Supporting Information

Living Radical Polymerization with Alkali and Alkaline Earth Metal Iodides as Catalysts

Jit Sarkar,[1] *Longqiang Xiao,*[1] *Atsushi Goto*[1]*

[1]Division of Chemistry and Biological Chemistry, School of Physical and Mathematical Sciences,
Nanyang Technological University, 21 Nanyang Link, 637371 Singapore

1. Experimental Section

Materials. Methyl methacrylate (MMA) (>99.8%, Tokyo Chemical Industry (TCI), Japan), styrene (St) (>99%, TCI), acrylonitrile (AN) (>99%, Kanto Chemical, Japan), lauryl methacrylate (LMA) (>95%, TCI), benzyl methacrylate (BzMA) (>98%, TCI), *N*,*N*-dimethylaminoethyl methacrylate (DMAEMA) (>98.5%, TCI), 2-hydroxyethyl methacrylate (HEMA) (>95%, TCI), and poly(ethylene glycol) methacrylate (PEGMA) (average molecular weight = 300) (98%, Aldrich) were purified through an alumina column. 2-Cyanopropyl iodide (CP-I) (>95%, TCI), NaI (>99.5%, Kanto), KI (>99.5%, Kanto), CsI (99.9%, Aldrich), CaI_2 (99%, Aldrich), MgI_2 (98%, Aldrich), 2,2′-azobis (2,4-dimethyl valeronitrile) (V65) (95%, Wako Pure Chemical, Japan), 2.2′-azobis(2-methylpropionitrile) (AIBN) (98%, Wako), 2,2′-azobis(4-methoxy-2.4-dimethyl valeronitrile) (V70) (95%, Wako), iodine (I_2) (>98%, TCI), diethylene glycol dimethyl ether (diglyme) (>99%, TCI), 18-crown-6-ether (>98%, TCI), and 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) (>98%, TCI) were used as received. Ethylene glycol bis(2-iodoisobutyrate) (EMA-II), glycerol tris(2-iodoisobutyrate) (EMA-III), 2-hydroxyethyl 2-iodo-2-phenylacetate (PhEOH-I) (>90%), 2-hydroxyethyl 2-iodoisobutyrate (HEMA-I) (>98%), and 6-(2-iodo-2-isobutyloxy)hexyltriethoxysilane (IHE) (>95%) were provided through the courtesy of Godo Shigen Co., Ltd. (Japan) and used as received.[1]

Measurements. The GPC analysis was performed on a Shodex GPC-101 liquid chromatograph (Tokyo, Japan) equipped with two Shodex KF-804L mixed gel columns (300 × 8.0 mm; bead size = 7 μm; pore size = 20–200 Å). The eluent was tetrahydrofuran (THF) or dimethyl formamide (DMF) at a flow rate of 1.0 mL/min (THF) or 0.8 mL/min (DMF) (40 °C). Sample detection and quantification were conducted using a Shodex differential refractometer RI-101 calibrated with known concentrations of polymer in solvent. The monomer conversion was determined from the peak area. The column system was calibrated with standard polystyrenes and poly(methyl methacrylate)s (PMMAs).

The NMR spectra in Figure 2 were recorded on a Bruker BBF0400 spectrometer (400 MHz) (Germany) at ambient temperature; ^{1}H: spectral width 4000.00 Hz, acquisition time 8.192 sec, and pulse delay 1.000 sec. The NMR spectra in Figures 4, 9, S2, and S3 were recorded on a Bruker AV500 spectrometer (500 MHz) at ambient temperature; ^{1}H: spectral width 5000.00 Hz, acquisition time 6.554 sec, and pulse delay 1.000 sec.

Some polymers were purified with a preparative GPC (LC-918, Japan Analytical Industry, Tokyo) equipped with JAIGEL 1H and 2H polystyrene gel columns (600×40 mm; bead size = 16 μm; pore size = 20-30 (1H) and 40-50 (2H) Å). Chloroform was used as eluent at a flow rate of 14 mL/min (room temperature).

Reaction of CP-I, NaI, 18-Crown-6-Ether, and TEMPO (Figure 2). A mixture of toluene-d_8 (1.8 mL), acetonitrile-d_3 (0.2 mL), CP–I (10 mM), NaI (80 mM), 18-crown-6-ether (80 mM), and TEMPO (80 mM) was heated in a Schlenk flask at 70 °C for 7 h under an argon atmosphere with magnetic stirring and subsequently quenched to room temperature. The mixtures before and after the heat treatment were analyzed by ^{1}H NMR.

