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Effect of monomer composition on apparent chain transfer coefficient in reversible addition fragmentation transfer (RAFT) copolymerization

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ABSTRACT

The effects of monomer composition on the apparent chain transfer coefficient ($\langle C_{tr} \rangle$) in reversible addition fragmentation transfer (RAFT) copolymerization were investigated. The studied RAFT systems included methyl methacrylate (MMA)/butyl acrylate (BA) mediated by 1-phenylethyl phenyldithioacetate (PEPDTA) (i.e. MMA/BA–PEPDTA), MMA/BA by 2-cyanoprop-2-yl dithiobenzoate (i.e. MMA/BA–CPDTB), and styrene (St)/BA by benzyl dithioisobutyrate (i.e. St/BA–BDTiB). The *R* groups of the RAFT agents were first converted to the corresponding copolymer oligomers having the same composition to facilitate the measurement of the main RAFT equilibrium transfer coefficients. It was found that there exist minimum values in the $\langle C_{tr} \rangle \sim f_1$ curves in MMA/BA–CPDTB and St/BA–BDTiB at $f_1 = 0.75$ and 0.25, respectively. The apparent transfer coefficients of the copolymerization systems within some composition range were lower than their homopolymerization values. The lower $\langle C_{tr} \rangle$ values resulted in broader copolymer molecular weight distributions. The composition dependence of $\langle C_{tr} \rangle$ was determined by the comonomer reactivity ratios and the Z group functionality of the RAFT agent. The experimental data could be well described by a simple equation derived from the terminal model:

$$\langle C_{tr} \rangle = \frac{\langle k_{tr} \rangle}{\langle k_p \rangle} = \psi_1 \frac{r_1 f_1 C_{tr,11} + r_2 f_2 C_{tr,21}}{r_1 f_1^2 + r_2 f_2^2 + 2 f_1 f_2} + \psi_2 \frac{r_1 f_1 C_{tr,12} + r_2 f_2 C_{tr,22}}{r_1 f_1^2 + r_2 f_2^2 + 2 f_1 f_2}.$$

1. Introduction

Reversible addition fragmentation chain transfer (RAFT) free radical polymerization has developed into a major controlled/living radical polymerization (CLRP) process since its discovery in 1998 [1]. The basic principle of the RAFT process is to activate/deactivate polymer chains by a RAFT agent between propagation radicals and dormant chains. The chain transfer constant C_{tr} is defined as the ratio of the rate constants of chain transfer and propagation ($C_{tr} = k_{tr}/k_p$). C_{tr} is one of the most important parameters in the RAFT mechanism. A high C_{tr} means a rapid switch of propagating radical to its dormant state. For a given chain length, the number of activation/deactivation cycles increases with an increase of C_{tr}, leading to narrow chain length distribution. The C_{tr} value, which can be evaluated by GPC [2–4], depends mainly on the structure of RAFT agent in the RAFT homopolymerization [5–8].

Copolymerization is an important approach for fine tuning polymer materials properties. Controlled/living free radical copolymerization (CLRcoP) offers a great opportunity for precise control over composition profile as well as chain architecture. Unique copolymer microstructures such as gradient copolymer have been synthesized by CLRcoP [11,12]. Compared to a huge number of reports on CLRP, there are only a few reports dealing with the fundamentals of CLRcoP. Feldermann et al. [13] reported the copolymer compositions derived from the RAFT copolymerization could be slightly different from their non-living counterparts at very low monomer conversions. Recently we have launched a research program to tailor-make gradient copolymers having precisely designed composition profiles via model-based semibatch copolymerization technologies [11]. A theoretical kinetic model was developed to predict monomer conversion, molecular weight and its distribution, and polymer composition. In our previous paper [14], a model was developed

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for the apparent equilibrium coefficient $\langle K \rangle$ of RAFT copolymerization. The apparent equilibrium coefficient at any initial monomer composition could be predicted if the corresponding equilibrium constants of the RAFT homopolymerization were given. The equation explained the particular retardation effect observed in the RAFT copolymerization of methyl methacrylate (MMA)/butyl acrylate (BA) mediated by benzyl dithioisobutyrate (i.e. MMA/BA–BDTiB). On the other hand, Fukuda et al. [15,16] investigated the influence of penultimate unit effect on the chain transfer constant of styrene (St)/MMA copolymerization mediated by dithioacetate. They found that the PUE becomes significant only in the addition process but not in the fragmentation process at the azeotropic composition ($f_1 = 0.53$) of St/MMA copolymerization. A theoretical expression was derived for the apparent chain transfer coefficient $\langle C_{tr} \rangle$ [16]. Fukuda's model is very sophisticated, taking into account the penultimate effect and thus inevitably involves many rate parameters that cannot be experimentally estimated independently. It is challenging to verify and use the model.

In this paper, the chain transfer constants in the homo- and random co-polymerization systems of MMA/BA mediated by 1-phenylethyl phenyldithioacetate (PEPDTA) (i.e. MMA/BA–PEPDTA), MMA/BA by 2-cyanoprop-2-yl dithiobenzoate (CPDTB) (i.e. MMA/BA–CPDTB), and St/BA by benzyl dithioisobutyrate (BDTiB) (i.e. ST/BA–BDTiB) were experimentally determined. The influence of monomer composition and RAFT agent structure on the apparent chain transfer coefficient was investigated in detail. To avoid the complication from the RAFT pre-equilibrium in the early stage of polymerization (during which the *R* groups are converted to polymer chains), the small molecular RAFT agents are first oligomerized with their corresponding comonomer systems having the same compositions. That is, PEPDTA is converted to oligo(MMAcoBA)-phenyldithioacetate (in abbreviation, oligoPDTA), CPDTB is converted to oligo(MMA-*co*-BA)-dithiobenzoate (in abbreviation, oligoDTB), and BDTiB is converted to oligo(ST-*co*-BA)-dithioisobutyrate (in abbreviation, oligoDTiB). The chain transfer constants thus measured are the ones of chain transfer to polymer in the main equilibrium. We observed an intriguing phenomenon in our experiment data, that is, the copolymerization chain transfer constants within some composition range were lower than those of the homopolymerization systems, exhibiting minima in the $\langle C_{tr} \rangle \sim f_1$ curves. We also found that this observation can be adequately explained by a theory based on the terminal model.

