Supporting Information to

Zero Valent Metal/RAFT Agent Mediated CRP of Functional Monomers at Room Temperature: a Promising Catalyst System for CRP

Yuwei Gu, Junfei Zhao, Qingqing Liu, Xiangqiang Pan, Wei Zhang, Zhengbiao Zhang*, Xiulin Zhu*

Jiangsu Key Laboratory of Advanced Functional Polymer Design and Application, Suzhou Key

Laboratory of Macromolecular Design and Precision Synthesis, Department of Polymer Science and

Engineering, College of Chemistry, Chemical Engineering and Materials Science, Soochow University,

Suzhou, 215123, P. R. China.

E-mail: zhangzhengbiao@suda.edu.cn (Zheng B. Zhang) or xlzhu@suda.edu.cn (Xiu L. Zhu)

1. Experimental

Materials

Glycidyl methacrylate (GMA, 99%, TCI Chemicals), methyl methacrylate (MMA, 99%, Shanghai Chemical Reagents), butyl methacrylate (BMA, 99%, Shanghai Chemical Reagents), 2-(dimethylamino)ethyl methacrylate (DMAEMA, 99%, Energy Chemical), 4-vinylpyridine (4VP, 99%, TCI Chemicals) were freshly distilled under reduced pressure. Poly (ethylene glycol) monomethyl ether methacrylate (PEGMA, M_n = 300 g mol^{-1}, 99%, Aldrich) was purified by making it pass through a column filled with neutral aluminum oxide. Zero-valent iron (Fe(0), 99%, Alfa Aesar), Zero-valent cobalt (Co(0), 99.998%, Alfa Aesar), Zero-valent nickel (Ni(0), 99.8%, Alfa Aesar), Zero-valent manganese (Mn(0), 99.95%, Alfa Aesar), Zero-valent zinc (Zn(0), 99.99%, Aladdin-reagent), Zero-valent copper (Cu(0), 99%, Aldrich), N,N,N',N'',N''-pentamethyldiethylenetriamine (PMDETA, 99%, Aldrich) were used as received without further treatment. 2-Cyanoprop-2-yl 1-dithionaphthalate (CPDN) was synthesized according to the method reported elsewhere.[1] 4-(4-cyanopentanoicacid) dithiobenzoate

(CPADB) was synthesized according to the literature.[2] All other chemicals were obtained from Shanghai Chemical Reagents and used as received unless mentioned.

Characterization

The number-average molecular weight (M_n) and polydispersity (M_w/M_n) of PGMA, PMMA, PBMA and PPEGMA were determined by a HLC-8320 size exclusion chromatography (SEC, TOSOH) equipped with a refractive index detector, using two TSKgel Super Mutipore HZ-N columns (4.6×150 mm, 3 μm particle size) in series with molecular weights ranging from $7×10^2$ - $2×10^5$ g mol^{-1}. THF was used as the eluent at a flow rate of 0.35 mL min^{-1} and 40 ^{o}C. These samples were calibrated with PMMA standards purchased from American Polymer Standards Corporation. The M_n and M_w/M_n of P4VP and PDMAEMA were determined by a HLC-8320 SEC (TOSOH) equipped with a refractive index detector, using two TSKgel Super HM-M columns (6.0×150 mm, 3 μm particle size) in series with molecular weights ranging from $1×10^3$ - $7×10^5$ g mol^{-1}. DMF (0.01 M LiBr) was used as an eluent at a flow rate of 0.60 mL min^{-1} operated at 40 ^{o}C. These samples were calibrated with PS standards purchased from TOSOH. ^{1}H NMR spectrum of the precipitated polymer was recorded on an INOVA 400 MHz nuclear magnetic resonance instrument using CDCl$_3$ as the solvent.

Fe(0)/RAFT Agent Mediated Polymerization of GMA

A typical Fe(0)/RAFT agent mediated polymerization for the molar ratio of $[GMA]_0/[CPDN]_0/[Fe(0)]_0$ = 200/1/1 was prepared as the following procedure: a mixture of GMA (1 mL, 7.33 mmol), CPDN (0.0099g, 0.0367 mmol), Fe(0) (0.0021 g, 0.0367 mmol) and DMSO (1 mL) was added to a clean ampoule and degassed through three standard freeze-pump-thaw cycles. The ampoule was flame sealed and then transferred into water bath at 25 ^{o}C and regulated with a precision of ± 0.1 ^{o}C under stirring. When the desired time was up, the ampoule was opened and the contents were diluted with THF and filtered through a column of neutral alumina to remove zero-valent iron. Finally, the polymer was precipitated in methanol and dried under vacuum until a constant weight at room temperature. Polymer yields were determined by gravimetry.