Polymerization. In a typical run, a mixture of monomer (3 mL), an alkyl iodide initiator, a catalyst, and an ether was heated in a Schlenk flask at 40-80 °C under an argon atmosphere with magnetic stirring. After a prescribed time *t*, an aliquot (0.1 mL) of the solution was taken out by a syringe, quenched to room temperature, diluted by THF or DMF to a known concentration, and analyzed by GPC.

Preparation of PMMA-I for Block Copolymerizations. A mixture of MMA (4 mL (8 M)), CP-I (80 mM), NaI (40 mM), and 18-crown-6-ether (40 mM) was heated in a Schlenk flask at 70 °C for 70 min under an argon atmosphere with magnetic stirring, yielding a PMMA-I with M_n = 4500 and M_w/M_n = 1.15 (monomer conversion = 38%) (before purification). The reaction mixture was diluted with THF and passed through a short alumina column to remove NaI. After purification by reprecipitation from cold hexane and with the preparative GPC, a PMMA-I with M_n = 4600 and M_w/M_n = 1.13 was obtained and used as a macroinitiator for the block copolymerization (Figures 8a, 8b, and 8c and Table 6).

Preparation of I-PLMA-I for Triblock Copolymerization. A mixture of LMA (1.8 mL (8 M)), EMA-II (40 mM), NaI (40 mM), V65 (20 mM), and diglyme (10 wt%) was heated in a Schlenk flask at 60 °C under an argon atmosphere for 3 h with magnetic stirring, yielding an I-PLMA-I with M_n = 25000 and M_w/M_n = 1.32 (monomer conversion = 69%) (before purification). The reaction mixture was diluted with THF and passed through a short alumina column to remove NaI. After purification by reprecipitation from acetonitrile, an I-PLMA-I with M_n = 26000 and M_w/M_n = 1.29 was obtained and used as a macroinitiator for the block copolymerization (Figures 8d and Table 7).

2. Polymerizations of MMA with Different Concentrations of NaI and 18-Crown-6-Ether.

Figure S1 shows the polymerizations of MMA (8 M) with a constant amount of CP-I (80 mM) and varied amounts of NaI (20-80 mM) and 18-crown-6-ether (20-80 mM) at 70 °C. The ratio of $[\mathrm{NaI}]_0/[\text{18-crown-6-ether}]_0$ was 1 in all cases in Figure S1.

