

## Electronic Supplementary Information

# Effect of Variations of $\text{Cu}^{\text{II}}\text{X}_2/\text{L}$ , Surface Area of $\text{Cu}^0$ , Solvent, and Temperature on Atom Transfer Radical Polyaddition of 4-Vinylbenzyl 2-Bromo-2-isobutyrate Inimers

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## Captions of ESI

Table S1. ATRPA of VBBiB: conditions and characterization of the products.

Figure S1. GPC traces for reactions performed using (A) PMDETA and (B) HMTETA ligands recorded at various reaction time; (C) Vinyl groups conversion vs reaction time for ATRPA performed with various ligands. Polyaddition conditions were as followed: VBBiB/ $\text{CuBr}_2/\text{Cu}^0$  powder/L = 50/1/2/3 (or 6 in the case of dNBpy) with  $[\text{VBBiB}]_0 = 1.8$  M in anisole at 10 °C.

Figure S2.  $^1\text{H}$  NMR spectra (400 MHz,  $\text{CDCl}_3$ ) of reaction mixture from the ATRPA in anisole performed with PMDETA after 8, 20, 45 h and after evaporation of solvent.

Figure S3.  $^1\text{H}$  NMR spectra (400 MHz,  $\text{CDCl}_3$ ) of reaction mixture from the ATRPA in anisole performed with HMTETA after 8, 20, 45, 70 and 168 h.

Figure S4. GPC traces for reactions performed in (A) DMF and (B) DMSO solvents recorded at various reaction time; (C) Vinyl groups conversion vs reaction time for ATRPA performed in various solvents. Polyaddition conditions were as followed: VBBiB/ $\text{CuBr}_2/\text{Cu}^0$  powder/dNBpy = 50/1/2/6 with  $[\text{VBBiB}]_0 = 1.8$  M at 10 °C.

Figure S5.  $^1\text{H}$  NMR spectra (400 MHz,  $\text{CDCl}_3$ ) of reaction mixture from the ATRPA in DMF performed with dNBpy after 7, 20, 45, 70 and 168 h.

Figure S6.  $^1\text{H}$  NMR spectra (400 MHz,  $\text{CDCl}_3$ ) of reaction mixture from the ATRPA in DMSO performed with dNBpy (A) after 20, 31, 50 and 70 h, and (B) after evaporation of solvent.

Table S1. ATRPA of VBBiB: conditions and characterization of the products.

Entry <sup>a</sup>	Composition <sup>a</sup>	Catalyst	Temp. (°C)	Time (h)	Conv. (%)	$M_w^b$	$\mathcal{D}^b$
S1	50/1/2/3	CuBr <sub>2</sub> /PMDETA/anisole	10	45	97	30800	8.86
S2	50/1/2/3	CuBr <sub>2</sub> /HMTETA/anisole	10	168	90	4950	2.45
S3	50/1/2/6	CuBr <sub>2</sub> /dNBpy/DMSO	10	168	51	640	1.41
S4	50/1/2/6	CuBr <sub>2</sub> /dNBpy/DMF	10	168	52	611	1.63

<sup>a</sup> Compositions consisted of VBBiB/CuX<sub>2</sub>/Cu<sup>0</sup>/Ligand, respectively.

<sup>b</sup>  $M_w$  and  $\mathcal{D}$  were determined by GPC using THF as an eluent and PS standards.

