Electronic Supplementary Information

Photo-selective chain end transformation of polyacrylate-iodide using cysteamine and its application to facile single-step preparation of patterned polymer brushes

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1. Experimental

Materials. Ethyl 2-iodopropanoate (EA-I) (> 99%, Tokyo Chemical Industry (TCI), Japan), cysteamine (> 95%, TCI), 2-iodo-2-methylpropionitrile (CP−I) (> 95%, TCI), butyl acrylate (BA) (> 97%, TCI), 2-methoxyethyl acrylate (MEA) (> 98%, TCI), tetrabutylammonium iodide (BNI) (> 98%, TCI), 4,4'-azobis(4-cyanovaleric acid) (V501) (> 75%, Sigma-Aldrich, United States), diethylene glycol dimethyl ether (diglyme) (> 99%, TCI), 1-butanol (> 99%, Kanto Chemical, Japan), iodine (I_2) (> 98%, TCI), tributylamine (TBA) (> 98%, TCI), 7-diethylamino-3-(4-maleimidophenyl)-4-methylcoumarin (CPM) (> 95%, Sigma-Aldrich), ammonia solution (28% in water, TCI), trans-2-[3-(4-t-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) (> 99%, Fluka Chemicals Ltd., UK), sodium trifluoroacetate (NaTFA) (> 98%, TCI), and tetrahydrofuran (THF) (> 99.5%, Kanto) were used as received. 6-(2-Iodo-2-isobutyloxy)hexyltriethoxysilane (IHE) was provided through the courtesy of Godo Shigen Co., Ltd. (Japan) and was used as received. The glass photomask (Hunan Omnisun Information Material Co., Ltd., China) is polished on both sides with a patterned low reflective chrome film on one side. The photomask was used as received. The Cu grid is carbon-coated on 200 mesh (Ted Pella, USA). The Cu grid was washed by acetone with sonication for 30 min before use.

Analytical GPC. 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 THF at a flow rate of 1.0 mL/min (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 poly(methyl methacrylate)s.

Preparative GPC. Polymers were purified with a preparative GPC (LC-9204, 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).

NMR. The NMR spectra were recorded on a BBFO400 spectrometer (400 MHz) (Bruker, Germany) at ambient temperature; ^{1}H: spectral width 4000.00 Hz, acquisition time 8.192 sec, and pulse delay 1.000 sec.

MALDI-TOF-MS. The MALDI-TOF-MS spectra were recorded on a JMS-S3000 Spiral-TOF (JEOL Ltd., Japan) at an accelerating potential of 20 kV in the positive spiral mode. We prepared polymer solution (10 g/L in THF), matrix solution (DCTB: 60 g/L in THF), and cationization agent solution (NaTFA: 10 g/L in THF). The polymer solution, the DCTB solution, and the cationization agent solution were mixed in a ratio of 1/2/1 (v/v/v). Then, 5 μL of the mixed solution was deposited on the target plate spot and dried in the air at room temperature.

UV-LED light. The UV-LED light source (C11924-101) (at 365 (± 10) nm), was purchased from Hamamatsu Photonics (Japan). The energy of the radiating light per area (mW/cm^2) (described below) was measured with a power meter (FieldMate, Coherent, USA).

Photo-Selective Reaction of EA-I with Cysteamine. Cysteamine (0.2 mmol, 5 eq) was pre-dissolved in a toluene-d_8/methanol-d_4 (w/w = 88/12) mixed solvent (0.4 mL) because of its slow dissolution. Then,

the solution was mixed with a solution of EA-I (0.04 mmol, 1 eq) in a toluene-d_8/methanol-d_4 (w/w = 88/12) mixed solvent (0.1 mL) in a reaction tube (hence 0.5 mL solution in total) and magnetically stirred under UV irradiation (365 nm) for 10 min or without UV irradiation for 1 h at ambient temperature.

