Supporting Material to

Methyl Acrylate Polymerizations in the Presence of a Copper/N$_3$S$_3$ Macrobicyclic Cage in DMSO at 25 $^{\mathrm{o}}$C.

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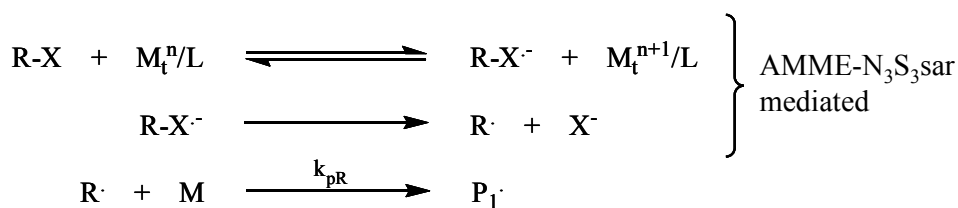
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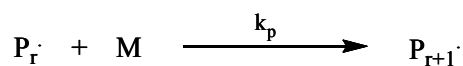[b] School of Chemistry and Molecular Biosciences, University of Queensland, Brisbane QLD 4072

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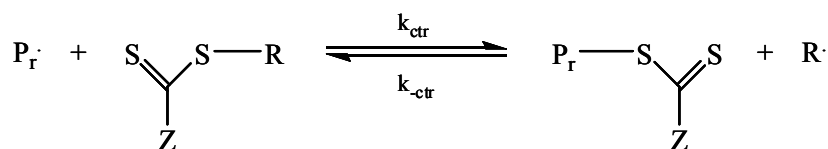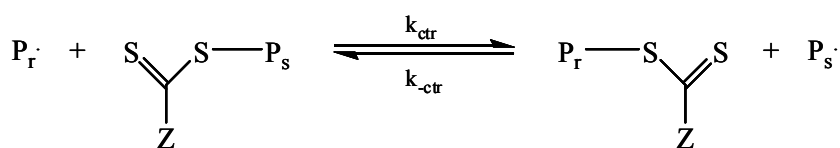
e-mail: m.monteiro@uq.edu.au

Initiation

$$R\text{-}X \;+\; M_t^n/L \;\rightleftharpoons\; R\text{-}X^{\cdot-} \;+\; M_t^{n+1}/L$$

$$R\text{-}X^{\cdot-} \;\longrightarrow\; R^{\cdot} \;+\; X^-$$

AMME-N_3S_3sar mediated

$$R^{\cdot} \;+\; M \;\xrightarrow{k_{pR}}\; P_1^{\cdot}$$

Propagation

$$P_r^{\cdot} \;+\; M \;\xrightarrow{k_p}\; P_{r+1}^{\cdot}$$

Pre-equilibrium

Main equilibrium

Termination

$$P_r^{\cdot} \;+\; P_s^{\cdot} \;\xrightarrow{k_{tc}}\; D_{r+s}$$

$$P_r^{\cdot} \;+\; P_s^{\cdot} \;\xrightarrow{k_{td}}\; D_r \;+\; D_s$$

Scheme S1. Mechanism for AMME-N_3S_3sar mediated initiation and RAFT mediated polymerizations.

$E_{1/2}$, V (vs Fc$^{+/0}$)

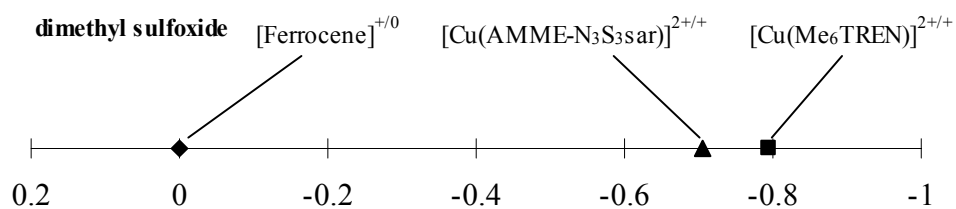**dimethyl sulfoxide**   [Ferrocene]$^{+/0}$ [Cu(AMME-N$_3$S$_3$sar)]$^{2+/+}$ [Cu(Me$_6$TREN)]$^{2+/+}$

| 0.2 | 0 | -0.2 | -0.4 | -0.6 | -0.8 | -1 |

Figure S1. Redox potentials of CuBr$_2$/AMME-N$_3$S$_3$sar, CuBr$_2$/Me$_6$TREN and

