A photo-selective chain-end modification of polyacrylate-iodide and its application to patterned polymer brush synthesis

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1. Materials and Measurement

Materials. 2-Iodo-2-methylpropionitrile (CP−I) (>95%, Tokyo Chemical Industry (TCI), Japan), butyl acrylate (BA) (>97%, TCI), 2-methoxyethyl acrylate (MEA) (>98%, TCI), 1\textsubscript{H},1\textsubscript{H},2\textsubscript{H},2\textsubscript{H}-nonafluorohexyl acrylate (NFHA) (> 98%, TCI), tetrabutylammonium iodide (BNI) (>98%, TCI), 2-phenylethylamine (>98%, TCI), 1-amylamine (>98%, TCI), 3-aminopropyltriethoxysilane (>98%, TCI), 4-amino-1-butanol (>98%, TCI), propargylamine (>97%, TCI), N,N-dimethylformamide (DMF) (>99.5%, Kanto Chemical, Japan), methanol (>99%, International Scientific, Singapore), tetrahydrofuran (THF) (>99.5%, Kanto Chemical), triethylamine (TEA) (>99%, TCI), tributylamine (TBA) (>98%, TCI), 4-dimethylaminopyridine (DMAP) (>99%, TCI), fluorescein 5-isothiocyanate (FITC) (>90%, Sigma-Aldrich, United States), 1,2-ethanedithiol (>99%, TCI), 2-hydroxy-4’-(2-hydroxyethoxy)-2-methylpropio phenone (Irgacure D-2959) (98%, Sigma-Aldrich), 7-diethylamino-3-(4-
maleimidophenyl)-4-methylcoumarin (CPM) (>95%, Sigma-Aldrich), formic acid (>98%, TCI), ammonia solution (28% in water, TCI), \textit{trans}-2-[3-(4-t-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) (>99%, Fluka Chemicals, UK) and sodium trifluoroacetate (NaTFA) (>98%, TCI) were used as received. 6-(2-Iodo-2-isobutoxy)hexyltriethoxysilane (IHE) was provided through the courtesy of Godo Shigen (Japan) and was used as received. Formic-\textit{d} acid (DCOOH) (95wt% in H\textsubscript{2}O) (Sigma-Aldrich) was dried by MgSO\textsubscript{4} before use. The glass photomasks (Hunan Omnisun Information Materia, China) polished on both sides with a patterned low reflective chrome film on one side were used as received.

**Analytical GPC.** The GPC analysis was performed on a Shimadzu LC-2030C Plus liquid chromatograph (Kyoto, Japan) equipped with a Shodex (Tokyo, Japan) KF-804L mixed gel column (300 × 8.0 mm; bead size = 7 \( \mu \)m; pore size = 20–200 Å) and a Shodex LF-804 mixed gel column (300 × 8.0 mm; bead size = 6 \( \mu \)m; pore size = 3000 Å). The eluent was tetrahydrofuran (THF) at a flow rate of 0.7 mL/min. Sample detection was conducted using a Shimadzu differential refractometer RID-20A. The column system was calibrated with standard poly(methyl methacrylate)s (PMMA).

**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 \( \mu \)m; pore size = 20-30 (1H) and 40-50 (2H) Å). Chloroform was used as the 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; 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 mg/mL in THF), matrix solution (\textit{trans}-2-[3-(4-t-butylphenyl)-2-...
methyl-2-propenyldiene]malononitrile (DCTB): 60 mg/mL in THF), and cationization agent solution (sodium trifluoroacetate (NaTFA): 10 mg/mL 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.

**Contact Angle.** The water-contact angle analysis of the polymer brushes was carried out with a DM-701 contact angle meter (Kyowa Interface Science, Japan).

**UV-LED light.** The UV-LED light source (C11924-101) (at 365 (± 10) nm) was purchased from Hamamatsu Photonics (Japan). The energy of the irradiating light per area was measured to be 900 mW/cm² with a power meter (FieldMate, Coherent, USA).

