# **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° 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° LS detector (LS90), RI detector, and intrinsic viscosity (DP) detector.



**Figure 3S.** <sup>1</sup>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	v Reactions of RAFT	<sup>C</sup> Copolymerizatior	of Vinvl/Divin	vl Monomer System
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Initiation	$I \xrightarrow{f,k_d} 2P_{0,1,0}$
	$P_{0,1,0} + M_i \xrightarrow{k_{p,i}} P_{1,1,0}$
Propagation with comonomer	$P_{n,r,c} + M_i \xrightarrow{k_{p,i}} P_{n+1,r,c}$
Transfer to RAFT species	$P_{n,r,c} + P_{m,s,d} \xrightarrow{rdk_{tr}} P_{n,r-1,c+1} + P_{m,s+1,d-1}$
Termination by disproportionation	$P_{n,r,c} + P_{m,s,d} \xrightarrow{-rsk_{td}} P_{n,r-1,c} + P_{m,s-1,d}$
Termination by recombination	$P_{n,r,c} + P_{m,s,d} \xrightarrow{-rsk_{tc}} P_{n+m,r+s-2,c+d}$
intermolecular cross-linking	$P_{n,r,c} + P_{m,s,d} \xrightarrow{-rmk_{inter}} P_{n+m,r+s,c+d}$
intramolecular cross-linking	$P_{n,r,c} \xrightarrow{-rnk_{intra}} P_{n,r,c}$

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<sup>S1</sup>) 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

$$k_{p,i} = \sum_{j} k_{p,ji} \phi_j \tag{1a}$$

$$k_{ir} = \sum_{j} k_{ir,j} \phi_j \tag{1b}$$

$$k_t = \sum_i \sum_j k_{t,ij} \phi_i \phi_j$$
(1c)

$$k_{\text{int}er} = \sum_{j} k_{\text{int}er,j}^* \phi_j (\overline{F_2} - \overline{C} - \overline{D})$$
(1d)

$$k_{\text{int}ra} = \sum_{j} k_{\text{int}ra,j}^* \phi_j (\overline{F_2} - \overline{C} - \overline{D})$$
(1f)

where  $\overline{F_2}$  is the divinyl density in the total copolymer,  $\overline{C}$  is the intermolecular cross-linkage density, and  $\overline{D}$  is the intramolecular cross-linkage density.

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

$$\frac{dP_{n,r,c}}{dt} = \sum_{i} rk_{p,i} M_{i} P_{n-1,r,c} - \sum_{i} rk_{p,i} M_{i} P_{n,r,c} 
+ \sum_{m=0}^{\infty} \sum_{s=0}^{\infty} \sum_{d=1}^{\infty} (r+1) dk_{tr} P_{n,r+1,c-1} P_{m,s,d} - \sum_{m=0}^{\infty} \sum_{s=0}^{\infty} \sum_{d=1}^{\infty} r dk_{tr} P_{n,r,c} P_{m,s,d} 
+ \sum_{m=0}^{\infty} \sum_{s=1}^{\infty} \sum_{d=0}^{\infty} s(c+1) k_{tr} P_{n,r-1,c+1} P_{m,s,d} - \sum_{m=0}^{\infty} \sum_{s=1}^{\infty} \sum_{d=0}^{\infty} sck_{tr} P_{n,r,c} P_{m,s,d} 
+ \sum_{m=0}^{\infty} \sum_{s=1}^{\infty} \sum_{d=0}^{\infty} (r+1) sk_{td} P_{n,r+1,c} P_{m,s,d} - \sum_{m=0}^{\infty} \sum_{s=1}^{\infty} \sum_{d=0}^{\infty} r sk_{td} P_{n,r,c} P_{m,s,d} 
+ \frac{1}{2} \sum_{m=0}^{n} \sum_{s=1}^{r+1} \sum_{d=0}^{\infty} (r+2-s) sk_{tc} P_{m,s,d} P_{n-m,r+2-s,c-d} - \sum_{m=0}^{\infty} \sum_{s=1}^{\infty} \sum_{d=0}^{\infty} r sk_{tc} P_{n,r,c} P_{m,s,d} 
+ \sum_{m=0}^{n} \sum_{s=1}^{r} \sum_{d=0}^{c} s(n-m) k_{p,int\,er} P_{m,s,d} P_{n-m,r-s,c-d} - \sum_{m=0}^{\infty} \sum_{s=0}^{\infty} \sum_{d=0}^{\infty} r m k_{p,int\,er} P_{n,r,c} P_{m,s,d} 
- \sum_{m=0}^{\infty} \sum_{s=1}^{\infty} \sum_{d=0}^{\infty} snk_{p,int\,er} P_{n,r,c} P_{m,s,d}$$
(2)

