Supporting Information

**ARGET ATRP Synthesis of Thermally Responsive Polymers with Oligo(ethylene oxide) Units**

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**Experimental**

**Materials**

Ethyl 2-bromoisoobutyrate (EBiB), tin (II) 2-ethylhexanoate (Sn(EH)$_2$), copper(II) bromide, and solvents were purchased from Aldrich at the highest purity available and used as received without further purification. Di(ethylene glycol) methyl ether methacrylate (MEO$_2$MA) (Aldrich, 95%) was purified by vacuum distillation before use. The ligand, tris[(2-pyridyl)methyl]amine (TPMA), was prepared according to the reported procedure.$^1$

**Analysis**

The apparent molecular weight and molecular weight distribution of the polymers were measured by GPC (Waters Microstyragel columns (guard, 10$^2$, 10$^3$, and 10$^5$ Å), using THF as the eluent at 35 °C, and a flow rate of 1.00 mL/min) with a calibration based on poly(methyl methacrylate) (PMMA) standards using GPCWin software from Polymer Standards Service. Conversions were determined by gas chromatography (GC) using a Shimadzu GC-14A gas chromatograph equipped with a FID detector and ValcoBond 30 m VB WAX Megabore column. $^1$H-NMR spectra of polymer were examined in CDCl$_3$ at 30 °C using a Bruker Advance 300 MHz spectrometer. UV-vis spectra were recorded using a Varian Cary 7 Bio UV-vis spectrophotometer equipped with a digital temperature controller. The 600 nm wavelength was used for the determination of the LCST. The temperature range was from 20 °C to 60 °C, and heating and cooling rates were 1 °C/min (Figure 3).
General procedure for ARGET ATRP of di(ethylene glycol) methyl ether methacrylate (PMEO₂MA). 0.16 mg (0.75 µmol) of CuBr₂, 1.09 mg (3.75 µmol) of TPMA, 11 µL (75 µmol) of EBiB, 2.8 mL (15 mmol) of MEO₂MA, and 1.8 mL of anisole were added to a 25 mL Schlenk flask, and oxygen was removed by subjecting the contents of the flask to three freeze-pump-thaw cycles. A solution of Sn(EH)₂ (2.4 µL, 7.5 µmol) in anisole (1 mL) was purged with nitrogen gas then added to the Schlenk flask via syringe. The stirred flask was placed in an oil bath controlled at 40 °C, samples were withdrawn periodically to monitor monomer conversion (GC) and molecular weight (GPC). The polymerization was stopped after 4 h (Mₙ, GPC = 34 800, Mₓ/Mₙ = 1.26, conversion = 68%) by opening the flask and exposing the catalyst to air.

Figure S1. GPC traces for ARGET ATRP of MEO₂MA (Entry 3). Conditions: [MEO₂MA]₀/[EBiB]₀/[CuBr₂]₀/[TPMA]₀/[Sn(EH)₂]₀=200/1/0.01/0.05/0.1 in anisole 40 °C.

General procedure for ARGET ATRP of MEO₂MA in the presence of air. A 22 mL glass vial containing a small stir bar was charged with 9.0 mL (48 mmol) of MEO₂MA, 15 µL (0.10 mmol) of EBiB, and 6 mL of anisole. Then a solution of CuBr₂ (0.22 mg, 1.0 µmol) and TPMA ligand (1.5 mg, 5.0 µmol) in anisole (2 mL) was added. After sealing the vial with a rubber septum, a solution of Sn(EH)₂ (81 µL, 0.20 mmol) in anisole (1 mL) was injected. The initial sample was taken and the sealed vial was placed in an oil bath thermostated at 40 °C. Samples were taken at timed intervals and analyzed by GC and GPC. The polymerization was stopped after 12 h (Mₙ, GPC = 41 200, Mₓ/Mₙ = 1.22, conversion = 53%) by opening the flask and exposing the catalyst to air.
Figure S2. (A) First order kinetic plots, (B) Evolution of molecular weights with conversion of ARGET ATRP of MEO₂MA in the presence of limited amount of air (entry 9). Condition: [MEO₂MA]₀/[EBiB₂]/[CuBr₂]/[TPMA]/[Sn(EH)₂]₀ = 480/1/0.01/0.05/2.0 in anisole 40 °C.

Transmittance Measurement.

Figure S3. Temperature dependence of optical transmittance at 600 nm for 0.3 wt% aqueous solution of PMEO₂MA.

Reference