Preparation of Purified EA-SH. The reaction mixture of EA-I and cysteamine in the dark condition (without UV irradiation) after 1 h was washed with brine three times and deionized water once. The organic phase was collected and dried under vacuum, giving EA-SH. ^{1}H NMR (toluene-d_8/methanol-d_4 (w/w = 88/12)) is given in Fig. 1d. ^{13}C NMR (toluene-d_8/methanol-d_4 (w/w = 88/12)) is given in Fig. S1a.

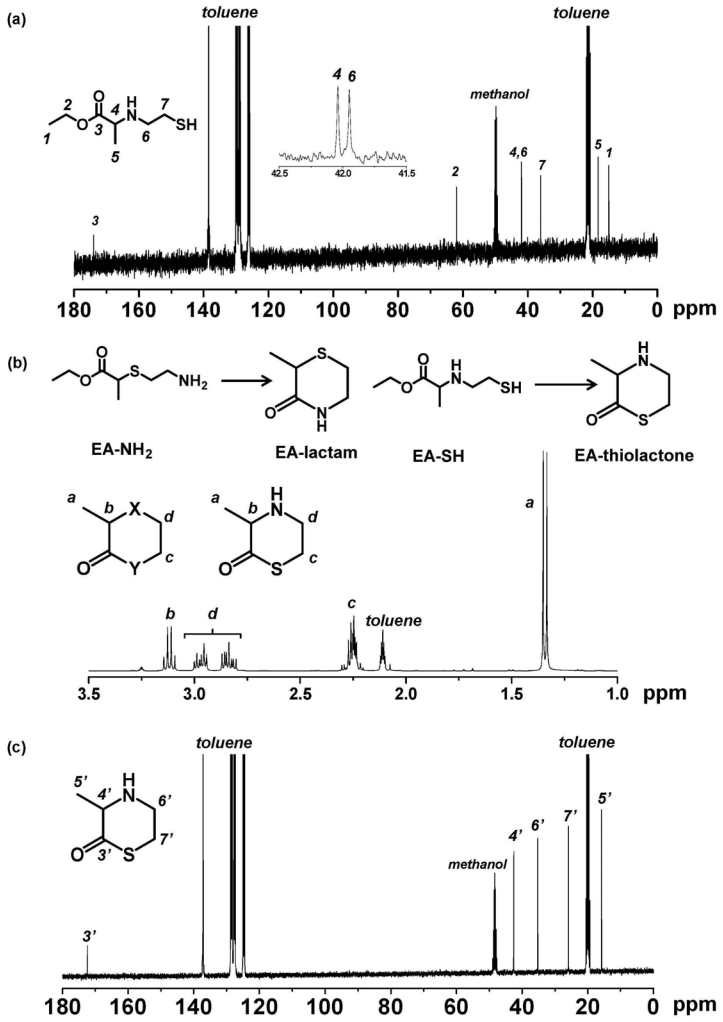

Fig. S1. NMR spectra in a mixture of toluene-d_8 and methanol-d_4 (w/w = 88/12). (a) ^{13}C NMR spectrum of EA-SH. (b and c) ^{1}H and ^{13}C NMR spectra of EA-thiolactone.

Preparation of polymer-I (PBA-I and PMEA-I). A mixture of monomer (BA or MEA) (15 g, 50 eq), CP-I (1 eq), and BNI (4 eq) was heated in a 100 mL flask at 110 °C for 5 h under an argon atmosphere with magnetic stirring**.** The reaction mixture was diluted with THF, and the polymer was reprecipitated in a non-solvent (methanol/water mixture (w/w = 1/1) for PBA and hexane for PMEA). The polymer was further purified with preparative GPC.

Preparation of HOOC-PMEA-I. A mixture of MEA (10 g, 100 eq), V501 (3.75 eq), I_2 (1 eq), BNI (1 eq) and diglyme (50 wt%) was heated in a 100 mL flask at 110 °C for 1 h under an argon atmosphere with magnetic stirring**.** The reaction mixture was diluted with THF, and the polymer was reprecipitated in hexane. The polymer was further purified with preparative GPC.

