

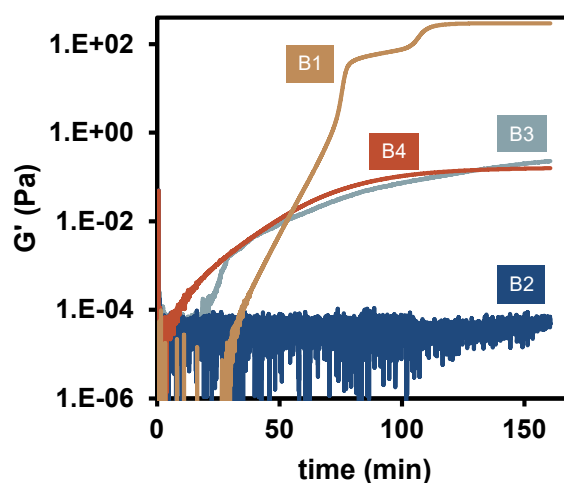
## Supporting Information

### Insights into the Bulk Kinetics of a 2K Radical Polymerization System Based on the Copper Catalyzed Cleavage of Diboranes and its Perspectives

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#### Materials

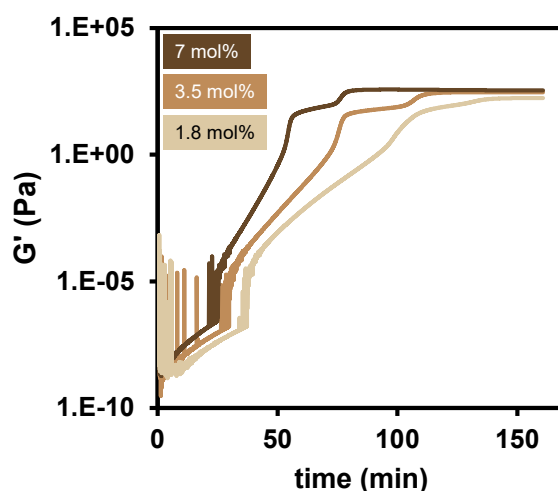
B1 (5,5,5',5'-Tetramethyl-2,2'-bi-1,3,2-dioxaborinan) (98%, BLD Pharm), B3 (4,8-Dimethyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,3,6,2-dioxazaborocane) (95%, abcr), B4 (2-(Dimethylphenylsilyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolan) (95%, Merck), Cu(acac)<sub>2</sub> (99.9%, Merck), tetrakis(dimethylamino)diboron (98%, BLD Pharm), 3-methylbutane-1,3-diol (97%, Merck), benzylmethacrylate (Sigma), methylmethacrylate (VWR), benzylacrylate (TCI), isobutylvinylether (TCI), dimethylacrylamide (Sigma), acrylomorpholine (Sigma), acetonitrile (ACROS) and styrene (ACROS) were used as received.



**SI Figure 1:**  $G'$  resulting from rheology/IR measurements of the polymerization of BzMA using either 3.5 mol% B1, B2, B3 or B4 and 0.2 mol% Cu(acac)<sub>2</sub> with logarithmic scale of the y-axis.

**SI-Table 1:** Summarized data derived from rheology/IR measurements of the polymerization of BzMA using 3.5 mol% of the respective diborane B1, B2, B3 or B4 and 0.2 mol% Cu(acac)<sub>2</sub>. SEC measurements of polymers derived from the same concentrations, but prepared in larger bulk scale (500 mg) are included.

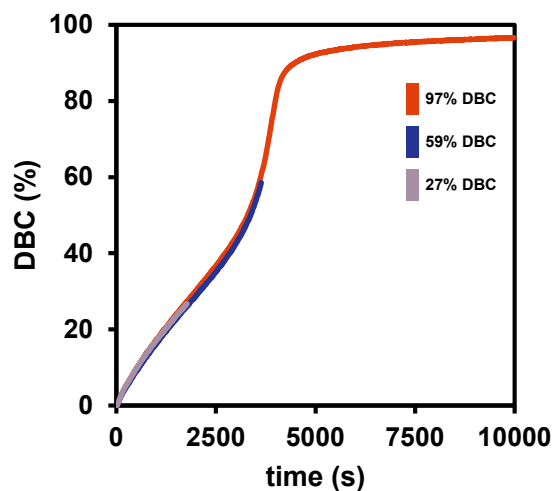
	$t_{\text{gel}}$ (min)	$\text{DBC}_{\text{end}}$ (%)	$k_p$ (db% s <sup>-1</sup> )	$R_p$ (mol s <sup>-1</sup> )	$M_n$ (kDa)	$M_w$ (kDa)	PDI ( )
B1	108	96	0.018	$2.01 \cdot 10^{-5}$	660	1984	3.0
B2	-	5.7	0.001	$1.59 \cdot 10^{-6}$	632	2127	3.4
B3	-	9.1	0.002	$2.50 \cdot 10^{-6}$	-	-	-
B4	-	56	0.015	$1.75 \cdot 10^{-5}$	696	2339	3.4



