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Supporting Information

Surface Grafting "Band-Aid" for "Everyone": Filter Paper-Assisted Surface-Initiated Polymerization in the Presence of Air

Wei Li, Wenbo Sheng, Bin Li,* and Rainer Jordan**

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Experimental Procedures

Materials

Monomers: *N*-isopropylacrylamide (NIPAAm), [2-(Methacryloyloxy)ethyl]dimethyl-(3-sulfopropyl)ammonium hydroxide (SBMA), (methacryloyloxy)ethyl trimethylammonium chloride (METAC), 3-sulfopropyl methacrylate potassium salt (SPMA), 2-Hydroxypropyl methacrylamide (HPMAAm), and 1*H*,1*H*,2*H*,2*H*-nonafluorohexyl methacrylate (FHMA) were used as received. Methyl methacrylate (MMA), 2-hydroxyethyl methacrylate (HEMA), 2-(dimethylamino)ethyl methacrylate (DMAEMA), styrene, 4-vinyl pyridine (4VP), methyl acrylate (MA), n-butyl acrylate (nBA), tert-butyl methacrylate (tBuMA), 2-hydroxyethyl acrylate (HEA), and 2-(dimethylamino)ethyl acrylate (DMAEA) were purified by passing through a basic alumina column (Sigma). The chemical structures of the above monomers are shown in Figure S6. 3-(Trimethoxysilyl)propyl 2-bromo-2-methylpropanoate, tetraethoxysilane (TEOS), 2-bromoisobutryl bromide (BIBB), 3-aminopropyltriethoxysilane (APTES), *N,N,N',N',N'*-pentamethyldiethylenetriamine (PMDETA), triethylamine (TEA) were purchased from Sigma-Aldrich. Cu plates (MicroChemicals GmbH, Germany) with a thickness of 200 nm (purity >99.9%, RMS < 10 nm) were washed with ultrapure water and ethanol under ultrasonication prior to use. Silicon wafers with an oxide layer (~300 nm) (Si/SiO_2) were purchased from Wacker AG (Burghausen, Germany). Filter paper (RC 55) was purchased from Whatman (Germany). A photoresist (BP212-37 positive photoresist) was purchased from Kempur (Beijing) Microelectronics, Inc. All chemicals were used as received unless specified.

Preparation of initiator-modified substrate

For silicon wafer, the substrate was ultrasonicated in acetone and ethanol for 5 min and was dried with a stream of nitrogen, then was treated by oxygen plasma for 15 min. Afterward, the substrate was immersed in dry acetone solution containing 5% (*v*/*v*) APTES and sonicated for 45 min, and followed by washing with acetone, water, and ethanol. The APTES-modified substrate was immersed into dry DCM with 2% (*v*/*v*) TEA and cooled at 0°C. Then DCM containing 2% BIBB was added into the above solution and allowed to react for 1 h at room temperature for 23 h. The substrate was washed with DCM, water, ethanol, and acetone and dried with a stream of N_2 gas.

For the glass vial, glass slide and mirror, the initiator 3-(Trimethoxysilyl)propyl 2-bromo-2-methylpropanoate (0.67 mL, 3.2 mmol) and TEOS (2.8 mL, 12.8 mmol) were added into 8.0 mL ethanol with 1 mL HCl (10 mM), the above initiator solution was sprayed onto the substrate and incubated overnight, the physically absorbed initiator was washed away by ethanol.

Paper-based surface-initiated Cu(0)-mediated controlled radical polymerization (PSI-CuCRP)

The polymerization solution was prepared by adding monomer into the water/methanol (2 : 1) mixture with PMDETA in the air. The filter paper wetted by the polymerization solution was placed onto an initiator-modified substrate and a copper plate was covered on the top of the filter paper. After the polymerization for a certain time, the substrate was thoroughly washed and dried by nitrogen gas. The thickness of the polymer brushes can be easily controlled by changing the amount of monomers.

