## Supporting information

# Toward Understanding of Branching in RAFT Copolymerization of Methyl Methacrylate through a Cleavable Dimethacrylate 

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Figure 1S. GPC traces of b-PMMA samples collected at different monomer conversions in Run 7
(a) $90^{\circ}$ light scattering (LS) detector and (b) refractive index (RI) detector


Figure 2S. GPC traces of b-PMMA sample at $99.6 \%$ conversion in Run 7 after cleavage acquired at $90^{\circ}$
LS detector (LS90), RI detector, and intrinsic viscosity (DP) detector.


Figure 3S. ${ }^{1} \mathrm{H}$ NMR spectra of b-PMMA sample at $42.1 \%$ conversion in Run 5 (a) before and (b) after cleavage

## Model Development for RAFT Copolymerization of Vinyl/Divinyl Monomer System with Branching

The equations and kinetic parameters are listed as follows. The details for the model development can also be seen in Ref S1.

## Polymerization scheme and kinetic equations

The elementary reactions of RAFT batch copolymerization of vinyl/divinyl monomer system are showed in Table 1S.

Table 1S. Elementary Reactions of RAFT Copolymerization of Vinyl/Divinyl Monomer System

| Initiation | $I \xrightarrow{f, k_{d}} 2 P_{0,1,0}$ |
| :---: | :---: |
|  | $P_{0,1,0}+M_{i} \xrightarrow{k_{p, i}} P_{1,1,0}$ |
| Propagation with comonomer | $P_{n, r, c}+M_{i} \xrightarrow{k_{p, i}} P_{n+1, r, c}$ |
| Transfer to RAFT species | $P_{n, r, c}+P_{m, s, d} \xrightarrow{r d k_{r r r}} P_{n, r-1, c+1}+P_{m, s+1, d-1}$ |
| Termination by disproportionation | $P_{n, r, c}+P_{m, s, d} \xrightarrow{r s k_{d, d}} P_{n, r-1, c}+P_{m, s-1, d}$ |
| Termination by recombination | $P_{n, r, c}+P_{m, s, d} \xrightarrow{r s k_{c c}} P_{n+m, r+s-2, c+d}$ |
| intermolecular cross-linking | $P_{n, r, c}+P_{m, s, d} \xrightarrow{r m k_{\text {inter }}} P_{n+m, r+s, c+d}$ |
| intramolecular cross-linking | $P_{n, r, c} \xrightarrow{r m k_{\text {intra }}} P_{n, r, c}$ |

Herein, $P_{n, r, c}$ denotes the macromolecule containing $n$ monomeric units, $r$ radical centers and $c$ RAFT moieties. $I$ and $M_{i}$ represent conventional initiator and monomer $i$, respectively. $M_{1}$ is vinyl monomer MMA and $M_{2}$ is divinyl monomer BMAODS.

The kinetic parameters (or pseudokinetic rate constants ${ }^{\text {S1 }}$ ) listed in Table 1S are the functions of radical fractions, $\phi_{i}$, which can be calculated by the instantaneous monomer composition, $f_{i}$. So the pseudo rate constants can be expressed as

$$
\begin{gather*}
k_{p, i}=\sum_{j} k_{p, j i} \phi_{j}  \tag{1a}\\
k_{t r}=\sum_{j} k_{t r, j} \phi_{j}  \tag{1b}\\
k_{t}=\sum_{i} \sum_{j} k_{t, i j} \phi_{i} \phi_{j}  \tag{1c}\\
k_{\text {inter }}=\sum_{j} k_{\text {inter }, j}^{*} \phi_{j}\left(\overline{F_{2}}-\bar{C}-\bar{D}\right)  \tag{1d}\\
k_{\text {intraa }}=\sum_{j} k_{\text {int } r a, j}^{*} \phi_{j}\left(\overline{F_{2}}-\bar{C}-\bar{D}\right) \tag{1f}
\end{gather*}
$$

where $\overline{F_{2}}$ is the divinyl density in the total copolymer, $\bar{C}$ is the intermolecular cross-linkage density, and $\bar{D}$ is the intramolecular cross-linkage density.