2. Experimental

2.1. Materials

Styrene (St, Shanghai Chemical Reagent Co., 98%), methyl methacrylate (MMA, Sinopharm Chemical Reagent Co., Ltd. 98%), and butyl acrylate (BA, Shanghai Chemical Reagent Co., 98%) were purified by vacuum distillation prior to use. 2,2′-Azobis-(isobutyronitrile) (AIBN, Shanghai Chemical Reagent Co., 98%) as an initiator was re-crystallized twice from methanol. 1-Phenylethyl phenyldithioacetate (PEPDTA), 2-cyanoprop-2-yl dithiobenzoate (CPDTB) and benzyl dithioisobutyrate (BDTiB) were synthesized according to Refs. [17–19]. The synthesis of cumyl phenyldithioacetate (CPDTA) was very similar to that of PEPDTA but styrene was replaced by α-methyl styrene to react with dithiophenylacetic acid for 8 h at 70 °C with carbon tetrachloride as solvent. The orange crystal CPDTA was obtained by evaporation of cold (268 K) methanol. It should be pointed out that CPDTA was used only in the preparation of oligoMMA–PDTA because PEPDTA did not give good control in the MMA homopolymerization.

2.2. Synthesis of oligomer-RAFT agents

A mixture solution of monomers, small molecular RAFT agent, and AIBN was thoroughly deoxygenated by N_2 purging with stirring for 30 min. The solution was then transferred to a five-necked flask, equipped with condenser, thermometer, nitrogen inlet, and mechanical stirrer. The reaction vessel was placed in a thermostated water bath at 70 °C for a given period of time under nitrogen atmosphere. For the synthesis of BA oligomer-RAFT agent, the temperature of water bath was set to 60 °C. The reaction mixture was then slowly poured with stirring into a large excess of methanol (for the BA oligomer-RAFT agent, 1/1 volume ratio of methanol/water was used as precipitant). The precipitated polymer was washed with the precipitant four times. Finally, the oligomer-RAFT agent was collected and dried at 35 °C in a vacuum oven for 16 h.

2.3. Determination of chain transfer constant

A mixture solution of monomers, oligomer-RAFT agent, and AIBN (oligomer-RAFT/AIBN/monomer = 2/3/10,000 in the molar ratio) was thoroughly deoxygenated by N_2 purging with stirring for 30 min. The solution was then transferred to a five-necked flask and heated at 60 °C for a preset time. The reaction mixture was firstly quenched with hydroquinone tetrahydrofuran (THF) solution. The polymer sample was collected by evaporating solvent and residual monomers. The monomer conversion was measured gravimetrically. The chain transfer constants were determined by the GPC method according to Refs. [3,4].

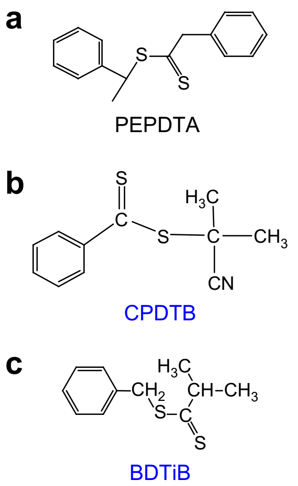
2.4. Sample characterization

The polymer molecular weight distribution was determined at 30 °C by gel permeation chromatography (Waters 1525/2414/2487). Three linear PL Waters Styragel columns (HR2, HR3, and HR4) were used. THF was used as an eluent at a flow rate of 1 mL/min at 25 °C. The GPC curves were calibrated using polystyrene (PS) standard samples with molecular weights ranging from 780 to 710,000 g/mol.

3. Results and discussion

3.1. Oligomerization of RAFT agents

In this work, we studied the influence of monomer composition on the apparent chain transfer coefficient using three representative systems: methyl methacrylate (MMA)/butyl acrylate (BA) mediated the MMA-*co*-BA oligomer of PEPDTA (MMA/BA–oligoPDTA), MMA/BA by the MMA-*co*-BA oligomer of CPDTB (MMA/BA–oligoDTB), and styrene (St)/BA by the St-*co*-BA oligomer of BDTiB (ST/BA–oligoDTiB). It is well known that RAFT polymerization is a complicated system that involves pre-equilibrium and main equilibrium [20,21]. The *R* group plays an important role in the chain transfer reaction. In the pre-equilibrium at the early stage of polymerization, the *R* group is a small functional moiety. As the polymerization proceeds, the *R* group is fragmented and becomes a radical that initiates with monomers. Upon addition, the *R* group becomes a polymer chain instead of a small moiety. The *R* groups of small moiety and polymer chain can have very different chain transfer rate constants. The reason of using the oligomer-RAFT agents is to avoid the complication from the pre-equilibrium. Scheme 1 gives the molecular structures of the small molecule RAFT agents used in this work (PEPDTA, CPDTB and BDTiB). The prepared oligomer-RAFT agents with various initial comonomer compositions ($f_{1,0}$) for the MMA/BA–oligoPDTA, MMA/BA–oligoDTB and St/BA–oligoDTiB copolymerization systems are listed in Tables 1–3, respectively. The



Scheme 1. Molecular structures of the small molecule RAFT agents used in this work (PEPDTA, CPDTB and BDTiB). These RAFT agents are oligomerized for the measurements of chain transfer constants.

monomer conversions were controlled to assure that all the small molecule RAFT agents were converted to their corresponding oligomer RAFT agents, which was confirmed via the disappearance of the original small RAFT agent by GPC. In Tables 1–3, the final comonomer compositions (f_1) calculated from the Mayo equation are also listed. In the case of MMA/BA–CPDTB, oligoDTB of MMA was not prepared since the transfer constant of MMA homopolymerization mediated by CPDTB is available in the literature [2]. As it can be seen, the experimental molecular weights are in good agreement with their theoretical values, suggesting that the *R* groups of the RAFT agents were consumed.

3.2. Copolymerization of MMA/BA mediated by MMA/BA–oligoPDTA

The apparent transfer coefficients $\langle C_{tr}\rangle$ were determined by the GPC curve resolution method [2–4]. The five runs of MMA/BA copolymerization (M_1 = MMA and M_2 = BA) were carried out in the presence of MMA/BA–oligoPDTA agents having the corresponding comonomer compositions, as shown in Table 1. The probe adduct molecules (MMA/BA–oligoPDTA) are fragmented into propagation radicals. With sufficiently low oligoPDTA concentration, a large number of monomer units are added to the radicals during a single activation/deactivation cycle, giving an accurate resolution in the GPC trace that shows two peaks. Fig. 1 presents a typical change in GPC trace as the copolymerization proceeded. The decrease in the oligPDTA concentration can be readily estimated. The change of the oligoPDTA concentration with the monomer conversion is approximated as follows [2,16]:

$$\ln\left(\frac{[\text{oligoPDTA}]_0}{[\text{oligoPDTA}]}\right) = \langle C_{tr}\rangle \ln\left(\frac{[\text{M}]_0}{[\text{M}]}\right) \tag{1}$$

where [oligoPDTA] is the concentration of oligoPDTA; [M] is the monomer concentration; $\langle C_{tr}\rangle$ is the chain transfer coefficient. The subscript 0 indicates an initial value.