Surface-initiated Cu(0)-mediated controlled radical polymerization (SI-CuCRP)

Polymerization solution in a glass tube was prepared by mixing the monomer, ligand PMDETA, and solvent (water/methanol 2:1, or DMSO). A sandwiched setup of a copper plate and an initiator-modified substrate was prepared with two spacers (0.5 mm), the setup was submerged into the monomer solution to initiate the polymerization. After the polymerization, the substrate was thoroughly washed and dried with N_2 gas.

Surface-initiated atom transfer radical polymerization (SI-ATRP) of SBMA under argon atmosphere

SBMA (0.5 g) was added into a glass tube containing water/methanol (2 : 1). The mixture was degassed with Argon for 30 min. Afterward, bpy (15 mg) and CuBr (5 mg) were added into the glass tube under argon flow. After degassing for another 30 min, the initiator-modified substrate was put into the tube. The polymerization was allowed to proceed at room temperature under the argon flow.

Fabrication of multiblock copolymer brushes via PSI-CuCRP

Polymerization solutions of 2-(Dimethylamino)ethyl acrylate (DMAEA) 1.65 M, and 2-hydroxyethyl acrylate (HEA) 2.18 M were prepared respectively. DMAEA solution wetted paper was placed onto an initiator-modified substrate and covered by a copper plate for 15 min. After thoroughly washing with water and dried by a stream of nitrogen. HEA-wetted paper was placed on a PDMAEA-modified substrate and covered by the same copper plate for 30 min. For the third and fourth layers, the procedure was repeated using the corresponding monomer solution for 50 min and 60 min, respectively. The brush thickness changes after each step of the polymerization were measured AFM.

Fabrication of negative, positive and binary patterned polymer brushes

For patterned polymer brushes, the initiator patterned substrate was prepared, detailed procedures were as follow:

For the positive pattern, the initiator-modified substrate was spin-coated with the positive photoresist, a copper grid was used as the photomask, the substrate was patterned by conventional photolithography, exposed areas of photoresist were removed by the oxygen plasma and the initiator exposed. Polymer brush growth on the initiator surface by PSI-CuCRP as mentioned above. Finally, the remaining photoresist was removed and positive patterns were obtained.
For the negative pattern, the initiator modified substrate was spin-coated with the photoresist, after the UV irradiation and oxygen plasma treatment, initiator exposed and followed by PSI-CuCRP.
For binary patterns, positive pattern after PSI-CuCRP was treated with oxygen plasma to remove the remaining photoresist. The second polymer brush was grown by PSI-CuCRP on the newly exposed initiator to yield the binary patterns.

Fabrication of patterned polymer brushes via the combination of paper cutting and PSI-CuCRP
Paper was cut into different shapes and was wetted by the monomer solution, placed on the initiator-modified substrate and covered with copper plate, the polymerization procedure is similar to the homogenous polymer grafting.

Fabrication of polymer brush arrays by PSI-CuCRP
Polymer brush arrays were prepared by using pieces of filter paper wetted by different monomer solutions and followed by polymerization.

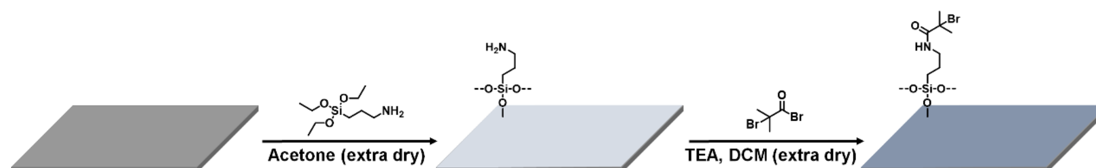
Characterization
The thickness of the polymer brushes on the silicon substrate was determined by ellipsometry (SENTECH Instruments GmbH, equipped with a He–Ne laser source λ = 632.8 nm and a fixed angle of incidence of 60°). Measurements were performed at least three times at different locations of three samples.