General Procedure of Photo-Selective Reaction for Polymers. A mixture (0.5 g) of polymer-I (1 eq, 20 wt%) and cysteamine (20 eq) in a mixed diglyme/1-butanol (w/w = 1/1) solvent was stirred in a reaction tube at room temperature in the dark condition (for 12 h for PBA and 24 h for PMEA) or under UV irradiation (for 2 h for PBA and 12 h for PMEA). The reaction mixture was diluted by THF, and then the polymer was reprecipitated in a non-solvent (methanol/water mixture (w/w = 1/1) for PBA and hexane for PMEA). The polymer was further purified with preparative GPC.

Preparation of IHE-Immobilized Silicon Wafer. A silicon wafer (0.8 cm × 0.8 cm) was washed with acetone (with sonication for 30 min), chloroform (with sonication for 30 min), and isopropanol (with sonication for 30 min). After drying under nitrogen flow, the wafer was placed in the ozone cleaner and radiated for 30 min. The wafer was immersed in a mixture of IHE, aqueous ammonia solution, and ethanol (1/89/10 (w/w/w)) for one day. The wafer was rinsed with ethanol, sonicated in ethanol for 30 min, and dried under nitrogen flow to give an IHE immobilized silicon wafer.

Preparation of PBA-I Brushes. The IHE-immobilized silicon wafer was heated in a mixture of BA (10 g, 1000 eq), CP−I (1 eq), and BNI (4 eq) in a Schlenk flask at 110 ^{o}C under argon atmosphere for 20 h (entry 1 in Table S1) and 48 h (entry 2 in Table S1). After the polymerization, the wafer was rinsed with acetone, sonicated in acetone for 30 min twice, and dried under nitrogen flow. The thickness of the

polymer brush in the dry state was determined by AFM. We scratched the brush and measured the height gap between the scratched and unscratched areas (Fig. S2). The M_n and $Đ$ of the non-immobilized polymers generated from CP-I (non-immobilized alkyl iodide initiator) and the height and surface occupancy (σ*) of the obtained PBA brushes are summarized in Table S1.

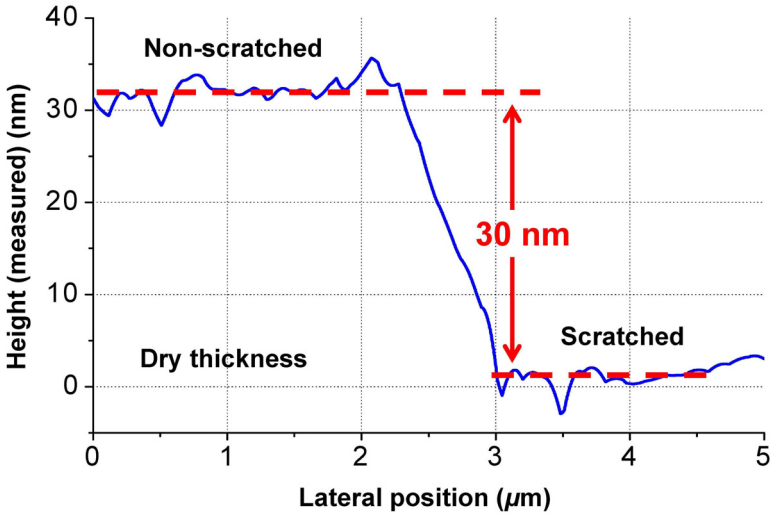

Fig. S2. AFM height profile in the scratched and non-scratched areas of the obtained brush (Table S1, entry 2).

Table S1. M_n and $Đ$ of the non-immobilized polymers generated from CP-I and the thickness and surface occupancy (σ*) of the obtained PBA brush.

entry	M_n	$Đ$	Dry thickness (nm)	σ*
1	61,000	1.92	20	0.19
2	139,000	1.80	30	0.11

Preparation of Patterned Brushes. A cysteamine solution (5 wt%) in a diglyme/1-butanol (w/w = 1/1) mixed solvent was dropped onto a silicon wafer fabricated with PBA-I brush. Then, a cover glass was placed to form a thin layer of solution between the cover glass and wafer. A photomask was then placed on the cover glass, and UV was irradiated (irradiation power = 900 mW/cm^2) for 2 h. The wafer was cleaned by ultra-sonication in THF for 30 min and dried under nitrogen flow.

