Electronic Supplementary Information

Is it ATRP or SET-LRP? I. Cu\(^0\)&Cu\(^{II}\)/PMDETA-mediated reversible - deactivation radical polymerization with PMDETA.

Yongsheng Gao\(^{ab}\), Tianyu Zhao\(^a\) and Wenxin Wang\(^*\)\(^a\)

\(^a\) Charles Institute of Dermatology, School of Medicine and Medical Science, University College Dublin, Belfield, Dublin 4, Ireland.
\(^b\) Department of Mechanical and Biomedical Engineering, College of Engineering and Informatics, National University of Ireland, Galway, Ireland.

wenxin.wang@ucd.ie

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Experimental details

Materials: methyl acrylate (MA, 99%, Aldrich), ethyl α-bromoisobutyrate (EBriB, 98%, Aldrich), ethyl 2-bromopropionate (CuBr₂, 99%, Aldrich), tris[2-(dimethylamino)ethyl]amine (Me₆TREN, 97%, Aldrich), and pentamethyldiethylenetriamine (PMDETA, 99%, Aldrich) were used as received. Cu(0)-wire (diameter 1 mm) was purchased from Sigma-Aldrich and was treated by immersion in conc. HCl prior to use. Solvents were purchased from Fisher Scientific and used as received.

Synthesis of PMA catalyzed by Cu₀/Me₆TREN: MA (100 mmol, 100 equiv), EBriB (1 mmol, 1 equiv), Me₆TREN (0.18 mmol, 0.18 equiv) and DMSO (9 ml) were added into the flask and oxygen was removed by bubbling argon through the solutions for 20 min at room temperature. Cu₀-wire (5 cm) was immersed in conc. HCl and then thoroughly rinsed with acetone and water before used. The solution was stirred at 600 rpm and the polymerization was conducted at 25 °C in an oil bath for the desired reaction time.

Synthesis of PMA catalyzed by Cu₀/PMDETA: MA (100 mmol, 100 equiv), EBriB (1 mmol, 1 equiv), PMDETA (0.18 mmol, 0.18 equiv) and DMSO (9 ml) were added into the flask and oxygen was removed by bubbling argon through the solutions for 20 min at room temperature. Cu₀-wire (5 cm) was immersed in conc. HCl and then thoroughly rinsed with acetone and water. The solution was stirred at 600 rpm and the polymerization was conducted at 25 °C in an oil bath for the desired reaction time.

Synthesis of PMA catalyzed by Cu/I/PMDETA: MA (100 mmol, 100 equiv), EBriB (1 mmol, 1 equiv), PMDETA (0.18 mmol, 0.18 equiv), pretreated CuCl (0.18 mmol, 0.18 equiv) and DMSO (9 ml) were added into the flask and oxygen was removed by bubbling argon through the solutions for 20 min at room temperature. The solution was stirred at 600 rpm and the polymerization was conducted at 25 °C in an oil bath for the desired reaction time.

Synthesis of PMA catalyzed by Cu₀/PMDETA: MA (100 mmol, 100 equiv), EBriB (1 mmol, 1 equiv), PMDETA (0.18 mmol, 0.18 equiv), CuBr₂ (0.05 mmol, 0.05 equiv) and DMSO (9 ml) were added into the flask and oxygen was removed by bubbling argon through the solutions for 20 min at room temperature. The solution was stirred at 600 rpm and the polymerization was conducted at 25 °C in an oil bath for the desired reaction time.

Synthesis of PMA catalyzed by Cu₀&CuII/PMDETA: MA (100 mmol, 100 equiv), EBriB (1 mmol, 1 equiv), PMDETA (0.18 mmol, 0.18 equiv), CuBr₂ (0.05 mmol, 0.05 equiv) and DMSO (9 ml) were added into the flask and oxygen was removed by bubbling argon through the solutions for 20 min at room temperature. Cu₀-wire (5 cm) was immersed in conc. HCl and then thoroughly rinsed with acetone and water. The solution was stirred at 600 rpm and the polymerization was conducted at 25 °C in an
oil bath for the desired reaction time.

**Size exclusion chromatography (SEC) characterizations:** Weight average molecular weight ($M_w$), number average molecular weight ($M_n$) and polydispersity ($M_w/M_n$) were obtained by SEC (Varian 920-LC) equipped with an RI and an LS detector. The columns (30 cm PLgel Mixed-C, two in series) were eluted using tetrahydrofuran (THF) and calibrated using a series of 12 near-monodisperse PMMA standards ($M_p$ from 690 to 1,944,000 g/mol). The polymers were analyzed in THF at a concentration of 5.0 mg/ml. All calibrations and analyses were performed at 40 °C and a flow rate of 1 ml/min.

**$^1$H NMR characterizations:** $^1$H NMR analysis was carried out on a S4 300 MHz Bruker NMR with JEOL Delta v5.0.1 processing software.
Scheme S1. The SARA ATRP mechanism\textsuperscript{1}
Scheme S2. The SET-LRP mechanism

-- Diagram of the SET-LRP mechanism with reactions and kinetics labeled --
Scheme S3. The mechanism of Cu$^0$/PMDETA catalyzed polymerization
Scheme S4. The mechanism of Cu$^{1}$/PMDETA catalyzed polymerization
Figure S1. SEC trace of Cu⁰/Me₆TREN catalyzed polymerization (entry 1-5 in Table 1)
Figure S2. SEC trace of Cu$^0$/PMDETA catalyzed polymerization (entry 6-9 in Table 1)
Figure S3. SEC trace of Cu$^{I}$/PMDETA catalyzed polymerization (entry 10-15 in Table 1)

- 27%($M_{n,SEC}$ = 2.06KDa)
- 31%($M_{n,SEC}$ = 2.86KDa)
- 56%($M_{n,SEC}$ = 4.20KDa)
- 67%($M_{n,SEC}$ = 5.11KDa)
- 83%($M_{n,SEC}$ = 6.19KDa)
Figure S4. $^1$H NMR results for PMA catalyzed by Cu$^0$/Me$_6$TREN
Figure S5. $^1$H NMR results for PMA catalyzed by Cu$^0$/PMDETA
Figure S6. $^1$H NMR results for PMA catalyzed by Cu$^{I}$/PMDETA
Figure S7. $^{1}H$ NMR results for PMA catalyzed by Cu$^{0}$&Cu$^{II}$/PMDETA

Equation S1.

$$
\text{Vinyl conversion} = \frac{\text{consumed vinyl groups}}{\text{original vinyl groups}} = 1 - \frac{\text{current vinyl groups}}{\text{original vinyl groups}} = 1 - \frac{\text{integrals of } k}{\text{integrals of } (h+q)/3}
$$

Reference