The infrared spectra were obtained on a photometric ellipsometry externally attached to a BRUKER IFS 55 FTIR spectrometer.

Contact angle measurements were carried on a Drop Shape Analysis System DSA10 from Krüss (drop volumes 1 μL).

Atomic force microscopy (AFM) measurements were performed on NT-MDT (Russia) under ambient conditions. The surface morphology, roughness, and brush thickness were obtained in tapping mode using the etalon silicon tip.

Supplementary Figures



Scheme S1. Schematic view of immobilizing initiator onto the substrate.

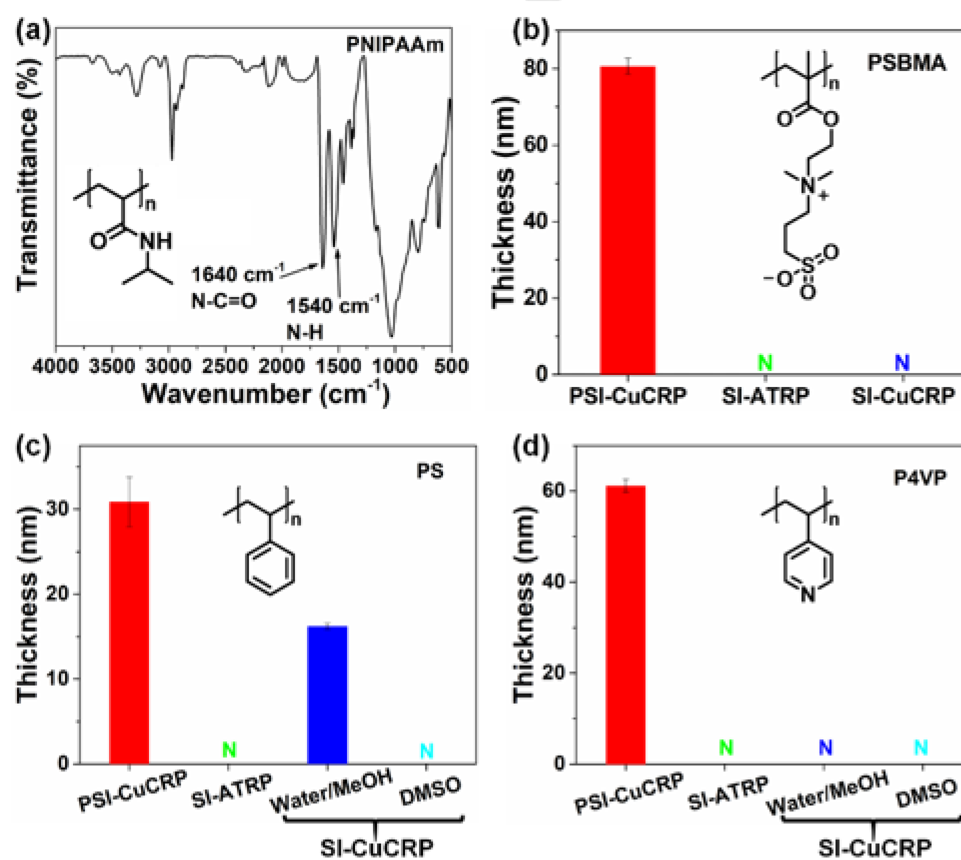


Figure S1. (a) FT-IR spectrum of PNIPAAm. (b-d) Surface polymerization of SBMA, St and 4VP through PSI-CuCRP, SI-ATRP and SI-CuCRP methods (water/MeOH and DMSO), respectively. Polymerization time: 30 min. N: not detected.

Table S1. Grafting density of polymer brushes via PSI-CuCRP.

