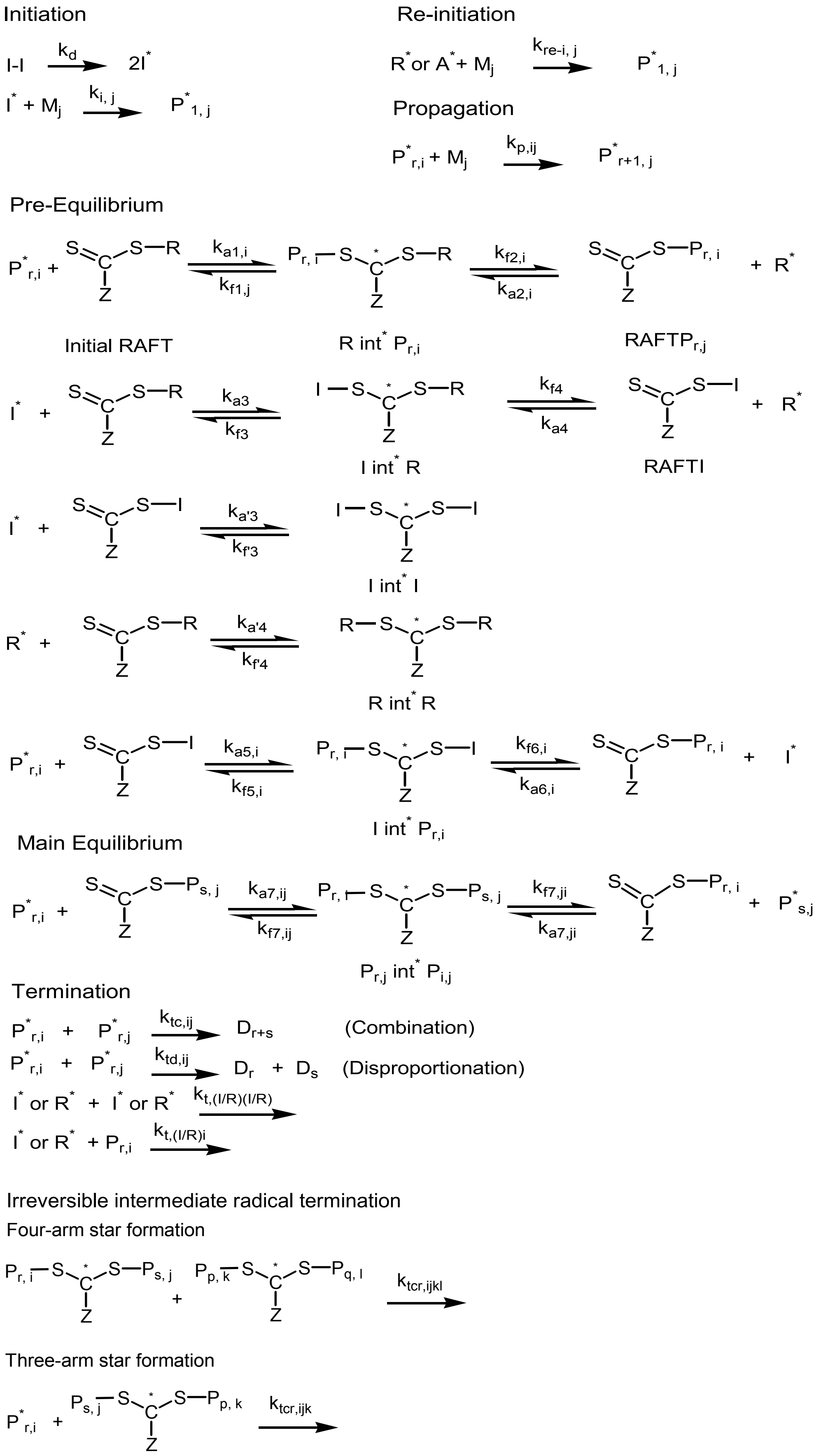
According to the points mentioned above, one should consider the complex kinetic scheme containing many side reactions. It should also be noted that the presence of each reaction varies by changing the type of both monomer and RAFT agent. McLeary et al. [27, 28] showed the effect of monomer/RAFT agent on the mechanism and kinetics of RAFT polymerization.

In the literature, Monte Carlo methods [33-36], methods of moments [37-39] and ordinary differential equations (ODE) [15,40,41] have been used to describe the kinetics of RAFT polymerization. Recently, Konkolewicz et al. [41] 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.

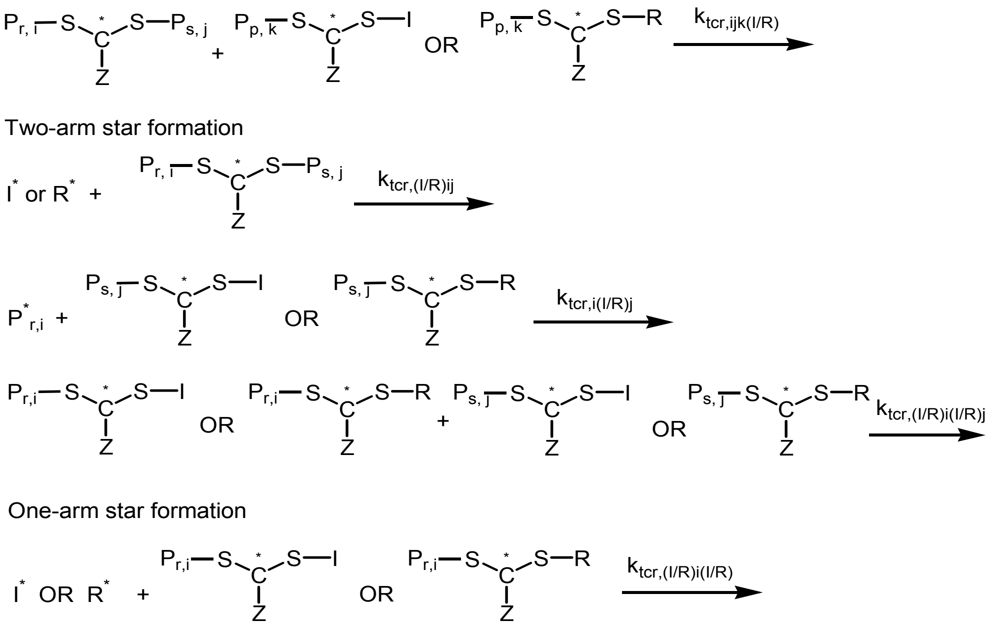
In this work, we developed a universal kinetic model including reactions probably occurring anchored in experimental data. Then, we applied our model to different monomer/RAFT agent systems in both homo- and copolymerization reactions. Our aim is to show that these confusing (sometimes contradicting) observations look like puzzle pieces which can be re-arranged 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 between its pieces.

KINETIC SCHEME

Scheme I shows the kinetic routes in which initiation can occur by thermal dissociation of initiator molecules. The initiator radical fragments can react with monomer molecules to form primary radicals or go through reversible transfer reactions with different types of RAFT agents. There are three types of RAFT agents in the system based on their leaving groups: initial RAFT (having R as a leaving group), RAFTI (having initiator moiety, I, as a leaving group) and $RAFTP_n$ (RAFT agent with a polymeric leaving group). Primary radicals propagate by reacting with


Initiation
Re-initiation
Propagation
Pre-Equilibrium
Initial RAFT
R int* P_{r,i}
RAFTP_{r,j}
I int* R
RAFTI
I int* I
R int* R
I int* P_{r,i}
Main Equilibrium
P_{r,j} int* P_{i,j}
Termination
(Combination)
(Disproportionation)
Irreversible intermediate radical termination
Four-arm star formation
Three-arm star formation

Continued



Scheme I. RAFT Mechanism including probable reactions.

monomer molecules. Another possible reaction of propagating radicals is transfer reaction 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 centres can transfer to some species (CTA) (not shown in Scheme I) in the reaction mixture to form a dead polymer or a small radical (denoted as A^* in Scheme I). The latter may undergo a reinitiation reaction with a monomer molecule.

Terminations between radicals can deactivate the radical centres and stop radical formation. In addition to common terminations which are present in free radical polymerization systems, we assume the possibility of reactions between intermediate radicals and 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 more similar to experimental observations [22]. This type of reaction leads to formation of star-like dead polymers. With respect to the number of polymeric arms, we have divided star-like products into four-, three-, two- and one-arm star polymer types. It is worth noting that star-like polymers with 2 polymeric arms or fewer are not different from linear polymers.