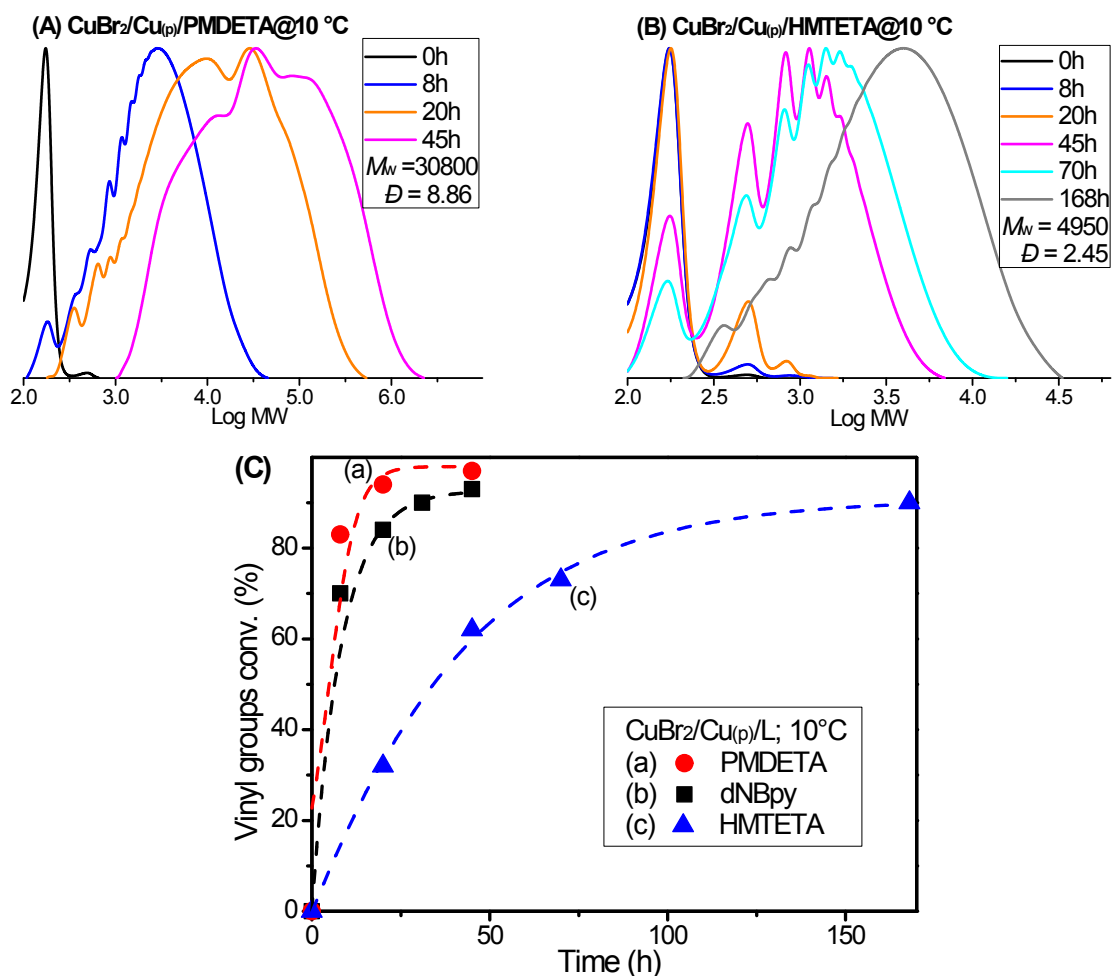


Figure S1. GPC traces for reactions performed using (A) PMDETA and (B) HMTETA ligands recorded at various reaction time; (C) Vinyl groups conversion vs reaction time for ATRPA performed with various ligands. Polyaddition conditions were as followed:  $\text{VBBiB}/\text{CuBr}_2/\text{Cu}^0$  powder/L = 50/1/2/3 (or 6 in the case of dNBpy) with  $[\text{VBBiB}]_0 = 1.8 \text{ M}$  in anisole at  $10^\circ\text{C}$ .