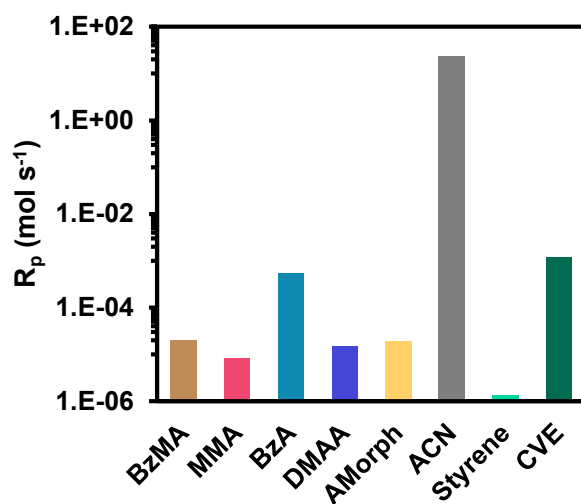
**SI-Figure 2:**  $G'$  resulting from rheology/IR measurements of the polymerization of BzMA using either 1.8 mol% B1, 3.5 mol% B1 or 7 mol% B1 and 0.2 mol% Cu(acac)<sub>2</sub> with logarithmic scale of the y-axis.

**SI-Table 2** Summarized data derived from rheology/IR measurements of the polymerization of BzMA using either 1.8 mol% B1, 3.5 mol% B1 or 7 mol% B1 and 0.2 mol% Cu(acac)<sub>2</sub>.

	$k_p$ (db% s <sup>-1</sup> )	$R_p$ (mol s <sup>-1</sup> )
7 mol%	0.018	$2.04 \cdot 10^{-5}$
3.5 mol%	0.018	$2.01 \cdot 10^{-5}$
1.8 mol%	0.012	$1.35 \cdot 10^{-5}$



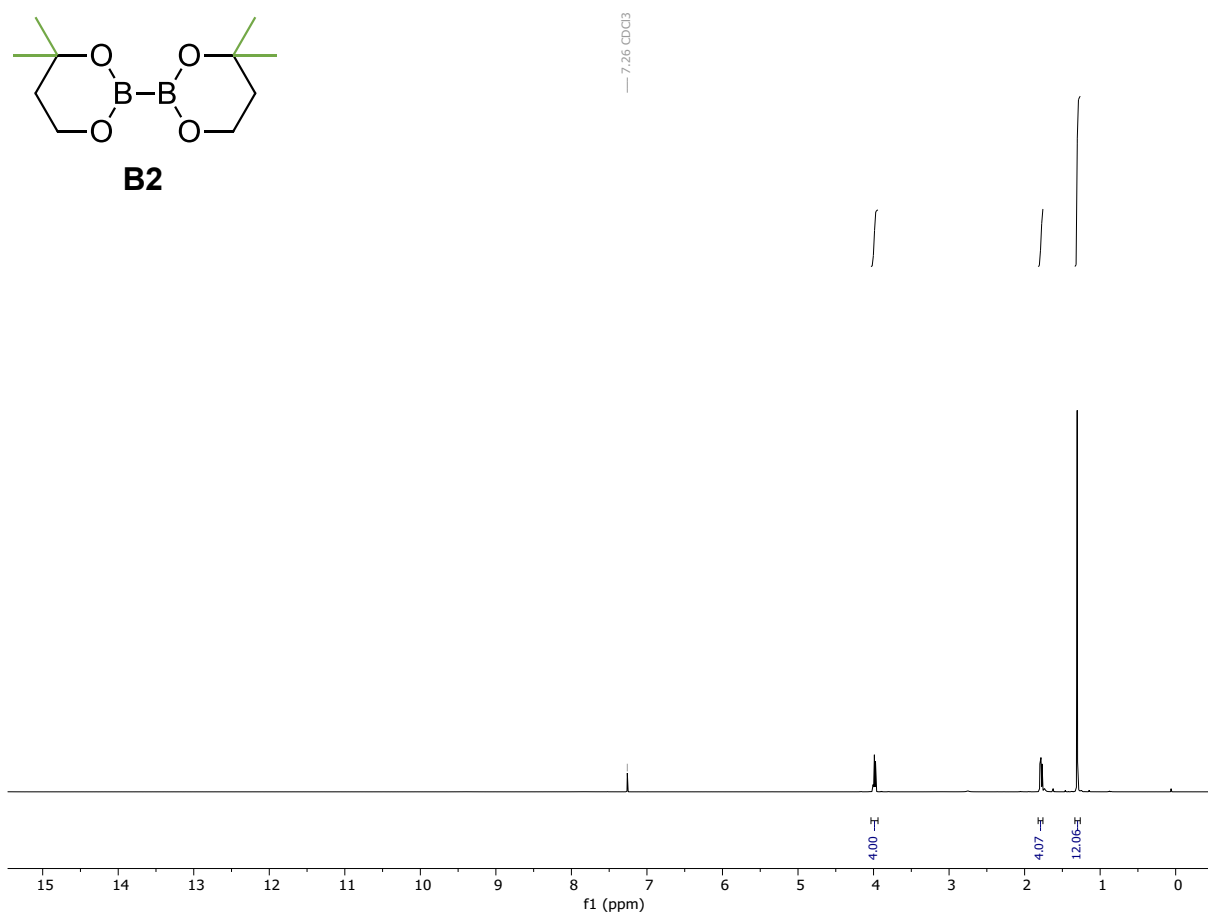
**SI-Figure 3:** IR measurements of the polymerization of BzMA using 3.5 mol% B1 and 0.2 mol% Cu(acac)<sub>2</sub> interrupted at certain times to evaluate molecular mass from SEC. The reproducibility of methods is highly emphasized.