Buback and coworkers [42,43] have proposed a new reaction called 'missing reaction step'. This step can be dominated for highly reactive radical chains such as acrylates. Due to missing theoretical studies on this topic, this reaction has not been considered in the kinetic scheme. We extended our scheme to a copolymerization system based on the terminal model. For macro-species, the first term of index relates to the chain length (number of monomer units) and the second term shows the monomer type of terminal unit. For small species, the index only relates to the type of monomer.

Model Development

As it may be seen in Scheme I, method of moments [44] used to model the RAFT polymerization is as follows:

Propagating radical:

$$\lambda_m^{(i)} = \sum_{r=1}^{\infty} r^m \left[P_{r,i}^* \right] \tag{1}$$

Dormant chain:

$$\upsilon_m^{(i)} = \sum_{r=1}^{\infty} r^m \left[RAFT\, P_{r,i} \right] \tag{2}$$

Intermediate radical:

$$\mu_{R,m}^{(i)} = \sum_{r=1}^{\infty} r^m \left[R\ Int^* P_{r,i} \right] \tag{3}$$

$$\mu_{I,m}^{(i)} = \sum_{r=1}^{\infty} r^m \left[I\ Int^* P_{r,i} \right] \tag{4}$$

$$\omega_{m,n}^{(i,j)} = \sum_{k=1}^{\infty} \sum_{r=1}^{\infty} r^m k^n \left[P_{r,i} Int^* P_{k,j} \right] \tag{5}$$

$$i = j \qquad \omega_{m,n}^{(i,j)} = \omega_{n,m}^{(i,j)}$$

Linear dead polymer:

$$\xi_m = \sum_{r=1}^{\infty} r^m \left[D_r \right] \tag{6}$$

One-arm star shaped polymer:

$$\xi_m''' = \sum_{r=1}^{\infty} r^m \left[RAFTD_r \right] \tag{7}$$

Two-arm star shaped polymer:

$$\xi_m'' = \sum_{r=1}^{\infty} r^m [RAFTD_{n,k}] \quad (n+k=r) \tag{8}$$

Three-arm star shaped polymer:

$$\xi_m' = \sum_{r=1}^{\infty} r^m [RAFTD_{n,k,l}] \quad (n+k+l=r) \tag{9}$$

Four-arm star shaped polymer:

$$\delta_m = \sum_{r=1}^{\infty} r^m [RAFTD_{n,k,l,h}] \quad (n+k+l+h=r) \tag{10}$$

By using this kinetic scheme, the mass balances of different species are summarized in Appendix which shows the details of the moment equations for the RAFT homo- and copolymerization systems. For simplicity and reduction of some unknown parameters, a terminal model has been applied in the case of copolymerization. As it may be observed later, this assumption does not have any significant effect on the results. The reactions between macro-species are chain-length dependent and controlled by diffusion limitations. To this end, a single power law is used for the chain length dependency of termination reactions. Geometric and diffusive means have been used for long-long terminations and short-long terminations, respectively [45].

Following the derivation of mass balance equations, the set of ODE's can be solved by a commercial ODE solver (ode23tb, ode23s, or ode15s in MATLAB R2006B). The concentration profiles and desired data can be obtained as shown in Schemes II and III:

Number-average degree of polymerization

$$\overline{X}_n = \frac{\sum_i \lambda_1^{(i)} + \sum_i \upsilon_1^{(i)} + \sum_i \mu_{R,1}^{(i)} + \sum_i \mu_{I,1}^{(i)} + \sum_j \sum_i \omega_{1,0}^{(i,j)} + \delta_1 + \xi_1 + \xi_1' + \xi_1'' + \xi_1'''}{\sum_i \lambda_0^{(i)} + \sum_i \upsilon_0^{(i)} + \sum_i \mu_{R,0}^{(i)} + \sum_i \mu_{I,0}^{(i)} + \frac{1}{2} \sum_j \sum_i \omega_{0,0}^{(i,j)} + \delta_0 + \xi_0 + \xi_0' + \xi_0'' + \xi_0'''} \tag{11}$$

Weight-average degree of polymerization:

$$\overline{X}_w = \frac{\sum_i \lambda_2^{(i)} + \sum_i \upsilon_2^{(i)} + \sum_i \mu_{R,2}^{(i)} + \sum_i \mu_{I,2}^{(i)} + \sum_j \sum_i \omega_{2,0}^{(i,j)} + \sum_j \sum_i \omega_{1,1}^{(i,j)} + \delta_2 + \xi_2 + \xi_2' + \xi_2'' + \xi_2'''}{\sum_i \lambda_1^{(i)} + \sum_i \upsilon_1^{(i)} + \sum_i \mu_{R,1}^{(i)} + \sum_i \mu_{I,1}^{(i)} + \sum_j \sum_i \omega_{1,0}^{(i,j)} + \delta_1 + \xi_1 + \xi_1' + \xi_1'' + \xi_1'''} \tag{12}$$

Polydispersity index:

$$PDI = \frac{\overline{X}_w}{\overline{X}_n} \tag{13}$$

Scheme II

Cumulative copolymer composition:

$$F_{cum_i} = \frac{[M_i]_0 - [M_i]_t}{\sum_j [M_i]_0 - [M_i]_t} \tag{14}$$

Number-average molecular weight:

$$\overline{M_n} = \sum_i \overline{X}_n . F_{cum_i} . M_{w_i} \tag{15}$$

Weight-average molecular weight:

$$\overline{M_w} = \sum_i \overline{X}_w . F_{cum_i} . M_{w_i} \tag{16}$$

Fraction of dormant (living) chains:

$$x_{living} = \frac{\sum_i \upsilon_0^{(i)}}{\sum_i \lambda_0^{(i)} + \sum_i \upsilon_0^{(i)} + \sum_i \mu_{R,0}^{(i)} + \sum_i \mu_{I,0}^{(i)} + \frac{1}{2}\sum_j \sum_i \omega_{0,0}^{(i,j)} + \delta_0 + \xi_0 + \xi_0' + \xi_0'' + \xi_0'''} \tag{17}$$

Scheme III

RESULTS AND DISCUSSION

Homopolymerization

Homopolymerization of Styrene-mediated Polystyryl Dithiobenzoate

Based on the ESR findings [21], the polymerization system reaches the stationary-state in a few seconds by using polymeric RAFT agents. Applying the polymeric RAFT agent eliminates most pre-equilibrium steps reactions. Both propagating and intermediate radicals reach their equilibrium values at the same time, as a result of small value of equilibrium constant for main equilibrium reactions. We used the obtained data for a closer investigation of the main equilibrium. The experimental conditions used by Kwak et al. [21] and the rate constants used in this work are listed in Table 1.

For better understanding, we also compared our results with SF model [15] (K_{eq} = 1.6×10^7, no intermediate radical termination) and IRT model [21,22] (K_{eq} = 55, $k_{t(cross)} \approx 0.5\ k_t$, only considered three-arm star-shaped products).

Many of unknown parameters have been determined by applying other researchers' investigations. It is obvious that the rate constant of addition of propagating radical to RAFT (and *PolyRAFT*) agents is independent of the type of leaving group (and stabilizing group in some cases) [31]. Therefore, the rate constants k_{a5}, k_{a6}, and k_{a7} are supposed to be equal. Moreover, the error caused by a slight difference between these values is negligible. However, the above statement is not true for the rate constant of fragmentation reactions, k_{f7}, which can be calculated by using simple equilibrium equation for reversible transfer reaction as follows [13]:

$$K_{eq7} = \frac{k_{a7}}{k_{f7}} = \frac{\left[P_n \ \text{int}^* \ P_m\right]}{\left[P_r^*\right]\left[PolyRAFT\right]} \tag{18}$$

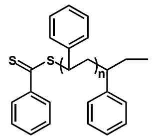
The experimental values for the concentrations of both propagating and intermediate radicals can easily be obtained from Figure 1. The concentration of polymeric RAFT agent has been approximated by the initial concentration of RAFT agent.