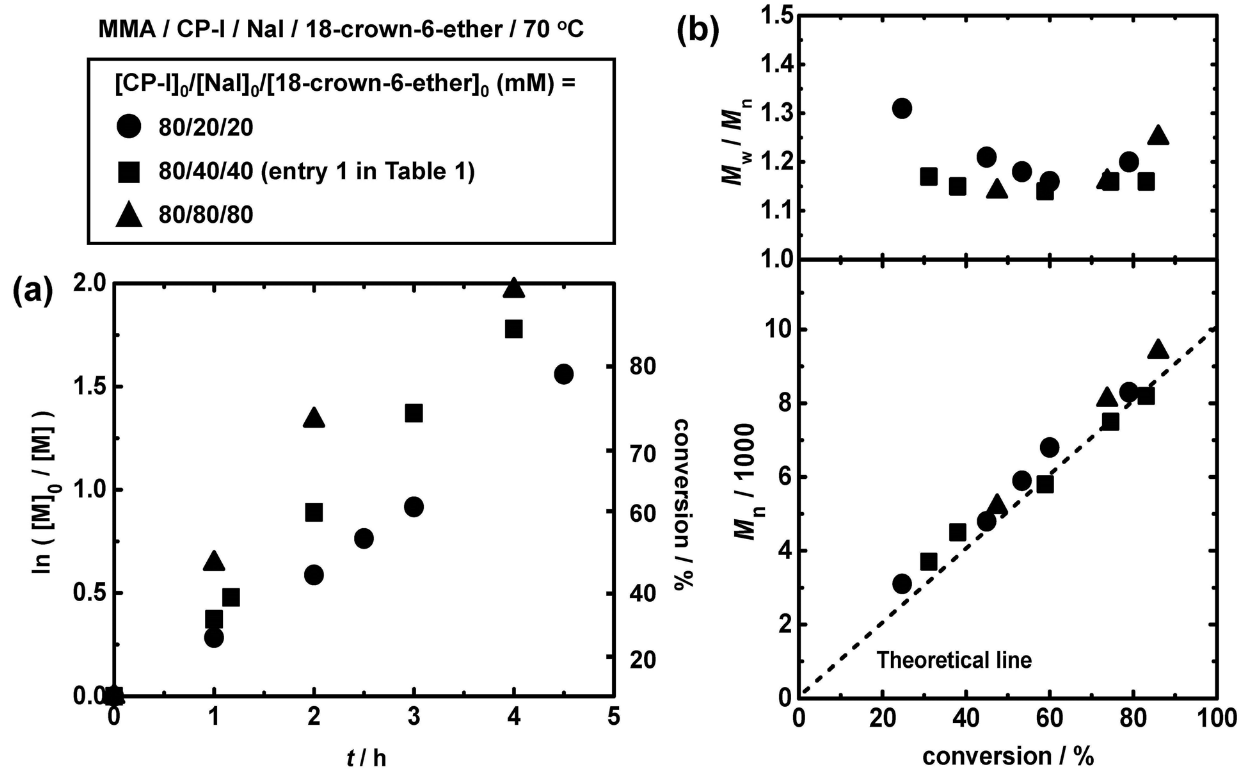

Figure S1. Plots of (a) $\ln([M]_0/[M])$ vs t and (b) M_n and M_w/M_n vs conversion for the MMA/CP-I/NaI/18-crown-ether systems in bulk (70 °C): $[\mathrm{MMA}]_0$ = 8 M; $[\text{CP-I}]_0$ = 80 mM; $[\mathrm{NaI}]_0$ = 20-80 mM; $[\text{18-crown-6-ether}]_0$ = 20-80 mM. The symbols and concentrations are indicated in the figure.

3. ^{1}H NMR Spectra of Telechelic Polymers.

Figure S2 shows the ^{1}H NMR spectrum of the polymer synthesized from HEMA-I (monomer conversion = 78%) and purified with a preparative GPC (M_n = 8400 and PDI = 1.38 after purification). The chain-end functionality can be estimated from the relative peak areas of this initiating moiety (peak **e**) and the monomer units (peak **a**, **a'**, and **a"**). We calculated the number of monomer units (= 81) using the M_n determined by GPC and estimated the chain-end functionality to be 100% (with ± 10% experimental error).