Fluorescent Labeling of Thiol Patterned PBA Brushes. The wafer with the thiol patterned PBA brush was immersed in a mixture of CPM (0.5 mg/mL, 1 eq), TBA (2 eq), and DMF in dark at room temperature for 4 h. The wafer was cleaned by ultra-sonication in THF for 30 min and dried under nitrogen flow. The fluorescence picture was taken with Zeiss Observer Z1 (Germany) using the filter set 49 under autoexposure.

2. Proof of NH_2 (instead of SH) as Nucleophile in the Studied Condition.

If SH is a nucleophile, the substitution reaction of EA-I with cysteamine generates EA-$SCH_2CH_2NH_2$ with a terminal NH_2 group (EA-NH_2). EA-NH_2 would subsequently readily undergo an intra-molecular amidation to generate a 6-memberred lactam (EA-lactam, Fig. S1b).

For the reaction of EA-I with cysteamine in the dark condition (Fig. 1b), we observed EA-SH after 1 h. We further prolonged the reaction time from 1 h to 12 h. EA-SH was stable and underwent no further reaction. To this reaction mixture, for a characterization purpose, silica gel was added to induce the ring closure reaction. After the purification by chromatography**,** a product with a 6-membered ring was obtained, which should be either EA-thiolactone or EA-lactam if any (Fig. S1b). Fig. S1b shows the ^{1}H NMR spectrum of the 6-membered ring product. The two split signals (2.79–2.88 ppm and 2.93–3.02 ppm) belong to XCH_2 (protons d), because the axial proton d interacts with the axial proton b (the methyl group is bulkier and equatorial) and the equatorial proton d does not, resulting in the two different chemical shifts (protons d). The non-split signal at 2.22–2.31 ppm belongs to YCH_2 (protons c). In comparison of N and S, the chemical shift of NCH_2 (down-field) should be higher than SCH_2 (up-field). This means that XCH_2 (down-field protons d) is NCH_2, and YCH_2 (up-field protons c) is SCH_2. The product obtained must be EA-thiolactone (not EA-lactam), demonstrating that only NH_2 worked as a nucleophile in the studied reaction condition. The ^{1}H NMR and ^{13}C NMR spectra (toluene-d_8/methanol-d_4 (w/w = 88/12)) and the assignment are given in Figs. S1b and S1c.

3. Calculation of Theoretical Molecular Mass for MALDI-TOF-MS.

The chemical formula of PBA-H with 21 BA repeating units and CP (C_4H_6N) at the initiating chain is $C_{151}H_{259}O_{42}N$. The theoretical molecular mass value (with the additive cation Na^+) without ^{13}C atoms is (Fig. 2d):

$$151 \times 12\ (C) + 259 \times 1.00783\ (H) + 42 \times 15.99491\ (O) + 1 \times 14.00307\ (N) + 22.98977\ (Na) = 2781.81$$

4. ^{1}H NMR Analysis of PBA-I, PBA-SH, and PBA-H.

Fig. S3a shows the ^{1}H NMR spectrum of the obtained PBA-I (M_n = 2900 and $Đ$ = 1.29 according to PMMA-calibrated GPC). Fig. S3b shows the obtained PBA-SH (polymer **2**) (the polymer given in Fig. 2a), confirming the presence of the CH_2CH_2SH moiety (protons *l* and *m*). Fig. S3c shows the obtained PBA-H (the polymer given in Fig. 2b).

