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Kinetic study on reversible addition–fragmentation chain transfer (RAFT) process for block and random copolymerizations of styrene and methyl methacrylate

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Abstract

The degenerative (exchange) chain transfer constant C_{ex} was determined for the dithioacetate-mediated living radical block and random copolymerizations of styrene (St) and methyl methacrylate (MMA) at 40 °C. The addition of the polystyrene (PSt) radical to a polymer–dithioacetate adduct (P–X) to form the intermediate radical (PSt–(X$^\bullet$)–P) was (about twice) faster than that of the poly(methyl methacrylate) (PMMA) radical to form the intermediate radical PMMA–(X$^\bullet$)–P. The fragmentation (release) of the PMMA radical from the PSt–(X$^\bullet$)–PMMA intermediate formed at the initiating stage of block copolymerization was much (about 100 times) faster than the release of the PSt radical, explaining why the block copolymerization of MMA from a PSt–dithiocarbonate adduct is not so satisfactory as that of St from a PMMA–dithiocarbonate adduct. In the random copolymerization, there was implicit penultimate unit effect on the exchange chain transfer process, which appeared in the addition process but not in the fragmentation process.

Keywords: Living radical polymerization; Reversible addition–fragmentation chain transfer (RAFT); Copolymerization

1. Introduction

The dithioester-mediated living radical polymerization has attracted much attention as a robust and versatile synthetic route for well-defined polymers [1–3]. It is based on a reversible addition–fragmentation chain transfer (RAFT) process (Scheme 1(a)), which involves the addition of the propagating radical $P_A^\bullet$ to the dormant species P_B–X (rate constant $k_{adA\cdot B}$) to form the intermediate radical P_A–(X$^\bullet$)–P_B, followed by the fragmentation of the intermediate to release either $P_A^\bullet$ (rate constant $k_{frB\cdot A}$) or $P_B^\bullet$ (rate constant $k_{frA\cdot B}$). When $P_B^\bullet$ is released, a RAFT process, viewed as a degenerative chain transfer or exchange process (rate constant $k_{exA\cdot B}$) (Scheme 1(b)), is completed.

We previously determined k_{ex} for the homopolymerizations of styrene (St) with Z = methyl (CH_3) and phenyl (Ph) (Scheme 1(a)) and of methyl methacrylate (MMA) with Z = Ph [4]. The k_{ex} values for these systems were large enough to provide low-polydispersity polymers from an early stage of polymerization. The RAFT polymerization can provide not only homopolymers but also block and random copolymers with controlled structures [3,5,6]. To obtain a well-defined block copolymer, the synthetic order for the block formation (AB or BA block copolymerization) is often important. For example, the block copolymerization of MMA with a polystyrene (PSt)–dithioester (PSt–macroinitiator) is not so satisfactory as that of St with a poly(methyl methacrylate) (PMMA)–dithioester (PMMA–macroinitiator) [5]. This may be ascribed to a large difference in the exchange (initiation) rate for the two systems, but this is still to be confirmed experimentally. For random copolymerization, it has been established that the penultimate unit of P$^\bullet$ generally affects the propagation rate constant k_p and hence the polymerization rate [7–9]. The penultimate unit effect (PUE) also appears on chain transfer reactions [8,10–14]. Hence it would be interesting and important to study the PUE on the RAFT process. In these regards, we determined k_{ex} for the block and random

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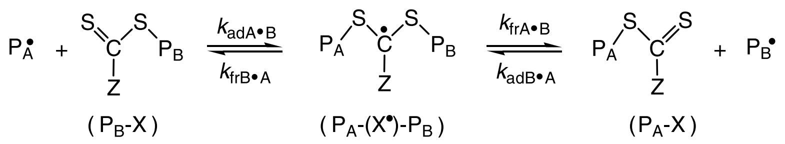
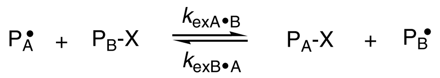
(a) RAFT ($Z = CH_3$ etc.)



(b) Degenerative (Exchange) Chain Transfer



Scheme 1. (a) RAFT and (b) degenerative (exchange) chain transfer.

copolymerizations of St and MMA with $Z = CH_3$ at 40 °C. Results were partly and briefly introduced in previous reviews [15,16]. In this paper, we will give full details along with discussion.

2. Definitions

2.1. Block copolymerization

In Scheme 1, P_A and P_B denote poly(A) and poly(B), respectively, where A and B are different monomers in this case. According to this scheme, $k_{exA \cdot B}$ can take the form [4]

$$k_{exA \cdot B} = P_{rB} k_{adA \cdot B} \tag{1}$$

where P_{rB} is the relative probability for P_A–($X^\cdot$)–P_B to release $P_B^\cdot$, given by

$$P_{rB} = \frac{k_{frA \cdot B}}{k_{frA \cdot B} + k_{frB \cdot A}} \tag{2}$$

(Eq. (1) assumes that the system is in a stationary state with respect to radical concentrations [16]). The exchange constant $C_{exA \cdot B}$ is defined by

$$C_{exA \cdot B} = \frac{k_{exA \cdot B}}{k_{pA}} \tag{3}$$

where k_{pA} is the propagation rate constant for $P_A^\cdot$ to react with monomer A.

