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ARTICLE

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

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A photo-selective chain-end modification of polyacrylate-iodide (polymer-I) was developed. In the presence of functional primary amine (NH₂-R-X with an X functionality) and formic acid, by simply switching the ultraviolet (UV) light on and off, polymer-I was selectively converted to hydrogen-terminated polymer-H and chain-end functionalized polymer-NH-R-X (polymer-X), respectively. The scopes of the amenable functional X groups and polyacrylates are wide, and hence this method may serve as a general and versatile method for the selective chain-end modification. As a useful application, this method was successfully used to fabricate chain-end patterned binary polymer brushes on surfaces. This method is free from metal, amenable to various functionalities, and useful for designing a range of chain-end functionalized polymers and surface-functionalized materials.

Introduction

Chain-end functionalized polymers are of great interest for their use as building blocks to create architecturally designed polymers.^{1–3} They can connect with small molecules and other polymers to produce labelled polymers,⁴ block copolymers,^{5,6} and bio-conjugates,^{7,8} yielding advanced polymer materials such as bio-imaging, drug or gene delivery, self-assembly, and stimuli-responsive materials. The chain-end functionalized polymer brushes on solid surfaces also provide smart surfaces.^{9,10}

Living radical polymerization, also termed reversible-deactivation radical polymerization, is a useful approach for synthesizing well-defined polymers possessing a capping agent at the growing chain end.^{11–14} Chain-end functionalized polymers are accessible by using functional initiators to give functional groups at the initiating chain end or by the post-transformation of the capping agent to functional groups to give functional groups at the growing chain end.¹

Besides the functionalization, the removal of the capping agent from the polymer chain end is often required for the long-term stability of the obtained polymers. Hydrogen-terminated polymers (polymer-H) can be obtained *via* photo-redox catalysis in the presence of reducing agents from halide- and thiocarbonate-terminated polymers prepared *via* atom

transfer radical polymerization (ATRP) and reversible addition-fragmentation chain transfer (RAFT) polymerization.^{15–19} This transformation was used to obtain hydrogen-terminated polymer brushes on surfaces in patterned manners.¹⁹

Our research group developed reversible complexation mediated polymerization (RCMP) using an alkyl iodide (R-I) as an initiator and an organic molecule as a catalyst, yielding a polymer-iodide (polymer-I) possessing an iodide at the growing chain end.^{20–25} Mechanistically, polymer-I reversibly generates the propagating radical (polymer•) by the work of the catalyst. The catalysts include organic salts such as tetrabutylammonium iodide (Bu₄N⁺I[−] (BNI)). The polymerization is metal-free, odor-free, and amenable to a wide range of monomers and polymer structures, which are attractive features. The terminal iodide chain end can be modified using primary amines (NH₂-R-X), converting polymer-I to chain-end functionalized polymers (polymer-NH-R-X) with various functional X groups.²⁶

Selective reaction is important in organic synthesis and polymer chemistry.^{17,27–31} By applying different external stimuli, the reaction proceeds under different pathways, yielding different products from the same reactants. Our group previously utilized polymer-I and cysteamine (NH₂CH₂CH₂SH) to selectively produce polymer-H and a thiol-terminated polymer (polymer-SH) with and without photo-irradiation, respectively.³² The SH of cysteamine worked as a radical chain transfer agent (a hydrogen donor) with the irradiation to generate polymer-H, while the NH₂ of cysteamine worked as a substitution agent without the irradiation to generate polymer-NHCH₂CH₂SH (polymer-SH). However, this method can give only an SH functional chain end, and a more general method accessible to various functional X chain ends is desirable.