Based on elementary reactions, the population balance for $P_{n, r, c}$ is

$$
\begin{align*}
\frac{d P_{n, r, c}}{d t}= & \sum_{i} r k_{p, i} M_{i} P_{n-1, r, c}-\sum_{i} r k_{p, i} M_{i} P_{n, r, c} \\
& +\sum_{m=0}^{\infty} \sum_{s=0}^{\infty} \sum_{d=1}^{\infty}(r+1) d k_{t r} P_{n, r+1, c-1} P_{m, s, d}-\sum_{m=0}^{\infty} \sum_{s=0}^{\infty} \sum_{d=1}^{\infty} r d k_{t r} P_{n, r, c} P_{m, s, d} \\
& +\sum_{m=0}^{\infty} \sum_{s=1}^{\infty} \sum_{d=0}^{\infty} s(c+1) k_{t r} P_{n, r-1, c+1} P_{m, s, d}-\sum_{m=0}^{\infty} \sum_{0}^{\infty} \sum_{s=1}^{\infty} s c k_{t r} P_{n, r, c} P_{m, s, d} \\
& +\sum_{m=0}^{\infty} \sum_{s=1}^{\infty} \sum_{d=0}^{\infty}(r+1) s k_{t d} P_{n, r+1, c} P_{m, s, d}-\sum_{m=0}^{\infty} \sum_{s=1}^{\infty} \sum_{d=0}^{\infty} r s k_{t d} P_{n, r, c} P_{m, s, d} \\
& +\frac{1}{2} \sum_{m=0}^{n} \sum_{s=1}^{r+1} \sum_{d=0}^{\infty}(r+2-s) s k_{t c} P_{m, s, d} P_{n-m, r+2-s, c-d}-\sum_{m=0}^{\infty} \sum_{s=1}^{\infty} \sum_{d=0}^{\infty} r s k_{t c} P_{n, r, c} P_{m, s, d} \\
& +\sum_{m=0}^{n} \sum_{s=0}^{r} \sum_{d=0}^{c} s(n-m) k_{p, \text { inter }} P_{m, s, d} P_{n-m, r-s, c-d}-\sum_{m=0}^{\infty} \sum_{s=0}^{\infty} \sum_{d=0}^{\infty} r m k_{p, \text { inter }} P_{n, r, c} P_{m, s, d} \\
& -\sum_{m=0}^{\infty} \sum_{s=1}^{\infty} \sum_{d=0}^{\infty} s n k_{p, \text { inter }} P_{n, r, c} P_{m, s, d} \tag{2}
\end{align*}
$$

## Method of moments

The moments of $P_{n, r, c}$ are defined as

$$
\begin{equation*}
Y_{i, j, k}=\sum_{n=0}^{\infty} \sum_{r=0}^{\infty} \sum_{c=0}^{\infty} n^{i} r^{j} c^{k} P_{n, r, c} \tag{3}
\end{equation*}
$$

A complete set of moment equations can be derived as summarized in Table 2S.

Table 2S. Different Moment Equations

| zeroth-order moments | $\frac{d Y_{0,0,0}}{d t}=2 f k_{d}[I]-\frac{1}{2} k_{t c} Y_{0,1,0}^{2}-k_{p, \text { inter }} Y_{1,0,0} Y_{0,1,0}$ |
| :--- | :--- |
| first-order moments | $\frac{d Y_{1,0,0}}{d t}=\sum_{i} k_{p, i} M_{i} Y_{0,1,0}$ |
| $\frac{d Y_{0,1,0}}{d t}=2 f k_{d}[I]-k_{t d} Y_{0,1,0}^{2}-k_{t c} Y_{0,1,0}^{2}$ |  |
| $\frac{d Y_{0,0,1}}{d t}=0$ |  |