2.2. Random (statistical) copolymerization

We consider the random (statistical) copolymerization of two monomers 1 and 2 (M_1 and M_2), which include two propagating radicals $P_1^\cdot$ and $P_2^\cdot$ with the terminal units 1 and 2, respectively. $P_1^\cdot$ reacts with M_1 and M_2 with the generalized rate constants $\bar{k}_{11}$ and $\bar{k}_{12}$, respectively, and reacts (exchanges) with P_B–X with the generalized rate constant $\bar{k}_{ex1 \cdot B}$ (we attach a bar '–' over those variables which can be a function of monomer composition and/or other variables [8]). Similarly, $P_2^\cdot$ reacts with M_1, M_2, and P_B–X with the rate constants $\bar{k}_{21}$, $\bar{k}_{22}$ and $\bar{k}_{ex2 \cdot B}$, respectively. The generalized monomer reactivity ratios are defined by $\bar{r}_1 = \bar{k}_{11}/\bar{k}_{12}$ and $\bar{r}_2 = \bar{k}_{22}/\bar{k}_{21}$.

The penultimate model distinguishes four propagating radicals $P_{ij}^\cdot$, where i and j denote the penultimate and terminal units, respectively (i, $j = 1$ or 2), and thus it is characterized by the eight propagation rate constants k_{ijk} for $P_{ij}^\cdot$ to react with monomer M_k ($k = 1$ or 2) and the four exchange rate constants $k_{exij \cdot B}$ for $P_{ij}^\cdot$ to undergo the exchange reaction with the adduct or dormant species P_B–X. The penultimate-model monomer reactivity ratios r_{ij} are defined by

$$r_{11} = \frac{k_{111}}{k_{112}} \tag{4a}$$

$$r_{21} = \frac{k_{211}}{k_{212}} \tag{4b}$$

$$r_{12} = \frac{k_{122}}{k_{121}} \tag{4c}$$

$$r_{22} = \frac{k_{222}}{k_{221}} \tag{4d}$$

and the radical reactivity ratios s_i are defined by

$$s_1 = \frac{k_{211}}{k_{111}} \tag{5a}$$

$$s_2 = \frac{k_{122}}{k_{222}} \tag{5b}$$

At this stage, we need to redefine P_A and P_B in Scheme 1 such that they are random copolymers characterized by these parameters. Hence the generalized exchange constant $\bar{C}_{exA \cdot B}$ is given, in terms of the penultimate model, by Eq. (6) with the reactivity ratio $\bar{r}_i$ given by Eq. (7) and the exchange constant $\bar{C}_{exi \cdot B}$ given by Eq. (8) with Eq. (9) [8]:

$$\bar{C}_{\mathrm{exA \cdot B}} = \frac{\bar{k}_{\mathrm{exA \cdot B}}}{\bar{k}_{\mathrm{pA}}} = \frac{\sum_{i,j} k_{\mathrm{ex}ij\cdot \mathrm{B}}\left[\mathrm{P}_{ij}^{\cdot}\right] / \sum_{i,j}\left[\mathrm{P}_{ij}^{\cdot}\right]}{\sum_{i,j,k} k_{ijk}\left[\mathrm{P}_{ij}^{\cdot}\right][\mathrm{M}_k] / \sum_{i,j}\left[\mathrm{P}_{ij}^{\cdot}\right] / \sum_k [\mathrm{M}_k]} = \frac{\bar{r}_1 f_1 \bar{C}_{\mathrm{ex1\cdot B}} + \bar{r}_2 f_2 \bar{C}_{\mathrm{ex2\cdot B}}}{\bar{r}_1 f_1^2 + \bar{r}_2 f_2^2 + 2 f_1 f_2} \tag{6}$$

$(i,\ j,\ k = 1 \text{ or } 2)$

$$\bar{r}_i = r_{ji}\frac{f_i r_{ii} + f_j}{f_i r_{ji} + f_j} \quad (j \neq i = 1 \text{ or } 2) \tag{7}$$

$$\bar{C}_{\mathrm{ex}i\cdot \mathrm{B}} = \frac{\bar{k}_{\mathrm{ex}i\cdot \mathrm{B}}}{\bar{k}_{ii}} = \frac{\left(k_{\mathrm{ex}ii\cdot \mathrm{B}}\left[\mathrm{P}_{ii}^{\cdot}\right] + k_{\mathrm{ex}ji\cdot \mathrm{B}}\left[\mathrm{P}_{ji}^{\cdot}\right]\right) / \left(\left[\mathrm{P}_{ii}^{\cdot}\right] + \left[\mathrm{P}_{ji}^{\cdot}\right]\right)}{\left(k_{iii}\left[\mathrm{P}_{ii}^{\cdot}\right] + k_{jii}\left[\mathrm{P}_{ji}^{\cdot}\right]\right) / \left(\left[\mathrm{P}_{ii}^{\cdot}\right] + \left[\mathrm{P}_{ji}^{\cdot}\right]\right)} = \frac{r_{ii} f_i C_{\mathrm{ex}ii\cdot \mathrm{B}} + f_j C_{\mathrm{ex}ji\cdot \mathrm{B}}}{r_{ii} f_i + f_j} \tag{8}$$

$(j \neq i = 1 \text{ or } 2)$

$$C_{\mathrm{ex}ij\cdot \mathrm{B}} = \frac{k_{\mathrm{ex}ij\cdot \mathrm{B}}}{k_{ijj}} \quad (i,\ j = 1 \text{ or } 2) \tag{9}$$

where f_1 and f_2 are the mole-compositions of the feed-monomers 1 and 2, respectively. When we specifically refer to the dormant species P_j–X and P_{ij}–X, we should replace the B appearing in these equations by j and ij, respectively.