### Method of moments

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

$$Y_{i,j,k} = \sum_{n=0}^{\infty} \sum_{r=0}^{\infty} \sum_{c=0}^{\infty} n^{i} r^{j} c^{k} P_{n,r,c}$$
(3)

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

Table 28. Different Moment Equations				
zeroth-order moments	$\frac{dY_{0,0,0}}{dt} = 2fk_d[I] - \frac{1}{2}k_{tc}Y_{0,1,0}^2 - k_{p,\text{int}er}Y_{1,0,0}Y_{0,1,0}$			
first-order moments	$\frac{dY_{1,0,0}}{dt} = \sum_{i} k_{p,i} M_i Y_{0,1,0}$			
	$\frac{dY_{0,1,0}}{dt} = 2fk_d[I] - k_{td}Y_{0,1,0}^2 - k_{tc}Y_{0,1,0}^2$			
	$\frac{dY_{0,0,1}}{dt} = 0$			

#### Table 2S. Different Moment Equations

second-order moments

$$\begin{aligned} \frac{dY_{2,0,0}}{dt} &= 2\sum_{i} k_{p,i} M_{i} Y_{1,1,0} + \sum_{i} k_{p,i} M_{i} Y_{0,1,0} + k_{k} Y_{1,1,0}^{2} \\ &+ 2k_{p,inter} Y_{1,1,0} Y_{2,0,0} \end{aligned}$$

$$\begin{aligned} \frac{dY_{0,2,0}}{dt} &= 2f k_{d} [I] - 2k_{ul} Y_{0,2,0} Y_{0,1,0} + k_{ul} Y_{0,2,0}^{2} \\ &+ 2k_{k} Y_{0,2,0}^{2} - 4k_{k} Y_{0,2,0} Y_{0,1,0} + k_{kl} Y_{0,2,0}^{2} \\ &- 2k_{kr} Y_{0,2,0} Y_{0,0,1} + 2k_{kr} Y_{0,1,0} Y_{0,0,1} + 2k_{kr} Y_{0,1,1} Y_{0,0,1} + 2k_{kr} Y_{0,1,0} Y_{0,0,1} \\ &+ 2k_{p,inter} Y_{0,2,0} Y_{1,1,0} \end{aligned}$$

$$\begin{aligned} \frac{dY_{0,0,2}}{dt} &= k_{kr} Y_{0,1,1}^{2} - 2k_{kr} Y_{0,0,2} Y_{0,1,0} + 2k_{kr} Y_{0,1,1} Y_{0,0,1} + 2k_{kr} Y_{0,1,0} Y_{0,0,1} \\ &+ 2k_{p,inter} Y_{0,2,0} Y_{1,1,0} \end{aligned}$$