It is worth noting that though all these approximations led to some errors in modelling results, the sensitivity analysis (not presented herein) has revealed that these small errors do not affect the

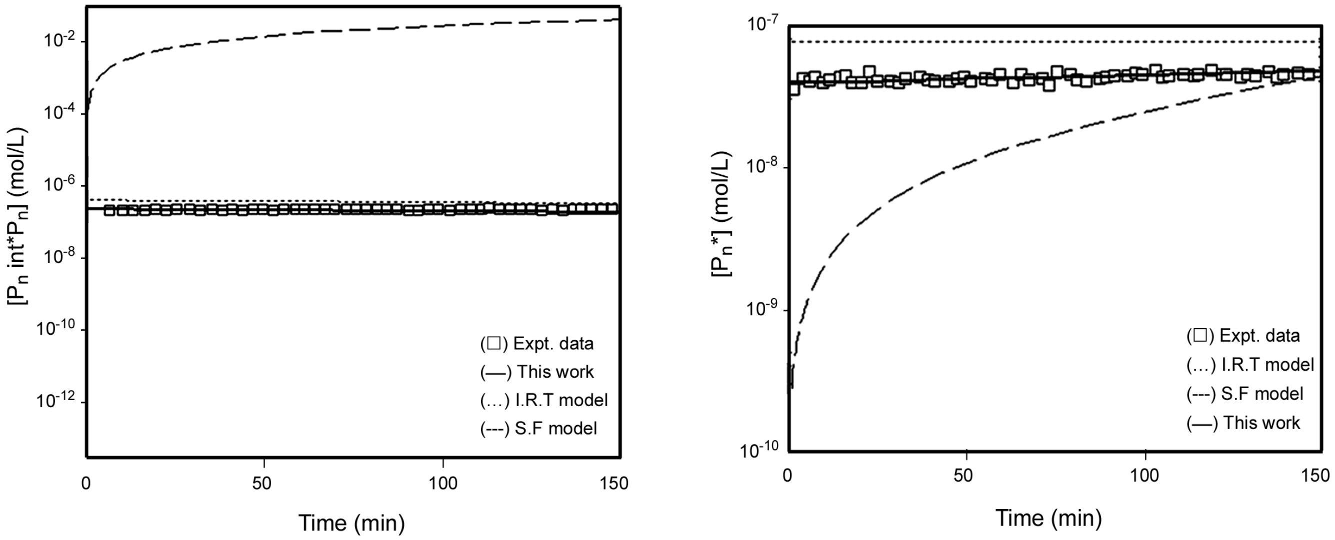
Table 1. Experimental conditions and rate constants of polystyryl dithiobenzoate^{a}-mediated styrene polymerization at 60°C ^{b}.

Parameter	Value	Reference	Unit
$[AIBN]_0$	0.3	21	mol/L
$[RAFT]_0$	0.1	21	mol/L
$[Styrene]_0$	8.74	21	mol/L
$f^{c} \times k_d$	$8.256\times10^{14}\times\exp(-127600/R^{d}\,T)$	46	1/s
k_i, and $k_{re\text{-}i}$	$3.2\times10^{7}\times\exp(-24300/RT)$	47	L/(mol.s)
k_p	$4.2\times10^{7}\times\exp(-32500/RT)$	46	L/(mol.s)
k_{tc}	$3.904\times10^{8}\times L^{-0.16\ e}$	45	L/(mol.s)
k_{a5}, k_{a6} and k_{a7}	1×10^{6}	31	L/(mol.s)
k_{f5}	0.5	-	1/s
k_{f6}	1×10^{5}	31	1/s
k_{f7}	1.67×10^{4}	13	1/s
k_{ti}	$0.5\,(k_{tc}(1)+k_{tc}(L))$	45	L/(mol.s)
$k_{tcr,111}$	$0.6\,k_{tc}(L)$	22	L/(mol.s)
$k_{tcr,i11}$	$0.5\,(k_{tc}(1)+k_{tcr,111})$	45	L/(mol.s)
$k_{tcr,i1i1}$, $k_{tcr,i1i}$ and $k_{tcr,1i1}$	$k_{tc}\,(L)$	45	L/(mol.s)
$k_{tcr,i111}$	$k_{tcr,111}$	45	L/(mol.s)
$k_{tcr,1111}$	$0.08\,k_{tcr,111}$	-	L/(mol.s)

(a)



(b) Other coefficients have supposed to be zero; (c) initiator efficiency (0.64); (d) 8.314 (J/mol.k); (e) number-average chain length.



(a) (b)

Figure 1. (a) Macro-intermediate and (b) propagating radical concentration in polystyryl dithiobenzoate-mediated styrene polymerization at 60°C (experimental data taken from Ref. 21).

results, considerably. The value of k_{f6} has been estimated by the fact that the rate of fragmentation of cyanoisopropyl leaving group is about an order of magnitude faster than that of polystyryl leaving group [30,31]. For termination of intermediate radicals, analogy has been used to estimate the value of rate constants.

For short-long termination reactions, diffusion mean has been used which has proved to give a better estimation. The value of $k_{tcr,111}$ has the same magnitude of k_{tc} by a factor of 0.4 to 0.8. The value of $k_{tcr,111}$ is also reproduced by the same procedure addressed elsewhere [22].

Two remaining parameters have been obtained by using monomer conversion data and applying the least square method. These two parameters do not appear in monomer rate equation but affect the concentration of propagating radicals, indirectly. Other parameters (not given in Table 1) are supposed to be zero. In fact, these parameters are not considered in this system and omitting the related reactions is acceptable.

Figures 1a and 1b show the concentration profiles of macro-intermediate radicals and propagating radicals. It is obvious that the SF model fails to predict the radical species concentrations as a result of assuming a high equilibrium constant. Both our model and the IRT model predictions are in good agreements with the experimental data which indicates that the system reaches equilibrium in a short time and the fragmentation of polymeric intermediate radical species is fast.

The monomer conversion profiles can be seen in Figure 2. Although IRT model predicts the concentration profile of radicals, owing to ignoring some side reactions, its prediction is not in accordance with experimental monomer conversion data. Also, the value of equilibrium constants in our model is different from what has been used in the IRT model. Additionally, we have used an extended kinetic scheme based on more termination reactions between intermediate radicals. Ignoring some termination reactions leads to faster monomer consumption. This is clearly shown in Figure 2 for the IRT model.

The SF model also predicts values which are not in agreement with the experimental data. In the SF model, due to assuming high stability for intermediate radicals, the concentration of propagating radicals is very low until the equilibrium is reached (Figure 1b). Therefore, the rate of monomer consumption is very small in the non-stationary state.

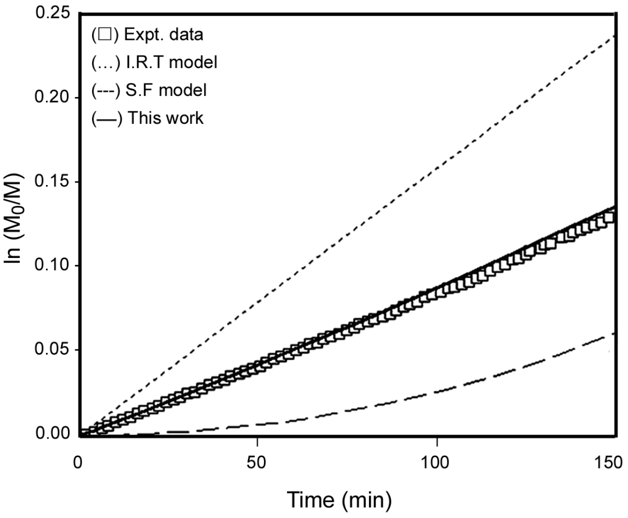


Figure 2. Monomer consumption as a function of time in polystyryl dithiobenzoate-mediated styrene polymerization at 60°C (experimental data taken from Ref. 21).

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

Homopolymerization of Styrene in the Presence of a Relatively High Amount of Cynoisopropyl Dithiobenzoate

As it is stated already, 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 causes of rate retardation are different from inhibition process. Inhibition step has been observed at the early stage of RAFT polymerization and it 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 high amount of RAFT agent, the induction period extends further and its kinetic effects can be observed clearly. In this respect, some facts have been ratified: (i) radical storage experiments [19] have revealed the stability of some species in reaction mixture which retards monomer conversion to polymer although, it is not clear whether those species are radicals or not; besides, (ii) in situ ^{1}H NMR investigations [27] imply that there is a high tendency towards 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 [30-32] have shown that the equilibrium constants are chain length dependent. We developed our model based on these findings. Validation of our model has been tested by comparing the modelling results with experimental data. The reaction conditions and kinetic parameters are presented in Table 2. The details of the experiments can be read in McLeary's work [28].

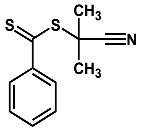
Rate constants have been obtained similar to previous section. As discussed earlier, rate constants for addition reactions are supposed to be equal. The temperature dependency of addition rate constants has not been investigated yet, but considering the changes of C_{tr} [21] with temperature could be useful to estimate fairly accurate values. The radical storage experiments [19] have shown the stability of intermediate radicals in pre-equilibrium stage. At this stage of reaction, no reaction was reported between the intermediate radicals in literature. Based on the above statement, all intermediate termination reactions are supposed to be zero which is in agreement with experiments.