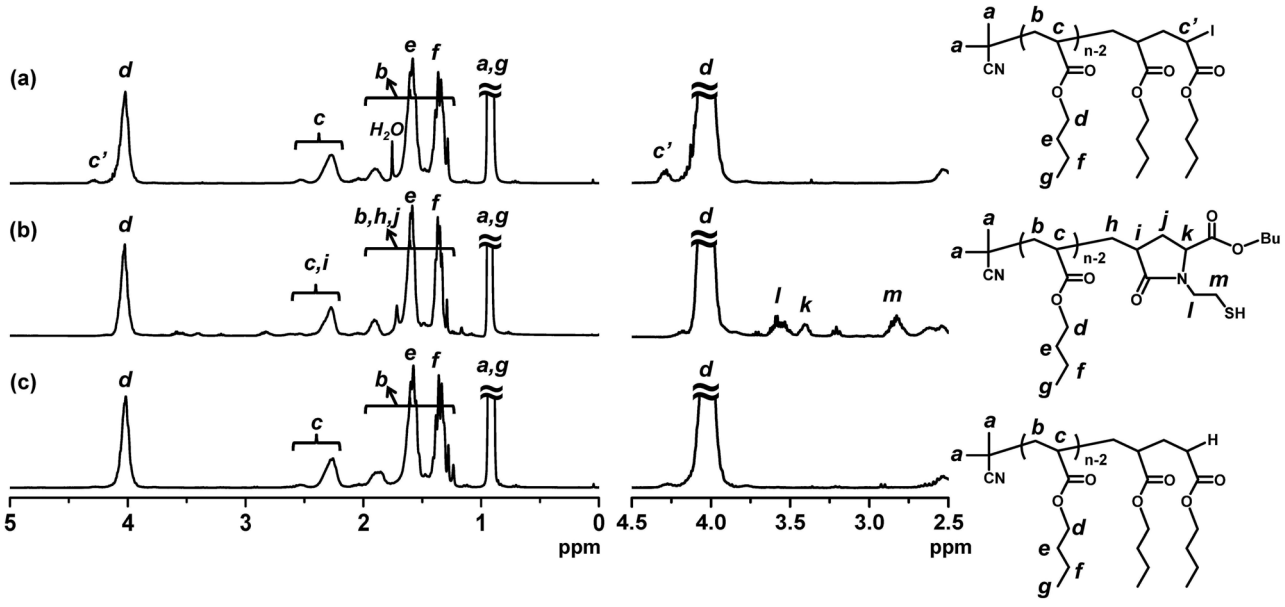

Fig. S3. ^{1}H NMR (400 MHz) spectra ($CDCl_3$) of (a) PBA-I, (b) PBA-SH (polymer **2**), and (c) PBA-H.

4. MALDI-TOF-MS Analysis for Reaction of PMEA-I and Cysteamine.

Fig. S4 shows the MALDI-TOF-MS spectra of the products in the reaction of PMEA-I and cysteamine in the dark condition (24 h) and under UV irradiation (12 h). In the dark condition, PMEA-SH was obtained (Fig. S4a); the experimental mass (2692.21) matched the theoretical mass of PMEA-SH (2692.27). Under UV irradiation, PMEA-H was obtained (Fig. S4b); the experimental mass (2693.27) matched the theoretical mass of PMEA-SH (2693.31).

