ARGET ATRP of 2-(Dimethylamino)ethyl Methacrylate as an Intrinsic Reducing Agent

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Supporting Information

Materials. 2-(Dimethylamino)ethyl methacrylate (DMAEMA) (Aldrich, 98%) was purified by passing through a column filled with basic alumina. Tris[(2-pyridyl)methyl]amine (TPMA) was synthesized following previously reported procedures.[1] The initiator, 1-(chlorodimethylsilyl)propyl 2-bromoisobutyrate, was grafted on the surface of a silicon wafer as described elsewhere.[2] According to the literature, the cross-sectional area of alkyldimethylsilyl groups in a densely packed monolayer on the surface is 32-38 Å^2.[3] Therefore, it is estimated the initiator density on silicon wafer is ca. 3 bromoester groups per nm^2. Ethyl 2-bromoisobutyrate (EBiB) (Acros, 98%), copper(II) chloride (Acros, 99%), tin(II) 2-ethylhexanoate (Sn(EH)_2) (Aldrich, 95%), α-D-glucose (Aldrich, 96%), L-ascorbic acid (Aldrich, > 99%), anhydrous hydrazine (Aldrich, 98%) and dimethyl sulfoxide (DMSO) (Fisher, 99.9%) were used as received.

Synthetic Procedures.

Activators Re-Generated by Electron Transfer (ARGET) Atom Transfer Radical Polymerization (ATRP) of DMAEMA with Internal Reducing Agent under Nitrogen (Table 1, entry 1). A dry 10 mL Schlenk flask was charged with DMAEMA (3.0 mL, 17.8 mmol), anisole (1.0 mL) and ethyl 2-bromoisobutyrate (5.2 μL, 0.036 mmol). The resulting mixture was degassed by four freeze-pump-thaw cycles. After melting the mixture, a bubbled solution of $CuCl_2$ (0.24 mg, 0.0018 mmol) and TPMA ligand (2.6 mg, 0.009 mmol) in anisole (0.5 mL) was slowly added to the reaction medium. The sealed flask was placed in an oil bath thermostated at 30 °C. Samples were taken at timed intervals and analyzed by ^{1}H-NMR and gel permeation chromatography (GPC) to follow the progress of the reaction. The polymerization was stopped by opening the flask and exposing the catalyst to air.

ARGET ATRP of DMAEMA with Internal Reducing Agent in The Presence of Air (Table 1, entry 2). A 22 mL glass vial containing a stir bar was charged with DMAEMA (12.0 mL, 71.2 mmol), anisole (5.6 mL), and ethyl 2-bromoisobutyrate (20.9 μL, 0.142 mmol). Then a solution of $CuCl_2$ (0.95 mg, 0.0071 mmol) and TPMA ligand (10.3 mg, 0.036 mmol) in anisole (0.4 mL) was added. After sealing the vial with a rubber septum, the vial was placed in an oil bath thermostated at 30 °C. Samples were taken at timed intervals and analyzed by ^{1}H-NMR and GPC to follow the progress of the reaction. The polymerization was stopped by opening the flask and exposing the catalyst to air.