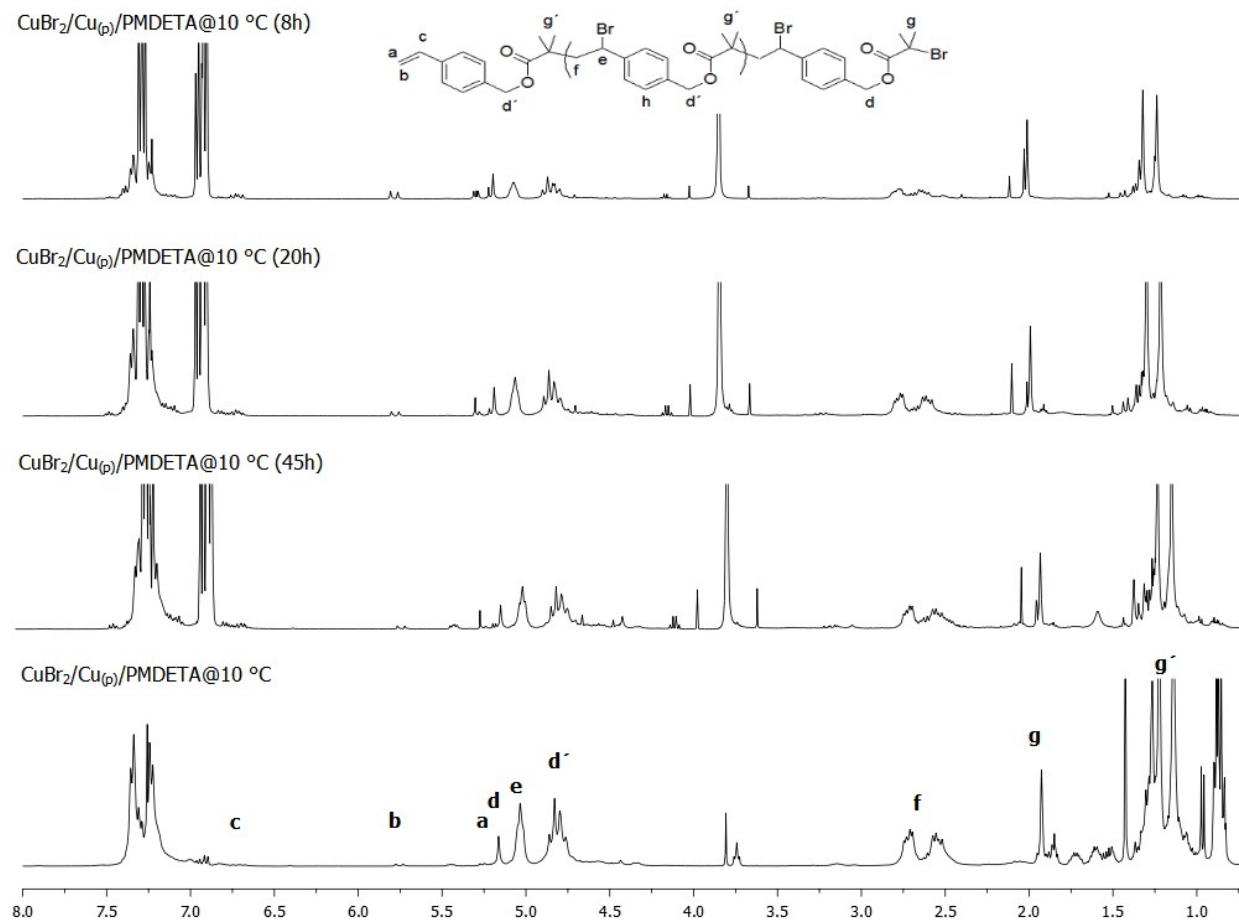


Figure S2. <sup>1</sup>H NMR spectra (400 MHz, CDCl<sub>3</sub>) of reaction mixture from the ATRPA in anisole performed with PMDETA after 8, 20, 45 h and after evaporation of solvent.