Monomer	h_{dry} (nm)	$h_{swollen}$ (nm)	$h_{dry}/h_{swollen}$	Polymerization degree, N (a)	Grafting density (chains/nm^2) (b)	Distance between grafting site D (nm) (c)
NIPAAm	440 ± 6	743 ± 30	1.69	7230	0.29	2.11
nBA	495.4 ± 5	1553 ± 37.8	3.13	29530	0.070	4.26
MA	1229.7 ± 5	4886 ± 916	3.97	104605	0.072	4.21
tBuMA	84 ± 1	208.9 ± 2	2.49	3537	0.088	3.81
MMA	92 ± 2	355.9 ± 16	3.87	7517	0.069	4.29

(a) Degree of polymerization N = $[1.074(h_{swollen})^{3/2}]/[(h_{dry}(\text{Å}^2))^{1/2}]$ (the constant related to excluded volume parameter, 1.074 was used independently of the type of monomers); (b) grafting density $\sigma = [\rho h_{dry} N_A]/[M_0 N]$; (c) the distance between grafting sites $D = [4/(\pi\sigma)]^{1/2}$, where N: degree of polymerization, ρ: polymer density, N_A: Avogadro's number, M_0: monomer molecular weight.[1]

Table S2. Polymer brush growth rate for PSI-CuCRP, SI-CuCRP (air, O_2 free), SI-photo ATRP, SI-sa-ATRP and eATRP of thermoresponsive NIPAAm, zwitterionic SBMA, hydrophobic St, and pH-responsive 4VP.

Monomer	PSI-CuCRP (nm/h)	SI-CuCRP (in air) (nm/h)	SI-CuCRP (O_2 free) (nm/h)	SI-photo ATRP (nm/h)	SI-sa-ATRP (nm/h)	eATRP (nm/h)
NIPAAm	880	279[2]	190[3]	95[4]	100[5]	180[6]
SBMA	160	0	0	-	-	-
St	62	32	31[3]	-	-	-
4VP	122	0	56[3]	-	-	-