Ferrocene in both dimethyl sulfoxide and acetonitrile. All complex concentrations are 1

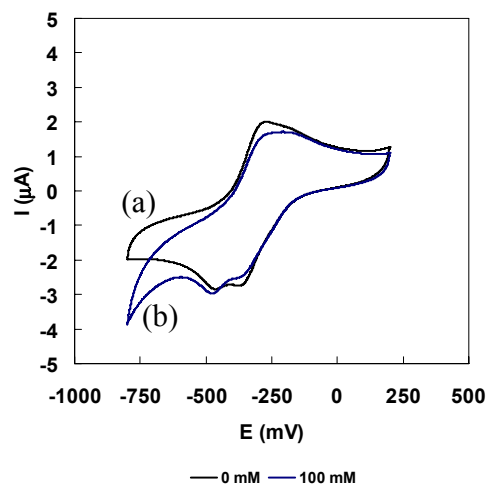mM, contain 0.1 M Et$_4$NClO$_4$ and are referenced to Fc$^{+/0}$.

Figure S2. Cyclic voltammograms of $[Cu(AMME-N_3S_3sar)]^{2+/+}$ (a) without EBiB and (b) with EBiB (100 mM) in DMSO. Complex concentrations are 1 mM and all voltammograms are recorded at 50 mV/s scanning rate in 0.1 M Et_4NClO_4 and are referenced to $Ag/AgNO_3$.