**AFM.** The polymer brush thickness was determined with an atomic force microscope (AFM) (Probe Station AFM5000II, Hitachi High-Technologies, Japan) using a cantilever PRC-DF40P.
2. AFM Height Profile of Synthesized PBA-I Brushes

**Fig. S1** AFM height profile in the scratched and non-scratched areas of the PBA-I brush.
3. NMR Spectra of CPS-SH

Fig. S2 (a) $^1$H and (b) $^{13}$C NMR spectra (DMSO-$d_6$) of CPS-SH.
4. Calculation of Theoretical Molecular Mass for MALDI-TOF-MS.

For example, the chemical formula of PBA-Ph with 21 BA repeating units with CP (C₄H₈N) at the
initiating chain and NHCH₂CH₂Ph (C₈H₁₀N) at the growing chain end is C₁₅₉H₂₆₈O₄₂N₂ (Fig. 1). The
theoretical molecular mass value (with the additive cation Na⁺) without ^{13}C atom is given by
159 × 12 (C) + 268 × 1.00783 (H) + 42 × 15.99491 (O) + 2 × 14.00307 (N) + 22.98977 (Na) = 2900.88

5. ^1H NMR Analysis of Reactions Using NH₂CH₂CH₂Ph with and without UV Irradiation.

Fig. 2a shows the ^1H NMR spectrum of PBA-I. From the peak areas of the terminal monomer unit
(peak c’, CH, 4.3 ppm) and the whole monomer units (peak d, OCH₂, 3.8–4.2 ppm), we calculated the
degree of polymerization (DP) to be 27. Figs. 2b and 2c show the ^1H NMR spectra of the products
obtained in the reactions of PBA-I (1 eq, 20wt%), NH₂CH₂CH₂Ph (20 eq), and HCOOH (4 eq) in the
dark and under the UV irradiation, respectively. The products were purified by preparative GPC to
remove trace amounts of NH₂CH₂CH₂Ph and other low-molecular-weight species. In the dark, the
signal of C₆H₅ (peak j, 7.1–7.4 ppm) was clearly observed, demonstrating the introduction of the
NHCH₂CH₂Ph moiety. The yield of PBA-Ph was calculated to be 88% from the relative peak areas of
C₆H₅ and the monomer units (peak d, OCH₂, 3.8–4.2 ppm) with DP = 27. Under the UV irradiation, the
yield of PBA-Ph was calculated to be 11%. Assuming that PBA-I was converted to either PBA-Ph or
PBA-H (100% in total), we calculated the yield of PBA-H to be 89% (= 100% − 11%).
6. Mechanistic Study Using Formic-\textit{d} Acid (DCOOH).

Fig. S3 shows the MALDI-TOF-MS spectrum of the product obtained in the reaction of PBA-I (20 wt\%, 1 eq), DCOOH (4 eq), and TBA (20 eq) in DMF under the UV irradiation at room temperature for 2 h. A minor signal at 2395.72 belongs to an HI elimination product from PBA-I (PBA-ene (theoretical mass value = 2395.66 (with the repeating unit \(n = 18\))) without \(^{13}\text{C}\) atom. The signal intensity was 2720, which is given in the parenthesis in the figure. The signal at 2397.73 (with the intensity of 23900) belongs to PBA-H (theoretical mass value = 2397.68 (\(n = 18\))) without \(^{13}\text{C}\) atom and PBA-ene with two \(^{13}\text{C}\) atoms (theoretical mass value = 2397.67). The signal at 2398.73 (with the intensity of 37000) belongs to PBA-D (theoretical mass value = 2398.69 (\(n = 18\))) without \(^{13}\text{C}\) atom, PBA-H with one \(^{13}\text{C}\) atom (theoretical mass value = 2398.68), and PBA-ene with three \(^{13}\text{C}\) atoms (theoretical mass value = 2398.67). Because all of PBA-ene, PBA-H, and PBA-D have the same number of carbons, the isotopic distribution is the same. The theoretical relative intensities at \(n = 18\) for zero, one, two, and three \(^{13}\text{C}\) atoms are given in Fig. S3. The experimental ratio of PBA-H/PBA-D is calculated as follows:

\[
\frac{\text{PBA-H}}{\text{PBA-D}} = \frac{23900 - \frac{2720}{69.008} \times 77.035}{37000 - \frac{23900 - \frac{2720}{69.008} \times 77.035}{69.008} \times 100 - \frac{2720}{69.008} \times 41.637} = 80/20
\]