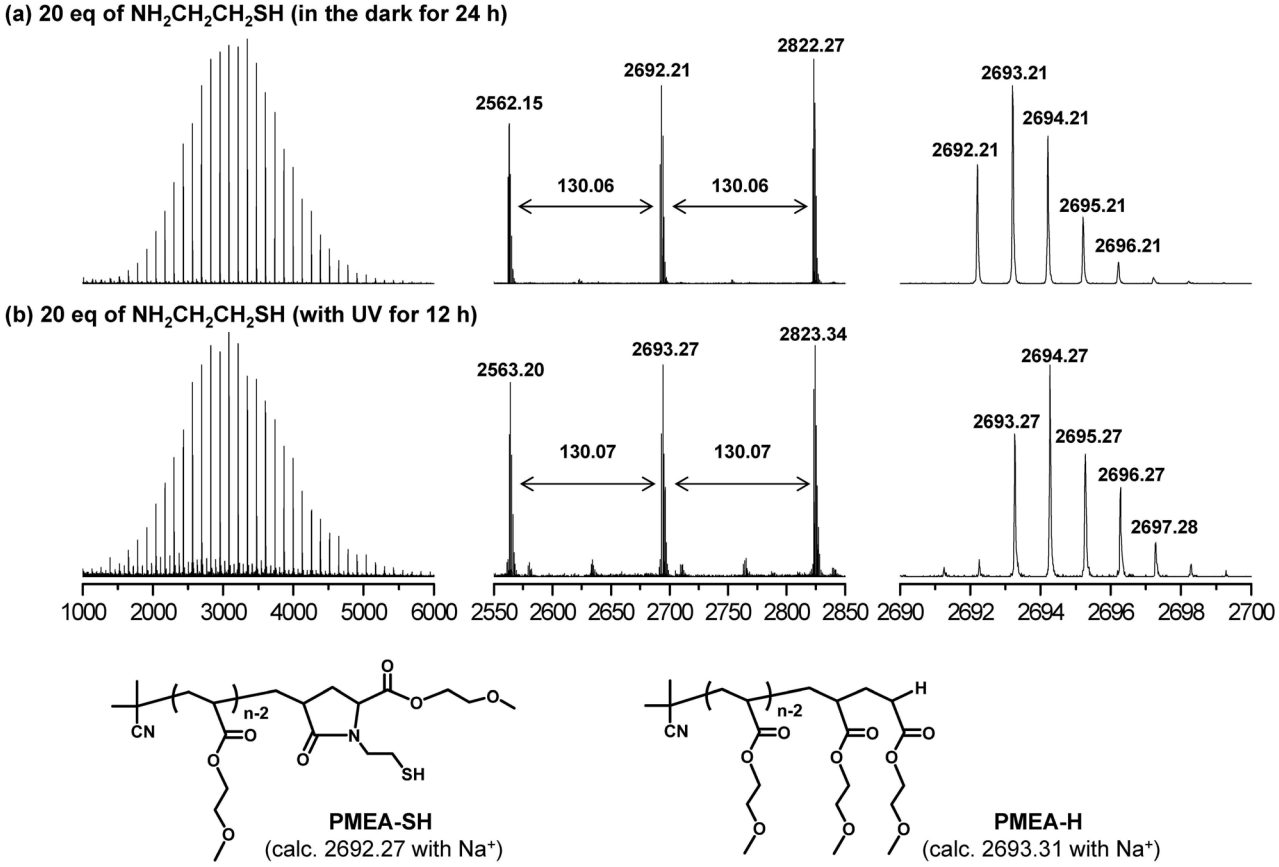

Fig. S4. MALDI-TOF-MS spectra of the polymers obtained via a reaction of PMEA-I (1 equiv) and cysteamine (20 equiv) (a) without UV after 24 h and (b) with UV after 12 h.

5. MALDI-TOF-MS Analysis for Reaction of HOOC-PMEA-I and Cysteamine.

Fig. S5 shows the MALDI-TOF-MS spectra of the products in the reaction of HOOC-PMEA-I and cysteamine in the dark condition (24 h) and under UV irradiation (12 h). In the dark condition, HOOC-

PMEA-SH was obtained (Fig. S5a); we observed two series, i.e., HOOC-PMEA-SH (theoretical mass = 2619.92) without Na^+ (main peak) and NaOOC-PMEA-SH (theoretical mass = 2641.90) with replacement of H^+ with Na^+ (minor peak). Under UV irradiation, HOOC-PMEA-H was obtained (Fig. S5b); we observed HOOC-PMEA-H (theoretical mass = 2620.96) without Na^+ (main peak) and NaOOC-PMEA-H (theoretical mass = 2642.94) with replacement of H^+ with Na^+ (minor peak) in the MALDI-TOF-MS spectrum (Fig. S5b).