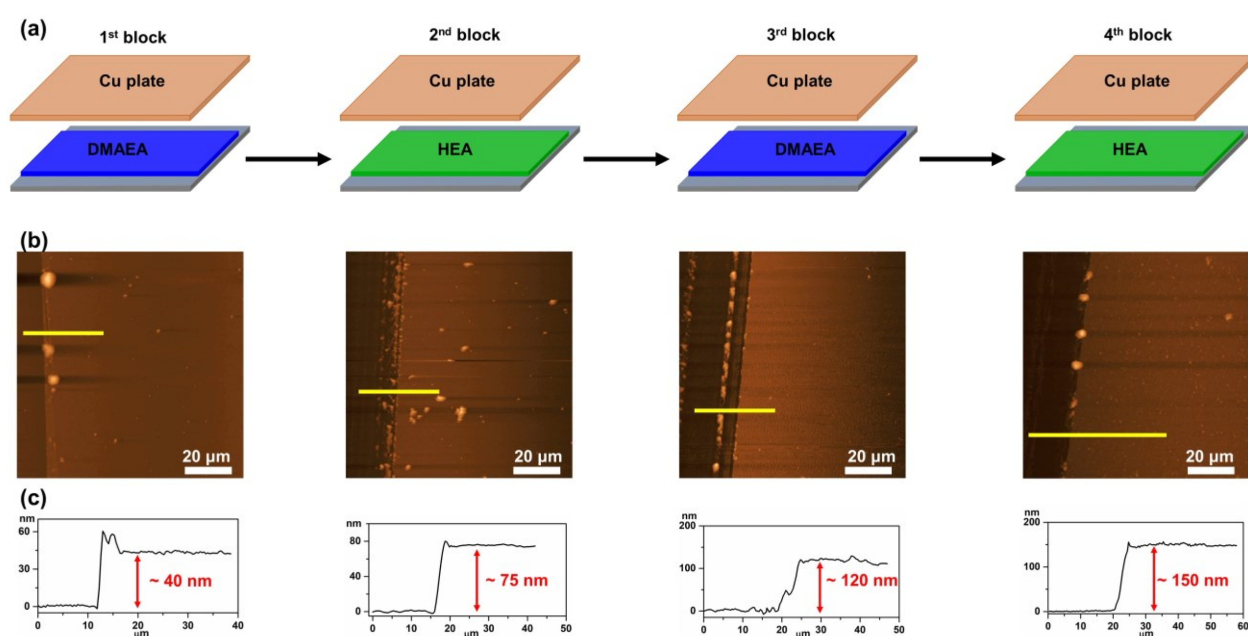


Figure S2. (a) Schematic procedures for preparing tetra-block copolymer brushes. (b) AFM topography images and the corresponding height profiles (c) of the block copolymer brushes.

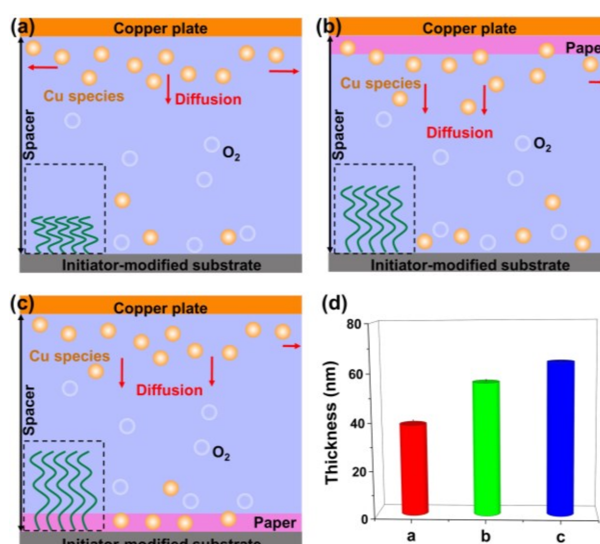


Figure S3. Schematic illustration of the role of the filter paper in PSI-CuCRP (a) without filter paper, (b) with the filter paper close to the copper plate, (c) with the filter paper close to the initiator-modified substrate, the copper plate and the substrate are separated by a spacer (Si wafer, 600 μm thick). (d) Thicknesses of POEGMA prepared under the three conditions showing in a, b and c.

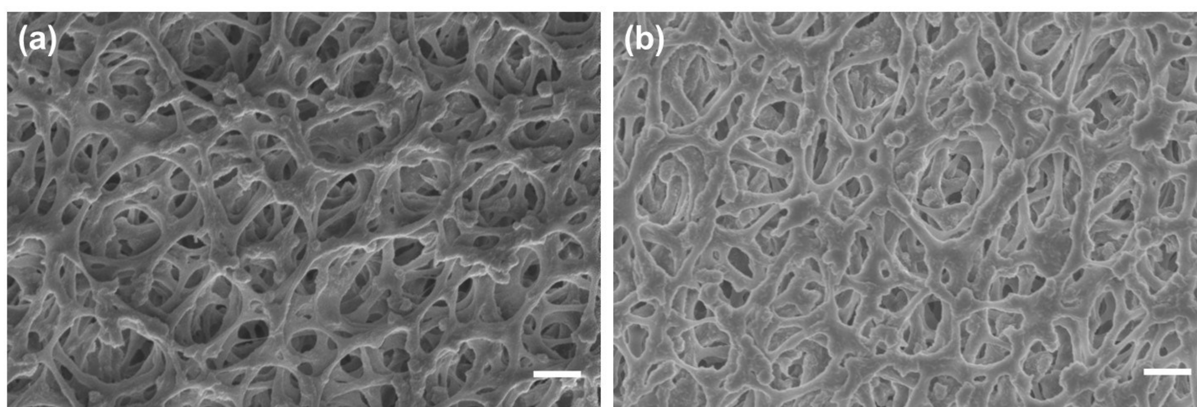


Figure S4. Scanning electron microscope (SEM) images of filter paper before (a) and after polymerization (b) (scale bar: 1 μm).