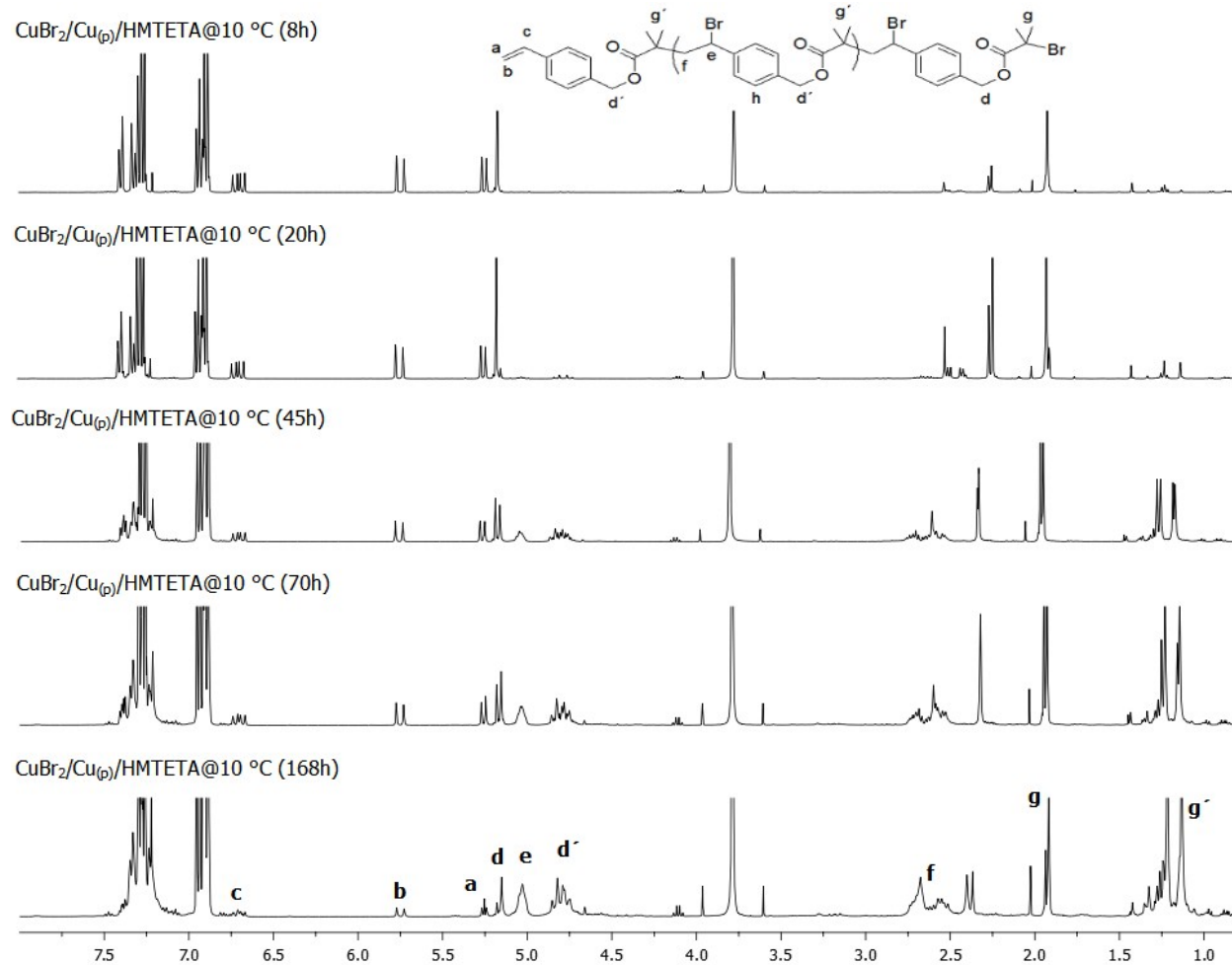


Figure S3. <sup>1</sup>H NMR spectra (400 MHz, CDCl<sub>3</sub>) of reaction mixture from the ATRPA in anisole performed with HMTETA after 8, 20, 45, 70 and 168 h.