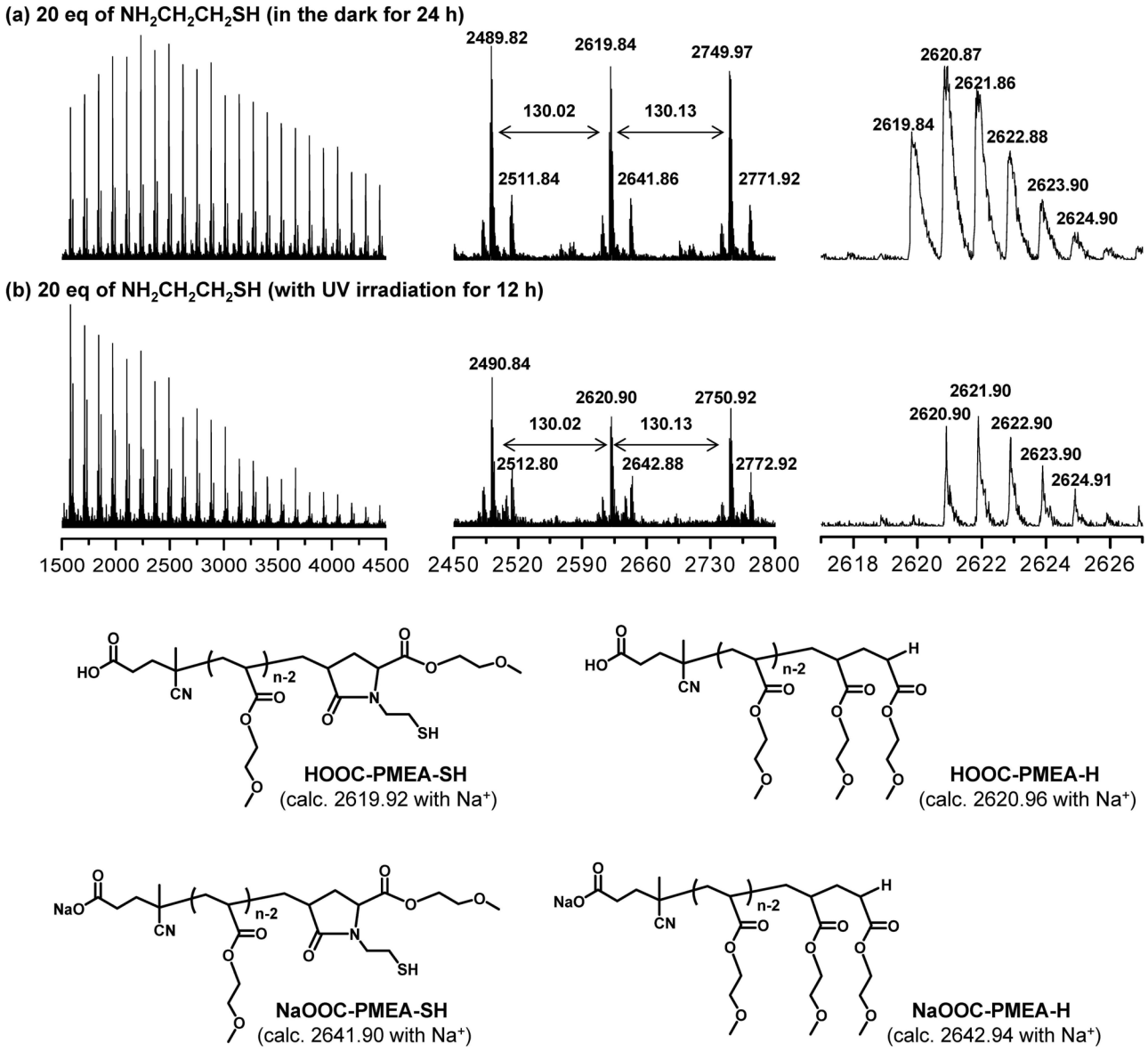

Fig. S5. MALDI-TOF-MS spectra of the polymers obtained via a reaction of HOOC-PMEA-I (1 equiv) and cysteamine (20 equiv) (a) without UV after 24 h and (b) with UV after 12 h.