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In the present work, we developed the first general method to selectively produce polymer-H and polymer-X with various functional X groups. We co-used formic acid as a hydrogen donor and a primary amine $\text{NH}_2\text{-R-X}$ as a substitution agent to selectively convert polymer-I to polymer-H and polymer-X (polymer-NH-R-X) with and without photo-irradiation, respectively. The use of primary amines with different functional X groups generates various polymer-X, significantly widening the scope of the X groups. This method is robust and practically attractive, since formic acid is inexpensive and various primary amines are commercially available. We focused on polyacrylates because this amine-based substitution is limited to polyacrylate-iodides (not amenable to polymethacrylate-iodides).²⁶ As a useful application, this method also enabled a facile preparation of patterned binary polymer brushes with hydrogen and various functional X groups at the chain ends, as described below.

Experimental section

Preparation of Polymer-I (PBA-I and PMEAI-I). A mixture of monomer (butyl acrylate (BA) or 2-methoxyethyl acrylate (MEA)) (15 g, 50 eq), 2-iodo-2-methylpropionitrile (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 tetrahydrofuran (THF), and the polymer was reprecipitated in a non-solvent (methanol/water mixture (v/v = 1/1) for poly(butyl acrylate)-iodide (PBA-I) and hexane for poly(methoxyethyl acrylate)-iodide (PMEAI-I). The polymer was further purified with preparative gel permeation chromatography (GPC).

General Procedure of Photo-Selective Chain-End Transformation of Polymer-I. A *N,N*-dimethylformamide (DMF) solution of polymer-I (20 wt%, 1 eq), formic acid (HCOOH) (4 eq), and a primary amine (20 eq) was stirred in a reaction tube at room temperature in the dark for 2 h or under the UV irradiation for 2 h. The reaction mixture was diluted with chloroform, and then the polymer was purified with preparative GPC.

Reaction of PBA-I with HCOOH. A DMF solution of PBA-I (20 wt%, 1 eq) and HCOOH (4 eq) was stirred in a reaction tube at room temperature under the UV irradiation for 2 h. The reaction mixture was diluted with THF, and then the polymer was reprecipitated in a methanol/water mixture (v/v = 1/1).

Reaction of PBA-I with TBA. A DMF solution of PBA-I (20 wt%, 1 eq) and tributylamine (TBA) (20 eq) was stirred in a reaction tube at room temperature under the UV irradiation for 2 h. The reaction mixture was diluted with THF, and then the polymer was reprecipitated in a methanol/water mixture (v/v = 1/1).

Reaction of PBA-I with DCOOH. A DMF solution of PBA-I (20 wt%, 1 eq), formic-*d* acid (DCOOH) (4 eq), and TBA (20 eq) was stirred in a reaction tube at room temperature under the UV irradiation for 2 h. The reaction mixture was diluted with THF,

and then the polymer was reprecipitated in a methanol/water mixture (v/v = 1/1).

Preparation of PBA-I Brush. The 6-(2-Iodo-2-isobutyloxy)hexyltriethoxysilane (IHE)-immobilized silicon wafer was heated in a mixture of BA (10 g, 1000 eq), CP-I (1 eq), and BNI (8 eq) in a Schlenk flask at 110 °C under argon atmosphere for 24 h. The M_n and $\bar{D}$ ($= M_w/M_n$) values of the non-immobilized polymer produced from CP-I were 23000 and 1.34, respectively, where M_n and M_w are the number- and weight-average molecular weights, respectively, and $\bar{D}$ is the dispersity. The M_n and $\bar{D}$ values are poly(methyl methacrylate) (PMMA)-calibrated GPC values. After the polymerization, the wafer was rinsed with acetone, sonicated in acetone for 30 min twice, and dried under nitrogen flow. The thickness (h) of the polymer brush in the dry state was determined by atomic force microscope (AFM) to be 20 nm (Fig. S1 in ESI). We scratched the brush and measured the height gap between the scratched and unscratched areas. Assuming that the M_n value of the polymer brush is 23000 (179 monomer units), the contour length of the polymer brush chain is 45 nm ($= 0.25$ nm (length of the monomer unit) $\times$ 179 units). (For the sp^3 carbon linkage, the C-C distance is 1.53 Å and the bond angle is 109.5°. The alternate C-C-C distance (length of the monomer unit) is thus calculated to be 0.25 nm.) The surface occupancy (σ^*) is calculated to be 0.45 ($= 20$ nm (brush thickness) / 45 nm (contour length of the polymer chain)). This σ^* value is viewed as an approximation, because we assume that the M_n value of the polymer brush is the same as that of the non-immobilized polymer and use the PMMA-calibrated M_n value.