$$
\text { second-order moments } \begin{aligned}
\frac{d Y_{2,0,0}}{d t}= & 2 \sum_{i} k_{p, i} M_{i} Y_{1,1,0}+\sum_{i} k_{p, i} M_{i} Y_{0,1,0}+k_{t c} Y_{1,1,0}^{2} \\
& +2 k_{p, \text { inter }} Y_{1,1,0} Y_{2,0,0} \\
\frac{d Y_{0,2,0}}{d t}= & 2 f k_{d}[I]-2 k_{t d} Y_{0,2,0} Y_{0,1,0}+k_{t d} Y_{0,1,0}^{2} \\
& +2 k_{t c} Y_{0,1,0}^{2}-4 k_{t c} Y_{0,2,0} Y_{0,1,0}+k_{t c} Y_{0,2,0}^{2} \\
& -2 k_{t r} Y_{0,2,0} Y_{0,0,1}+2 k_{t r} Y_{0,1,0} Y_{0,0,1}+2 k_{t r} Y_{0,1,1} I_{0,1,0} \\
& +2 k_{p, \text { inter }} Y_{0,2,0} Y_{1,1,0} \\
\frac{d Y_{0,0,2}}{d t}= & k_{t c} Y_{0,1,1}^{2}-2 k_{t r} Y_{0,0,2} Y_{0,1,0}+2 k_{t r} Y_{0,1,1} Y_{0,0,1}+2 k_{t r} Y_{0,1,0} Y_{0,0,1} \\
& +2 k_{p, \text { inter }} Y_{0,1,1} Y_{1,0,1} \\
\frac{d Y_{1,1,0}}{d t}= & \sum_{i} k_{p, i} M_{i} Y_{0,2,0}-k_{t d} Y_{1,1,0} Y_{0,1,0}+k_{t c} Y_{1,1,0} Y_{0,2,0}-2 k_{t c} Y_{1,1,0} Y_{0,1,0} \\
& -k_{t r} Y_{1,1,0} Y_{0,0,1}+k_{t r} Y_{1,0,1} Y_{0,1,0}+k_{p, \text { inter }} Y_{2,0,0} Y_{0,2,0}+k_{p, \text { inter }} Y_{1,1,0}^{2} \\
\frac{d Y_{1,0,1}}{d t}= & \sum_{i} k_{p, i} M_{i} Y_{0,1,1}+k_{t c} Y_{1,1,0} Y_{0,1,1}+k_{t r} Y_{1,1,0} Y_{0,0,1}-k_{t r} Y_{1,0,1} Y_{0,1,0} \\
& +k_{p, \text { inter }} Y_{2,0,0} Y_{0,1,1}+k_{p, \text { inter }} Y_{1,1,0} Y_{1,0,1} \\
\frac{d Y_{0,1,1}}{d t}= & -k_{t d} Y_{0,1,1} Y_{0,1,0}+k_{t c} Y_{0,1,1} Y_{0,2,0}-2 k_{t c} Y_{0,1,1} Y_{0,1,0}+k_{t r} Y_{0,2,0} Y_{0,0,1} \\
& +k_{t r} Y_{0,0,2} Y_{0,1,0}-k_{t r} Y_{0,1,1} Y_{0,0,1}-k_{t r} Y_{0,1,1} Y_{0,1,0}-2 k_{t r} Y_{0,1,0} Y_{0,0,1} \\
& +k_{p, \text { inter }} Y_{0,1,1} Y_{1,1,0}+k_{p, \text { inter }} Y_{0,2,0} Y_{1,0,1}
\end{aligned}
$$

intermolecular
cross-linkage

$$
\frac{d[C]}{d t}=k_{p, \text { inter }} Y_{0,1,0} Y_{1,0,0}
$$

intramolecular
cross-linkage

$$
\frac{d[D]}{d t}=k_{p, \text { int } r a} Y_{1,1,0}
$$

pendant double bond
$\frac{d[P]}{d t}=k_{p, 2} Y_{0,1,0}\left[M_{2}\right]-\frac{d[C]}{d t}-\frac{d[D]}{d t}$
small molecules
initiator: $\frac{d[I]}{d t}=-k_{d}[I]$
monomer: $\frac{d\left[M_{i}\right]}{d t}=-k_{p, i} Y_{0,1,0}\left[M_{i}\right]$
polymerization volume

$$
\frac{d V}{d t}=-\sum_{i=1}^{2} m_{i} R_{p, i}\left(\frac{1}{\rho_{i}}-\frac{1}{\rho_{p}}\right) V
$$

The chain properties can be described within the above definitions as shown in Table 3S.

