

Electronic Supplementary Information

for

Use of Alcohols as Reducing Agent for Synthesis of Well-Defined Polymers by AGET-ATRP

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Experimental Section

Materials. All chemicals and reagents were purchased commercially unless otherwise stated. Methyl acrylate (MA), tert-butyl acrylate (^tBA), and styrene (St) were purified via column chromatography with basic alumina before use. 1-Bromoethylbenzene (PEBr), copper(II) bromide, alcohols, 2,2'-bipyridyl (bpy), and anisole were used as received.

Instrumentation. ¹H NMR spectra were recorded at room temperature on a Bruker AVANCE II spectrometer operating at 400 MHz. CDCl₃ and dimethyl sulfoxide (DMSO)-d₆ were used as solvents. The chemical shifts were referenced relative to the solvents. The number average molecular weights (M_n) and polydispersities (M_w/M_n) were measured by gel permeation chromatography (GPC) on a Waters 150 instrument equipped with 10³, 10⁴ and 10⁵ Å Waters Ultrastyrigel columns and using THF (1.0

mL / min) as the eluent. Calibration was against polystyrene standards. UV-Vis spectra of solutions were recorded with a Pgeneral UV-Vis TU-1901 spectrometer.

Reduction of CuBr₂/bpy by Alcohols. A typical procedure for the reduction of CuBr₂/bpy was as follows. A mixture of CuBr₂ (2.45 mg, 11 μmol), bpy (5.15 mg, 33 μmol), ethylene glycol (2.20 mg, 35 μmol), and DMF (4 mL) was added to a glass tube. The solution was degassed by three cycles of freezing-pumping-thawing. Then, the tube was sealed under vacuum and the solution was stirred at 75 °C for a prescribed time. After the reaction, the reaction mixture was characterized immediately by UV-Vis spectra.

AGET-ATRP with Alcohols as Reducing Agents. A typical procedure for the AGET-ATRP of MA was as follows. PEBr (20 mg, 0.11 mmol), MA (1 mL, 11 mmol), CuBr₂ (24.5 mg, 0.11 mmol), bpy (34.5 mg, 0.22 mmol), ethylene glycol (22.0 mg, 0.35 mmol), Na₂CO₃ (16 mg, 0.16 mmol), and anisole (0.5 mL) were charged into a 5 mL tube and, after being degassed by three freeze-vacuum-thaw cycles, the tube was sealed under vacuum. The tube was held in an oil bath at a temperature of 75 °C for a prescribed time and, after polymerization, the reaction mixture was dissolved in THF. Subsequently the solution was passed through a neutral alumina column and then precipitated in petroleum ether for three times. The precipitate was collected by filtration and dried in vacuo at 40 °C. The conversion of MA was determined gravimetrically. The molecular weight was measured by GPC and ¹H NMR.

Extension of PMA Macroinitiator with ^tBA via Glycol-based AGET-ATRP. A PMA macroinitiator (M_n , 7700; M_w/M_n , 1.19) (0.85 g, 0.11 mmol) prepared by AGET-ATRP was dissolved in anisole (2 mL) in a 5 mL tube. The tube was then charged with ^tBA (1.4 g, 11 mmol), CuBr₂ (24.5 mg, 0.11 mmol), bpy (34.5 mg, 0.22 mmol), ethylene glycol (22.0 mg, 0.35 mmol), Na₂CO₃ (16 mg, 0.16 mmol). After being degassed by three freeze-vacuum-thaw cycles, the tube was sealed under vacuum. The tube was held in an oil bath at a temperature of 75 °C for 25 h and, after polymerization, the reaction mixture was dissolved in THF. Subsequently the solution was passed through a neutral alumina column and then precipitated in a large excess of petroleum ether for three times. The precipitate was collected by filtration and dried in vacuo at 40 °C. Yield, 1.11 g; M_n , 11200; M_w/M_n , 1.25.

General Procedure for AGET-ATRP of MA in the Presence of a Limited Amount of Air. The polymerization was carried out in a sealed tube. PEBr (40 mg, 0.22 mmol), MA (2 ml, 22 mmol), CuBr₂ (49 mg, 0.22 mmol), bpy (69 mg, 0.44 mmol), ethylene glycol (44 mg, 0.70 mmol), Na₂CO₃ (32 mg, 0.32 mmol), and anisole (1 mL) were charged into a 5 mL tube and the tube was sealed under air. The tube was held in the oil bath at a temperature of 75 °C for 45 h and, after polymerization, the reaction mixture was dissolved in THF. Subsequently the solution was passed through a neutral alumina column and then precipitated in petroleum ether for three times. The polymer was obtained by filtration and dried in vacuo at 40 °C. Conversion, 75.2%; M_n , 6800; M_w/M_n , 1.12.