As the initiator radical fragment and RAFT leaving group are the same, the fragmentation rate constants, i.e., k_{f1}, k_{f2}, and k_{f3} are equal to k_{f5}, k_{f6}, and k_{f4} respectively. For simplicity and lowering the number of unknown parameters, the same value obtained in the previous subsection has been used for k_{f6} (and also k_{f2}). The other fragmentation rate constants (k_{f1}, k_{f3}, k_{f7}) have been obtained by applying the least

Table 2. Experimental conditions and rate constants of cyanoisopropyl dithiobenzoate[a]-mediated styrene polymerization at 70°C[b].

Parameter	Value	Reference	Unit
$[AIBN]_0$	0.1	28	mol/L
$[RAFT]_0$	0.736	28	mol/L
$[Styrene]_0$	3.65	28	mol/L
$[C_6D_6]_0$	5.4	28	mol/L
$f^c \times k_d$	$8.256\times10^{14}\times\exp(-127600/RT)$	46	1/s
k_i, and $k_{re\text{-}i}$	$3.2\times10^{7}\times\exp(-24300/RT)$	47	L/(mol.s)
k_p	$4.2\times10^{7}\times\exp(-32500/RT)$	46	L/(mol.s)
k_{tc}	$5\times10^{8}\times L^{-0.16\ d}$	45	L/(mol.s)
$k_{a1\text{-}7}$	1.2×10^{6}	31	L/(mol.s)
k_{f1}, k_{f5}	L=1: 0.3077 L>1: 0.0012	-	1/s
k_{f2}, k_{f6}	1×10^{5}	31	1/s
k_{f3}, k_{f4}, $k_{f'3}$, and $k_{f'4}$	4	-	1/s
k_{f7}	L=1: 74 L>2: 0.11	-	1/s
k_{ti}	$0.5\ (k_{tc}(1)+k_{tc}(L))$	45	L/(mol.s)

(a)



(b) Other coefficients have supposed to be zero; (c) initiator efficiency (0.64); (d) number-average chain length.

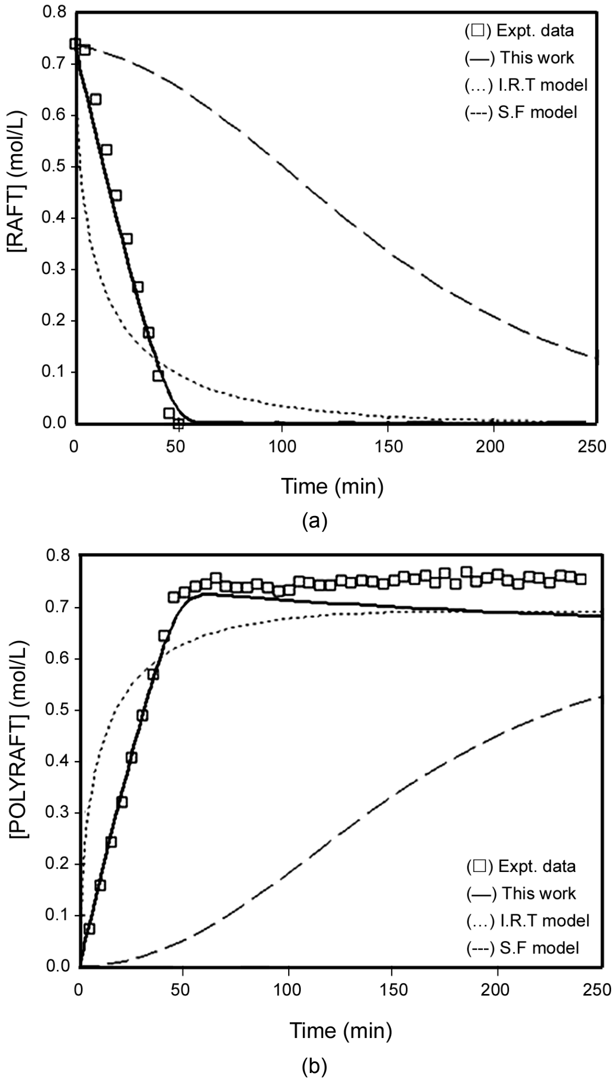


Figure 3. Comparing experimentally determined: (a) RAFT and (b) PolyRAFT concentrations and the theoretical results in cyanoisopropyl dithiobenzoate-mediated styrene polymerization at 70°C (experimental data taken from Ref. 28).

square method to fit the modelling results with the *RAFT*, *PolyRAFT*, and monomer experimental concentration profiles.

A more careful study of the equilibrium constants points out an asymmetric fragmentation of intermediate radicals and slower fragmentation compared to intermediate radicals which are presented in the main equilibrium (i.e., $P_n\ int^*\ P_n$).

Figure 3 shows the concentrations of *RAFT* and *PolyRAFT* as a function of polymerization time. The average chain length of *PolyRAFT* at this stage of the reaction is less than two (calculated by moment equations) which indicates that mono-adduct species are in the majority. When *RAFT* agent is consumed, the other dormant species (i.e., *PolyRAFT*) are produced. The modelling results are acceptably in agreement with the experimental data. Both the SF and IRT models fail to predict concentration profiles (details of kinetic parameters of each model is indicated above). The SF model assumes 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 a poor agreement with the experimental data. The total concentration of polymeric RAFT agents is equal to that of primary RAFT agent, implying that the cross terminations have not taken place.

In Figure 4, the monomer conversion data have been compared with the modelling results. The slope of the curve is proportional to the rate of the monomer consumption. Based on the mass balance equation for monomer, most of its concentration 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,

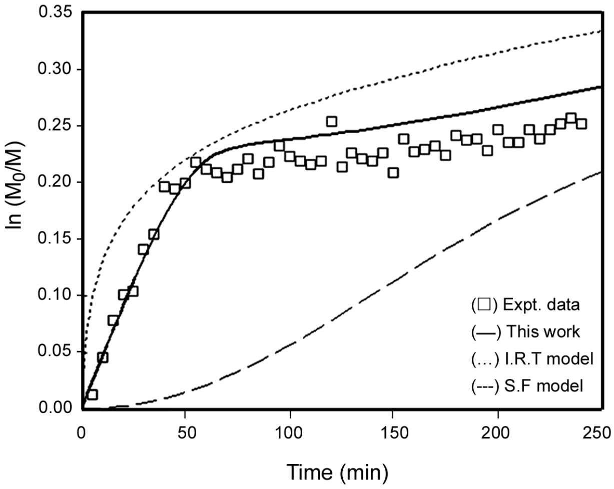


Figure 4. Comparison between the model predictions and experimental conversion data in cyanoisopropyl dithiobenzoate-mediated styrene polymerization at 70°C (experimental data taken from Ref. 28).

when all the initial RAFT agents are consumed (i.e., 50 min after the reaction initiation, as indicated in Figure 3a) the slope of the curve diminishes dramatically which implies that the equilibrium is moving towards the formation of mono-adduct species. In other words, the propagating radicals undergo transfer reactions and change into dormant species.

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

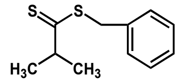
Copolymerization of Styrene and Butyl Acrylate Mediated by Benzyl Dithioisobutyrate

It is well known that copolymerization systems are more practical for obtaining desired architectures. Sun and coworkers [6] have accomplished some experiments on St/BA systems both in batch and semi-batch reactors. By the support of mathematical modelling, they synthesized uniform and linear gradient copolymers. Our aim was not to synthesize different copolymer architectures, but we intended to investigate the kinetics of RAFT polymerization from a different point of view. The details of each experiment given in Table 3 can be found in the original work [6]. Once again, unknown parameters

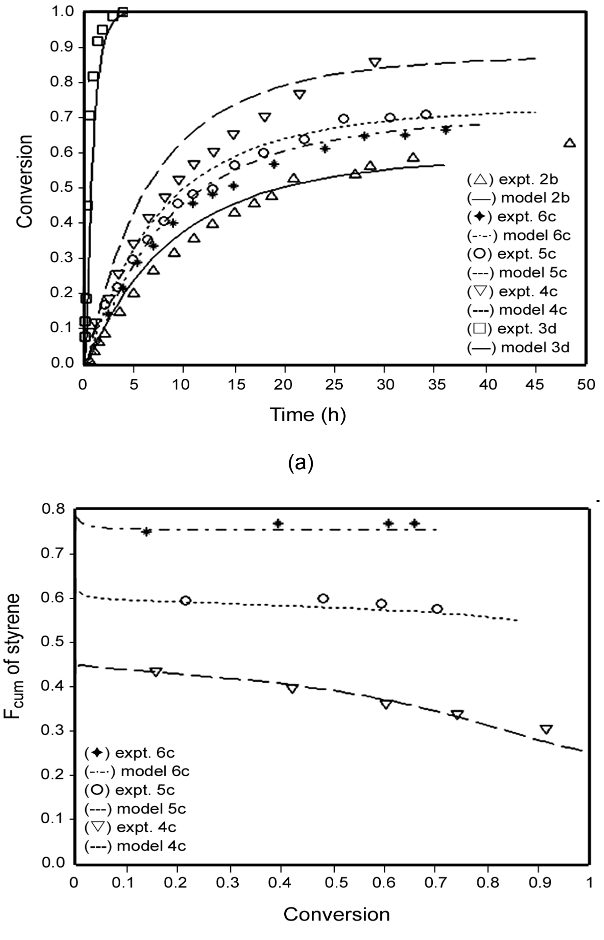
Table 3. Experimental conditions and rate constants of copolymerization of styrene and butyl acrylate mediated by benzyl dithioisobutyrate [a] at 70°C [b].