Table 3S. Definition of Important Chain Structural Properties

| chain property | Expression |
| :---: | :---: |
| number-average chain length | $r_{n}=\frac{Y_{1,0,0}}{Y_{0,0,0}}$ |
| weight-average chain length | $r_{w}=\frac{Y_{2,0,0}}{Y_{1,0,0}}$ |
| polydispersity index | $P D I=\frac{r_{w}}{r_{n}}$ |
| divinyl density in copolymer* | $\bar{F}_{2}=\frac{n_{20}-n_{2}}{n_{10}-n_{1}+n_{20}-n_{2}}$ |
| intermolecular cross-linkage density | $\bar{C}=\frac{C}{Y_{1,0,0}}$ |
| intramolecular cross-linkage density | $\bar{D}=\frac{D}{Y_{1,0,0}}$ |
| number-average molecular weight** | $M_{n}=r_{n} \times\left[\overline{F_{2}} \times m_{2}+\left(1-\overline{F_{2}}\right) \times m_{1}\right]$ |
| branching density | $B D=1000 \times \frac{C \times V}{n_{10}-n_{1}+2\left(n_{20}-n_{2}\right)}$ |
| cyclization density | $C D=1000 \times \frac{D \times V}{n_{10}-n_{1}+2\left(n_{20}-n_{2}\right)}$ |
| branching frequency | $B F=\frac{M_{n}}{m_{1}} \times \frac{B D}{1000}$ |
| cyclization frequency | $C F=\frac{M_{n}}{m_{1}} \times \frac{C D}{1000}$ |

* $\mathrm{n}_{10}$ and $\mathrm{n}_{20}$ are initial mole number of vinyl and divinyl monomers, respectively. $\mathrm{n}_{1}, \mathrm{n}_{2}$ are mole number of unreacted vinyl and divinyl monomers, respectively
${ }^{* *} \mathrm{~m}_{1}$ and $\mathrm{m}_{2}$ are molecular weight of vinyl and divinyl monomers, respectively.

The kinetic parameters at $70^{\circ} \mathrm{C}$ are summarized in Table 4S
Table 4S. Kinetic Rate Constants in RAFT Copolymerization of MMA/BMAODS

| Parameter Description | Value | Reference |
| :---: | :---: | :---: |
| $f k_{d}\left(s^{-1}\right) \quad$ decomposition rate constant | $1.61 \times 10^{-5}$ | [S2] |
| $k_{p 11}\left(L \cdot \mathrm{~mol}^{-1} \cdot s^{-1}\right)$ propagation rate constant of MMA | $1.05 \times 10^{3}$ | [S3] |
| $k_{p 22}\left(L \cdot \mathrm{~mol}^{-1} \cdot s^{-1}\right)$ propagation rate constant of BMAODS | $2.15 \times 10^{3}$ | [S4] |
| $k_{p 12}\left(L \cdot m o l^{-1} \cdot s^{-1}\right) \quad$ cross propagation rate constant of BMAODS | $3.22 \times 10^{3}$ | $k_{p 12}=k_{p 11} / r_{1}$ |
| $k_{p 21}\left(L \cdot m o l^{-1} \cdot s^{-1}\right)$ cross propagation rate constant of MMA | $1.43 \times 10^{3}$ | $k_{p 21}=k_{p 22} / r_{2}$ |
| $k_{t c 11}\left(L \cdot \mathrm{~mol}^{-1} \cdot s^{-1}\right)$ recombination termination rate constant of MMA | $2.07 \times 10^{7}$ | [S5, S6] |
| $k_{t c 22}\left(L \cdot \mathrm{~mol}^{-1} \cdot \mathrm{~s}^{-1}\right)$ recombination termination rate constant of BMAODS | $2.07 \times 10^{7}$ | Equal to $k_{\text {tol1 }}$ |
| $k_{t d 11}\left(L \cdot m o l^{-1} \cdot s^{-1}\right)$ disproportionation termination rate constant of MMA | $3.11 \times 10^{7}$ | [S5, S6] |
| $k_{t d 22}\left(L \cdot \mathrm{~mol}^{-1} \cdot \mathrm{~s}^{-1}\right)$ disproportionation termination rate constant of MMA | $3.11 \times 10^{7}$ | Equal to $k_{t d 11}$ |
| $k_{t 12}, k_{t 21}\left(L \cdot \mathrm{~mol}^{-1} \cdot \mathrm{~s}^{-1}\right)$ cross termination rate constant | $\left(k_{t 11} \times k_{t 22}\right)^{1 / 2}$ | [S7] |
| $k_{t r 1}\left(L \cdot m o l^{-1} \cdot s^{-1}\right) \quad$ chain transfer rate constant of MMA | $1 \times 10^{7}$ | [S1] |
| $k_{t r 2}\left(L \cdot \mathrm{~mol}^{-1} \cdot s^{-1}\right) \quad$ chain transfer rate constant of BMAODS | $1 \times 10^{7}$ | Equal to $k_{t r 2}$ |
| $k_{p, \text { inter1 }}^{*}\left(L \cdot m o l^{-1} \cdot s^{-1}\right)$ intermolecular cross-linkage rate constant of MMA | 500 | This work |
| $k_{p, \text { inter } 2}^{*}\left(L \cdot m o l^{-1} \cdot s^{-1}\right.$ intermolecular cross-linkage rate constant of BMAODS | 500 | Equal to $k_{p, \text { inter } 1}^{*}$ |
| $k_{p, \text { intral }}^{*}\left(L \cdot \mathrm{~mol}^{-1} \cdot s^{-1}\right)^{\text {intramolecular cross-linkage rate constant of MMA }}$ | 30 | This work |
| $k_{p, \text { intr } a_{2}}^{*}\left(L \cdot m o l l^{-1} \cdot s^{-1}\right)^{\text {intramolecular cross-linkage rate constant of BMAODS }}$ | 30 | Equal to $k_{p, \text { intral }}^{*}$ |