In what follows, we will let 1 and 2 denote St and MMA, respectively. The k_{111} and k_{222} and the monomer and radical reactivity ratios have been evaluated at 40 °C [7,17], which are listed in Table 1. These parameters will be used in the following discussion. The PUE on propagation was found to be essentially implicit for this system [7], namely, the penultimate unit affects reactivity ($s_1 \neq 1$ and $s_2 \neq 1$) but not selectivity ($r_{11} = r_{21} (= \bar{r}_1 = r_1)$ and $r_{12} = r_{22} (= \bar{r}_2 = r_2)$) and hence affects k_p but not copolymer composition, where r_1 and r_2 refer to the terminal model.

Table 1
Propagation rate constants and the related reactivity ratios for the St (1) /MMA (2) system (40 °C)

Parameter	Value	Ref.
k_{111} ($\mathrm{M^{-1}\,s^{-1}}$)	160	[17]
k_{222} ($\mathrm{M^{-1}\,s^{-1}}$)	500	[17]
$r_{11} = r_{21} (= \bar{r}_1)$	0.52	[7]
$r_{12} = r_{22} (= \bar{r}_2)$	0.46	[7]
s_1	0.30	[7]
s_2	0.52	[7]

3. Experimental section

3.1. Materials

St (99%), MMA (99%), benzene (99.5%), azobis(isobutyronitrile) (AIBN, 98%), and benzoyl peroxide (BPO, 75% containing 25% water) were purchased from Nacalai Tesque (Japan) and purified by fractional distillation or recrystallization. 1-Phenylethyl dithioacetate and cumyl dithioacetate were prepared according to the CSIRO group [1].

3.2. Preparation of polymer–dithioacetate adducts

A St solution of 1-phenylethyl dithioacetate (17 mM) and BPO (10 mM) in a glass tube was degassed by several freeze–pump–thaw cycles, sealed off under vacuum, and heated at 60 °C for 3 h. After purification [18], a PSt–dithioacetate adduct (PSt–$\mathrm{SCSCH_3}$) was isolated. This polymer had the number- and weight-average molecular weights M_n and M_w of 1900 and 2300, respectively, ($M_\mathrm{w}/M_\mathrm{n}$ of 1.17) according to gel permeation chromatography (GPC). A chain extension test [19] showed that this polymer contains 6% ($f_\mathrm{dead} = 0.06$) of potentially inactive species (without dithioacetate moiety at the chain end). An MMA/benzene (3/1 v/v) solution of cumyl dithioacetate (280 mM) and AIBN (27 mM) was heated at 60 °C for 3 h. After purification, a PMMA–dithioacetate adduct (PMMA–$\mathrm{SCSCH_3}$) with $M_\mathrm{n} = 5500$, $M_\mathrm{w}/M_\mathrm{n} = 1.19$, and $f_\mathrm{dead} = 0.08$ was isolated.

3.3. Determination of C_{ex}

The polymer–dithioacetate adducts described above were used as probe polymers. A probe polymer (0.7 mM) and AIBN (30 mM) were dissolved in monomer (St and/or MMA), degassed, sealed off under vacuum, and heated at 40 °C for a prescribed time t. The reaction mixture was diluted with tetrahydrofran (THF) to a known concentration and analyzed by GPC. The experimental data shown below have been corrected for the inactive species mentioned above [4].

3.4. GPC

The analysis was made on a Shodex GPC-101 liquid chromatography (Tokyo, Japan) equipped with two Shodex KF-804L polystyrene mixed gel columns (300 × 8.0 mm; bead size = 7 μm; pore size = 20–200 Å). THF was used as eluent (40 °C) at a flow rare of 0.8 mL/min. The column system was calibrated with standard PSts. Sample detection and quantification were made with a Shodex differential refractometer RI-101 (equipped with tungsten lamp).

4. Results and discussion

4.1. Determination of k_{ex}

We carried out homopolymerizations and random copolymerization of St (1) and MMA (2) in the presence of PSt–SCSCH$_3$ (0.7 mM) or PMMA–SCSCH$_3$ (0.7 mM) as a probe adduct and AIBN (30 mM) as a radical initiator at 40 °C. The random copolymerization was carried out at the azeotropic composition ($f_1 = 0.53$). The k_{ex} was determined by GPC curve resolution [4,20,21]. When a probe adduct is activated to P$^\cdot$, the P$^\cdot$ will propagate until it is deactivated to give a new adduct. Since the probe and new adducts are generally different in chain length and its distribution, they may be distinguishable by GPC. By following the decay of the concentration I of the probe, k_{ex} can be determined from