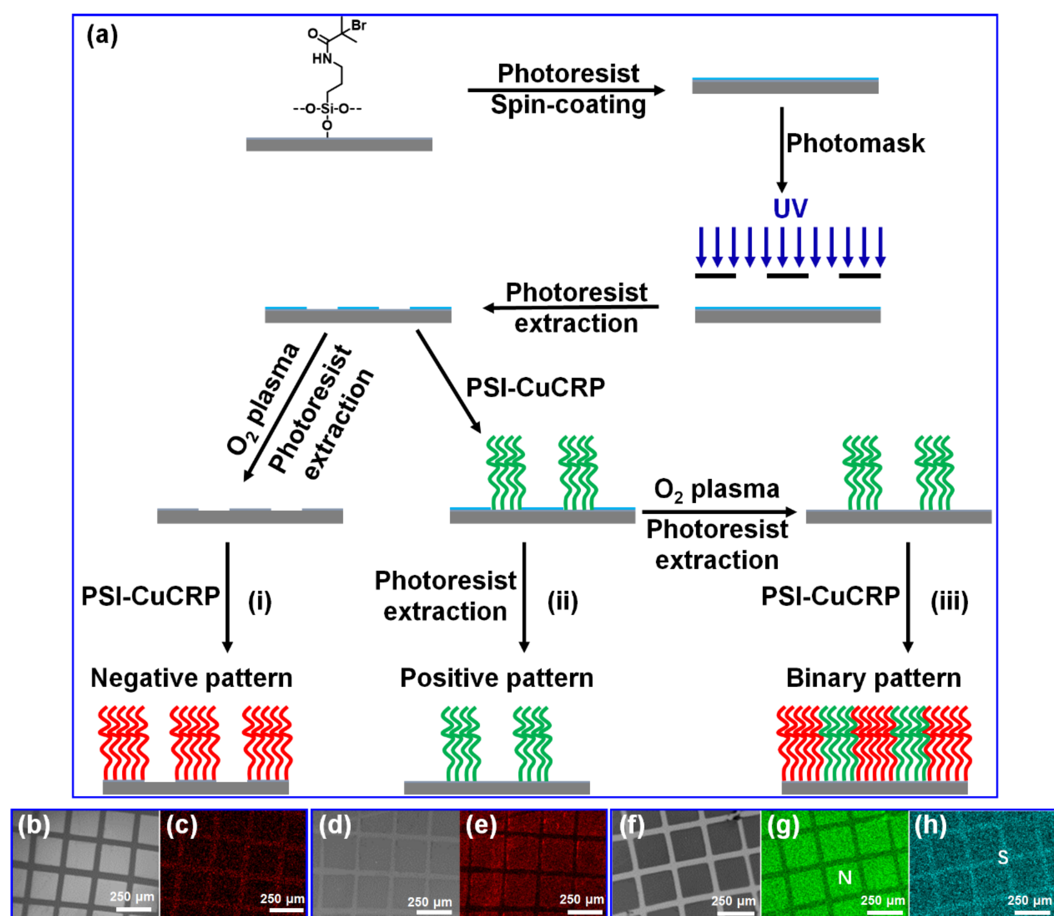


Figure S5. (a) Schematic of negative (i), positive (ii) and binary (iii) patterned polymer brushes () via PSI-CuCRP. (b) SEM image and (c) EDS carbon distribution map of the negative pattern. (d) SEM image and (e) EDS carbon distribution map of the positive pattern. (f) SEM image, (g) EDS nitrogen distribution map, and (h) EDS sulfur distribution map of the binary pattern.