The overall conversion $X$ correlated to $\mathrm{M}_{1}$ conversion $x_{1}$ and $\mathrm{M}_{2}$ conversion $x_{2}$ can be expressed as

$$
\begin{equation*}
X=\frac{w_{1}+w_{2}}{w_{1,0}+w_{2,0}}=\frac{x_{1} w_{1,0}+x_{2} w_{2,0}}{w_{1,0}+w_{2,0}} \tag{4}
\end{equation*}
$$

where $w_{1,0}$ and $w_{2,0}$ are the initial mass of $\mathrm{M}_{1}$ and $\mathrm{M}_{2}$ in the solution, respectively. $w_{1}$ and $w_{2}$ are the mass of $M_{1}$ and $M_{2}$ incorporated in the polymer chains, respectively.

The numbers of $M_{1}$ and $M_{2}$ monomer units bound in the polymer chains were determined by ${ }^{1} \mathrm{H}$ NMR spectra (listed in Table S2). Therefore, conversions of MMA and BMAODS can be calculated using the following equations

$$
\begin{align*}
& x_{1}=\frac{X\left(\frac{n_{2,0} m_{2}}{n_{1,0} m_{1}}+1\right)}{\frac{n_{2} m_{2}}{n_{1} m_{1}}+1}  \tag{5}\\
& x_{2}=\frac{X\left(\frac{n_{1,0} m_{1}}{n_{2,0} m_{2}}+1\right)}{\frac{n_{1} m_{1}}{n_{2} m_{2}}+1} \tag{6}
\end{align*}
$$

where $\mathrm{m}_{1}$ and $\mathrm{m}_{2}$ are the molecular weight of $\mathrm{M}_{1}$ and $\mathrm{M}_{2}$, respectively. $\mathrm{n}_{1,0}$ and $\mathrm{n}_{2,0}$ are the initial moles of $M_{1}$ and $M_{2}$ in the solution while $n_{1}$ and $n_{2}$ are the accumulated moles of $M_{1}$ and $M_{2}$ in polymer chains.


Figure 4S. Evolution of overall conversion in RAFT copolymerization of MMA (1) and BMAODS (2) at various $\left[\mathrm{M}_{1}\right]_{0} /\left[\mathrm{M}_{2}\right]_{0}$ (Run $1=50 / 0.5$, Run $2=50 / 1$, and Run $3=50 / 1.5$ ). Curves are model prediction values.


Figure 5S. Evolution of overall conversion in RAFT copolymerization of MMA (1) and BMAODS (2) at various primary chain lengths by controlling $[\mathrm{CTA}]_{0} /\left[\mathrm{M}_{1}\right]_{0}$ at $1 / 50$ (Run 2), $1 / 75$ (Run 4), and $1 / 100$ (Run 5).

Curves are model prediction values.


Figure 5S. Evolution of overall conversion in RAFT copolymerization of MMA (1) and BMAODS (2) at various initial monomer concentrations of $15 \mathrm{wt} \%$ (Run 6), $30 \mathrm{wt} \%$ (Run 2), and $45 \mathrm{wt} \%$ (Run 7). Curves are model prediction values.


Figure 7S. Deconvolution of GPC trace of the b-PMMA sample from Run 6

## REFFERENCE

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