Fig. 2 shows the linear relationship between ln([oligoPDTA]$_0$/[oligoPDTA]) and ln([M]$_0$/[M]). The slopes of the lines give an estimate of the ($\langle C_{tr}\rangle$) values. $\langle C_{tr}\rangle$ decreases with increased MMA composition. The estimated $\langle C_{tr}\rangle$ values are plotted against the monomer composition in Fig. 3. The $\langle C_{tr}\rangle$ decreases steadily from 116 of the BA homopolymerization to 11 of the MMA homopolymerization.

Based on the terminal model, we derived the following equation to describe the change of $\langle C_{tr}\rangle$ with f_1 (refer to Appendix for the details of derivation):

$$\begin{aligned}\langle C_{tr}\rangle &= \frac{\langle k_{tr}\rangle}{\langle k_p\rangle} \\ &= \psi_1\frac{r_1f_1C_{tr,11}+r_2f_2C_{tr,21}}{r_1f_1^2+r_2f_2^2+2f_1f_2}+\psi_2\frac{r_1f_1C_{tr,12}+r_2f_2C_{tr,22}}{r_1f_1^2+r_2f_2^2+2f_1f_2}\end{aligned} \tag{2}$$

where

$$\psi_1 = C_{tr,12}r_1f_1/(C_{tr,12}r_1f_1+C_{tr,21}r_2f_2) \tag{3}$$

$$\psi_2 = 1-\psi_1 \tag{4}$$

$$C_{tr,12} = k_{tr,12}/k_{p,11} = k_{a,11}k_{f,22}/\left(k_{f,11}+k_{f,22}\right)/k_{p,11} \tag{5}$$

$$C_{tr,21} = k_{tr,21}/k_{p,22} = k_{a,22}k_{f,11}/\left(k_{f,11}+k_{f,22}\right)/k_{p,22} \tag{6}$$

$$\frac{C_{tr,12}}{C_{tr,11}}+\frac{C_{tr,21}}{C_{tr,22}} = 2 \tag{7}$$

Table 1
Molecular weight and PDI of MMA/BA–oligoPDTA RAFT agent prepared from MMA/BA–PEPDTA with various comonomer compositions.

f_{10}[a]	0[b]	0.29[b]	0.49[b]	0.79[b]	1[c]
Time, min.	75	85	88	130	190
x, %	6.0	11.9	12.9	16.2	20.0
f_1	0	0.26	0.46	0.77	1
$M_{n,\,theo}$[d]	1536	2752	2894	3497	4000
$M_{n,\,exp}$	1525	2715	2960	3584	4211
PDI	1.13	1.24	1.43	1.45	1.28

[a] [RAFT]$_0$/[I]$_0$/[M]$_0$ = 5/1/1000 (in molar ratio).
[b] PEPDTA as the original RAFT agent.
[c] CPDTA as the original RAFT agent for the homopolymerization of MMA.
[d] $M_{n,theo} = x\ [\text{M}]_0M_M/[\text{RAFT}]_0 + M_{RAFT}$ where [M]$_0$ and [RAFT]$_0$ are the initial concentrations of monomer and RAFT agent, respectively; M_M and M_{RAFT} are the molar masses of monomer and RAFT agent; and *x* is the total monomer conversion.

Table 2
Molecular weight and PDI of MMA/BA–oligoDTB RAFT agent prepared from MMA/BA–CPDTB with various comonomer compositions.

$f_{1,0}$	0[a]	0.2[b]	0.8[b]
Time, min.	350	630	168
x, %	15.3	20.8	19.8
f_1	0	0.17	0.78
$M_{n\ ,theo}$	4119	4448	3698
$M_{n,\ exp}$	4271	7850	5000
PDI	1.17	1.15	1.44

[a] [CPDTB]$_0$/[I]$_0$/[M]$_0$ = 5/1/1000 (molar ratio).
[b] [CPDTB]$_0$/[I]$_0$/[M]$_0$ = 6/1/1000 (molar ratio).

Table 3
Molecular weight and PDI of St/BA–oligoDTiB RAFT agent prepared from St/BA–BDTiB with various comonomer compositions.[a]

$f_{1,0}$	0	0.23	0.74[b]	1
Time, min.	51	175	180	120
x, %	18.8	20.4	22.0	29
f_1	0	0.18	0.74	1
$M_{n,\,theo}$	2406	2244	2420	3016
$M_{n,\,exp}$	2627	2709	3163	3760
PDI	1.34	1.45	1.38	1.35

[a] [BDTiB]$_0$/[I]$_0$/[M]$_0$ = 10/1/1000 (molar ratio).
[b] Azeotropic composition.

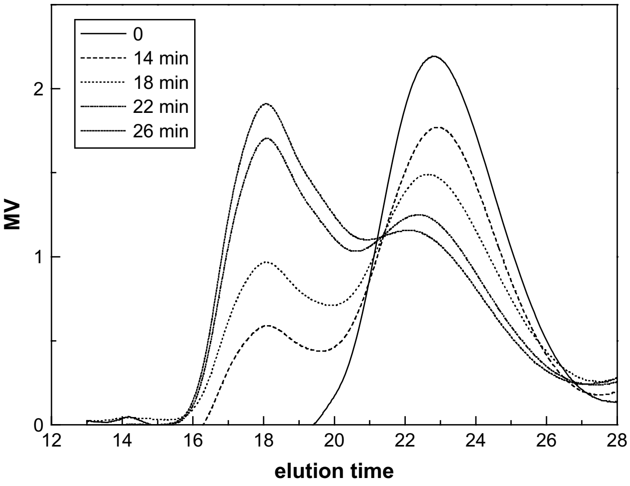


Fig. 1. The change of GPC chromatograms in the MMA/BA copolymerization mediated by oligoPDTA of the composition corresponding to $f_1 = 0.77$ at 60 °C.

ψ_i is the molar fraction of dormant chains with terminal unit i, $k_{tr,ij}$ is the transfer rate constant of radical i to dormant chain j, $k_{a,\,ii}$ is the RAFT addition rate constant of monomer i in its homopolymerization, $k_{f,ii}$ is the RAFT fragmentation rate constant of monomer i in its homopolymerization, r_i is the reactivity ratio of monomer i; f_i is the molar fraction of monomer i, $\langle k_{tr} \rangle$ and $\langle k_p \rangle$ are the apparent transfer and propagation rate coefficients, respectively.