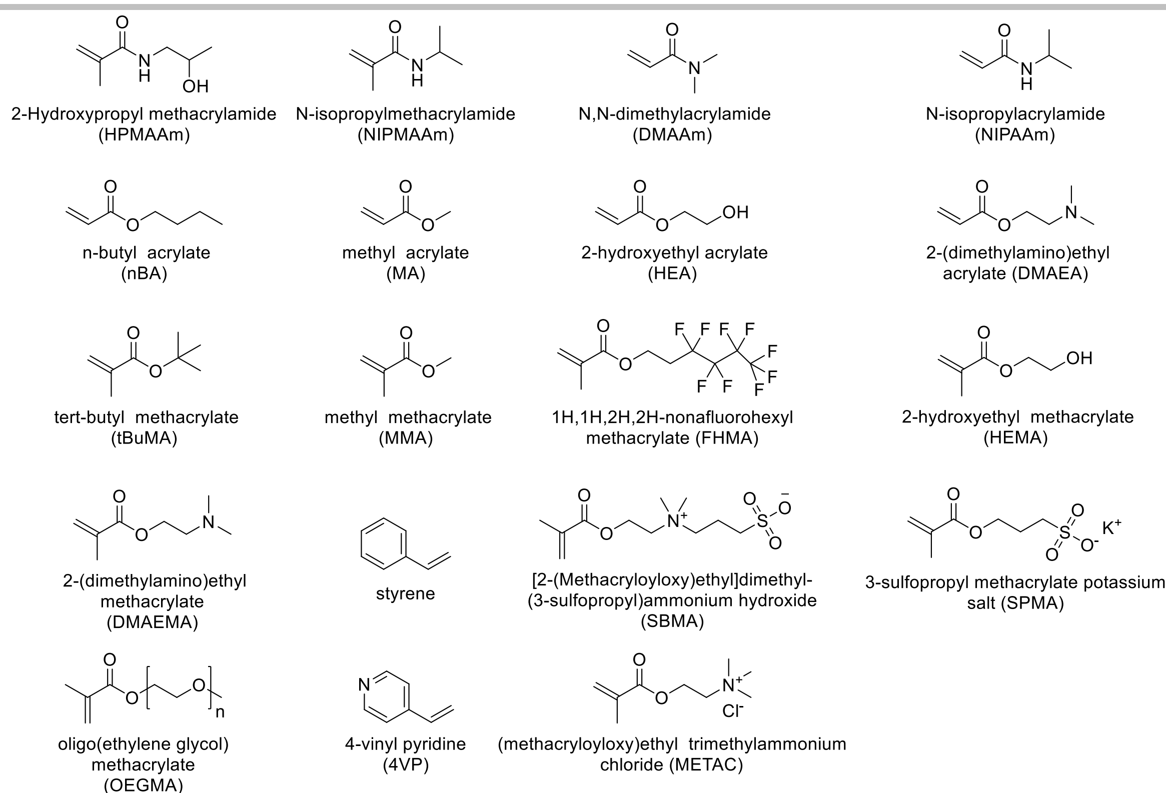


Figure S6. Chemical structures of monomers used for PSI-CuCRP.

References

[1] R. Jordan, A. Ulman, J. F. Kang, M. H. Rafailovich, J. Sokolov, *J. Am. Chem. Soc.* **1999**, *121*, 1016-1022.
[2] T. Zhang, Y. Du, J. Kalbacova, R. Schubel, R. D. Rodriguez, T. Chen, D. R. T. Zahn, R. Jordan, *Polym. Chem.* **2015**, *6*, 8176-8183.
[3] T. Zhang, Y. Du, F. Müller, I. Amin, R. Jordan, *Polym. Chem.* **2015**, *6*, 2726-2733.
[4] J. Yan, B. Li, F. Zhou, W. Liu, *ACS Macro Lett.* **2013**, *2*, 592-596.
[5] J. Yan, B. Li, B. Yu, W. T. Huck, W. Liu, F. Zhou, *Angew. Chem. Int. Ed.* **2013**, *52*, 9125-9129.
[6] N. Shida, Y. Koizumi, H. Nishiyama, I. Tomita, S. Inagi, *Angew. Chem. Int. Ed.* **2015**, *127*, 3994-3998.