ARGET ATRP of DMAEMA with External Reducing Agent in The Presence of Air (Table 1, entry 3). A 22 mL glass vial containing initiator-modified silicon wafer
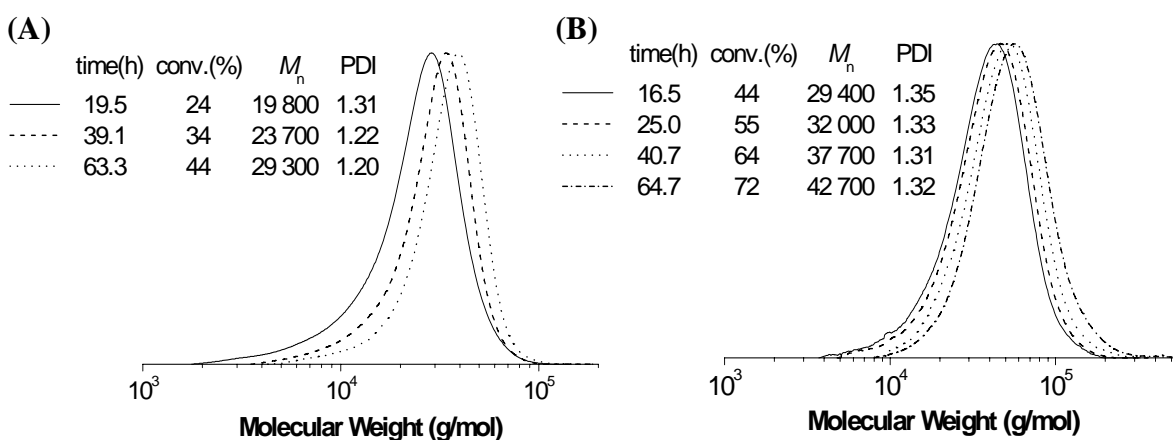
and a stir bar was charged with DMAEMA (12.0 mL, 71.2 mmol), anisole (4.6 mL), and ethyl 2-bromoisobutyrate (20.9 μL, 0.142 mmol). Then a solution of $CuCl_2$ (0.95 mg, 0.0071 mmol) and TPMA ligand (10.3 mg, 0.036 mmol) in anisole (0.4 mL) was added. After sealing the vial with a rubber septum, the solution of tin(II) 2-ethylhexanoate (230 μL, 0.71 mmol) in anisole (1 mL) was injected. The sealed vial was placed in an oil bath thermostated at 30 °C. Samples were taken at timed intervals and analyzed by ^{1}H-NMR and GPC to follow the progress of the reaction. The polymerization was stopped by opening the flask and exposing the catalyst to air.

Surface-initiated ARGET ATRP of DMAEMA from Silicon Wafer (Figure S2). A 22 mL glass vial containing initiator-modified silicon wafer and a stir bar was charged with DMAEMA (12.0 mL, 71.2 mmol), anisole (4.6 mL), and sacrificial initiator, ethyl 2-bromoisobutyrate (20.9 μL, 0.142 mmol). Then a solution of $CuCl_2$ (0.95 mg, 0.0071 mmol) and TPMA ligand (10.3 mg, 0.036 mmol) in anisole (0.4 mL) was added. After sealing the vial with a rubber septum, the solution of tin(II) 2-ethylhexanoate (69.3 μL, 0.214 mmol) in anisole (1 mL) was injected. The initial sample was taken and the sealed vial was placed in an oil bath thermostated at 30 °C. Samples were taken at timed intervals and analyzed by ^{1}H-NMR and GPC to follow the progress of the reaction. The polymerization was stopped by opening the flask and exposing the catalyst to air. The resulting silicon wafer was washed with acetone in a Soxhlet extractor for 24 hours. The thickness (h) of the dry PDMAEMA brushes was measured by ellipsometry in air. The grafting density (σ) was calculated using the following equation: $\sigma = N_A h \rho / M_w$, where M_w is the weight average molecular weight of polymer formed from sacrificial initiator

(which is assumed to be equal to that of polymer growing from the wafer), N_A is Avogadro's number, and $\rho = 1.3$ g/cm^3 is the bulk PDMAEMA density.

Analyses. Molecular weight and molecular weight distribution were measured by a GPC system consisting of a Waters 510 HPLC pump, three Waters Ultrastyragel columns (500, 10^3, and 10^5 Å), and a Waters 410 DRI detector, with DMF as an eluent (50 ^{o}C, flow rate = 1.0 mL/min). Linear polystyrene standards were used for calibration. Conversion of DMAEMA was determined by ^{1}H NMR in CDCl$_3$ on a Bruker AM 300 MHz spectrometer. UV-vis spectra were recorded on a Varian Cary 5000 UV-vis-NIR spectrophotometer using a 1-cm-wide glass cuvette. The thicknesses of the grafted PDMAEMA brushes were obtained by a discrete wavelength ellipsometer PhE-101 (Micro Photonics Inc.) with a He-Ne laser ($\lambda = 632.8$ nm) at a 70 ° incidence angle. The refractive index of the polymer brushes on the substrates was assumed to be n = 1.50. The data were collected at four spots on each wafer.