$$\ln\left(\frac{I_0}{I}\right) = k_{ex}[\mathrm{P}^\cdot]t \tag{10}$$

where I_0 is the I at $t = 0$. Fig. 1 shows the GPC chromatograms for the random copolymerization in the presence of PSt–SCSCH$_3$, as an example. A lower I_0 would lead to a larger number of monomer units added to P$^\cdot$ during an activation–deactivation cycle [4]. In fact, with a sufficiently low I_0 (0.7 mM in this work), the chromatograms were composed of two peaks, allowing accurate resolution. The lower-molecular-weight component corresponds to the probe, and the higher-molecular-weight one corresponds to the new adduct and other minor species such as AIBN-initiated chains. (Since we injected a constant volume of sample (diluted to a known concentration) to the GPC system, we could follow the concentration I of the lower-molecular-weight component (probe) in an absolute scale (Fig. 1), not relative to that of the higher-molecular-weight component. In other words, the analysis was independent of the origins and amounts of the higher-molecular weight component [4,20,21]). Figs. 2 and 3 show the first-order plots of I and the monomer concentration [M], respectively, for the system in Fig. 1. Both plots were linear, from the slope of which we obtained $\bar{k}_{ex}[\mathrm{P}^\cdot] = 1.1 \times 10^{-4}\ \mathrm{s}^{-1}$ (Fig. 2) and $\bar{k}_p[\mathrm{P}^\cdot] = 1.5 \times 10^{-6}\ \mathrm{s}^{-1}$ (Fig. 3) and calculated $\bar{C}_{ex} = (\bar{k}_{ex}[\mathrm{P}^\cdot])/(\bar{k}_p[\mathrm{P}^\cdot])$ to be 75. We similarly obtained C_{ex} (or $\bar{C}_{ex}$) for the other systems. Table 2 lists the C_{ex} (or $\bar{C}_{ex}$) values. (For the activation of P–X, the contribution of the thermal homolysis of P–X was negligible for the present systems: we observed that the activation rate was approximately zero when [AIBN] and hence [P$^\cdot$] were zero.)

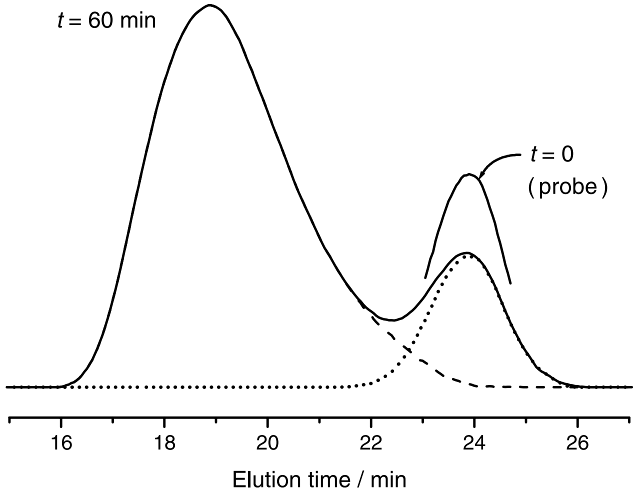


Fig. 1. Examples of GPC chromatograms for the random copolymerization of St (1) and MMA (2) with PSt–SCSCH$_3$ (probe) and AIBN (40 °C): $f_1 = 0.53$; [PSt–SCSCH$_3$]$_0 = 0.7$ mM; [AIBN]$_0 = 30$ mM. The dotted line represents the probe adduct and the broken line represents the new adduct formed after activation.

4.2. Homopolymerization

Referring to Eqs. (1)–(3) with A = B, we have

$$k_{adA\cdot A} = 2C_{exA\cdot A}k_{pA} \tag{11}$$

for homopolymerization. The results (Table 2), with the known k_p values (Table 1), show that $k_{ad11\cdot 11} = 70{,}000\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$ and $k_{ad22\cdot 22} = 40{,}000\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$ (in the penultimate model terminology, PSt and PMMA homopolymers can be expressed by 11 and 22, respectively). Since k_{ad} should not strongly depend on the polymer moiety of P–X, which is far apart from the C=S bond, we may consider that $k_{adA\cdot A} \approx k_{adA\cdot B}$ for any B polymer. Thus, the addition of PSt$^\cdot$ to a dithioacetate is about twice faster than that of PMMA$^\cdot$. To a dithiobenzoate (Z = Ph), the former is about 20 times faster than the latter, as previously reported [4]. The selectivity for $\mathrm{P}_A^\cdot$ to add to P–X relative to M$_A$ is given by $k_{adA\cdot A}/k_{pA}$ ($= 2C_{exA\cdot A}$), which is about six times larger in the St system than in the MMA system (Table 2).

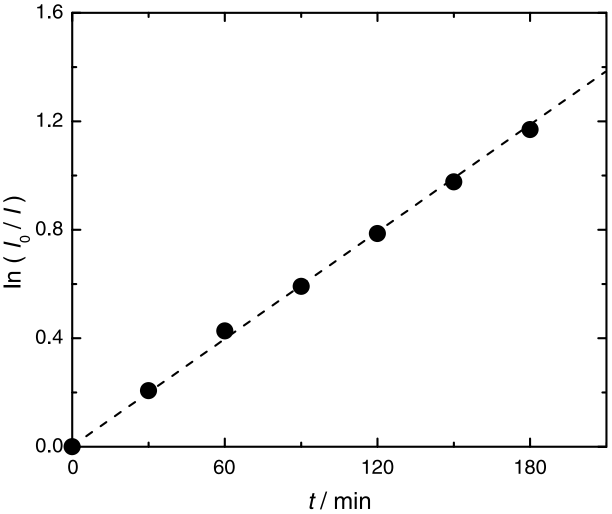


Fig. 2. Plot of $\ln(I_0/I)$ vs t for the system in Fig. 1.