Preparation of OH and Alkyne Chain-End Patterned Brushes. A DMF solution of HCOOH (1 eq, 1 wt%) and a primary amine (5 eq) ($\text{NH}_2(\text{CH}_2)_4\text{OH}$ or $\text{NH}_2\text{CH}_2\text{C}\equiv\text{CH}$) was dropped onto the silicon wafer fabricated with the PBA-I brush. A cover glass was placed to form a thin layer of the solution between the cover glass and the wafer. Then, a photomask was placed on the cover glass, and UV was irradiated for 2 h. The wafer was cleaned by ultra-sonication in THF for 30 min and dried under nitrogen flow.

FITC Labeling of OH Chain-End Patterned PBA Brush. The OH patterned silicon wafer was heated in a DMF solution of fluorescein 5-isothiocyanate (FITC) (1 wt%, 0.026 mM, 1 eq), TBA (0.026 mM, 1 eq), and 4-dimethylaminopyridine (DMAP) (0.026 mM, 1 eq) in a reaction tube at 60 °C for 12 h. The wafer was then cleaned by ultra-sonication in THF for 30 min and dried under nitrogen flow. The fluorescence image was taken with Zeiss Observer Z1 (Germany) using the filter set 38 under autoexposure.

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 stirred in a reaction tube at 60 °C for 12 h. The reaction mixture was diluted with THF, and then the polymer was reprecipitated in a methanol/water mixture (v/v = 1/1). The polymer was further purified with preparative GPC.

Preparation of Fluorescence Molecule CPS-SH. A dichloromethane solution of 7-diethylamino-3-(4-maleimidophenyl)-4-methylcoumarin (CPM) (0.0034 g, 0.035 mM, 1 eq), 1,2-ethanedithiol (2 eq), and triethylamine (TEA) (1.4 eq) was stirred at room temperature for 2 h. The crude solution was then purified by chromatography (dichloromethane/methanol (v/v = 40/1)), yielding 7-diethylamino-3-(4-((3-(2-mercaptoethyl)thio)succinimido)phenyl)-4-methylcoumarin (CPS-SH) (yellow powder). ^1H and ^{13}C NMR spectra of CPS-SH (dimethyl sulfoxide ($\text{DMSO}-d_6$)) are given in Fig. S2 in ESI.

CPS Labeling of Alkyne Chain-End Patterned PBA Brush. A DMF solution of CPS-SH (1wt%) and 2-hydroxy-4'-(2-hydroxyethoxy)-2-methylpropiophenone (Irgacure D-2959) (1wt%) was dropped onto the silicon wafer with the alkyne chain-end patterned PBA brush. A cover glass was placed to form a thin layer of the solution between the cover glass and the wafer. The wafer was irradiated with UV for 20 min and was cleaned by ultra-sonication in THF for 30 min. The fluorescence image was taken with Zeiss Observer Z1 using the filter set 49 under autoexposure.

Attaching Hydrophobic Polymer Chain to Alkyne Patterned PBA Brush. The silicon wafer with the alkyne chain-end patterned PBA brush was heated in a mixture of 1*H*,1*H*,2*H*,2*H*-nonafluorohexyl acrylate (NFHA) (10 g, 500 eq), CP-I (1 eq), and BNI (8 eq) in a Schlenk flask at 110 °C under argon atmosphere for 24 h. The wafer was rinsed with acetone (a good solvent of the NFHA polymer), sonicated in acetone for 30 min twice, and dried under nitrogen flow.