(A)

	time(h)	conv.(%)	M_n	PDI
——	19.5	24	19 800	1.31
-----	39.1	34	23 700	1.22
······	63.3	44	29 300	1.20

(B)

	time(h)	conv.(%)	M_n	PDI
——	16.5	44	29 400	1.35
-----	25.0	55	32 000	1.33
······	40.7	64	37 700	1.31
-·-·-	64.7	72	42 700	1.32

Molecular Weight (g/mol) (x-axis for A)

Molecular Weight (g/mol) (x-axis for B)

Figure S1. Evolution of molecular weight distribution during ARGET ATRP of DMAEMA under N$_2$ (A, Table 1, entry 1) and in the presence of air (B, Table 1, entry 2).

**Table S1. ARGET ATRP of DMAEMA in Presence of Air with Various Amount of Sn(EH)$_2$**[a]

entry	[Sn(EH)$_2$]$_0$ / [CuCl$_2$]$_0$	time (h)	conversion (%)	M_n[b] (theo)	M_n[c] (GPC)	PDI[c]
S1	15	48.2	52	40 700	46 400	1.28
S2	30	48.2	53	41 300	41 600	1.17
S3	50	48.2	74	58 300	49 900	1.22
S4	100	18.0	90	70 600	61 500	1.35
S5	200	18.0	97	76 200	78 400	1.54

[a] DMAEMA: EtBiB: CuCl$_2$: TPMA = 500: 1: 0.05: 0.25 at 30 ^{o}C in anisole. V(free space) = 4 mL. [DMAEMA]$_0$ = 3.96 M. [b] M_n(theo) = ([DMAEMA]$_0$/ [EBiB]$_0$) x conversion. [c] Determined by SEC in DMF, based on polystyrene standards.
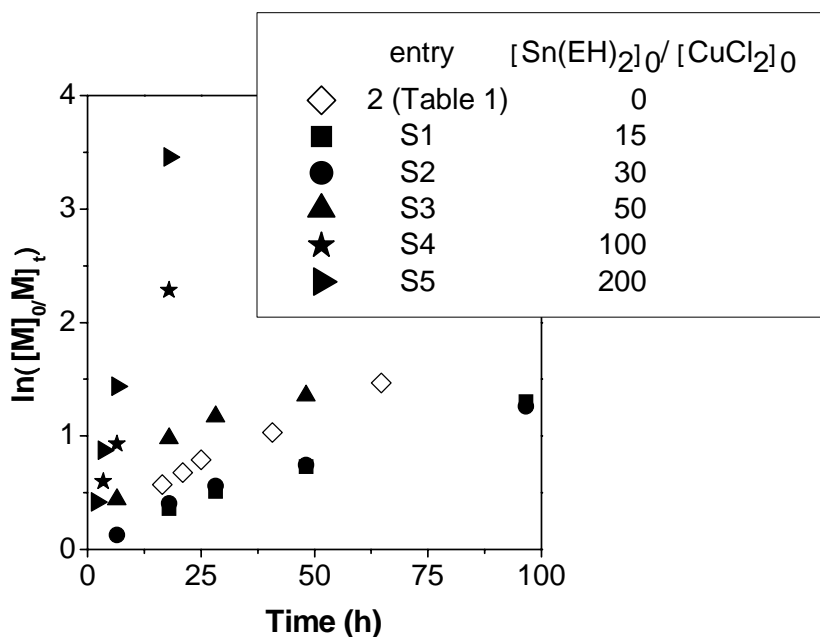