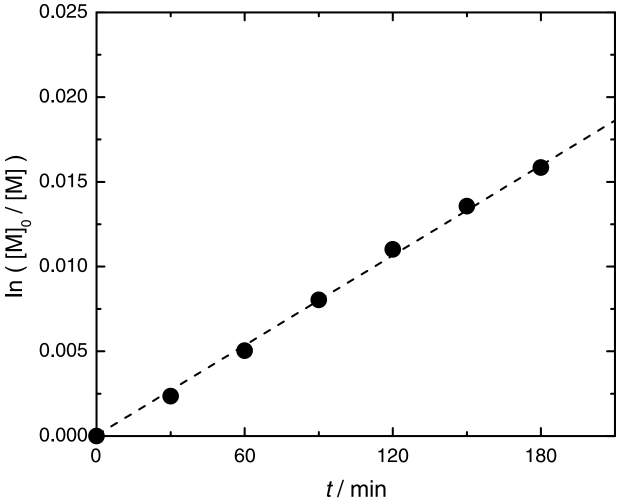


Fig. 3. Plot of $\ln([M]_0/[M])$ vs t for the system in Fig. 1.

4.3. Block copolymerization

When $A \neq B$, Eqs. (1)–(3) yield

$$\frac{C_{\mathrm{exA}\cdot\mathrm{B}}}{C_{\mathrm{exA}\cdot\mathrm{A}}} = 2P_{\mathrm{rB}}\left(\frac{k_{\mathrm{adA}\cdot\mathrm{B}}}{k_{\mathrm{adA}\cdot\mathrm{A}}}\right) \tag{12}$$

The results (Table 2) show that $C_{\mathrm{ex}11\cdot 22}/C_{\mathrm{ex}11\cdot 11} = 1.9$. We may assume that $k_{\mathrm{ad}11\cdot 22}/k_{\mathrm{ad}11\cdot 11} \sim 1$ (see above). Hence we estimate that $P_{\mathrm{r}22}$ $(= 1 - P_{\mathrm{r}11} = k_{\mathrm{fr}11\cdot 22}/(k_{\mathrm{fr}11\cdot 22} + k_{\mathrm{fr}22\cdot 11})) \sim 0.95$. This estimate is supported by the other set of experimental data showing that $C_{\mathrm{ex}22\cdot 11}/C_{\mathrm{ex}22\cdot 22} = 0.02$, from which we estimate that $P_{\mathrm{r}11} \sim 0.01$ or $P_{\mathrm{r}22} = 1 - P_{\mathrm{r}11} \sim 0.99$. In both cases, fragmentation of the intermediate P_{11}–$(X^{\bullet})$–P_{22} predominantly occurs by releasing $P_{22}^{\bullet}$ (PMMA$^{\bullet}$) rather than $P_{11}^{\bullet}$ (PSt$^{\bullet}$). This, along with the slower addition of PMMA$^{\bullet}$ than PSt$^{\bullet}$ to the dithioacetate (see above), explains why the polymerization (block copolymerization) of MMA with a PSt–dithiocarbonate macroinitiator is not so satisfactory as that of St with a PMMA macroinitiator. Chong et al. determined the C_{ex} for PMMA$^{\bullet}$ to the low-mass (unimer) model dithiobenzoates of PSt and PMMA to be 0.15 and 1.7, respectively (60 °C) [22]. Although the unimer values are not quantitatively applicable to polymers (hence block copolymerization) due to possibly strong chain length dependence of C_{ex} [16], the tendency observed for the C_{ex} (0.15 vs 1.7) to the low-mass homologues qualitatively agrees with the present result with the polymer system (0.83 vs 40 (Table 2)).

For a batch block copolymerization, we can calculate the (remaining) macroinitiator concentration I at a given conversion (fractional conversion c) by [23]

$$\ln\left(\frac{I_0}{I}\right) = C_{\mathrm{exA}\cdot\mathrm{B}} \ln\left(\frac{1}{1-c}\right) \tag{13}$$

With $C_{\mathrm{ex}11\cdot 22} = 420$ and $C_{\mathrm{ex}22\cdot 11} = 0.83$ (Table 2), we estimate that the PMMA macroinitiator in St is half consumed at the conversion of 0.16%, while the PSt macroinitiator in MMA is half consumed much later, at a 57% conversion.

4.4. Random copolymerization

Table 2 shows that, for a given polymer–dithioacetate adduct P–X, the C_{ex} of PMMA$^{\bullet}$ is more than one order of magnitude smaller than that of PSt$^{\bullet}$. This means that the $\bar{C}_{\mathrm{ex}}$ values observed for the copolymer radical predominantly reflect those of $P_1^{\bullet}$. Namely, since $\bar{C}_{\mathrm{ex}2\cdot\mathrm{B}} \ll \bar{C}_{\mathrm{ex}1\cdot\mathrm{B}}$ and $\bar{r}_1 f_1 \approx \bar{r}_2 f_2$, the $\bar{C}_{\mathrm{ex}2\cdot\mathrm{B}}$ term in Eq. (6) is relatively so small that $\bar{C}_{\mathrm{ex}2\cdot\mathrm{B}}$ may be approximated by $C_{\mathrm{ex}22\cdot\mathrm{B}}$, whether there is PUE in $\bar{C}_{\mathrm{ex}2\cdot\mathrm{B}}$ or not.