It should be pointed out that the derivation of Eq. (2) involves the following assumptions. (1) We used the terminal model, i.e. the reaction rate constant is determined only by chain end unit. It should be pointed out that both MMA/BA and St/BA copolymerization showed the penultimate unit effect as $\langle k_p \rangle$ cannot be accurately described by the terminal models [9,10]. However, in this study, we found that the simplest terminal model is sufficient in describing the variation of apparent transfer coefficient with monomer composition. A possible explanation is that the penultimate unit effect is significant on the reactivity (k_{tr}) but minor on the selectivity ($\langle C_{tr} \rangle$). That is, their influences on chain transfer and propagation rate constants compensate each other to a certain degree, as long the ratio $\langle C_{tr} \rangle$ is considered [9,22]. (2) k_a and k_f are assumed to be independent of terminal monomer units of dormant chains (i.e. $k_{a,12} = k_{a,11}$, $k_{a,21} = k_{a,22}$, $k_{f,12} = k_{f,11}$, $k_{f,21} = k_{f,22}$). (3) The RAFT equilibrium and the steady state of radical population are fully established.

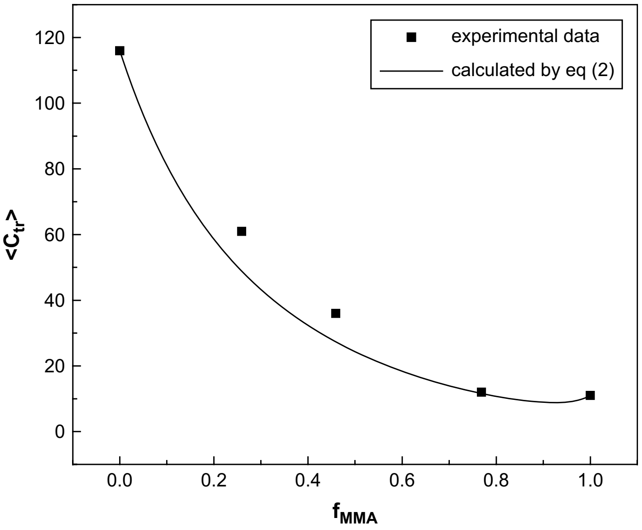


Fig. 3. The change of $\langle C_{tr} \rangle$ with f_1 in the MMA/BA–oligoPDTA. The points are experimental data, the line is calculated by Eq. (2).

Using Eq. (2), we can calculate $\langle C_{tr} \rangle$ at any given monomer composition if the reactivity ratios and the C_{trij} $(i, j = 1, 2)$ values are known. $C_{tr,11}$ and $C_{tr,22}$ were obtained from Fig. 1. The cross transfer reaction constants $C_{tr,ij}$ $(i \neq j)$ (i.e. $C_{tr,12}$ and $C_{tr,21}$) can also be determined by the similar approach. In the experiments, oligoMMA–PDTA was used to mediate the BA polymerization and oligoBA–PDTA was used for the MMA polymerization. $C_{tr,21}$ was estimated to be 205, as shown in Fig. 4. $C_{tr,\,12}$ was calculated to be 2.6 from Eq. (7). We then calculated the $\langle C_{tr} \rangle$ values at various monomer compositions with the estimated $C_{tr,ij}$ data and the literature-reported reactivity ratios $r_1 = 2.15$ and $r_2 = 0.4$ [23]. The calculation results are compared to the experimental data in Fig. 3. It is evident that Eq. (2) can predict very well the $\langle C_{tr} \rangle$ values at various monomer compositions without an adjusting parameter.

The values of ψ_1 and ψ_2 were calculated from Eqs. (3) and (4). Fig. 5 suggests that the dormant chain ended with BA unit is predominant when $f_1 < 0.8$. ψ_2 decreases sharply to zero with f_1 approaching 1. Such a trend of variation is due to that the

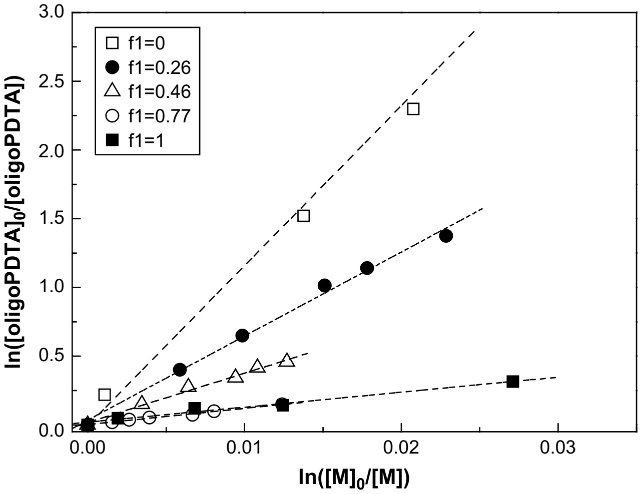


Fig. 2. ln([oligoPDTA]$_0$/[oligoPDTA]) versus ln([M]$_0$/[M]) in the MMA/BA copolymerization mediated by oligoPDTA having the corresponding compositions.

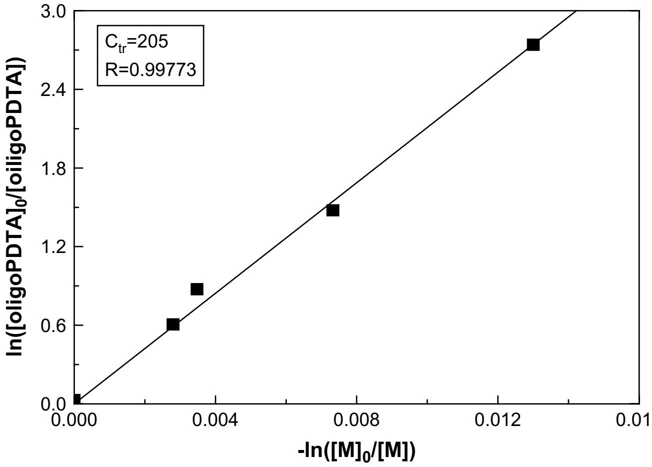


Fig. 4. ln([oligoPDTA]$_0$/[oligoPDTA]) versus ln([M]$_0$/[M]) in the BA polymerization mediated by oligoMMA–PDTA at 60 °C. The oligoMMA–PDTA was prepared from the oligomerization of MMA mediated by CPDTA.