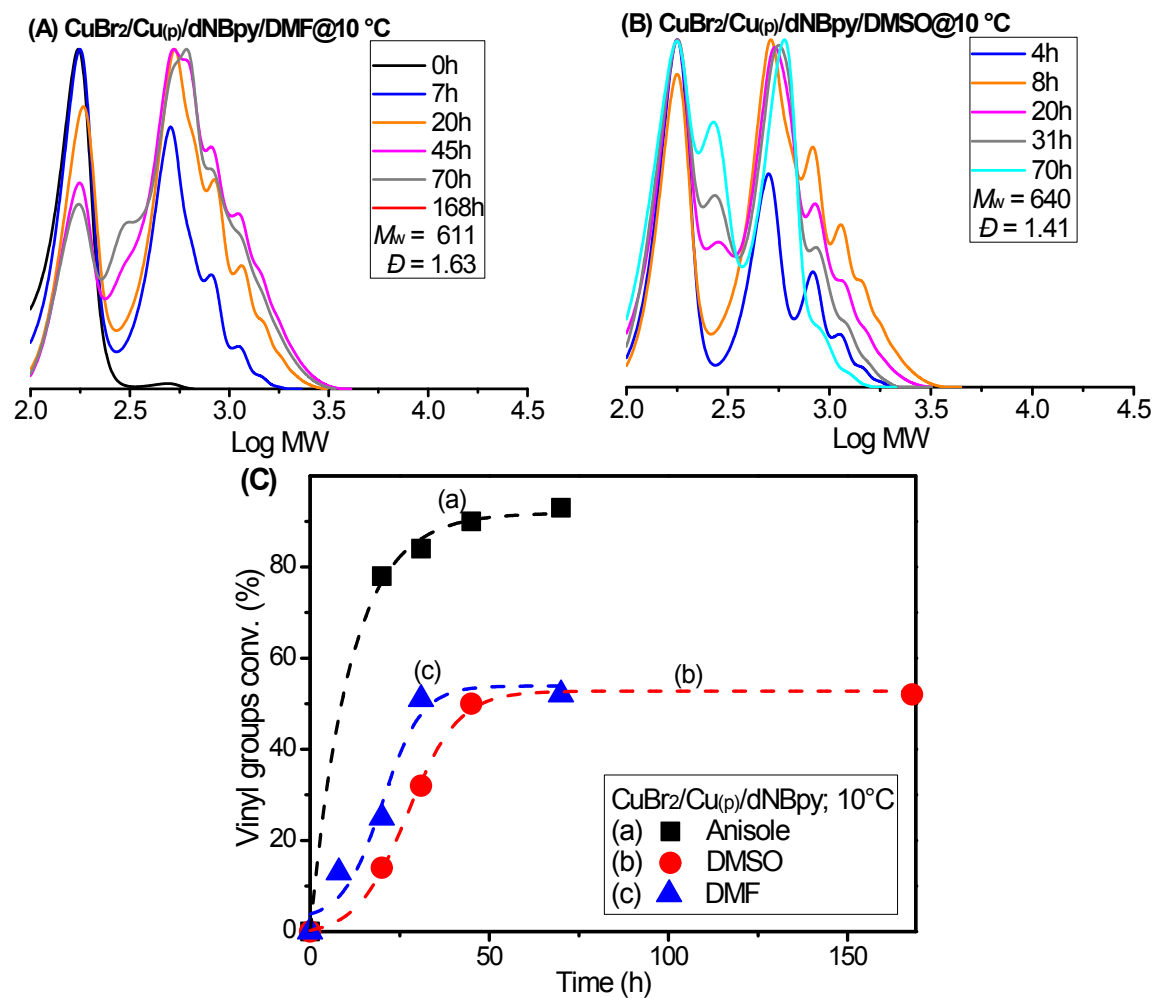


Figure S4. GPC traces for reactions performed in (A) DMF and (B) DMSO solvents recorded at various reaction time; (C) Vinyl groups conversion vs reaction time for ATRPA performed in various solvents. Polyaddition conditions were as followed: VBBiB/CuBr<sub>2</sub>/Cu<sup>0</sup> powder/dNBpy = 50/1/2/6 with [VBBiB]<sub>0</sub> = 1.8 M at 10 °C.