Then, from the data for PSt–X ($\bar{C}_{\mathrm{exA}\cdot 11} = 75$ and $C_{\mathrm{ex}22\cdot 11} = 0.83$) with Eq. (6), we have $\bar{C}_{\mathrm{ex}1\cdot 11} = 200$. With this value and the $C_{\mathrm{ex}11\cdot 11}$ value of 220 (Table 1) applied to Eq. (8), we estimate that $C_{\mathrm{ex}21\cdot 11}/C_{\mathrm{ex}11\cdot 11} = 0.9$, namely, $C_{\mathrm{ex}21\cdot 11} \approx C_{\mathrm{ex}11\cdot 11}$. In a similar way, from the data for PMMA–X ($\bar{C}_{\mathrm{exA}\cdot 22} = 155$, $C_{\mathrm{ex}22\cdot 22} = 40$, and $C_{\mathrm{ex}11\cdot 22} = 420$), we estimate that $C_{\mathrm{ex}21\cdot 22}/C_{\mathrm{ex}11\cdot 22} = 0.9$, namely, $C_{\mathrm{ex}21\cdot 22} \approx C_{\mathrm{ex}11\cdot 22}$. These give the following relation:

$$s_1 = \frac{k_{211}}{k_{111}} \approx \frac{k_{\mathrm{ex}21\cdot 11}}{k_{\mathrm{ex}11\cdot 11}} \approx \frac{k_{\mathrm{ex}21\cdot 22}}{k_{\mathrm{ex}11\cdot 22}} \tag{14}$$

We should remember that the s_1 in this system was evaluated to be 0.30 [7]. This means that PUE exists in the RAFT process and it is implicit (the penultimate unit affects reactivity (k_{ex}) but not selectivity ($k_{\mathrm{ex}}/k_{\mathrm{p}}$)). The implicit nature can be more directly seen in Table 2, where the observed $\bar{C}_{\mathrm{ex}}$ (random) values are nearly equal to the values in parenthesis which were calculated with the terminal model ($\bar{C}_{\mathrm{ex}1\cdot\mathrm{B}} = C_{\mathrm{ex}11\cdot\mathrm{B}}$ and $\bar{C}_{\mathrm{ex}2\cdot\mathrm{B}} = C_{\mathrm{ex}22\cdot\mathrm{B}}$). This result is in line with the fact that the chain transfer reactions of a majority of systems are under the influence of implicit PUE [8,10–12,24,25], and only a minority of systems, e.g. those with CBr_4 [10,26] and CCl_4 [26] used as a chain transfer agent, are explicit, i.e. exhibit PUE on chain transfer constant.

Table 2
Values of C_{ex} (or $\bar{C}_{\mathrm{ex}}$) for X = dithioacetate (40 °C)

	PSt$^{\bullet}$	PMMA$^{\bullet}$	Copolymer$^{\bullet a}$
PSt–X	$C_{\mathrm{ex}11\cdot 11} = 220$	$C_{\mathrm{ex}22\cdot 11} = 0.83$	$\bar{C}_{\mathrm{exA}\cdot 11} = 75$ (82^{b})
PMMA–X	$C_{\mathrm{ex}11\cdot 22} = 420$	$C_{\mathrm{ex}22\cdot 22} = 40$	$\bar{C}_{\mathrm{exA}\cdot 22} = 155$ (167^{b})

[a] Random copolymer radical $P_A^{\bullet}$ with $f_1 = 0.53$ (azeotropic composition).
[b] Terminal-model value.

Another important implication of the approximate relation in Eq. (14) is that PUE exists in the addition process but not in the fragmentation process: the PUE on addition ($k_{\mathrm{ad21\cdot B}}/k_{\mathrm{ad11\cdot B}}$) affects both $k_{\mathrm{ex21\cdot 11}}/k_{\mathrm{ex11\cdot 11}}$ and $k_{\mathrm{ex21\cdot 22}}/k_{\mathrm{ex11\cdot 22}}$ ratios, while the PUE on fragmentation ($k_{\mathrm{frA\cdot 21}}/k_{\mathrm{frA\cdot 11}}$), if any present, affects the former but little affects the latter, since the fragmentation of $\mathrm{P}_{22}^{\cdot}$ (PMMA$^{\cdot}$) is predominant over those of $\mathrm{P}_{21}^{\cdot}$ and $\mathrm{P}_{11}^{\cdot}$ (PSt$^{\cdot}$ homologues). The approximate equality in Eq. (14), therefore, suggests the absence of significant PUE on fragmentation. (Namely, $k_{\mathrm{ad21\cdot B}}/k_{\mathrm{ad11\cdot B}} \approx 0.3$ and $k_{\mathrm{frA\cdot 21}}/k_{\mathrm{frA\cdot 11}} \approx 1$.)