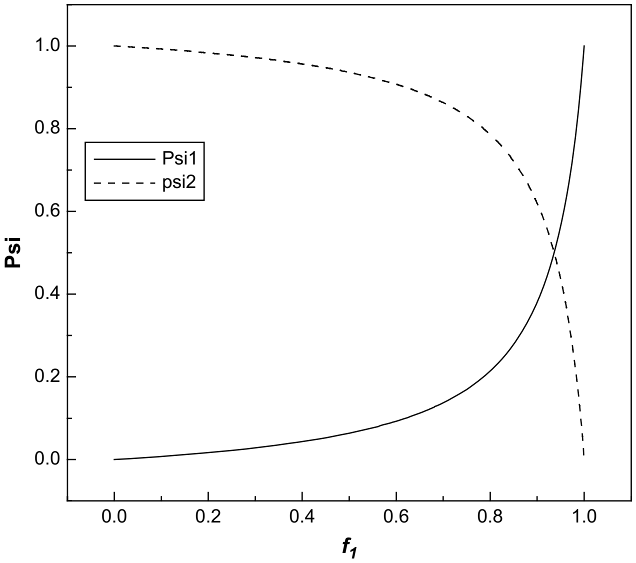


Fig. 5. The evolution of ψ_1 and ψ_2 with f_1 in MMA/BA/oligoPDTA copolymerization system.

intermediate radical $P_1T^{\bullet}P_2$ is much more likely to release $P_1^{\bullet}$ than $P_2^{\bullet}$. Using $C_{tr,21} = 205$ and $C_{tr,22} = 116$, we estimated $k_{f,11}/k_{f,22}$ to be 7.3 (see Eq. (6) and note that $C_{tr,22} = k_{a22}/2\,k_{p,22}$).

3.3. Copolymerization of MMA/BA mediated by MMA/BA/oligoDTB

In MMA/BA–oligoDTB system, the Z group of RAFT agent is a phenyl group. The apparent transfer coefficient of homo- and copolymerization of this system was determined using the similar method as above. The properties of oligoDTB were summarized in Table 2. Fig. 6 shows the measured $\langle C_{tr}\rangle$ values. Comparing Fig. 6 to Fig. 3, we can see how the *Z* group influences the trend of $\langle C_{tr}\rangle$ variation with monomer composition. When the *Z* group is changed from benzyl to phenyl, both $C_{tr,11}$ and $C_{tr,22}$ increased, suggesting a higher activating ability of the phenyl group. An increase of over ten times in $C_{tr,11}$ was observed while $C_{tr,22}$ increased only by a factor of 2. Interestingly, a minimum was observed at $f_1 = 0.75$ in the $\langle C_{tr}\rangle \sim f_1$ curve. We tried to measure $C_{tr,12}$ without success. It was found that the oligoBA–DTB cannot give good control over the MMA polymerization, indicating that the $C_{tr,12}$ value must be lower than 10. We therefore assumed $C_{tr,12} = 5$ and calculated $C_{tr,21} = 482$ from Eq. (7). The apparent transfer coefficients of the copolymerization were thus accurately predicted by Eq. (2), as evident in Fig. 6.

As shown in Fig. 7, the $\psi_i \sim f_1$ profile appeared to be similar to that in Fig. 5. However, the decrease of ψ_1 in the high f_1 region becomes more dramatic.

3.4. Copolymerization of St/BA mediated by St/BA–oligoDTiB

St/BA (M_1 = St and M_2 = BA) is another representative comonomer pair in the radical copolymerization. The apparent transfer coefficients at various monomer compositions and the cross transfer coefficients were experimentally determined. The properties of the used oligoDT*i*B are summarized in Table 3. Fig. 8 presents the measured $\langle C_{tr}\rangle$ data. Again the apparent transfer coefficient $\langle C_{tr}\rangle$ showed a minimum but at $f_1 = 0.25$. The cross transfer coefficients were experimentally measured to be $C_{tr,12} = 54$ and $C_{tr,21} = 50$. The theoretical values calculated by Eq. (2) with $r_1 = 0.723$ and $r_2 = 0.189$ [24] are compared to the experimental data and good agreement was found.

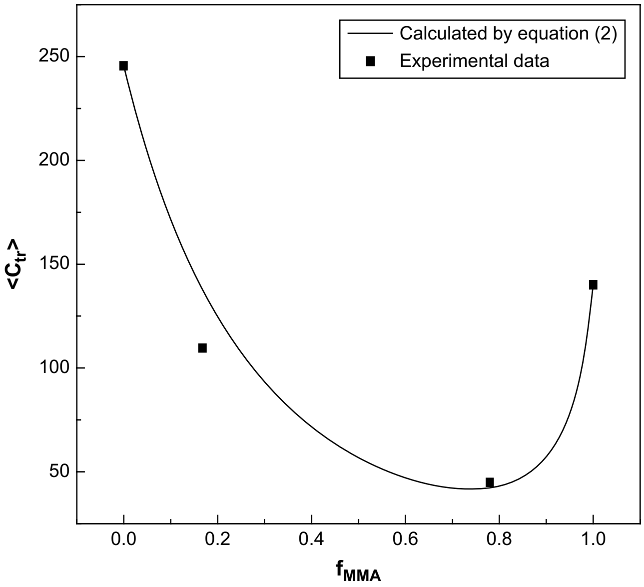


Fig. 6. The change of $\langle C_{tr}\rangle$ with f_1 in the MMA/BA–oligoDTB. The points are experimental data, the line is calculated by Eq. (2). $C_{tr,\,11} = 140$ is cited from the literature [2].

The $C_{tr,11}$ value in the St homo-polymerization is higher than that in the BA homo-polymerization. Using the propagation rate constants $k_{p11} = 340\ M^{-1}\,s^{-1}$ [25] and $k_{p22} = 35541\ M^{-1}\,s^{-1}$ [26], we estimated $k_{a,11}$ and $k_{a,22}$ to be 4.01e4 L mol^{-1} s^{-1} and 2.98e6 L mol^{-1} s^{-1}, respectively (note: $C_{tr,11} = k_{a,11}/2\,k_{p11}$, $C_{tr,22} = k_{a,\,22}/2\,k_{p22}$). The $k_{f,11}/k_{f,\,22}$ ratio was estimated to be 1.5 from Eq. (5) and 1.17 from Eq. (6) based on $C_{tr,12} = 54$ and $C_{tr,21} = 50$. PSt$^{\bullet}$ and PBA$^{\bullet}$ have close probability of fragmentation from their RAFT intermediate radicals. On the other hand, using $k_{a,11}/k_{a,\,22}$ and $k_{f,11}/k_{f,22}$, we estimated $K_1/K_2 \approx 74$. The rate retardation in the BA polymerization was reported to be much more severe than that in the St polymerization [27]. It becomes clear that the severe