Results and discussion

Preparation of PBA-I

We carried out the RCMP of butyl acrylate (BA) using 2-iodo-2-methylpropionitrile (CP-I) as an alkyl iodide initiator and BNI as a catalyst and prepared a poly(butyl acrylate)-iodide (PBA-I) possessing a CP group at the initiating chain end and an iodide at the growing chain end. The polymer was purified by reprecipitation with a mixture of methanol and water (v/v = 50/50) and subsequently by preparative GPC to remove trace amounts of impurities, yielding a PBA-I with $M_n = 3700$ and $\mathcal{D} = 1.27$.

Selective chain-end modification of PBA-I using formic acid and $\text{NH}_2\text{CH}_2\text{CH}_2\text{Ph}$

We studied the selective chain-end modification of the obtained PBA-I (1 eq, 20 wt%) in the presence of formic acid (4 eq, a hydrogen donor) and $\text{NH}_2\text{CH}_2\text{CH}_2\text{Ph}$ (20 eq, a substitution agent) in DMF (solvent) at room temperature in the dark and under a UV irradiation (365 nm wavelength) for 2 h. After the reaction, the obtained polymer was purified by reprecipitation and preparative GPC.

In the dark, PBA-I was selectively converted to PBA-NHCH₂CH₂Ph (PBA-Ph) *via* the substitution after 2 h. Figs. 1a and 1b show the matrix-assisted laser desorption/ionization

time-of-flight mass spectrometry (MALDI-TOF-MS) spectra before and after the reaction. We used *trans*-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) and CF_3COONa as a matrix and an additive salt, respectively. The polymers contain ^{12}C and ^{13}C atoms. For simplicity, the theoretical molecular weights discussed below and the experimental values given in the figures are the polymers possessing only ^{12}C atoms. In Fig. 1b, we observed a predominant peak with the experiment mass value 2900.85, which matches the theoretical mass value 2900.88 of PBA-NHCH₂CH₂Ph ($n = 21$) (ESI), where n is the degree of polymerization of PBA. This result suggests that the substitution product was predominant. A minor series of peak (experimental mass value = 2925.91) was also observed and belongs to a side product hydroxyl-terminated PBA (PBA-OH) (theoretical mass value = 2925.88) generated in the preparation of PBA-I. The ^1H NMR spectra (Figs. 2a and 2b) also confirmed the consumption of PBA-I (peak *c'*, CH, 4.3 ppm) and the formation of PBA-NHCH₂CH₂Ph (peak *j*, C_6H_5 , 7.1–7.4 ppm) at a high conversion (88%) (ESI). The intramolecular amidation of PBA-NHCH₂CH₂Ph can yield PBA-lactam-CH₂CH₂Ph possessing a lactam ring with a CH₂CH₂Ph group at the chain end.²⁶ In the present condition (reacted for 2 h), a small amount of PBA-lactam-CH₂CH₂Ph (theoretical mass value = 2826.81) was observed in the MALDI-TOF-MS spectrum (experimental mass value = 2826.95) (Fig. 1b). For a longer reaction time or at a higher reaction temperature, PBA-NHCH₂CH₂Ph would predominantly be converted to PBA-lactam-CH₂CH₂Ph as a thermodynamically stable product.

Fig. 1 MALDI-TOF-MS spectra of (a) PBA-I and the products obtained *via* the reactions of PBA-I (1 eq, 20 wt%), formic acid (4 eq), and $\text{NH}_2\text{CH}_2\text{CH}_2\text{Ph}$ (20 eq) in DMF (b) without the UV irradiation after 2 h and (c) with the UV irradiation after 2 h (Table 1 (entry 1)).

In contrast, under the UV irradiation, PBA-I was predominantly converted to PBA-H. In the MALDI-TOF-MS spectrum (Fig. 1c), we observed a single series of the main peak as well as several minor peaks. The experimental mass value (2909.78) in the main peak matches the theoretical mass value (2909.88) of PBA-H, suggesting that PBA-H was a major product. While the substitution also did occur in a parallel manner, the hydrogenation was much faster in the studied UV condition, resulting in a selective formation of PBA-H. The ^1H NMR spectrum (Fig. 2c) confirmed the generation of PBA-NHCH₂CH₂Ph (11%) as a minor product and PBA-H (89%) as the main product. These results demonstrate the selective chain-end conversion of PBA-I to PBA-H and PBA-Ph with and without photo-irradiation, respectively.