Based on these results, we can estimate the $\bar{C}_{\mathrm{ex}}$ for the actual random copolymerization where *both* P$^{\cdot}$ and P–X are random copolymer. In such a system, $\bar{C}_{\mathrm{ex}}$ depends on the composition (near the chain end) of P–X as well as P$^{\cdot}$. For the present system, since PUE is approximately absent on fragmentation, the penultimate unit of P–X should not significantly affect $\bar{C}_{\mathrm{ex}}$. Hence we may consider only the terminal unit of P–X. Then, referring to Eq. (6), we have the $\bar{C}_{\mathrm{ex}}$ as

$$\bar{C}_{\mathrm{ex}} = \frac{\bar{k}_{\mathrm{ex}}}{\bar{k}_{\mathrm{p}}} = \frac{\sum_{i,j,l} k_{\mathrm{ex}ij\cdot l}\left[\mathrm{P}_{ij}^{\cdot}\right][\mathrm{P}_l\text{–X}]/\sum_{i,j}\left[\mathrm{P}_{ij}^{\cdot}\right]/\sum_l[\mathrm{P}_l\text{–X}]}{\sum_{i,j,k} k_{ijk}\left[\mathrm{P}_{ij}^{\cdot}\right][\mathrm{M}_k]/\sum_{i,j}\left[\mathrm{P}_{ij}^{\cdot}\right]/\sum_k[\mathrm{M}_k]}$$

$$(i,\ j,\ k,\ l = 1 \text{ or } 2) \qquad (15)$$

$$= f_{\mathrm{P_1\text{–}X}}\frac{\bar{r}_1 f_1 \bar{C}_{\mathrm{ex1\cdot 1}} + \bar{r}_2 f_2 \bar{C}_{\mathrm{ex2\cdot 1}}}{\bar{r}_1 f_1^2 + \bar{r}_2 f_2^2 + 2 f_1 f_2} + f_{\mathrm{P_2\text{–}X}}\frac{\bar{r}_1 f_1 \bar{C}_{\mathrm{ex1\cdot 2}} + \bar{r}_2 f_2 \bar{C}_{\mathrm{ex2\cdot 2}}}{\bar{r}_1 f_1^2 + \bar{r}_2 f_2^2 + 2 f_1 f_2}$$

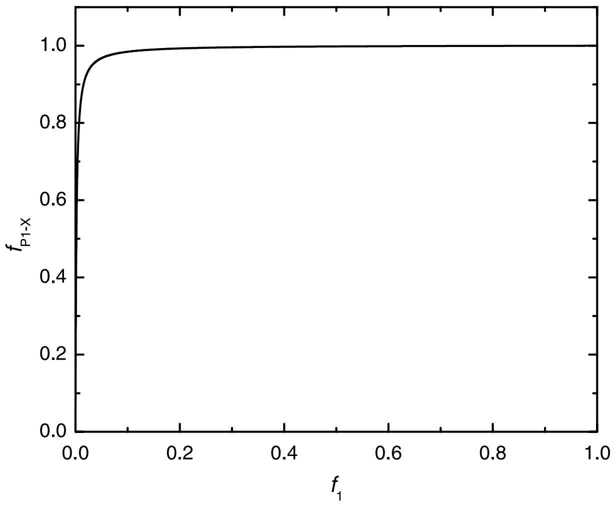


Fig. 4. The $f_{\mathrm{P_1\text{–}X}}$ as a function of f_1 calculated from Eq. (21) for the dithioacetate-mediated random copolymerization of St (1) and MMA (2) (40 °C).

where $f_{\mathrm{P_1\text{–}X}}$ and $f_{\mathrm{P_2\text{–}X}}$ are the mole-fractions of P$_1$–X and P$_2$–X, respectively. The $f_{\mathrm{P_1\text{–}X}}$ and $f_{\mathrm{P_2\text{–}X}}$ in this equation can be estimated as follows. When the polymerization is in the stationary state, the following equations should hold with respect to P–X and P$^{\cdot}$:

$$0 = \frac{\mathrm{d}[\mathrm{P_1\text{–}X}]}{\mathrm{d}t} = \frac{-\mathrm{d}[\mathrm{P_2\text{–}X}]}{\mathrm{d}t} = \bar{k}_{\mathrm{ex1\cdot 2}}\left[\mathrm{P}_1^{\cdot}\right][\mathrm{P_2\text{–}X}] - \bar{k}_{\mathrm{ex2\cdot 1}}\left[\mathrm{P}_2^{\cdot}\right][\mathrm{P_1\text{–}X}] \qquad (16)$$

$$0 = \frac{\mathrm{d}\left[\mathrm{P}_1^{\cdot}\right]}{\mathrm{d}t} = \frac{-\mathrm{d}\left[\mathrm{P}_2^{\cdot}\right]}{\mathrm{d}t} = \bar{k}_{21}\left[\mathrm{P}_2^{\cdot}\right][\mathrm{M}_1] - \bar{k}_{12}\left[\mathrm{P}_1^{\cdot}\right][\mathrm{M}_2] - \bar{k}_{\mathrm{ex1\cdot 2}}\left[\mathrm{P}_1^{\cdot}\right][\mathrm{P_2\text{–}X}] + \bar{k}_{\mathrm{ex2\cdot 1}}\left[\mathrm{P}_2^{\cdot}\right][\mathrm{P_1\text{–}X}] \qquad (17)$$

Eq. (16) gives

$$\frac{[\mathrm{P_1\text{–}X}]}{[\mathrm{P_2\text{–}X}]} = \frac{f_{\mathrm{P_1\text{–}X}}}{f_{\mathrm{P_2\text{–}X}}} = \frac{\bar{k}_{\mathrm{ex1\cdot 2}}}{\bar{k}_{\mathrm{ex2\cdot 1}}}\frac{\left[\mathrm{P}_1^{\cdot}\right]}{\left[\mathrm{P}_2^{\cdot}\right]} \qquad (18)$$