$$\begin{aligned} \frac{dY_{1,0,0}}{dt} &= \sum_{i} k_{p,i} M_{i} Y_{0,2,0} - k_{id} Y_{1,1,0} Y_{0,1,0} + k_{re} Y_{1,1,0} Y_{0,2,0} - 2k_{ic} Y_{1,1,0} Y_{0,1,0} \\ &- k_{o} Y_{1,1,0} Y_{0,0,1} + k_{o} Y_{1,0,1} Y_{0,1,0} + k_{p,inter} Y_{2,0,0} Y_{0,2,0} + k_{p,inter} Y_{1,1,0} Y_{0,1,0} \\ &- k_{o} Y_{1,1,0} Y_{0,0,1} + k_{o} Y_{1,0,1} Y_{0,1,0} + k_{r,0,1} Y_{0,1,0} - k_{rr} Y_{1,0,1} Y_{0,1,0} \\ &- k_{o} Y_{1,0,1} Y_{0,1,0} + k_{ic} Y_{0,1,1} Y_{0,2,0} - 2k_{ic} Y_{0,1,1} Y_{0,1,0} \\ &+ k_{p,inter} Y_{2,0,0} Y_{0,1,1} + k_{kr} Y_{1,0,0} Y_{0,0,1} \\ &+ k_{r,j} Y_{0,0,2} Y_{0,1,0} - k_{kr} Y_{0,1,1} Y_{1,0,0} \\ &- k_{kr} Y_{0,0,2} Y_{0,1,0} - k_{kr} Y_{0,1,1} Y_{0,0,0} - k_{kr} Y_{0,1,0} Y_{0,0,0} \\ &+ k_{p,inter} Y_{0,1,0} Y_{1,0,0} \\ \\ \frac{d[C]}{dt} = k_{p,inter} Y_{1,1,0} \\ \\ \frac{d[C]}{dt} = k_{p,inter} Y_{1,1,0} \\ \frac{d[C]}{dt} = -k_{cl} I \end{bmatrix}$$
monomer: 
$$\frac{d[M_{i}]}{dt} = -k_{cl} I_{0,1} \\ \\ \frac{dW_{i}}{dt} = -\sum_{i=1}^{2} m_{i} R_{p,i} (\frac{1}{\rho_{i}} - \frac{1}{\rho_{p}}) W$$

polymerization volume

intermolecular

cross-linkage intramolecular

cross-linkage

small molecules

pendant double bond

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

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	$PDI = \frac{r_w}{r_n}$
divinyl density in copolymer <sup>*</sup>	$\overline{F}_2 = \frac{n_{20} - n_2}{n_{10} - n_1 + n_{20} - n_2}$
intermolecular cross-linkage density	$\overline{C} = \frac{C}{Y_{1,0,0}}$
intramolecular cross-linkage density	$\overline{D} = \frac{D}{Y_{1,0,0}}$
number-average molecular weight**	$M_n = r_n \times [\overline{F_2} \times m_2 + (1 - \overline{F_2}) \times m_1]$
branching density	$BD = 1000 \times \frac{C \times V}{n_{10} - n_1 + 2(n_{20} - n_2)}$
cyclization density	$CD = 1000 \times \frac{D \times V}{n_{10} - n_1 + 2(n_{20} - n_2)}$
branching frequency	$BF = \frac{M_n}{m_1} \times \frac{BD}{1000}$
cyclization frequency	$CF = \frac{M_n}{m_1} \times \frac{CD}{1000}$

Table 3S. Definition of Important Chain Structural Properties

\*  $n_{10}$  and  $n_{20}$  are initial mole number of vinyl and divinyl monomers, respectively.  $n_1$ ,  $n_2$  are mole number of unreacted vinyl and divinyl monomers, respectively

\*\* m<sub>1</sub> and m<sub>2</sub> are molecular weight of vinyl and divinyl monomers, respectively.