Fig. 2 ^1H NMR (400 MHz) spectra of (a) PBA-I (in CDCl_3) and products (in acetone- d_6) obtained via the reactions of PBA-I (1 eq, 20wt%), formic acid (4 eq), and $\text{NH}_2\text{CH}_2\text{CH}_2\text{Ph}$ (20 eq) in DMF (b) without the UV irradiation after 2 h and (c) with the UV irradiation after 2 h (Table 1 (entry 1)).

Mechanism study

The photo-induced hydrogenation of alkyl halides using formic acid and amines was previously reported in small molecule systems and polymer systems,^{19,33} although the detailed mechanism was not clarified. In the present system, in the absence of amine, PBA-I and formic acid did not give PBA-H, meaning that the reaction is amine-catalyzed. PBA-I and amine would form a PBA-I...amine complex, which facilitates the generation of PBA $^{\bullet}$ under the UV irradiation (Scheme 1a). Subsequently, PBA $^{\bullet}$ reacts with formic acid to generate PBA-H (Schemes 1b and 1c). To further probe the mechanism, we used a deuterated formic acid (DCOOH) and tributylamine (TBA) to reduce PBA-I under the UV irradiation. (A primary amine (RNH₂) contains two active protons. To avoid the possible proton exchange with DCOOH, we used the tertiary amine (TBA with no active proton) for this mechanistic study

purpose.) Both PBA-D (20%) and PBA-H (80%) were observed in the MALDI-TOF-MS analysis (Fig. S3 in ESI), suggesting that PBA $^{\bullet}$ abstracts the aldehyde deuterium (D) as well as the carboxylic acid proton (H) from DCOOH (Schemes 1b and 1c). However, it should be noted that the reactivity of aldehyde and carboxylic acid (20/80) may not be quantitative because of possible intramolecular and intermolecular proton exchange of DCOOH during the reaction. PBA $^{\bullet}$ may also abstract H from TBA. However, without formic acid (namely, in a reaction of PBA-I and TBA only), no PBA-H was observed, meaning that PBA $^{\bullet}$ did not significantly abstract H from TBA.

Scheme. 1 (a) PBA-I...amine complex generates PBA $^{\bullet}$. PBA $^{\bullet}$ abstracts (b) the aldehyde deuterium (D) or (c) the carboxylic acid proton (H) from DCOOH.

Fig. 3 MALDI-TOF-MS spectra of the products obtained via the reactions of PBA-I (1 eq, 20wt%), formic acid (4 eq), and different amines $\text{NH}_2\text{-R-X}$ (20 eq) in DMF with and without the UV irradiation after 2 h (Table 1 (entries 2–4)). The amine and condition (with or without UV) are given in the figure.

Expansion of chain-end functionality and polymer scopes

We widened the scope of this reaction to other amines ($\text{NH}_2\text{-R-X}$) and polymer. The MALDI-TOF-MS spectra (Figs. 3 and S4) confirmed the selective formation of PBA-X (PBA-NH-R-X) and PBA-H in the dark and under the UV irradiation, respectively, for 2 h, with X = alkyl, hydroxyl, triethoxysilyl, and alkynyl functional groups. The reaction yields determined with ^1H NMR (Fig. S6 in ESI) were high for both PBA-X (57–100%) and PBA-H (85–97%) in all cases (Table 1). In the dark, the yield of PBA-X with X = alkynyl (57%) was lower than those with other X groups (84–100%). The reason is unclear at the moment. Under the UV irradiation, not only the reduction to give PBA-H (85–97%) but also the substitution to give PBA-X (3–15%) occurred. Because they are parallel reactions, the results suggest that the reduction was 6–30 times faster than the substitution in the studied conditions.