Figure S3: Cyclic voltammograms of $[Cu(Me_6TREN)]^{2+/+}$ with varying concentrations of EBiB (0 - 10 mM) in DMSO. Complex concentrations are 1 mM and all voltammograms are recorded at 100 mV/s scanning rate in 0.1 M Et_4NClO_4 and are referenced to $Ag/AgNO_3$.
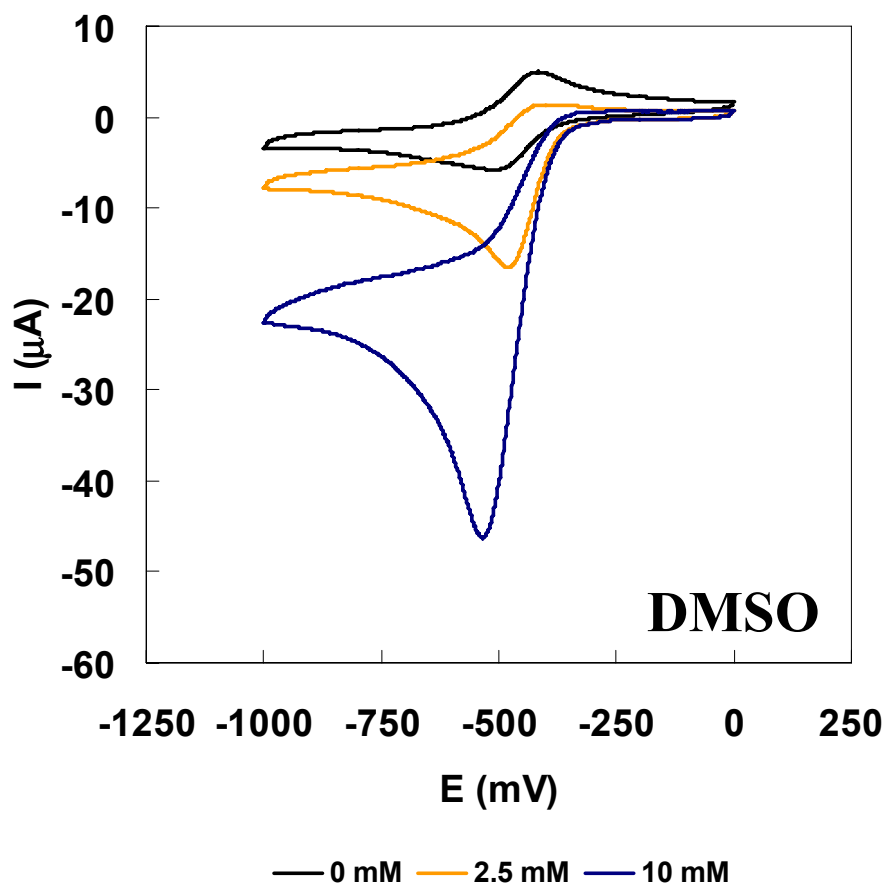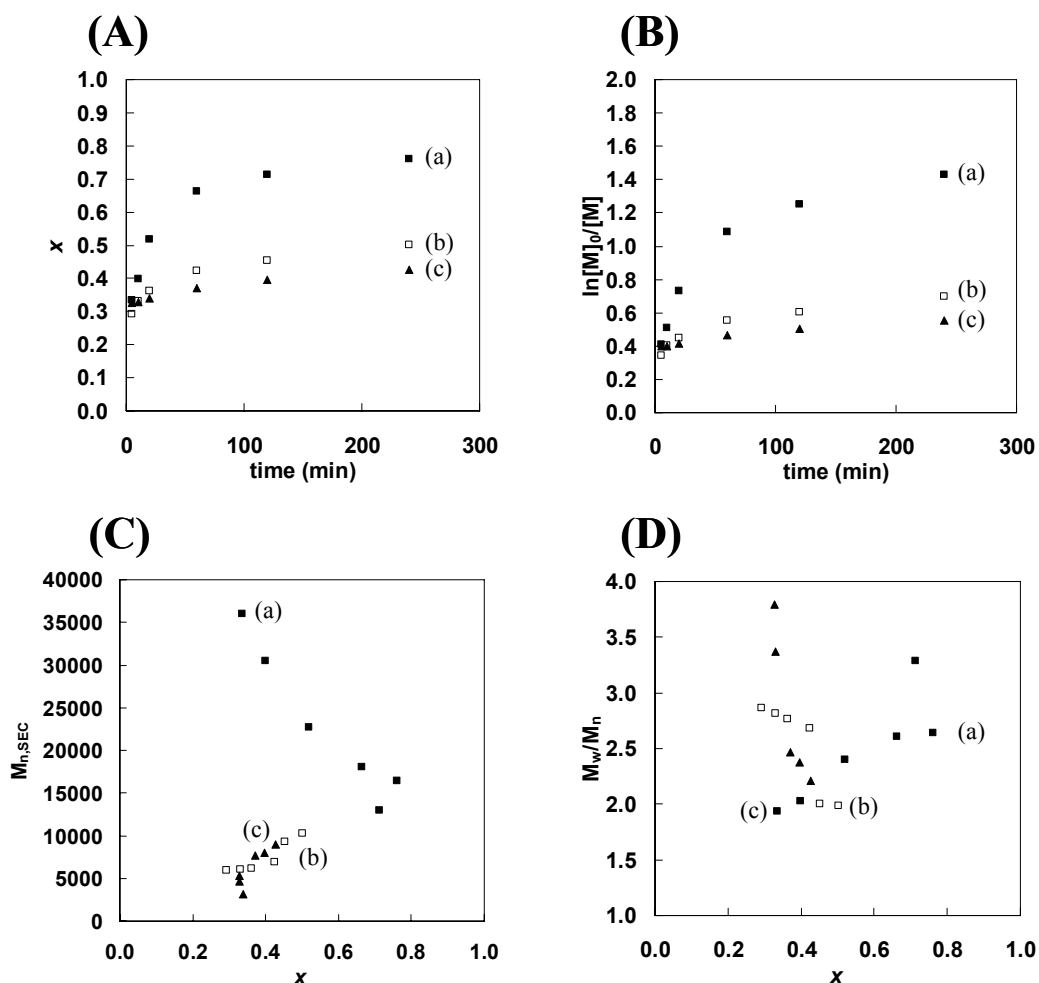
(A)

(B)

(C)

(D)