6. Optical Microscope Image of Copper Grid and Fluorescence Microscope Images of Patterned Polymer Brushes.

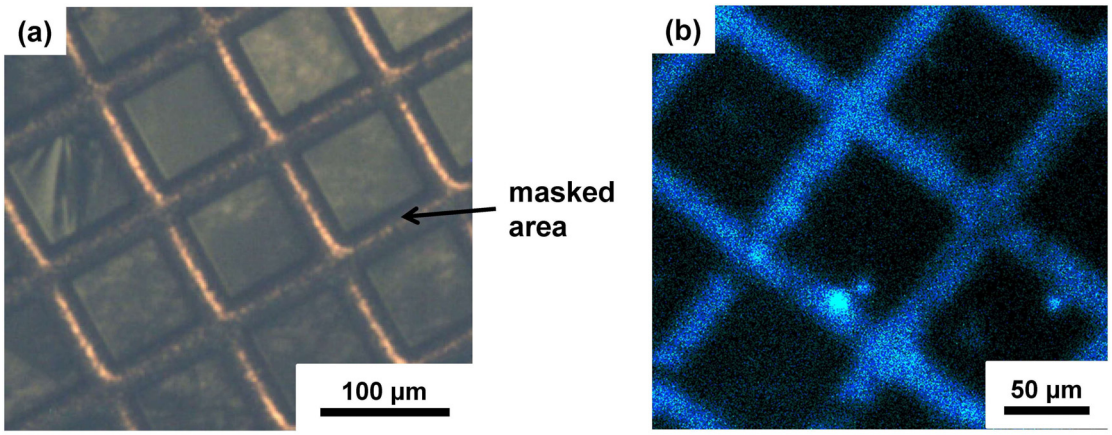

Fig. S6. (a) Optical microscope image of the copper grid. (b) Fluorescence microscope image of CPM-attached patterned PBA brush (thickness = 30 nm) with use of the copper grid.

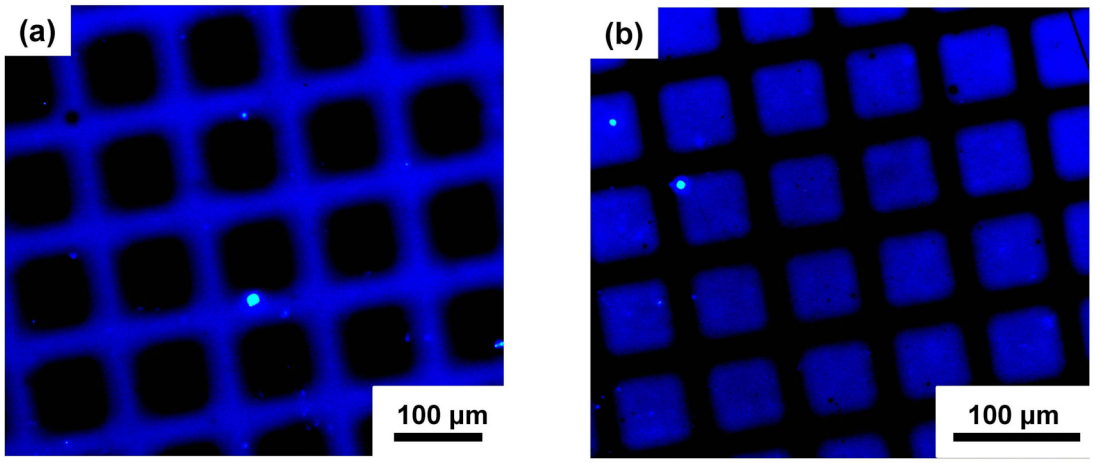

Fig. S7. Fluorescence microscope images of CPM-attached patterned PBA brushes (thickness = 20 nm) with use of (a) copper grid and (b) glass photomask.