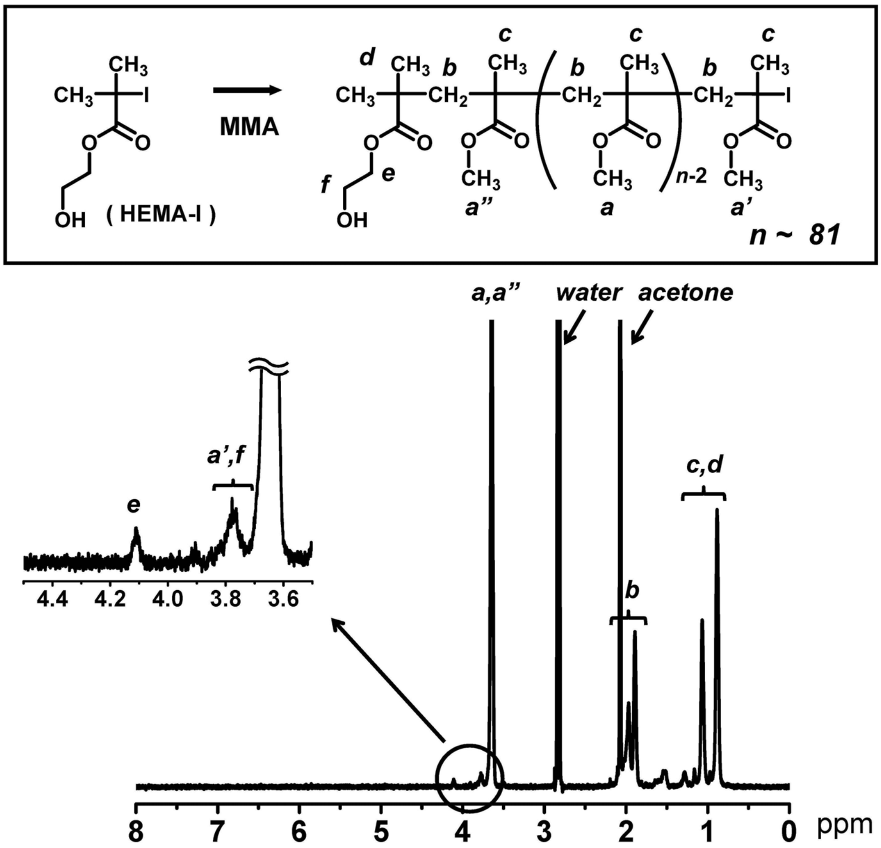

Figure S2. ^{1}H NMR spectrum (acetone-d_6) of PMMA-I obtained from HEMA-I and purified with preparative GPC (M_n = 8400 and PDI = 1.38 after purification). The polymerization condition is given in Table 8 (entry 1 for 6 h).

Figure S3 shows the ^{1}H NMR spectrum of the polymer synthesized from IHE (monomer conversion = 74%) and purified with a preparative GPC (M_n = 8300 and PDI = 1.30 after purification). The chain-end functionality can be estimated from the relative peak areas of this initiating moiety (peak **e**) and the monomer units (peak **a**, **a'**, and **a"**). We calculated the number of monomer units (= 78) using the M_n determined by GPC and estimated the chain-end functionality to be 89% (with ± 10% experimental error).

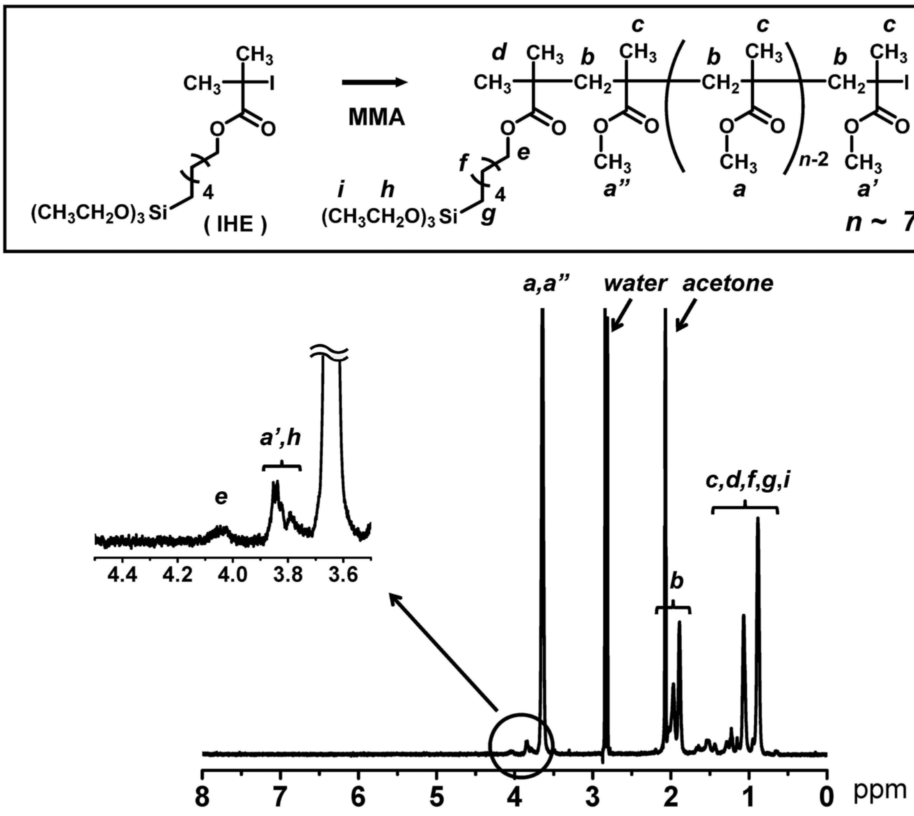

Figure S3. ^{1}H NMR spectrum (acetone-d_6) of PMMA-I obtained from IHE and purified with preparative GPC (M_n = 8300 and PDI = 1.30 after purification). The polymerization condition is given in Table 8 (entry 2).

Reference

(1) Lei, L.; Tanishima, M.; Goto, A.; Kaji, H.; Yamaguchi, Y.; Komatsu, H.; Jitsukawa, T.; Miyamoto, M. Systematic Study on Alkyl Iodide Initiators in Living Radical Polymerization with Organic Catalysts. *Macromolecules* **2014**, *47*, 6610-6618.