Figure S4: Kinetic data for the polymerization of methyl acrylate (3.67 M) in DMSO (9.36 M) at 25 ^{o}C with EBiB (1.83 x 10^{-2} M), CuBr (1.83 x 10^{-2} M) and AMME-N$_3$S$_3$sar. (A) conversion versus time, (B) ln[M]$_0$/[M] versus time (C) number-average molecular weight (M$_{n,SEC}$) versus conversion, and (D) polydispersity index versus conversion. The concentration ratios of reactants [MA]/[EBiB]/[CuBr]/[AMME-N$_3$S$_3$sar] are (a) 200/1/1/1, (b) 200/1/1/2, and (c) 200/1/1/3
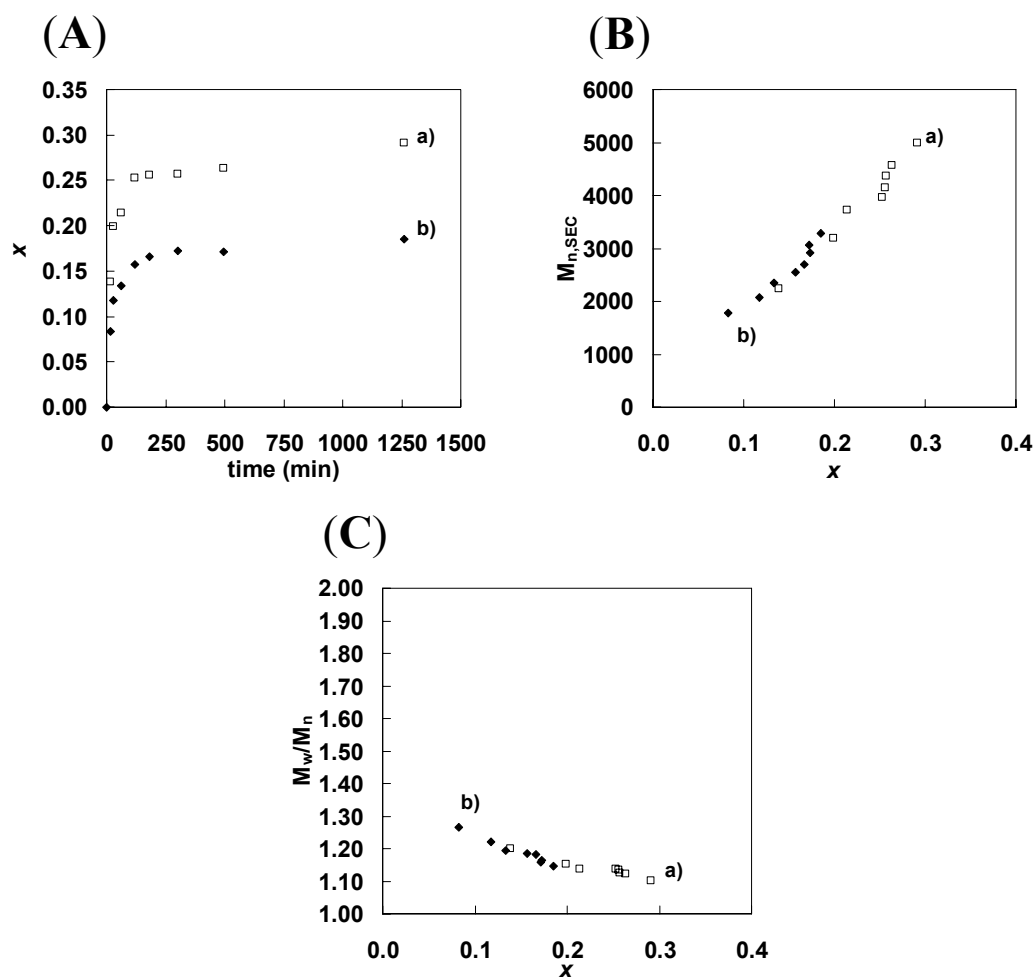
(A)

(B)

(C)