Besides PBA-I, we also selectively converted a biocompatible polyacrylate, i.e., poly(methoxyethyl acrylate)-iodide (PMEA-I), to PMEA-H and PMEA-Ph with and without the UV irradiation, respectively (Fig. S5 in ESI). These results demonstrate that this method serves as a versatile method to selectively convert polymer-I to polymer-H and polymer-X with various functional X groups for various polyacrylates. (In the case of PMEA, PMEA-NHCH₂CH₂Ph was first generated. The intramolecular amidation subsequently yielded a relatively large amount of PMEA-lactam-CH₂CH₂Ph (Fig. S5 in ESI)).

Table 1 Reaction of PBA-I (1 eq) with formic acid (4 eq) and an amine (20 eq) in the dark and under UV irradiation for 2 h.

Entry	Amine	Product (%) (with 10% error)	
		In the dark	Under UV irradiation
		PBA-X ^a	PBA-H ^b
1	$\text{NH}_2(\text{CH}_2)_2\text{Ph}$	88	89
2	$\text{NH}_2\text{-}n\text{C}_5\text{H}_{11}$	89	92
3	$\text{NH}_2(\text{CH}_2)_4\text{OH}$	84	85
4	$\text{NH}_2(\text{CH}_2)_3\text{Si}(\text{OEt})_3$	~100	92
5	$\text{NH}_2\text{CH}_2\text{C}\equiv\text{CH}$	57	97

^aThe amount of PBA-X (PBA-NH-R-X) was determined with ^1H NMR. ^bThe amount of PBA-X (PBA-NH-R-X) was determined with ^1H NMR. Assuming 100% of the total amount of PBA-X and PBA-H, the amount of PBA-H was calculated.

Chain-end patterned polymer brushes

An interesting application is to create chain-end patterned polymer brushes on surfaces. The fabrication of polymer brushes on surfaces can dramatically alter the surface properties such as thermodynamic, optical, and biological properties.³⁴ Surface-initiated living radical polymerization is a useful approach to prepare concentrated polymer brushes with high graft densities.³⁵ Patterned polymer brushes on surface with multiple polymers and different brush thicknesses have widely been prepared,^{36,37} finding applications in, e.g., peptide arrays and smart sensors for environmental changes.³⁸ However, the preparation of chain-end patterned polymer brushes is still limited. In the present work, we applied our method to obtain chain-end patterned polymer brushes. For the concentrated polymer brushes, because of the steric

hindrance of the neighboring chains, the polymer chains are forced to extend, and the growing polymer chain ends tend to be localized at the outermost surface in solution. We used a photomask under the UV irradiation and converted the iodide chain ends of polymer brushes to hydrogen and various functional groups in patterned manners.

Fig. 4 (a) Synthesis of PBA-I brush *via* surface-initiated RCMP. (b) Surface patterning of H and OH chain-end functionalized PBA brushes and attachment of FITC. (c) Fluorescence microscope image of FITC-attached patterned PBA brush.

Fig. 4a illustrates the fabrication of a polymer brush with the iodide chain end on a silicon wafer in a uniform (non-patterned) manner *via* surface-initiated RCMP. A concentrated PBA-I brush ($\sigma^* =$ approximately 0.45) with a thickness of 20 nm were prepared (Fig. S1 in ESI). A DMF solution of HCOOH (1 eq, 1wt%) and $\text{NH}_2(\text{CH}_2)_4\text{OH}$ (4 eq) was dropped on the polymer brush, which was subsequently covered with a cover glass. A stripe photomask was placed on the cover glass. After the UV irradiation for 2 h, the chain-end iodine was modified to an OH functionality in the masked area and was reduced to an H atom in the unmasked area (Fig. 4b). The formation of the patterned surface was confirmed by labelling the OH functionality with a fluorescence molecule, i.e., fluorescein 5-isothiocyanate (FITC), through an isothiocyanate-hydroxyl addition (Fig. 4b).³⁹ A clear fluorescence pattern was observed in the fluorescence microscope image (Fig. 4c), demonstrating the successful fabrication of the chain-end patterned binary polymer brush. The secondary amine of PBA-NH(CH₂)₄OH may also react with FITC. However, because of the large steric hindrance at the NH moiety, FITC most probably reacted with the OH group rather than the secondary amine moiety. The unreacted PBA-I brush, if any present, may react with FITC. As a control experiment, we tested a reaction of non-immobilized PBA-I with FITC, resulting in insignificant generation of PBA-FITC polymer (Fig. S7 in ESI). The result means that the observed labeling proceeded through the addition of the OH group with FITC.