Figure S2. Kinetic plots in ARGET ATRP of DMAEMA with internal (Table 1, entry 2) and varied amount of external reducing agent Sn(EH)$_2$ (Table S1, entries 1-5).
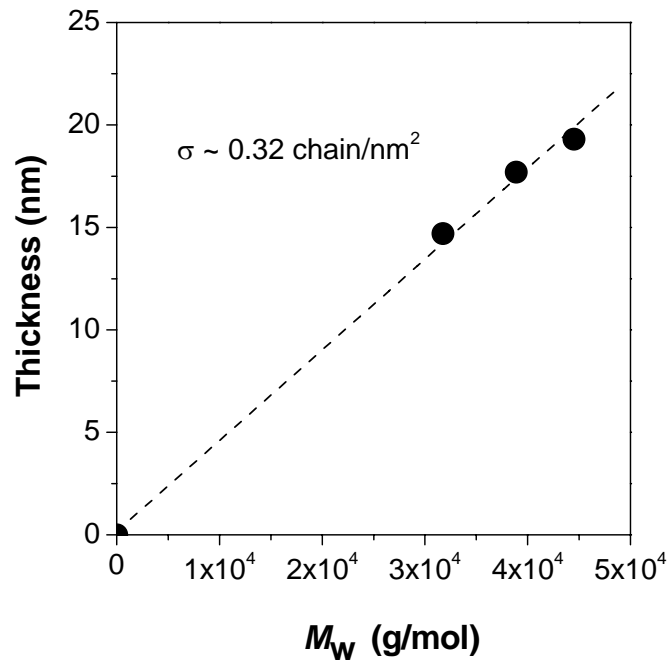
Figure S3. Relationship between grafted PDMAEMA brush thickness measured in air by ellipsometry and M_n of free PDMAEMA polymers. The reaction was conducted with chlorodimethylsilylpropyl 2-bromoisobutyrate-modified silicon wafer. DMAEMA: EtBiB: CuCl$_2$: TPMA = 500: 1: 0.05: 1.5 at 30 $^{\circ}$C in anisole. V(free space) = 4 mL. [DMAEMA]$_0$ = 3.96 M.

Scheme S1. Proposed Mechanism of Reduction of Cu(II)Cl$_2$/TPMA with DMAEMA
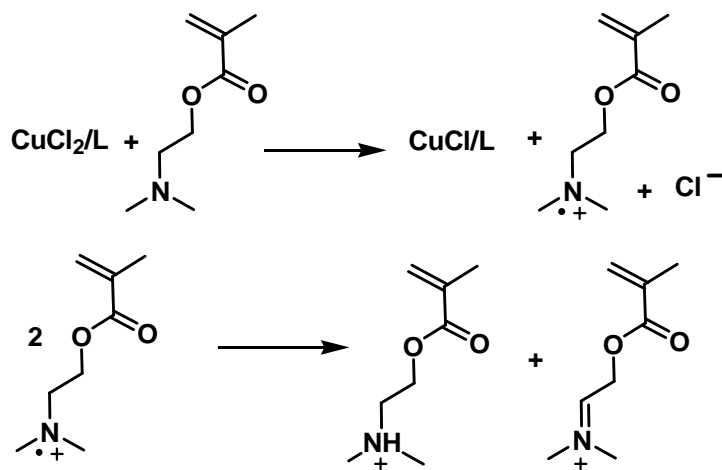
References

(1)   Tyeklar, Z.; Jacobson, R. R.; Wei, N.; Murthy, N. N.; Zubieta, J.; Karlin, K. D. *J. Am. Chem. Soc.* **1993**, *115*, 2677-2689.

(2)   Miller, P. J.; Matyjaszewski, K. *Macromolecules* **1999**, *32*, 8760-8767.

(3)   Fadeev, A. Y.; McCarthy, T. J. *Langmuir* **2000**, *16*, 7268-7274.