Parameter	Value					Reference	Unit
	2b	3d	4c	5c	6c		
$[AIBN]_0$	0.0070	0.00700	0.0070	0.00700	0.00700	6	mol/L
$[RAFT]_0$	0.02082	0.01672	0.01760	0.01860	0.01962	6	mol/L
$[Styrene]_0$	4.26070	0.00000	0.90020	1.90060	3.01390	6	mol/L
$[BA]_0$	0.00000	3.42610	2.70110	1.89780	1.00260	6	mol/L
$[Toluene]_0$	4.82340	4.77310	4.78530	4.79550	4.80870	6	mol/L
$f^c \times k_d$	$8.256\times10^{14}\times\exp(-127600/RT)$					46	1/s
k_{ij}, and k_{re-ij}	$3.2\times10^{7}\times\exp(-24300/RT)$					47	L/(mol.s)
k_{p11}	$4.2\times10^{7}\times\exp(-32500/RT)$					46	L/(mol.s)
k_{p22}	$10^{\exp(6.0123-784.4/RT)}$					46	L/(mol.s)
k_{tc11}	$5\times10^{8}\times L^{-0.16\ d}$					45	L/(mol.s)
k_{tc22}	$L\leq40$: $1\times10^{9}\times L^{-0.2}$ $L>40$: $2.217\times10^{10}\times L^{-1.04}$					45	L/(mol.s)
k_{tc12} or k_{tc21}	$(k_{tc11}\times k_{tc22})^{0.5}$					45	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}					46	-
$C_{tr,m22}$	1.05×10^{-4}					46	-
k_{tir}	5×10^{8}					45	1/s
k_{ti}	$0.5\ (k_{tci}(1)+k_{tci}(L))$					45	L/(mol.s)
k_{tcrijk}	$\langle k_t\rangle^{e}\times10^{-3}\times\exp(-f_{sty}^{\ f}/0.02)$					6	L/(mol.s)
r_{st}	0.723					6	-
r_{BA}	0.189					6	-

(a)



(b) Other coefficients have supposed to be zero; (c) initiator efficiency (0.64); (d) number-average chain length; (e) $\langle k_t\rangle=P_1^2k_{t,11}+2P_1P_2k_{t,12}+P_2^2k_{t,22}$, where P_i is the relative concentration of the terminal radical i; (f) styrene molar fraction.



(a)

(b)

Figure 5. Comparing (a) conversion data and (b) cumulative styrene copolymer composition with the modelling data in the copolymerization of styrene and butyl acrylate mediated by benzyl dithioisobutyrate at 70°C (experimental data taken from Ref. 6).

were also calculated by using conversion data and applying the least square method to obtain the best fit.

The conversion data and model results are illustrated in Figure 5. As expected, an increment in the initial molar fraction of BA increases monomer consumption due to a higher propagation rate. As a consequence of the existence of solvent, gel effect does not play a significant role in the polymerization rate, and slope of all curves (i.e., rate of monomer consumption) does not increase during the course of the polymerization.

Figure 5b shows the cumulative copolymer composition. Based on Feldermann's results, RAFT agent does not play a significant role in the change of monomer reactivity ratios [48]. By using the Lewis-Mayo copolymerization equation [49] the azeotrope point ($F_1 = f_1$) of the system can be calculated as follows:

$$f_1 = F_1 = \frac{1 - r_2}{2 - r_1 - r_2} \tag{19}$$

By substituting the values of r_1 (styrene reactivity ratio) and r_2 (butyl acrylate reactivity ratio), the azeotrope point becomes 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.

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 is raised which results in a reduction in the amount of living species.

Polydispersity index (PDI) depends on many reaction parameters which differs for different polymerization systems. In general, using RAFT agents narrows molecular weight distribution (MWD) and lowers polydispersity index. The homopolymerization curves of 2b and 3d in Figure 7 are

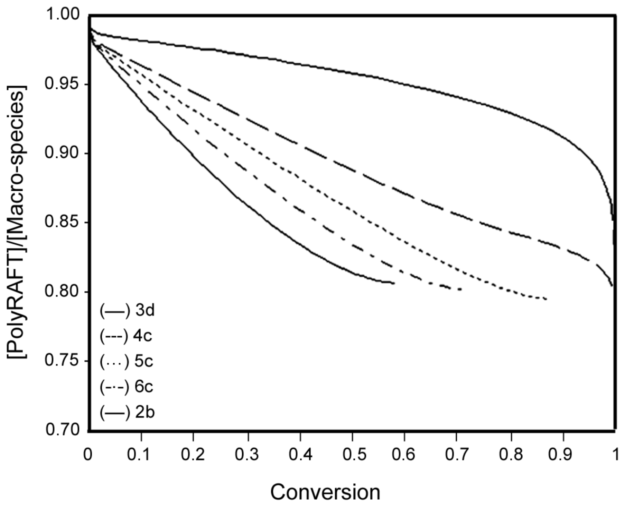


Figure 6. Variation of molar fraction of living polymer chains among macro-species during the copolymerization of styrene and butyl acrylate mediated by benzyl dithioisobutyrate at 70°C.

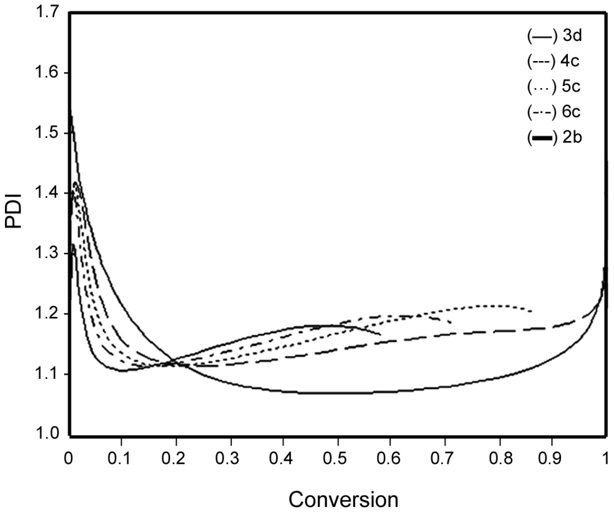


Figure 7. Polydispersity index as a function of conversion during the copolymerization of styrene and butyl acrylate mediated by benzyl dithioisobutyrate at 70°C.

different in terms of shape and value. Increasing the initial molar fraction of each monomer leads to the change of polydispersity index behaviour towards the one similar to that of the homopolymerization of the same monomer. At conversion smaller than 20%, higher amounts of styrene can lower polydispersity index. However, beyond this amount, conversion trend would be quite the opposite.

CONCLUSION

In this work, a detailed kinetic scheme was introduced and examined for three types of dithioester-mediated RAFT homo- and copolymerization systems. The method of moments was used to model the polymerization. The validity of this kinetic scheme was verified by comparing the model predictions and experimental data. Some of the kinetic rate constants were obtained by least square method which has not been considered before. The validity of the obtained values has been supported by previous experimental studies and exact theoretical calculations. Although acceptable results were obtained in this work, further experiments are required for both reducing the size of the model and correlating some apparently contradictory data.