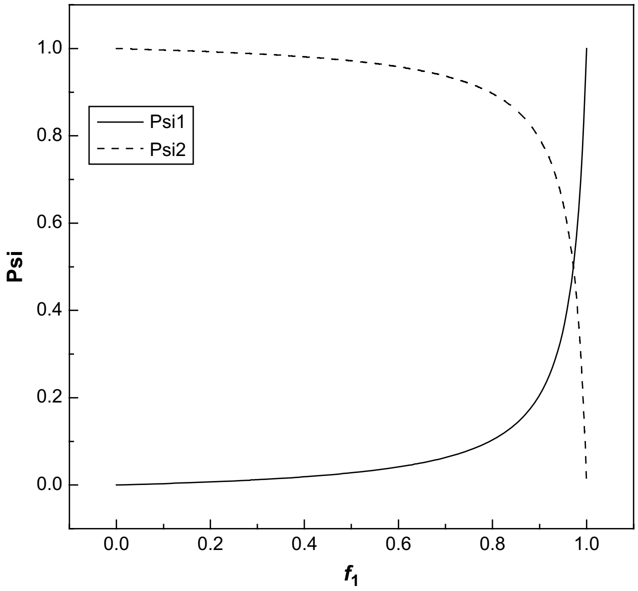


Fig. 7. The evolution of ψ_1 and ψ_2 with f_1 in MMA/BA/oligoDTB copolymerization system.

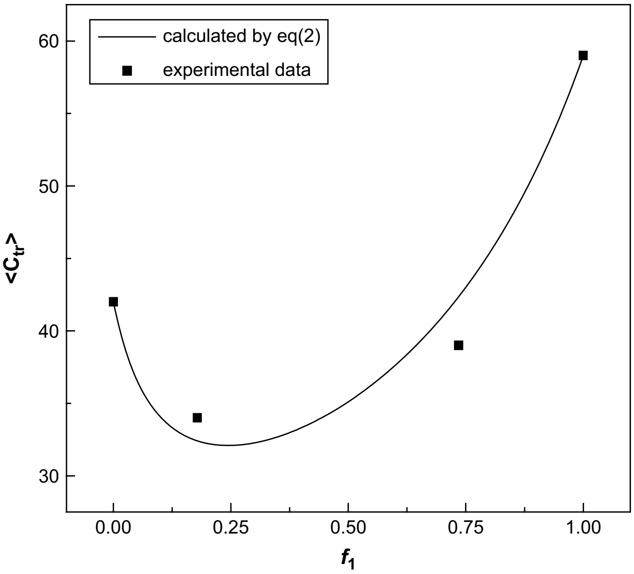


Fig. 8. The change of $\langle C_{tr}\rangle$ with f_1 in the St/BA–oligoDT*i*B. The points are experimental data, the line is calculated by Eq. (2).

retardation in the BA RAFT polymerization was not caused by slow fragmentation but by very fast addition, leading to a high equilibrium constant.

Fig. 9 shows ψ_1 and ψ_2 as a function of f_1. ψ_1 increased steadily with the increase of f_1 because the fragmentation probabilities of $PSt^{\bullet}$ and $PBA^{\bullet}$ from the intermediate radical $P_1\dot{T}P_2$ are similar.

3.5. Copolymerization effect on molecular weight distribution

As shown in Figs. 3, 6 and 8, the variation of $\langle C_{tr}\rangle$ with monomer composition is complicated and is influenced by many factors. These influences are non-linear, resulting in some unexpected observations. The chain transfer constants also affect copolymer molecular weight. The copolymer molecular weight distributions could be very different from their homopolymerization counterparts. Fig. 10 demonstrates such an effect. When f_1 gradually changes from 0.39 through 0.56 to 0.72, the PDIs of the copolymers generally increases. However, when f_1 increases further from 0.72 to 1, the PDIs decrease. This non-monotonous changing trend is in an excellent agreement with Fig. 6. In the case of BA homogeneous polymerization ($f_1 = 0$), Fig. 6 predicts the lowest PDI. This is true before conversion 20%. The PDIs of BA homo-polymerization steadily increase with conversion after 10% probably due to the severely irreversible termination (Note: the rate of BA homopolymerization is the lowest due to the severe retardation effect caused by PDTB) [14]. As a result, the PDIs of BA homo-polymerization become higher than those of MMA homopolymerization and copolymerization at $f_1 = 0.39$.

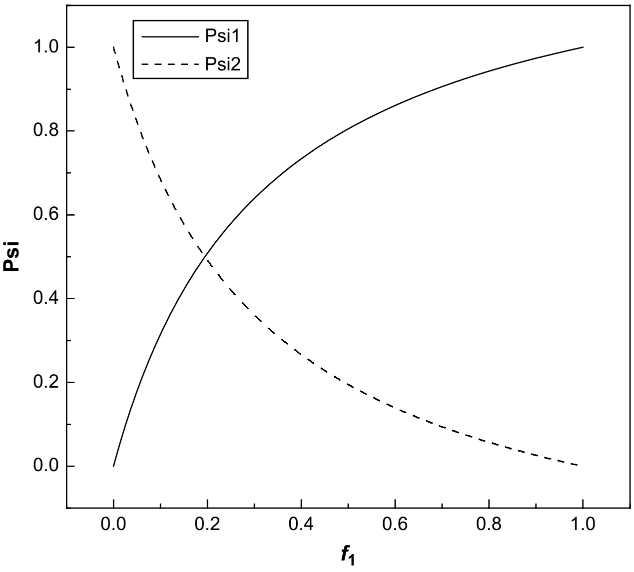


Fig. 9. The evolution of ψ_1 and ψ_2 with f_1 in St/BA–oligoDT*i*B copolymerization system.

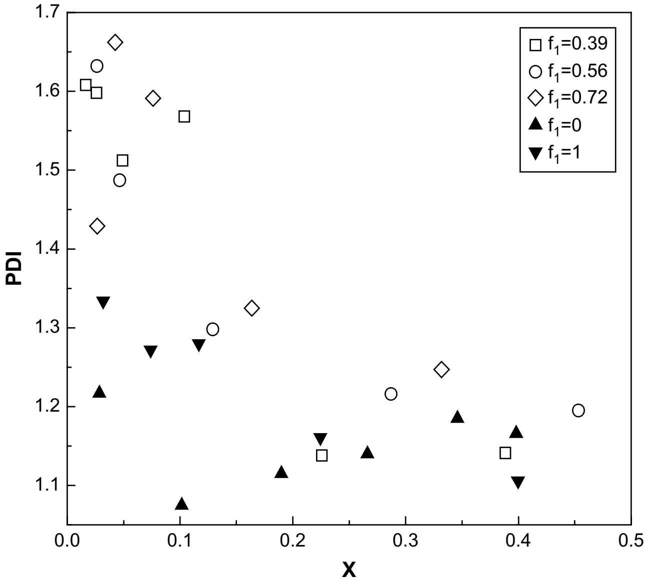


Fig. 10. The effect of monomer composition on the PDI of MMA/BA–PDTB copolymerization at 60 °C and [PDTB] = 17 mM.

