Supporting Information

Effects of Various Cu(0), Fe(0), and Proanthocyanidins Reducing Agents on Fe(III)-Catalysed ATRP to the Synthesis of PMMA Block Copolymers and Their Selfassembly Behaviours

Yi-Shen Huang[†]^a, Han-Yu Hsueh[†]^b, Junko Aimi^c, Li-Chieh Chou^a, Yu-Chi Lu^a, Shiao-Wei Kuo^{d,e}, Chung-Chi Wang^f, Kuo-Yu Chen^{*}^g and Chih-Feng Huang^{*}^a

- ^a Department of Chemical Engineering, i-Center for Advanced Science and Technology (iCAST), National Chung Hsing University, 145 Xingda Road, South District, Taichung 40227, Taiwan.
- ^{b.}Department of Materials Science and Engineering, National Chung Hsing University, Taichung 40227, Taiwan.
- ^{c.} Molecular Design & Function Group, Research Center for Functional Materials, National Institute for Materials Science, 1-2-1 Sengen, Tsukuba, Ibaraki 305-0047, Japan.
- ^{d.}Department of Materials and Optoelectronic Science, Center of Crystal Research, National Sun Yat-Sen University, Kaohsiung 80424, Taiwan.
- ^{e.}Department of Medicinal and Applied Chemistry, Kaohsiung Medical University, Kaohsiung 80708, Taiwan.
- ^{f.} Division of Cardiovascular Surgery, Veterans General Hospital, Taichung, Taiwan.
- ^{g.} Department of Chemical and Materials Engineering, National Yunlin University of Science and Technology, Yunlin 64002, Taiwan.

* Correspondence: <u>chenkuo@yuntech.edu.tw</u> and <u>HuangCF@dragon.nchu.edu.tw</u>

Captions:

- Figure S1. Kinetics of Cu(II)-catalyzed ARGET ATRP (a) with and (b) without PC at 60 °C (MMA/EBiB/PC/CuBr₂/PMDETA = 500/1/0.5/0.1/1 in anisole; [MMA]₀ = 4.5 M).
- Figure S2. Kinetics of Cu(II)-catalyzed ATRP with different M/I ratios in the presence of PC (MMA/EBiB/PC/CuBr₂/PMDETA = 100 (or 500)/1/0.1/0.5/1 in anisole; [MMA]₀ = 4.5 M).
- Figure S3. GPC traces of Cu(II)-catalyzed ATRP with different M/I ratios in the presence of PC (MMA/EBiB/CuBr₂/PC/PMDETA = 100 (or 500)/1/0.1/0.5/1 in anisole; [MMA]₀ = 4.5 M).
- Figure S4. Kinetics of ATRP of MMA without degassing using (a) Cu(0) and (b) PC as RAs $(MMA/EBiB/RA/FeCl_3/PPh_3 = 200/1/5/0.1/0.5 \text{ in anisole; } [MMA]_0 = 4.5 \text{ M}).$
- Figure S5. FT-IR spectra (4000–400 cm⁻¹) of (a) PMMA-*b*-PBzMA and (b) PMMA-*b*-PBMA block copolymers.



Figure S1. Kinetics of Cu(II)-catalyzed ARGET ATRP (a) with and (b) without PC at 60 °C (MMA/EBiB/PC/CuBr₂/PMDETA = 500/1/0.5/0.1/1 in anisole; [MMA]₀ = 4.5 M).



Figure S2. Kinetics of Cu(II)-catalyzed ATRP with different M/I ratios in the presence of PC (MMA/EBiB/PC/CuBr₂/PMDETA = 100 (or 500)/1/0.5/0.1/1 in anisole; $[MMA]_0 = 4.5 M$).



Figure S3. GPC traces of Cu(II)-catalyzed ATRP with different M/I ratios in the presence of PC (MMA/EBiB/PC/CuBr₂/PMDETA = 100 (or 500)/1/0.5/0.1/1 in anisole; [MMA]₀ = 4.5 M).



Figure S4. Kinetics of ATRP of MMA without degassing using (a) Cu(0) and (b) PC as RAs $(MMA/EBiB/RA/FeCl_3/PPh_3 = 200/1/5/0.1/0.5 \text{ in anisole}; [MMA]_0 = 4.5 \text{ M}).$



Figure S5. FT-IR spectra (4000–400 cm⁻¹) of (a) PMMA-*b*-PBzMA and (b) PMMA-*b*-PBMA block copolymers.