Chain Extension of PGMA

The chain extension reaction procedure was the same as the general procedure of Fe(0)/RAFT agent mediated polymerization of GMA. The only difference was that RAFT agent was replaced by a predetermined PGMA macroinitiator.
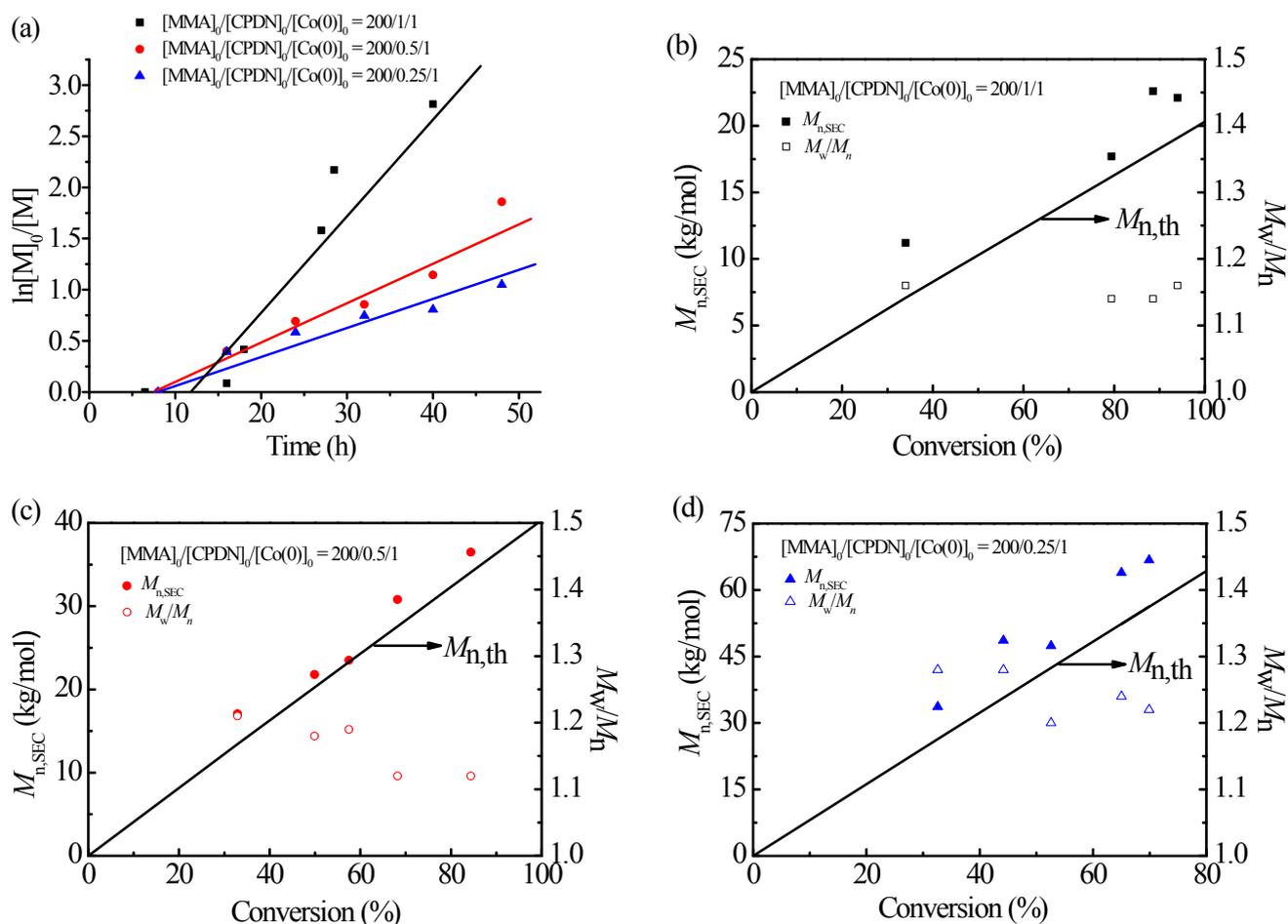
2. Results and Discussion