4. Conclusion

The effect of monomer composition on the apparent chain transfer coefficient in RAFT copolymerization was investigated with three representative systems, i.e. MMA/BA–oligoPDTA, MMA/BA–oligoDTB and St/BA–oligoDT*i*B. It was found that in the MMA/BA–oligoDTB and St/BA–oligoDT*i*B systems, there exists a minimum $\langle C_{tr}\rangle$ value in the $\langle C_{tr}\rangle \sim f_1$ profile. The copolymerization $\langle C_{tr}\rangle$ values in a large range of monomer compositions are lower than their homopolymerization values $C_{tr,11}$ and $C_{tr,22}$. This minimum value is determined by comonomer reactivity ratios and the *Z* group structure of the RAFT agent. It was found that the intriguing phenomenon can be explained by the terminal model of apparent transfer coefficient. The experimental data are well correlated with a simple expression, Eq. (2). The variation of $\langle C_{tr}\rangle$ with composition also explains the unexpected observation of higher PDIs of the resulting copolymers. The copolymer molecular weight distributions of the RAFT copolymerization systems are intrinsically broader than those of their homopolymerization counterparts.

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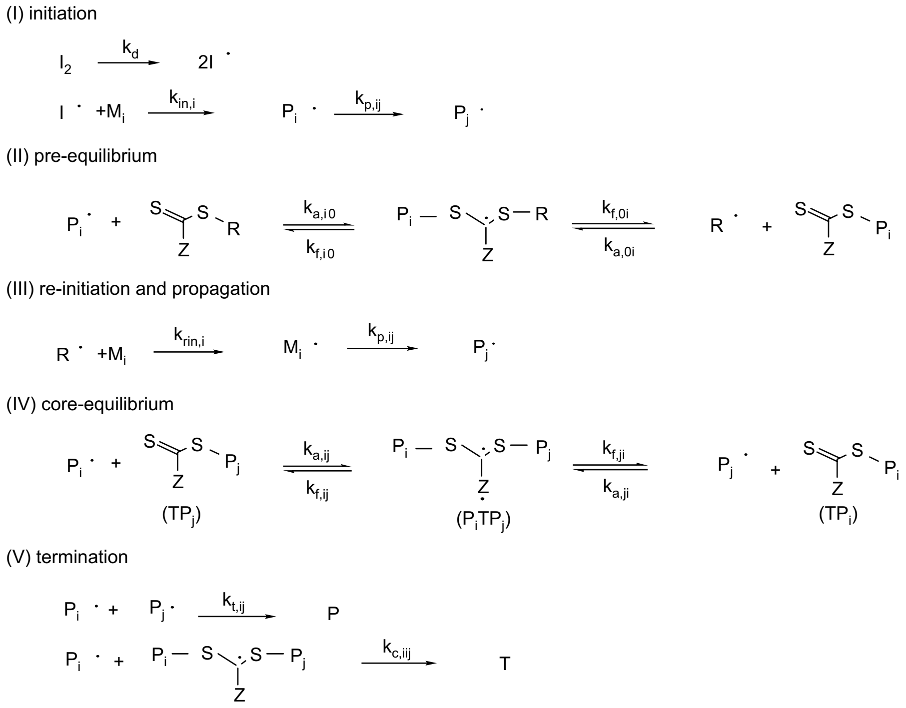
Appendix

Scheme A1 is a well-accepted RAFT polymerization mechanism. The pre-equilibrium reaction is ignored in developing the model for apparent transfer coefficient since we only account for the situation after the RAFT equilibrium is fully established.



Scheme A1. The mechanism of RAFT copolymerization.

The terminal model is used to derive the expression for the apparent transfer coefficient. According to Scheme 1, the chain transfer rate in the RAFT copolymerization can be expressed as:

$$R_{\mathrm{tr}} = k_{\mathrm{tr},11}[\mathrm{P}_1^{\bullet}][\mathrm{TP}_1] + k_{\mathrm{tr},12}[\mathrm{P}_1^{\bullet}][\mathrm{TP}_2] + k_{\mathrm{tr},21}[\mathrm{P}_2^{\bullet}][\mathrm{TP}_1] + k_{\mathrm{tr},22}[\mathrm{P}_2^{\bullet}][\mathrm{TP}_2] \equiv \langle k_{\mathrm{tr}}\rangle([\mathrm{P}_1^{\bullet}] + [\mathrm{P}_2^{\bullet}])([\mathrm{TP}_1] + [\mathrm{TP}_2]) \qquad \text{(A1)}$$

where $k_{\mathrm{tr}\ ,ii}$ and $k_{\mathrm{tr},ij}$ $(i \neq j = 1,\ 2)$ are the rate constants of chain transfer reactions in homopolymerization and cross-polymerization respectively, and they are defined as:

$$k_{\mathrm{tr},ii} = \frac{k_{\mathrm{a},ii}}{2} \quad k_{\mathrm{tr},ij} = \frac{k_{\mathrm{a},ij}k_{\mathrm{f},ji}}{k_{f,ij} + k_{f,ji}} \qquad \text{(A2)}$$

TP_i is the dormant chains (polymeric RAFT agent) with the terminal monomer unit *i*. The apparent chain transfer rate coefficient is defined as:

$$\langle k_{\mathrm{tr}}\rangle = \varphi_1\psi_1 k_{\mathrm{tr},11} + \varphi_1\psi_2 k_{\mathrm{tr},12} + \varphi_2\psi_1 k_{\mathrm{tr},21} + \varphi_2\psi_2 k_{\mathrm{tr},22} \qquad \text{(A3)}$$

where φ_i is defined as the fraction of $\mathrm{P}_i^{\bullet}$ in the total radical concentration (i.e.$[\mathrm{P}_i^{\bullet}] = \varphi_i[\mathrm{P}^{\bullet}]$), and ψ_i as the fraction of TP_i in the total dormant chain concentration (i.e. $[\mathrm{TP}_i] = \psi_i[\mathrm{TP}]$). φ_i can be calculated from Eq. (4), which was derived from the steady state assumption:

$$\varphi_1 = r_1 f_1 k_{\mathrm{p},22}/(r_1 f_1 k_{\mathrm{p},22} + r_2 f_2 k_{\mathrm{p},11}) \text{and}\ \varphi_2 = 1 - \varphi_1 \qquad \text{(A4)}$$