Figure S5: Kinetic data for the polymerization of methyl acrylate (3.67 M) in DMSO (9.36 M) at 25 ^{o}C with EBiB, MCEBTTC, CuBr and either AMME-N_3S_3sar or Me_6TREN where [MA]/[RAFT]/[EBiB] = 200/1/0.1. For all reactions, [EBiB]/[CuBr]/[ligand] = 1/1/1. (A) conversion vs time, (B) number-average molecular weight ($M_{n,SEC}$) vs conversion, and (C) polydispersity index vs conversion. Curves (a) CuBr/AMME-N_3S_3sar (b) CuBr/Me_6TREN.
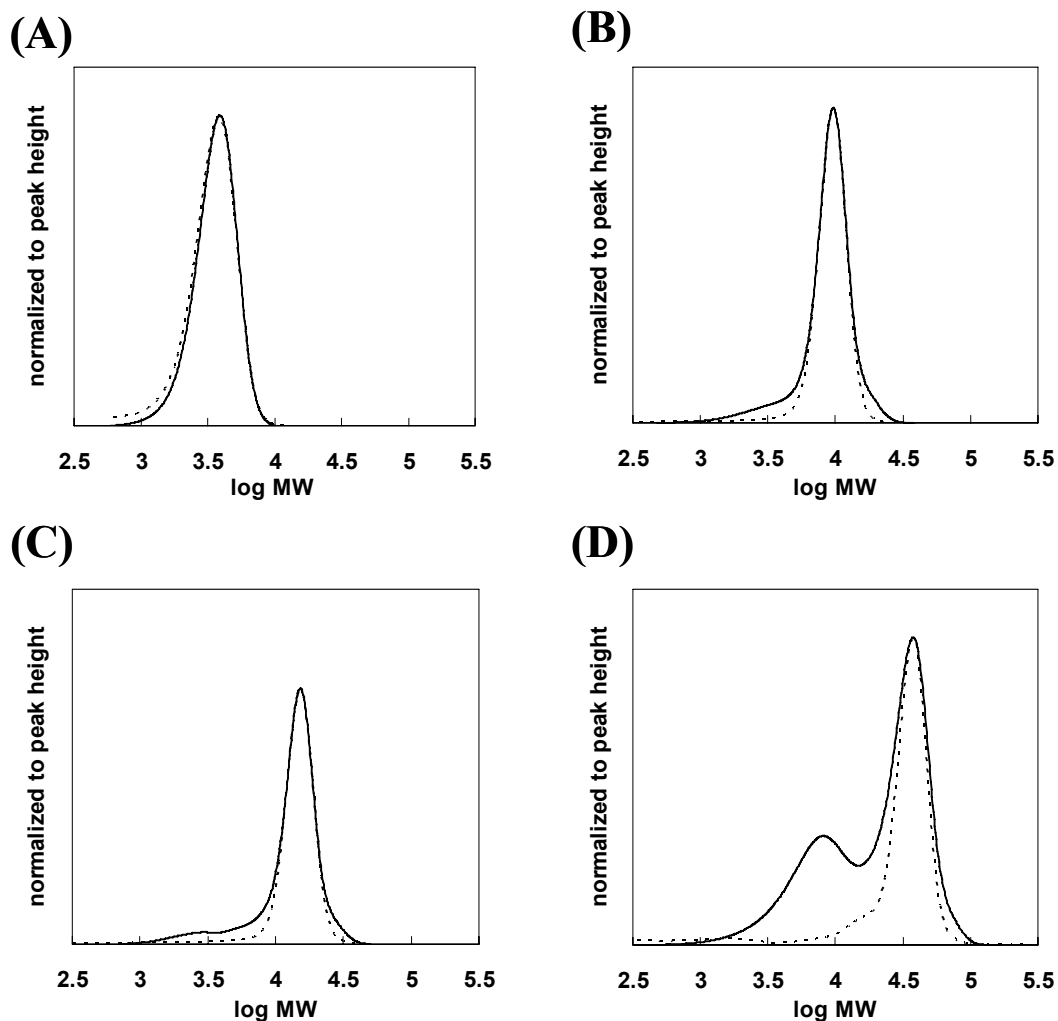
(A)

(B)

(C)

(D)