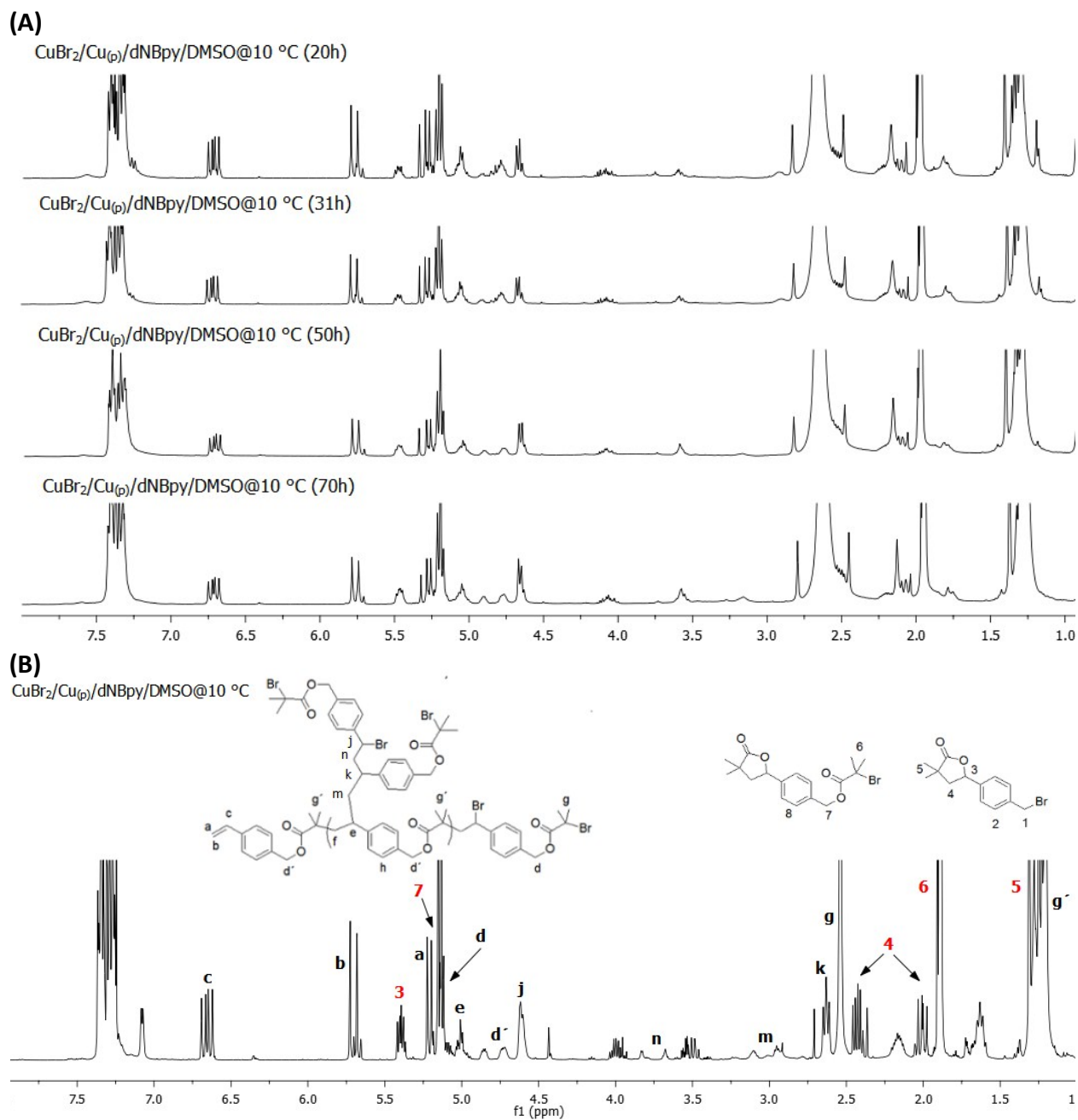


Figure S6. <sup>1</sup>H NMR spectra (400 MHz, CDCl<sub>3</sub>) of reaction mixture from the ATRPA in DMSO performed with dNBpy (A) after 20, 31, 50, and 70 h and (B) after evaporation of solvent.