SYMBOLS AND ABBREVIATIONS

AIBN : Azobisisobutyronitrile
BA : Butyl acrylate monomer
CTA : Chain transfer agent
C_{tr} : Transfer constant for reversible transfer
$C_{tr,m}$: Transfer to monomer constant
f : Initiator efficiency
f_i : Monomer feed composition in a copolymerization system
F_i : Instantaneous copolymer composition
F_{cum} : Cumulative copolymer composition
k_a : Addition rate constant (L/mol.s)
k_d : Initiator decomposition rate constant (1/s)
K_{eq} : Equilibrium constant for addition-fragmentation step (L/mol)
k_f : Fragmentation rate constant (1/s)
k_i : Initiation rate constant (L/mol.s)
k_{re-i} : Re-initiation rate constant (L/mol.s)
k_{tc} : Rate constant for termination reaction between two propagating radicals via combination (L/mol.s)
k_{tcr} : Rate constant for cross-termination reaction between intermediate radicals and other radical species (L/mol.s)
k_{ti} : Rate constant for termination reaction between propagating radicals and initiator or leaving group radicals (L/mol.s)
k_{tir} : Rate constant for termination reaction between initiator and leaving group radicals (L/mol.s)
$\overline{M}_n$: Number average molecular weight
$\overline{M}_w$: Weight average molecular weight
NMR : Nuclear magnetic resonance
PDI : Polydispersity index
P_n int* P_n : Intermediate radical with two polymeric arms
PolyRAFT : RAFT Agent with polymeric leaving group, $RAFTP_n$
r : Monomer reactivity ratio in a

copolymerization system

Sty : Styrene monomer

x_{living} : Molar fraction of dormant chains

$\overline{X}_n$: Number average degree of polymerization

$\overline{X}_w$: Weight average degree of polymerization

Greek Letters

δ : Four-arm star shaped dead polymers chain length distribution moment

λ : Propagating radicals chain length distribution moment

μ_R : Intermediate radicals, with a polymeric chain and leaving group as two-arms, chain length distribution moment

μ_I : Intermediate radicals, with a polymeric chain and initiator fragment as two-arms, chain length distribution moment

ξ : Linear dead polymers chain length distribution moment

ξ′ : Three-arm star shaped dead polymers chain length distribution moment

ξ″ : Two-arm star shaped dead polymers chain length distribution moment

ξ‴ : One-arm star shaped dead polymers chain length distribution moment

υ : Dormant chains chain length distribution moment

ω : Intermediate radical, with two polymeric arms, chain length distribution moment

APPENDIX

The details of the moment equations for the RAFT homo- and copolymerization systems.

Propagating radical:

$$Q^{(i)} = \Bigg[k_{a1,i}\,[RAFT] + k_{a5,i}\,[RAFTI] + \sum_j k_{a7,ij}\,\upsilon_0^{(j)} + \sum_j k_{p,ij}\,[M_j] + \sum_j k_{tc,ij}\,\lambda_0^{(j)} + \sum_j k_{td,ij}\,\lambda_0^{(i)}$$

$$+ \frac{1}{2}\sum_j\sum_k k_{tcr,ijk}\,\omega_{0,0}^{(j,k)} + k_{trA_j,i}\,[A_j] + \sum_j k_{tcr,jI1}\,\mu_{I,0}^{(j)} + \sum_j k_{tcr,jR1}\,\mu_{R,0}^{(j)} \Bigg]$$

$$\frac{d\lambda_0^{(i)}}{dt} = \left(k_{i,i}\left[I^*\right] + k_{re-i,i}\left[R^*\right] + k_{re-iA_j,i}\left[A_j^*\right] + \sum_j k_{p,ji}\,\lambda_0^{(j)} \right)[M_i] + \left[k_{f1,i}\,\mu_{R,0}^{(i)} + k_{f5,i}\,\mu_{I,0}^{(i)} + \frac{1}{2}\sum_j k_{f7,ij}\,\omega_{0,0}^{(i,j)} \right] - Q^{(i)}\lambda_0^{(i)}$$

$$\frac{d\lambda_1^{(i)}}{dt} = \left(k_{i,i}\left[I^*\right] + k_{re-i,i}\left[R^*\right] + k_{re-iA_j,i}\left[A_j^*\right] + \sum_j k_{P,ji}\left(\lambda_0^{(j)} + \lambda_1^{(j)}\right) \right)[M_i]$$

$$+ \left[k_{f1,i}\,\mu_{R,1}^{(i)} + k_{f5,i}\,\mu_{I,1}^{(i)} + \frac{1}{2}\sum_j k_{f7,ij}\,\omega_{1,0}^{(i,j)} \right] - Q^{(i)}\lambda_1^{(i)}$$

$$\frac{d\lambda_2^{(i)}}{dt} = \left(k_{i,i}\left[I^*\right] + k_{re-i,i}\left[R^*\right] + k_{re-iA_j,i}\left[A_j^*\right] + \sum_j k_{P,ji}\left(\lambda_0^{(i)} + \lambda_2^{(i)} + 2\lambda_1^{(i)}\right) \right)[M_i]$$

$$+ \left[k_{f1,i}\,\mu_{R,2}^{(i)} + k_{f5,i}\,\mu_{I,2}^{(i)} + \frac{1}{2}\sum_j k_{f7,ij}\,\omega_{2,0}^{(i,j)} \right] - Q^{(i)}\lambda_2^{(i)}$$

Dormant species:

$$\frac{d\upsilon_0^{(i)}}{dt} = \left[k_{f2,i}\,\mu_{R,0}^{(i)} + k_{f6,i}\,\mu_{I,0}^{(i)} + \frac{1}{2}\sum_j k_{f7,ij}\,\omega_{0,0}^{(i,j)} \right] - \left(k_{a2,i}\left[R^*\right] + k_{a6,i}\left[I^*\right] + \sum_j k_{a7,ji}\,\lambda_0^{(j)} \right)\upsilon_0^{(i)}$$

$$\frac{d\upsilon_1^{(i)}}{dt} = \left[k_{f\,2,i}\,\mu_{R,1}^{(i)} + k_{f\,6,i}\,\mu_{I,1}^{(i)} + \frac{1}{2}\sum_j k_{f\,7,ij}\,\omega_{1,0}^{(i,j)} \right] - \left(k_{a2,i}\left[R^*\right] + k_{a6,i}\left[I^*\right] + \sum_j k_{a7,ji}\,\lambda_0^{(j)} \right)\upsilon_1^{(i)}$$

$$\frac{d\upsilon_2^{(i)}}{dt} = \left[k_{f\,2,i}\,\mu_{R,2}^{(i)} + k_{f\,6,i}\,\mu_{I,2}^{(i)} + \frac{1}{2}\sum_j k_{f\,7,ij}\,\omega_{2,0}^{(i,j)} \right] - \left(k_{a2,i}\left[R^*\right] + k_{a6,i}\left[I^*\right] + \sum_j k_{a7,ji}\,\lambda_0^{(j)} \right)\upsilon_2^{(i)}$$

Intermediate radicals:

$$Q''^{(i)} = k_{f\,1,i} + k_{f\,2,i} + \sum_j k_{tcr,jRi}\,\lambda_0^{(j)} + k_{tcr,IRi}\left[I^*\right] + k_{tcr,RRi}\left[R^*\right] + \sum_j k_{tcr,RiRj}\,\mu_{R,0}^{(j)} + \sum_j k_{tcr,RiIj}\,\mu_{I,0}^{(j)} + \frac{1}{2}\sum_j\sum_k k_{tcr,Rijk}\,\omega_{0,0}^{(j,k)}$$

$$\frac{d\mu_{R,0}^{(i)}}{dt} = k_{a1,i}\left[RAFT\right]\lambda_0^{(i)} + k_{a2,i}\upsilon_0^{(i)}\left[R^*\right] - Q''^{(i)}\,\mu_{R,0}^{(i)}$$

$$\frac{d\mu_{R,1}^{(i)}}{dt} = k_{a1,i}\left[RAFT\right]\lambda_1^{(i)} + k_{a2,i}\upsilon_1^{(i)}\left[R^*\right] - Q''^{(i)}\mu_{R,1}^{(i)}$$

$$\frac{d\mu_{R,2}^{(i)}}{dt} = k_{a1,i}\left[RAFT\right]\lambda_2^{(i)} + k_{a2,i}\upsilon_2^{(i)}\left[R^*\right] - Q''^{(i)}\mu_{R,2}^{(i)}$$

$$Q'''^{(i)} = k_{f\,5,i} + k_{f\,6,i} + \sum_j k_{tcr,jIi}\,\lambda_0^{(j)} + k_{tcr,IIi}\left[I^*\right] + k_{tcr,RIi}\left[R^*\right] + \sum_j k_{tcr,IiRj}\,\mu_{R,0}^{(j)} + \sum_j k_{tcr,IiIj}\,\mu_{I,0}^{(j)} + \frac{1}{2}\sum_j\sum_k k_{tcr,Iijk}\,\omega_{0,0}^{(j,k)}$$