Invoking the steady assumption with regard to TP_i leads to:

$$k_{\mathrm{tr},12}[\mathrm{P}_1^{\bullet}][\mathrm{TP}_2] = k_{\mathrm{tr},21}[\mathrm{P}_2^{\bullet}][\mathrm{TP}_1] \qquad \text{(A5)}$$

Combining Eqs. (4) and (5) gives:

$$\psi_1 = C_{\mathrm{tr},12}r_1 f_1/(C_{\mathrm{tr},12}r_1 f_1 + C_{\mathrm{tr},21}r_2 f_2)$$

and

$$\psi_2 = 1 - \psi_1 \qquad \text{(A6)}$$

$C_{\mathrm{tr},\ ij}\,(i \neq j = 1, 2)$ are the cross transfer constants, which are defined as:

$$C_{\mathrm{tr},12} = k_{\mathrm{tr},12}/k_{\mathrm{p},11} = k_{\mathrm{a},12}k_{\mathrm{f},21}/\left(k_{\mathrm{f},12} + k_{\mathrm{f},21}\right)/k_{\mathrm{p},11} \qquad \text{(A7a)}$$

$$C_{\mathrm{tr},21} = k_{\mathrm{tr},21}/k_{\mathrm{p},22} = k_{\mathrm{a},21}k_{\mathrm{f},12}/\left(k_{\mathrm{f},12} + k_{\mathrm{f},21}\right)/k_{\mathrm{p},22} \qquad \text{(A7b)}$$

Inserting Eqs. (4) and (6) into Eq. (3), we obtain an expression for the apparent rate coefficient of chain transfer in the copolymerization:

$$\langle k_{\mathrm{tr}}\rangle = \frac{k_{\mathrm{p},11}k_{\mathrm{p},22}\left(r_1^2 f_1^2 C_{\mathrm{tr},12}C_{\mathrm{tr},11} + 2r_1 r_2 f_1 f_2 C_{\mathrm{tr},21}C_{\mathrm{tr},12} + r_2^2 f_1^2 C_{\mathrm{tr},21}C_{\mathrm{tr},22}\right)}{r_1^2 f_1^2 k_{\mathrm{p},22}C_{\mathrm{tr},12} + r_1 r_2 f_1 f_2 k_{\mathrm{p},22}C_{\mathrm{tr},21} + r_1 r_2 f_1 f_2 k_{\mathrm{p},11}C_{\mathrm{tr},12} + r_2^2 f_1^2 k_{\mathrm{p},11}C_{\mathrm{tr},21}} \qquad \text{(A8)}$$

The apparent chain transfer coefficient is defined as,

$$\langle C_{\mathrm{tr}}\rangle = \frac{\langle k_{\mathrm{tr}}\rangle}{\langle k_{\mathrm{p}}\rangle} \tag{A9}$$

where $\langle k_{\mathrm{p}}\rangle$ is apparent rate coefficient of propagation. With the terminal model, $\langle k_{\mathrm{p}}\rangle$ is written as [9],

$$\langle k_{\mathrm{p}}\rangle = \frac{r_1 f_1^2 + 2 f_1 f_2 + r_2 f_2^2}{r_1 \dfrac{f_1}{k_{\mathrm{p},11}} + r_2 \dfrac{f_2}{k_{\mathrm{p},22}}} \tag{A10}$$

Inserting Eqs. (A8) and (A10) into Eq. (A9), we obtained

$$\begin{aligned}\langle C_{\mathrm{tr}}\rangle &= \frac{\langle k_{\mathrm{tr}}\rangle}{\langle k_{\mathrm{p}}\rangle} \\ &= \psi_1 \frac{r_1 f_1 C_{\mathrm{tr},11} + r_2 f_2 C_{\mathrm{tr},21}}{r_1 f_1^2 + r_2 f_2^2 + 2 f_1 f_2} + \psi_2 \frac{r_1 f_1 C_{\mathrm{tr},12} + r_2 f_2 C_{\mathrm{tr},22}}{r_1 f_1^2 + r_2 f_2^2 + 2 f_1 f_2}\end{aligned} \tag{A11}$$

It is reasonable to assume that k_{a} and k_{f} are independent of the terminal monomer unit of TP$_i$ considering that the reactive C═S bond is far from the monomer unit (i.e. $k_{\mathrm{a},12} = k_{\mathrm{a},11}$, $k_{\mathrm{a},21} = k_{\mathrm{a},22}$, $k_{\mathrm{f},12} = k_{\mathrm{f},11}$, $k_{\mathrm{f},21} = k_{\mathrm{f},22}$). We then have [14],

$$C_{\mathrm{tr},12} = k_{\mathrm{tr},12}/k_{\mathrm{p},11} = k_{\mathrm{a},11} k_{\mathrm{f},22}/\left(k_{\mathrm{f},11} + k_{\mathrm{f},22}\right)/k_{\mathrm{p},11} \tag{A12}$$

$$C_{\mathrm{tr},21} = k_{\mathrm{tr},21}/k_{\mathrm{p},22} = k_{\mathrm{a},22} k_{\mathrm{f},11}/\left(k_{\mathrm{f},11} + k_{\mathrm{f},22}\right)/k_{\mathrm{p},22} \tag{A13}$$

$$\frac{C_{\mathrm{tr},12}}{C_{\mathrm{tr},11}} + \frac{C_{\mathrm{tr},21}}{C_{\mathrm{tr},22}} = 2 \tag{A14}$$

In the RAFT homopolymerization, the chain transfer constant is determined only by the RAFT addition and propagation rate constants ($C_{\mathrm{tr}} = k_{\mathrm{d}}/2\, k_{\mathrm{p}}$). However, from Eqs. (A6), (A10)–(A13), in the case of RAFT copolymerization, the situation becomes very complicated. From Eqs. (A6), (A10)–(A13), it is clear that the apparent transfer coefficient is a function of monomer composition, reactivity ratios, and reaction constants (k_{p11}, k_{p22}, k_{a11}, k_{a22}, k_{f11}, k_{f22}) of their corresponding homopolymerization systems. If these parameters are available, we can calculate the apparent transfer coefficient using the terminal model. In addition, the fragmentation rate constants, which have no influence on the chain transfer constant in homopolymerization, play a role in determining the apparent transfer coefficient in the copolymerization.

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