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<th>The number of (^{13}\text{C})</th>
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Fig. S3 MALDI-TOF-MS spectrum of the product obtained in a reaction of PBA-I (1 eq, 20 wt\%), DCOOH (4 eq), and TBA (20 eq) in DMF under the UV irradiation for 2 h.
7. MALDI-TOF-MS Spectra.

**Fig. S4** MALDI-TOF-MS spectra of the products obtained in the reactions of PBA-I (1 eq, 20wt%), formic acid (4 eq), and NH₂CH₂C≡CH (20 eq) in DMF (a) in the dark after 2 h and (b) with the UV irradiation after 2 h (Table 1 (entry 5)).

**Fig. S5** MALDI-TOF-MS spectra of the products obtained in the reactions of PMEA-I (1 eq, 20wt%), formic acid (4 eq), and NH₂CH₂CH₂Ph (20 eq) in DMF (a) in the dark after 2 h and (b) with the UV irradiation after 2 h.
8. $^1$H NMR Spectra

Fig. S6 $^1$H NMR spectra of the product (in CDCl$_3$) obtained via reactions of PBA-I (1 eq, 20wt%), formic acid (4 eq), and different amines NH$_2$-R-X (20 eq) in DMF with and without UV after 2 h (Table 1 (entries 2-5)). The amine and condition (with or without UV) are given in the figure.
9. Reaction of PBA-I with FITC

A DMF solution of non-immobilized PBA-I (20 wt%, 0.075 mM, 0.5 eq), FITC (5.7 wt%, 0.15 mM, 1 eq), TBA (0.15 mM, 1 eq), and DMAP (0.15 mM, 1 eq) was heated in a reaction tube at 60 °C for 12 h. The polymer was purified with preparative GPC. Fig. S7b shows the $^1$H NMR spectrum of the obtained polymer. The signals of the monomer units (peaks a-g, 0.8–4.2 ppm) and FITC (peak a’-f’, 6.5–8.2 ppm) were observed. The yield of PBA-FITC was calculated to be 9% from the relative peak areas of the monomer units (peak d, OCH$_2$, 3.8–4.2 ppm) (DP = 27) and FITC (peak d’, e’ and f’, 6.5–7.0 ppm), showing that the generation of PBA-FITC was insignificant. The concentrations of FITC, TBA, and DMAP (0.15 mM for all) in this reaction (using non-immobilized PBA-I) were 5.7 times higher than those (0.026 mM for all) in the reaction on surface (using surface-immobilized PBA-I) in Fig. 4, meaning that the generation of PBA-FITC was even less significant in the reaction studied for polymer brush on surface (Fig. 4).

Fig. S7 $^1$H NMR spectra of (a) FITC (in acetone-d$_6$) and (b) the polymer (in CDCl$_3$) obtained in a reaction of PBA-I (20 wt%, 0.075 mM, 0.5 eq), FITC (5.7 wt%, 0.15 mM, 1 eq), TBA (0.15 mM, 1 eq), and DMAP (0.15 mM, 1 eq) in DMF at 60 °C for 12 h.
10. Microscope image.

We prepared a binary patterned PNFHA-\textit{b}-PBA (squares) and PBA (wells) brush. Fig. S8 shows the microscope image. The squares (PNFHA-\textit{b}-PBA) were darker than the wells (PBA). This means that, in Fig. 5b, the darker and lighter stripes correspond to PNFHA-\textit{b}-PBA and PBA, respectively.

\textbf{Fig. S8} Optical microscope image of binary patterned PNFHA-\textit{b}-PBA and PBA-H brush using a well-shaped photomask.