Figure S6: Dual detector Size Exclusion Chromatograms of MCEBTTC mediated polymerization of methyl acrylate (3.67 M) in DMSO (9.36 M) at 25 ^{o}C with EBiB, MCEBTTC, CuBr and Me$_6$TREN at various ratios of initiator (— represents refractive index, --- represents UV absorbance at 306.6 nm). The concentration ratios of reactants [MA]/ [EBiB]/[CuBr]/[Me$_6$TREN]/[MCEBTTC] are (A) 200/0.1/0.1/0.1/1, (B) 200/1/1/1/1, (C) 200/1/1/1/0.5, and (D) 200/1/1/1/0.1
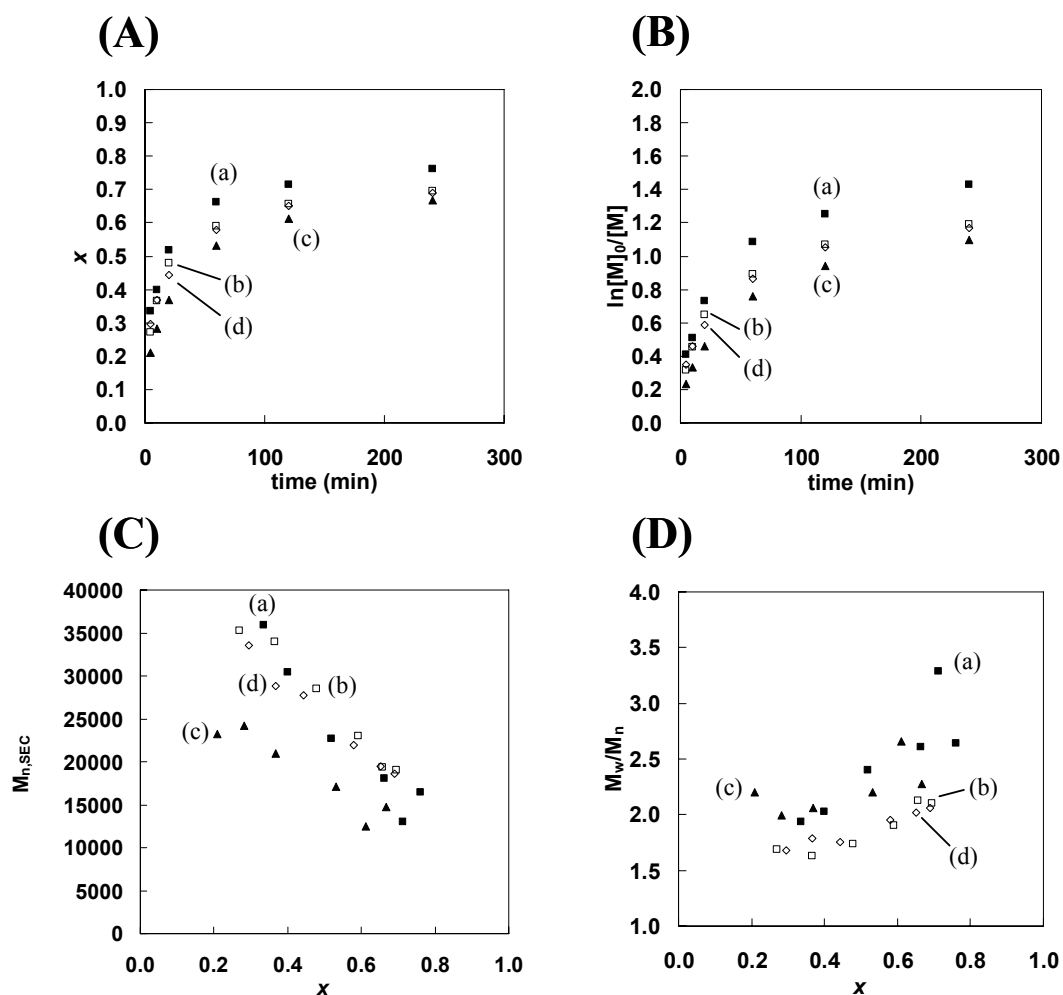
(A)

(B)

(C)

(D)

Figure S7: Kinetic data for the polymerization of methyl acrylate (3.67 M) in DMSO (9.36 M) at 25 ^{o}C with EBiB (1.83 x 10^{-2} M), CuBr, [Cu(AMME-N_3S_3sar)]Br$_2$ and AMME-N_3S_3sar. (A) conversion versus time, (B) ln[M]$_0$/[M] versus time (C) number-average molecular weight ($M_{n,SEC}$) versus conversion, and (D) polydispersity index versus conversion. The concentration ratios of reactants [MA]/[EBiB]/[CuBr]/[AMME-N_3S_3sar]/[[Cu(AMME-N_3S_3sar)]Br$_2$] are (a) 200/1/1/1/0, (b) 200/1/1/1/0.05, (c) 200/1/1/1/0.1, and (d) 200/1/1/1/0.3