$$\frac{d\mu_{I,0}^{(i)}}{dt} = k_{a5,i}\left[RAFTI\right]\lambda_0^{(i)} + k_{a6,i}\left[I^*\right]\upsilon_0^{(i)} - Q'''^{(i)}\,\mu_{I,0}^{(i)}$$

$$\frac{d\mu_{I,1}^{(i)}}{dt} = k_{a5,i}\left[RAFTI\right]\lambda_1^{(i)} + k_{a6,i}\left[I^*\right]\upsilon_1^{(i)} - Q'''^{(i)}\mu_{I,1}^{(i)}$$

$$\frac{d\mu_{I,2}^{(i)}}{dt} = k_{a5,i}\left[RAFTI\right]\lambda_2^{(i)} + k_{a6,i}\left[I^*\right]\upsilon_2^{(i)} - Q'''^{(i)}\mu_{I,2}^{(i)}$$

$$q^{(i,j)} = \frac{1}{2}\left(k_{f\,7,ij} + k_{f\,7,ji}\right) + \sum_k k_{tcr,kij}\,\lambda_0^{(k)} + k_{tcr,Iij}\left[I^*\right] + k_{tcr,Rij}\left[R^*\right] + \sum_k k_{tcr,ijRk}\,\mu_{R,0}^{(k)} + \sum_k k_{tcr,ijIk}\,\mu_{I,0}^{(k)} + \frac{1}{2}\sum_k\sum_l k_{tcr,ijkl}\,\omega_{0,0}^{(k,l)}$$

$$\frac{d\omega_{0,0}^{(i,j)}}{dt} = k_{a7,ij}\,\lambda_0^{(i)}\upsilon_0^{(j)} + k_{a7,ji}\,\lambda_0^{(j)}\upsilon_0^{(i)} - q^{(i,j)}\,\omega_{0,0}^{(i,j)}$$

$$\frac{d\omega_{1,0}^{(i,j)}}{dt} = k_{a7,ij}\,\lambda_1^{(i)}\upsilon_0^{(j)} + k_{a7,ji}\,\lambda_0^{(j)}\upsilon_1^{(i)} - q^{(i,j)}\omega_{1,0}^{(i,j)}$$

$$\frac{d\omega_{0,1}^{(i,j)}}{dt} = k_{a7,ij}\,\lambda_0^{(i)}\upsilon_1^{(j)} + k_{a7,ji}\,\lambda_1^{(j)}\upsilon_0^{(i)} - q^{(i,j)}\omega_{0,1}^{(i,j)}$$

$$\frac{d\omega_{1,1}^{(i,j)}}{dt} = k_{a7,ij}\,\lambda_1^{(i)}\upsilon_1^{(j)} + k_{a7,ij}\,\lambda_1^{(j)}\upsilon_1^{(i)} - q^{(i,j)}\omega_{1,1}^{(i,j)}$$

$$\frac{d\,\omega_{2,0}^{(i,j)}}{dt} = k_{a7,ij}\,\lambda_2^{(i)}\upsilon_0^{(j)} + k_{a7,ji}\,\lambda_0^{(j)}\upsilon_2^{(i)} - q^{(i,j)}\omega_{2,0}^{(i,j)}$$

$$\frac{d\,\omega_{0,2}^{(i,j)}}{dt} = k_{a7,ij}\,\lambda_0^{(i)}\upsilon_2^{(j)} + k_{a7,ji}\,\lambda_2^{(j)}\upsilon_0^{(i)} - q^{(i,j)}\omega_{0,2}^{(i,j)}$$

Linear dead polymer:

$$\frac{d\xi_0}{dt} = \frac{1}{2}\sum_i\sum_j k_{tc,ij}\,\lambda_0^{(i)}\lambda_0^{(j)} + \sum_i\sum_j k_{td,ij}\,\lambda_0^{(i)}\lambda_0^{(j)} + \sum_i k_{tR,i}\,\lambda_0^{(i)}\left[R^*\right] + \sum_i k_{tI,i}\,\lambda_0^{(i)}\left[I^*\right] + \sum_i k_{trA_j,i}\,\lambda_0^{(i)}\left[A_j\right]$$

$$\frac{d\xi_1}{dt} = \sum_i\sum_j k_{tc,ij}\,\lambda_0^{(i)}\lambda_1^{(j)} + \sum_i\sum_j k_{td,ij}\,\lambda_1^{(i)}\lambda_0^{(j)} + \sum_i k_{tR,i}\,\lambda_1^{(i)}\left[R^*\right] + \sum_i k_{tI,i}\,\lambda_1^{(i)}\left[I^*\right] + \sum_i k_{trA_j,i}\,\lambda_1^{(i)}\left[A_j\right]$$

$$\frac{d\xi_2}{dt} = \sum_i\sum_j k_{tc,ij}\left(\lambda_2^{(i)}\lambda_0^{(j)} + \lambda_1^{(i)}\lambda_1^{(j)}\right) + \sum_i\sum_j k_{td,ij}\,\lambda_2^{(i)}\lambda_0^{(j)} + \sum_i k_{tR,i}\,\lambda_2^{(i)}\left[R^*\right] + \sum_i k_{tI,1}\lambda_2^{(i)}\left[I^*\right] + \sum_i k_{trA_j,i}\,\lambda_2^{(i)}\left[A_j\right]$$

Three-arm star polymer:

$$\frac{d\xi_0'}{dt} = \frac{1}{2}\sum_i\sum_j\sum_k k_{tcr,ijk}\,\lambda_0^{(i)}\omega_{0,0}^{(j,k)} + \frac{1}{2}\sum_i\sum_j\sum_k k_{tcr,Rijk}\,\mu_{R,0}^{(i)}\omega_{0,0}^{(j,k)} + \frac{1}{2}\sum_i\sum_j\sum_k k_{tcr,Iijk}\,\mu_{I,0}^{(i)}\omega_{0,0}^{(j,k)}$$

$$\begin{aligned}\frac{d\xi_1'}{dt} = {}& \frac{1}{2}\sum_i\sum_j\sum_k k_{tcr,ijk}\,\lambda_1^{(i)}\omega_{0,0}^{(j,k)} + \sum_i\sum_j\sum_k k_{tcr,ijk}\,\lambda_0^{(i)}\omega_{1,0}^{(j,k)} + \frac{1}{2}\sum_i\sum_j\sum_k k_{tcr,Rijk}\,\mu_{R,1}^{(i)}\omega_{0,0}^{(j,k)}\\ &+ \sum_i\sum_j\sum_k k_{tcr,Rijk}\,\mu_{R,0}^{(i)}\omega_{1,0}^{(j,k)} + \frac{1}{2}\sum_i\sum_j\sum_k k_{tcr,Iijk}\,\mu_{I,1}^{(i)}\omega_{0,0}^{(j,k)} + \sum_i\sum_j\sum_k k_{tcr,Iijk}\,\mu_{I,0}^{(i)}\omega_{1,0}^{(j,k)}\end{aligned}$$

$$\begin{aligned}\frac{d\xi_2'}{dt} = {}& \frac{1}{2}\sum_i\sum_j\sum_k k_{tcr,ijk}\,\lambda_2^{(i)}\omega_{0,0}^{(j,k)} + 2\sum_i\sum_j\sum_k k_{tcr,ijk}\,\lambda_1^{(i)}\omega_{1,0}^{(j,k)} + \sum_i\sum_j\sum_k k_{tcr,ijk}\,\lambda_0^{(i)}\left(\omega_{2,0}^{(j,k)} + \omega_{1,1}^{(j,k)}\right) + \frac{1}{2}\sum_i\sum_j\sum_k k_{tcr,Rijk}\,\mu_{R,2}^{(i)}\omega_{0,0}^{(j,k)}\\ &+ 2\sum_i\sum_j\sum_k k_{tcr,Rijk}\,\mu_{R,1}^{(i)}\omega_{1,0}^{(j,k)} + \sum_i\sum_j\sum_k k_{tcr,Rijk}\,\mu_{R,0}^{(i)}\left(\omega_{2,0}^{(j,k)} + \omega_{1,1}^{(j,k)}\right) + \frac{1}{2}\sum_i\sum_j\sum_k k_{tcr,Iijk}\,\mu_{I,2}^{(i)}\omega_{0,0}^{(j,k)} + 2\sum_i\sum_j\sum_k k_{tcr,Iijk}\,\mu_{I,1}^{(i)}\omega_{1,0}^{(j,k)}\\ &+ \sum_i\sum_j\sum_k k_{tcr,Iijk}\,\mu_{I,1}^{(i)}\left(\omega_{2,0}^{(j,k)} + \omega_{1,1}^{(j,k)}\right)\end{aligned}$$