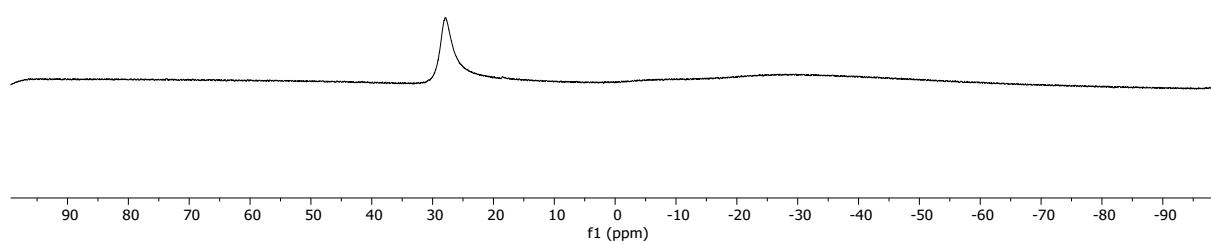
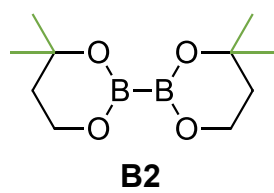
**SI Figure 4:** Rate of polymerization ( $R_p$ ) of different monomers using 3.5 mol% B1 and 0.2 mol% Cu(acac)<sub>2</sub> derived from the rheology/IR measurements shown in figure 5A.

**SI-Table 3:** Summarized data derived from rheology/IR measurements of the polymerization of different monomers including BzMA, MMA, BzA, DMAA, A-Morph, AN, Styrene and isoBVE and the evaluated  $t_{\text{gel}}$ ,  $\text{DBC}_{\text{gel}}$  and  $\text{DBC}_{\text{end}}$ . SEC measurements of polymers derived from the same concentrations, but prepared in larger bulk scale (500 mg) are included.

	$M_n$ (kDa)	$M_w$ (kDa)	PDI (-)	$k_p$ (db%/s <sup>-1</sup> )	$R_p$ (mol s <sup>-1</sup> )
BzMA	660	1984	3	0.018	$2.01 \cdot 10^{-5}$
MMA	57	116	2	0.004	$8.19 \cdot 10^{-6}$
BzA	88	754	6.4	0.441	$5.43 \cdot 10^{-4}$
DMAA	< 1	< 1	-	0.008	$1.51 \cdot 10^{-5}$
A-Morph	< 1	< 1	-	0.014	$1.96 \cdot 10^{-5}$
AN	n.s.	n.s.	n.s.	0.249	2.41
ST	24	56	2.4	0.001	$1.34 \cdot 10^{-6}$
isoBVE	3.5	8.4	4.5	0.601	$1.20 \cdot 10^{-3}$



**SI-Figure 5:**  $^1\text{H-NMR}$  of B2



SI-Figure 6:  $^{11}\text{B}$ -NMR of B2