The kinetic parameters at 70  $^{\circ}\mathrm{C}$  are summarized in Table 4S

Parameter	Description	Value	Reference
$fk_d(s^{-1})$	decomposition rate constant	$1.61 \times 10^{-5}$	[82]
$k_{p11}(L \cdot mol^{-1} \cdot s^{-1})$	propagation rate constant of MMA	$1.05 \times 10^{3}$	[83]
$k_{p22}(L \cdot mol^{-1} \cdot s^{-1})$	propagation rate constant of BMAODS	$2.15 \times 10^{3}$	[S4]
$k_{p12}(L \cdot mol^{-1} \cdot s^{-1})$	cross propagation rate constant of BMAODS	$3.22 \times 10^{3}$	$k_{p12} = k_{p11} / r_1$
$k_{p21}(L \cdot mol^{-1} \cdot s^{-1})$	cross propagation rate constant of MMA	$1.43 \times 10^{3}$	$k_{p21} = k_{p22} / r_2$
$k_{tc11}(L \cdot mol^{-1} \cdot s^{-1})$	recombination termination rate constant of MMA	$2.07 \times 10^{7}$	[S5, S6]
$k_{tc22}(L \cdot mol^{-1} \cdot s^{-1})$	recombination termination rate constant of BMAODS	$2.07 \times 10^{7}$	Equal to $k_{tc11}$
$k_{td11}(L \cdot mol^{-1} \cdot s^{-1})$	disproportionation termination rate constant of MMA	3.11×10 <sup>7</sup>	[S5, S6]
$k_{td22}(L \cdot mol^{-1} \cdot s^{-1})$	disproportionation termination rate constant of MMA	3.11×10 <sup>7</sup>	Equal to $k_{td11}$
$k_{t12}, k_{t21} (L \cdot mol^{-1} \cdot s^{-1})$	<sup>1</sup> )cross termination rate constant	$(k_{t11} \times k_{t22})^{1/2}$	[S7]
$k_{tr1}(L \cdot mol^{-1} \cdot s^{-1})$	chain transfer rate constant of MMA	$1 \times 10^{7}$	[S1]
$k_{tr2}(L \cdot mol^{-1} \cdot s^{-1})$	chain transfer rate constant of BMAODS	$1 \times 10^{7}$	Equal to $k_{tr2}$
$k_{p,\text{interl}}^*(L \cdot mol^{-1} \cdot s^{-1})$	) intermolecular cross-linkage rate constant of MMA	500	This work
$k_{p,\text{int}er2}^*(L \cdot mol^{-1} \cdot s^{-1})$	-1 intermolecular cross-linkage rate constant of BMAODS	500	Equal to $k_{p,\text{int}er1}^*$
$k_{p,\text{int}ra1}^*(L\cdot mol^{-1}\cdot s^{-1})$	)intramolecular cross-linkage rate constant of MMA	30	This work
$k_{p,\mathrm{int}ra2}^*(L\cdot mol^{-1}\cdot s^{-1})$	)intramolecular cross-linkage rate constant of BMAODS	30	Equal to $k_{p,\text{int }ral}^*$

The overall conversion X correlated to  $M_1$  conversion  $x_1$  and  $M_2$  conversion  $x_2$  can be expressed as

$$X = \frac{w_1 + w_2}{w_{1,0} + w_{2,0}} = \frac{x_1 w_{1,0} + x_2 w_{2,0}}{w_{1,0} + w_{2,0}}$$
(4)

where  $w_{1,0}$  and  $w_{2,0}$  are the initial mass of M<sub>1</sub> and M<sub>2</sub> in the solution, respectively.  $w_1$  and  $w_2$  are the mass of M<sub>1</sub> and M<sub>2</sub> incorporated in the polymer chains, respectively.

The numbers of  $M_1$  and  $M_2$  monomer units bound in the polymer chains were determined by <sup>1</sup>H NMR spectra (listed in Table S2). Therefore, conversions of MMA and BMAODS can be calculated using the following equations

$$x_{1} = \frac{X(\frac{n_{2,0}m_{2}}{n_{1,0}m_{1}} + 1)}{\frac{n_{2}m_{2}}{n_{1}m_{1}} + 1}$$
(5)

$$x_{2} = \frac{X(\frac{n_{1,0}m_{1}}{n_{2,0}m_{2}} + 1)}{\frac{n_{1}m_{1}}{n_{2}m_{2}} + 1}$$
(6)

where  $m_1$  and  $m_2$  are the molecular weight of  $M_1$  and  $M_2$ , respectively.  $n_{1,0}$  and  $n_{2,0}$  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  $[M_1]_0/[M_2]_0$  (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 [CTA]<sub>0</sub>/[M<sub>1</sub>]<sub>0</sub> 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 wt% (Run 6), 30 wt% (Run 2), and 45 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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