Eqs. (16) and (17) give

$$\frac{\left[\mathrm{P}_1^{\cdot}\right]}{\left[\mathrm{P}_2^{\cdot}\right]} = \frac{\bar{r}_1 \bar{k}_{22} f_1}{\bar{r}_2 \bar{k}_{11} f_2} \qquad (19)$$

as in the conventional (dithioester-free) system, where $\bar{k}_{ii}$ is given by [7]

$$\bar{k}_{ii} = k_{iii}\frac{r_{ii} f_i + f_j}{r_{ii} f_i + (f_j/s_i)} \quad (j \neq i = 1 \text{ or } 2) \qquad (20)$$

With Eqs. (18) and (19), we have the ratio $f_{\mathrm{P_1\text{–}X}}/f_{\mathrm{P_2\text{–}X}}$ by

$$\frac{f_{\mathrm{P_1\text{–}X}}}{f_{\mathrm{P_2\text{–}X}}} = \frac{\bar{C}_{\mathrm{ex1\cdot 2}}\bar{r}_1 f_1}{\bar{C}_{\mathrm{ex2\cdot 1}}\bar{r}_2 f_2} \qquad (21)$$

Figs. 4 and 5 (solid line) show the $f_{\mathrm{P_1\text{–}X}}$ (Eq. (21)) and the $\bar{C}_{\mathrm{ex}}$ (Eq. (15)) as a function of f_1, respectively, calculated with the known $\bar{r}_1$ and $\bar{r}_2$ (Table 1) and the relation that $\bar{C}_{\mathrm{ex}i\cdot j} = C_{\mathrm{ex}ii\cdot jj}$ (implicit PUE) (Table 2). Fig. 4 indicates that $f_{\mathrm{P_1\text{–}X}}$ rapidly increases with increasing f_1 and exceeds 0.99 even at $f_1 = 0.15$, which is due to the slow exchange of $\mathrm{P}_2^{\cdot}$ with P$_1$–X (see above). Therefore, when $f_1 \geq 0.15$, the $\bar{C}_{\mathrm{ex}}$ will predominantly be determined by the $f_{\mathrm{P_1\text{–}X}}$ term in Eq. (15), as shown in Fig. 5, where the broken and dotted lines represent the calculated $f_{\mathrm{P_1\text{–}X}}$ and $f_{\mathrm{P_2\text{–}X}}$ terms, respectively. Namely, in this range of f_1, the $\bar{C}_{\mathrm{ex}}$ in the actual polymerization may be approximated by the $\bar{C}_{\mathrm{ex}}$ to P$_1$–X. Fig. 5 also suggests that the $\bar{C}_{\mathrm{ex}}$ in the actual polymerization increases with f_1 (after initial sharp decrease until $f_1 = 0.02$). Since large C_{ex} is a requisite to produce a low-polydispersity polymer by the RAFT process [4,16], the mentioned result indicates that the polydispersity control in St–MMA random copolymerization becomes better with increasing f_{St} (for $f_{\mathrm{St}} \geq 0.02$).

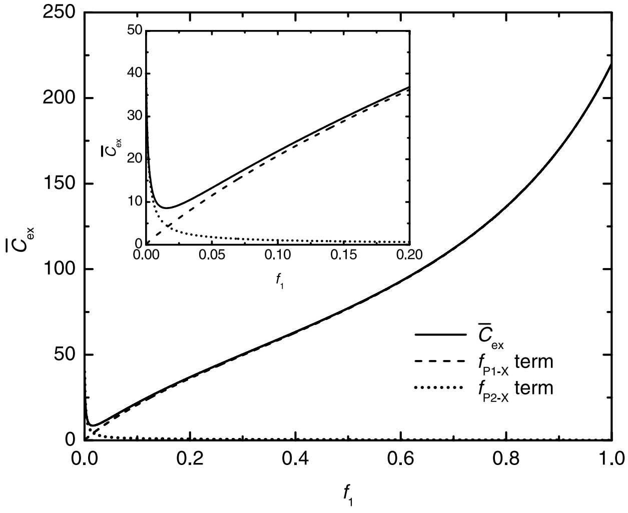


Fig. 5. The $\bar{C}_{ex}$ as a function of f_1 for the system in Fig. 4. The solid line shows the $\bar{C}_{ex}$ calculated from Eq. (15), the broken line shows the f_{P_1-X} term in Eq. (15), and the dotted line shows the f_{P_2-X} term in Eq. (15).

5. Conclusions

The C_{ex} was determined for systems related to St, MMA, and dithioacetate at 40 °C. The addition of PSt$^{\cdot}$ to a polymer–dithioacetate adduct was faster than that of PMMA$^{\cdot}$ to the same adduct. The fragmentation of PMMA$^{\cdot}$ from PSt–(X$^{\cdot}$)–PMMA was much faster than that of PSt$^{\cdot}$. These (mainly the latter) explain why the block copolymerization of MMA from a PSt–dithiocarbonate macroinitiator is not so satisfactory as that of St from a PMMA–dithiocarbonate macroinitiator. In the random copolymerization, there was PUE on the RAFT process, which appeared in the addition process but not significantly in the fragmentation process. The PUE was implicit, namely, the terminal model was formally valid to describe the exchange constant $\bar{C}_{ex} = \bar{k}_{ex}/\bar{k}_p$.

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