Two-arm star polymer:

$$\begin{aligned}\frac{d\xi_0''}{dt} = {}& \frac{1}{2}\sum_i\sum_j k_{tcr,Iij}\,\omega_{0,0}^{(i,j)}\left[I^*\right] + \frac{1}{2}\sum_i\sum_j k_{tcr,Rij}\,\omega_{0,0}^{(i,j)}\left[R^*\right] + \sum_i\sum_j k_{tcr,iIj}\,\mu_{I,0}^{(i)}\lambda_0^{(j)}\\ &+ \sum_i\sum_j k_{tcr,iRj}\,\mu_{R,0}^{(i)}\lambda_0^{(j)} + \frac{1}{2}\sum_i\sum_j k_{tcr,RiRj}\,\mu_{R,0}^{(i)}\mu_{R,0}^{(j)} + \sum_i\sum_j k_{tcr,IiRj}\,\mu_{I,0}^{(i)}\mu_{R,0}^{(j)} + \frac{1}{2}\sum_i\sum_j k_{tcr,IiIj}\,\mu_{I,0}^{(i)}\mu_{I,0}^{(j)}\end{aligned}$$

$$\begin{aligned}\frac{d\xi_1''}{dt} = {}& \sum_i\sum_j k_{tcr,Iij}\,\omega_{1,0}^{(i,j)}\left[I^*\right] + \sum_i\sum_j k_{tcr,Rij}\,\omega_{1,0}^{(i,j)}\left[R^*\right] + \sum_i\sum_j k_{tcr,iIj}\left(\mu_{I,1}^{(i)}\lambda_0^{(j)} + \mu_{I,0}^{(i)}\lambda_1^{(j)}\right)\\ &+ \sum_i\sum_j k_{tcr,iRj}\left(\mu_{R,1}^{(i)}\lambda_0^{(j)} + \mu_{R,0}^{(i)}\lambda_1^{(j)}\right) + \sum_i\sum_j k_{tcr,RiRj}\,\mu_{R,1}^{(i)}\mu_{R,0}^{(j)} + \sum_i\sum_j k_{tcr,IiRj}\left(\mu_{I,1}^{(i)}\mu_{R,0}^{(j)} + \mu_{I,0}^{(i)}\mu_{R,1}^{(j)}\right) + \sum_i\sum_j k_{tcr,IiIj}\,\mu_{I,1}^{(i)}\mu_{I,0}^{(j)}\end{aligned}$$

$$\frac{d\xi_2''}{dt}=\sum_i\sum_j k_{tcr,Iij}\left(\omega_{2,0}^{(i,j)}+\omega_{1,1}^{(i,j)}\right)\left[I^*\right]+\sum_i\sum_j k_{tcr,Rij}\left(\omega_{2,0}^{(i,j)}+\omega_{1,1}^{(i,j)}\right)\left[R^*\right]+\sum_i\sum_j k_{tcr,iIj}\left(\mu_{I,2}^{(i)}\lambda_0^{(j)}+2\mu_{I,1}^{(i)}\lambda_1^{(j)}+\mu_{I,0}^{(i)}\lambda_2^{(j)}\right)$$
$$+\sum_i\sum_j k_{tcr,iRj}\left(\mu_{R,2}^{(i)}\lambda_0^{(j)}+2\mu_{R,1}^{(i)}\lambda_1^{(j)}+\mu_{R,0}^{(i)}\lambda_2^{(j)}\right)+\sum_i\sum_j k_{tcr,RiRj}\left(\mu_{R,2}^{(i)}\mu_{R,0}^{(j)}+\mu_{R,1}^{(i)}\mu_{R,1}^{(j)}\right)$$
$$+\sum_i\sum_j k_{tcr,IiRj}\left(\mu_{I,2}^{(i)}\mu_{R,0}^{(j)}+2\mu_{I,1}^{(i)}\mu_{R,1}^{(j)}+\mu_{I,0}^{(i)}\mu_{R,2}^{(j)}\right)+\sum_i\sum_j k_{tcr,IiIj}\left(\mu_{I,2}^{(i)}\mu_{I,0}^{(j)}+\mu_{I,1}^{(i)}\mu_{I,1}^{(j)}\right)$$

One-arm star polymer:

$$\frac{d\xi_0'''}{dt}=\left(\sum_i k_{tcr,IRi}\,\mu_{R,0}^{(i)}+\sum_i k_{tcr,IIi}\,\mu_{I,0}^{(i)}\right)\left[I^*\right]+\left(\sum_i k_{tcr,RRi}\,\mu_{R,0}^{(i)}+\sum_i k_{tcr,RIi}\,\mu_{I,0}^{(i)}\right)\left[R^*\right]$$

$$\frac{d\xi_1'''}{dt}=\left(\sum_i k_{tcr,IRi}\,\mu_{R,1}^{(i)}+\sum_i k_{tcr,IIi}\,\mu_{I,1}^{(i)}\right)\left[I^*\right]+\left(\sum_i k_{tcr,RRi}\,\mu_{R,1}^{(i)}+\sum_i k_{tcr,RIi}\,\mu_{I,1}^{(i)}\right)\left[R^*\right]$$

$$\frac{d\xi_2'''}{dt}=\left(\sum_i k_{tcr,IRi}\,\mu_{R,2}^{(i)}+\sum_i k_{tcr,IIi}\,\mu_{I,2}^{(i)}\right)\left[I^*\right]+\left(\sum_i k_{tcr,RRi}\,\mu_{R,2}^{(i)}+\sum_i k_{tcr,RIi}\,\mu_{I,2}^{(i)}\right)\left[R^*\right]$$

Four-arm star polymer:

$$\frac{d\delta_0}{dt}=\frac{1}{4}\sum_i\sum_j\sum_k\sum_l\left(1+\left[\frac{i+j+k+l}{2}\right]-\frac{i+j+k+l}{2}\right)\left(1-\frac{\left|(i-j)(k-l)\right|}{2}\right)k_{tcr,ijkl}\,\omega_{0,0}^{(i,j)}\omega_{0,0}^{(k,l)}$$

$$\text{if }\ \mathrm{i}\neq\mathrm{j}\ \&\ \mathrm{k}\neq 1\ \Rightarrow\ \frac{d\delta_1}{dt}=\sum_i\sum_j\sum_k\sum_l\left(1+\left[\frac{i+j+k+l}{2}\right]-\frac{i+j+k+l}{2}\right)\left(1-\frac{\left|(i-j)(k-l)\right|}{2}\right)k_{tcr,ijkl}\,\omega_{0,0}^{(i,j)}\omega_{1,0}^{(k,l)}$$

$$\text{if }\ \mathrm{i}=\mathrm{j}\ \&\ \mathrm{k}=1\ \Rightarrow\ \frac{d\delta_1}{dt}=\frac{1}{2}\sum_i\sum_j\sum_k\sum_l\left(1+\left[\frac{i+j+k+l}{2}\right]-\frac{i+j+k+l}{2}\right)\left(1-\frac{\left|(i-j)(k-l)\right|}{2}\right)k_{tcr,ijkl}\,\omega_{0,0}^{(i,j)}\omega_{1,0}^{(k,l)}$$

$$\text{if }\ \mathrm{i}\neq\mathrm{j}\ \&\ \mathrm{k}\neq 1\ \Rightarrow\ \frac{d\delta_2}{dt}=\sum_i\sum_j\sum_k\sum_l\left(1+\left[\frac{i+j+k+l}{2}\right]-\frac{i+j+k+l}{2}\right)k_{tcr,ijkl}\left(\omega_{0,0}^{(i,j)}\left(\omega_{2,0}^{(k,l)}+\omega_{1,1}^{(k,l)}\right)+2\omega_{1,0}^{(i,j)}\omega_{1,0}^{(k,l)}\right)$$

$$\text{if }\ \mathrm{i}=\mathrm{j}\ \&\ \mathrm{k}=1\ \Rightarrow\ \frac{d\delta_2}{dt}=\frac{1}{2}\sum_i\sum_j\sum_k\sum_l\left(1+\left[\frac{i+j+k+l}{2}\right]-\frac{i+j+k+l}{2}\right)k_{tcr,ijkl}\left(\omega_{0,0}^{(i,j)}\left(\omega_{2,0}^{(k,l)}+\omega_{1,1}^{(k,l)}\right)+2\omega_{1,0}^{(i,j)}\omega_{1,0}^{(k,l)}\right)$$

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