Fig. S1 Kinetic investigation ($\ln([M]_0/[M])$ versus time) (a) and numberaverage molecular weight (M_n) and molecular weight distribution(M_w/M_n) (b-d) of Co(0)/CPDN mediated polymerization of MMA at different CPDN concentration at 25 ^{o}C in DMSO.
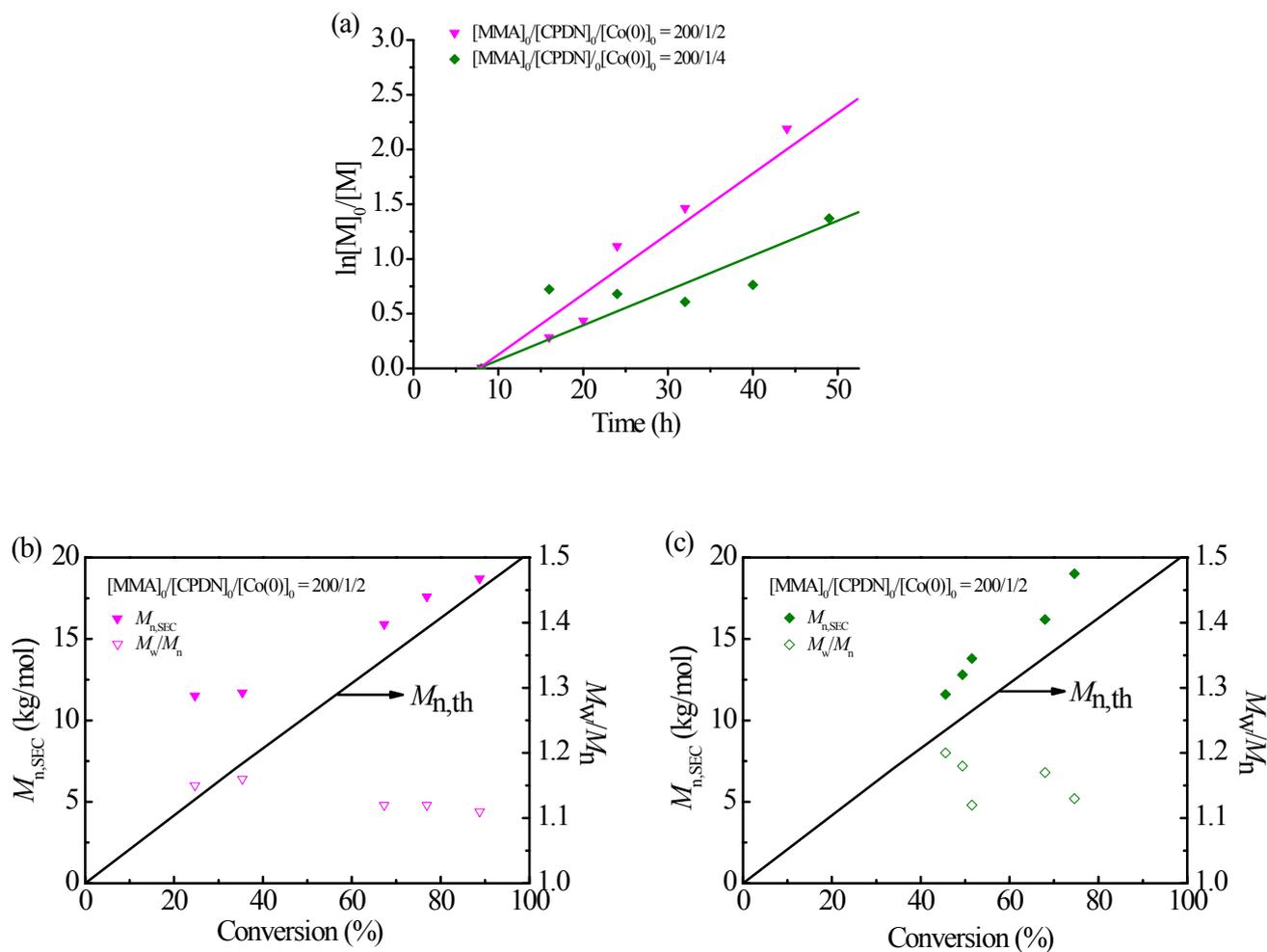
Fig. S2 Kinetic investigation ($\ln([M]_0/[M])$ versus time) (a) and numberaverage molecular weight (M_n) and molecular weight distribution(M_w/M_n) (b&c) of Co(0)/CPDN mediated polymerization of MMA at different Co(0) concentration at 25 °C in DMSO.

References

[1]. A. D. Asandei, V. Percec, *Journal of Polymer Science Part A: Polymer Chemistry*, 2001, **39**, 3392.

[2]. Y. Mitsukami, M. S. Donovan, A. B. Lowe, C. L. McCormick, *Macromolecules*, 2001, **34**, 2248.