Legends and Tables

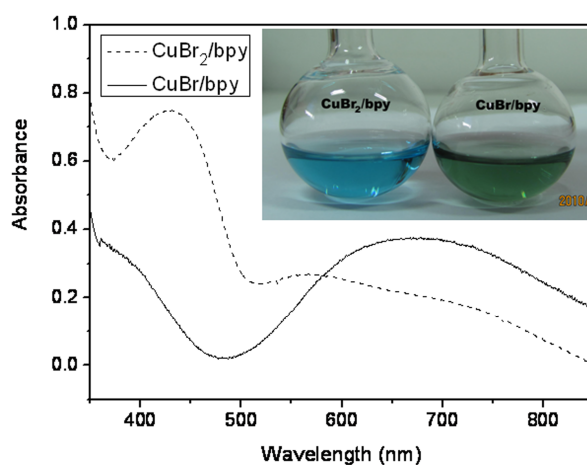


Figure S1. UV-Vis spectra of CuBr₂/bpy and ethylene glycol in DMF before (----) and after (—) the redox reaction. Condition: the tube was sealed under vacuum and heated at 75 °C for 5 h. Inset: photos taken before and after the reaction.

Table S1. AGET-ATRP of MA in anisole using simple alcohols as reducing agents^a

entry	alcohol	conv ^b (%)	M _{n,th} ^c (g/mol)	M _{n,GPC} ^d (g/mol)	M _w /M _n ^d
1	methanol	35.4	3200	3400	1.25
2	ethanol	20.6	2000	2400	1.32
3	isopropanol	32.5	3000	3300	1.25
4	tert-butanol	0	-	-	-
5	ethylene glycol	28.7	2500	2800	1.21
6	1,4-butanediol	48.5	4400	4500	1.29
7	glycerol	22.7	2100	2400	1.30

^a Conditions: MA/PEBr/CuBr₂/bpy/glycol/Na₂CO₃ = 200/2/2/4/6/3, [MA]₀ = 7.4 M, temperature = 70 °C, time = 20 h; ^b Determined gravimetrically; ^c Calculated from the equation: M_{n,th} = Conversion × 100 × 86 + 185; ^d Determined by GPC.

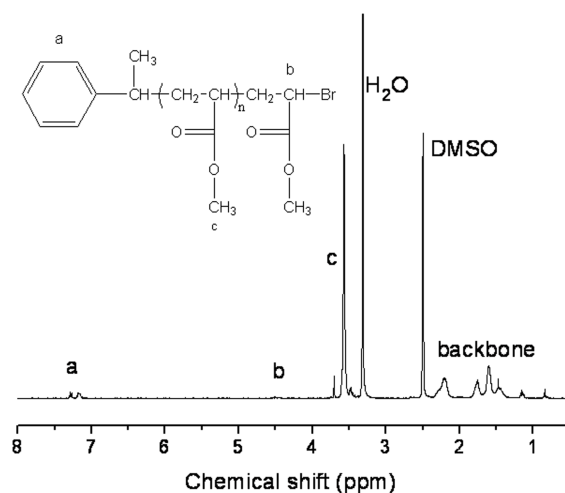


Figure S2. ¹H NMR spectrum of PMA obtained from the AGET-ATRP of MA (Entry 10 in Table 1).

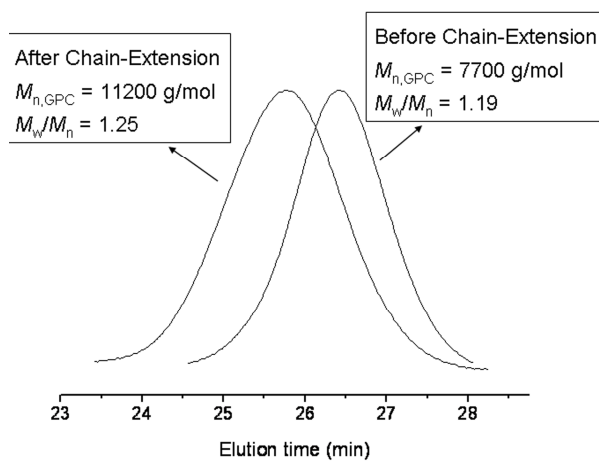


Figure S3. Chain extension of PMA as a macroinitiator with ^tBA via the ethylene glycol-based AGET-ATRP.

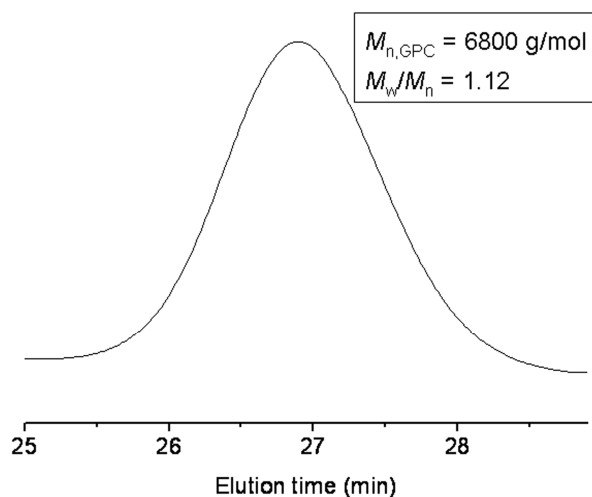


Figure S4. GPC curve of PMA obtained from the AGET-ATRP of MA in the presence of limited amount of air with conversion 75.2%. Condition: $[MA]_0/[PEBr]_0/[CuBr_2]_0/[bpy]_0/[ethylene \text{ glycol}]/[Na_2CO_3] = 200/2/2/4/6/3$, $[MA]_0 = 7.4 \text{ M}$, temperature = 75 °C, time = 45 h.