We also successfully used a different functional group and a different photomask. A patterned PBA brush with an H atom and an alkynyl functional group was synthesized using HCOOH and $\text{NH}_2\text{CH}_2\text{C}\equiv\text{CH}$ using a well-shaped photomask. The alkynyl

functionality is useful to attach various small molecules and polymers through so-called click reactions.⁴⁰ After the chain-end patterning, the alkynyl group was labelled with a fluorescence molecule CPS-SH (Fig. 5a) *via* a thiol-yne click reaction. A clear well-shaped fluorescence pattern was observed (Fig. 5a), demonstrating the successful fabrication of the hydrogen and alkyne chain-end patterned polymer brush.

The fabrication of the alkyne chain end was also used to alter a physical property of the polymer brush. A hydrogen and alkyne chain-end patterned PBA brush with a stripe pattern was prepared. Alkynes can react with radicals, although the reactivities of alkynes with radicals are generally much lower than those of alkenes. We immersed the wafer with the stripe pattern in a solution of a fluorinated acrylate (1*H*,1*H*,2*H*,2*H*-nonafluorohexyl acrylate (NFHA)), CP-I (16 mM), BNI (128 mM), and carried out the radical polymerization at 110 °C. A super-hydrophobic NFHA polymer (PNFHA) was grafted through the alkyne chain end of the PBA brush. An optical microscope image (Fig. 5b) showed a stripe pattern due to the different refractive indexes of PNFHA and PBA, where the darker and lighter stripes correspond to PNFHA-*b*-PBA and original PBA brushes, respectively. (We tested a well-shaped pattern with PNFHA-*b*-PBA square and PBA well, confirming that the darker part corresponds to PNFHA-*b*-PBA (Fig. S8 in ESI).) Figs. 5c and 5d show the contact angle analyses on the brush surfaces before and after the graft polymerization of NFHA, respectively. The contact angle increased from 85° to 110° after the polymerization of NFHA, showing the successful alteration of the surface hydrophobicity by the post-functionalization of the alkyne chain end.

The resolution limit of the patterning would correspond to the wavelength of the UV light used. This patterning is applicable to polyacrylate-iodide brushes (not polymethacrylate-iodide brushes).

Fig. 5 (a) Fluorescence microscope image of CPS-attached patterned polymer brushes. The structure of CPS-SH is given in the figure. (b) Microscope image of binary patterned PNFHA-*b*-PBA and PBA-H brushes. Contact angle analysis of (c) binary patterned PBA-C≡CH and PBA-H brushes and (d) binary patterned PNFHA-*b*-PBA and PBA-H brushes.

Conclusions

In summary, we developed a selective chain-end modification method of polymer-I to polymer-H and polymer-X with various functional X groups, using commercially available formic acid and primary amines. By simply switching the UV light on and off, polymer-H and polymer-X were selectively produced, respectively. This method is metal-free, and the scopes of the functional X groups and polyacrylates are wide. This method also enabled the fabrication of chain-end patterned binary polymer brushes. This method may serve as a platform technique for designing chain-end functionalized polymers and surface-functionalized materials for possible applications to, *e.g.*, molecular recognitions, sensors, and biomolecular arrays.

Conflicts of interest

There are no conflicts to declare.

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Graphical Abstract