

Supporting Information

Hydrophilic surfaces from simple dip-coating method: Amphiphilic block copolymers with zwitterionic group form antifouling coatings under atmospheric conditions

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Supporting Results

Synthesis of diblock copolymers of poly(MPC-b-MPTSSi) as b-120, and poly(MPC-b-MPTMSi) as c-120, and characterization of diblock polymer coated surface on glass

Polymer synthesis

P-120 and c-120 were synthesized in two steps via reversible addition fragmentation chain-transfer (RAFT) polymerization. The hydrophilic block poly(MPC) was first synthesized with the target molecular length of 120 units. MPC (2.953 g) was dissolved in 1-propanol to obtain 0.5-M monomer solution (volume: 20 mL). A chain transfer agent of 4-cyano-4-(phenylcarbonothioylthio)pentanoic acid (23.3 mg) and initiator of azobisisobutyronitrile (AIBN, 3.0 mg) were added to achieve the targeted molecular length of 120 units. The degassed mixture was heated in an oil bath at 65 °C for 24 h. In the second step, blocks of MPTSSi or MPTMSi were grown on the active chain end of poly(MPC). Considering that the extent of reaction was near 90% in previous trials, an excess of 90 equivalents were added into the mixture. The mixture was diluted to 0.25 M using 1-propanol and the concentration of the initiator was increased to 0.0025 M to ensure that the reaction would proceed. The degassed mixture was heated in an oil bath at 65 °C for 24 h. The chemical composition and molecular weight distribution were characterized with proton nuclear magnetic resonance (¹H-NMR) spectroscopy. The p-120 sample was reprecipitated in a mixture of acetone and ethanol (16:1 by volume) and dried with an evaporator. Reprecipitation of c-120 was

performed in a mixture of hexane and chloroform (20:1 by volume). The average molecular weight and dispersity were measured by gel permeation chromatography (GPC) using 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) as the solvent.

Polymer characterization

The chemical structures of the diblock copolymers were determined by signature peaks from the ¹H-NMR spectra. The approximate molecular weight and dispersity were determined by GPC. Films of the diblock copolymers p-120 and c-120 were prepared using the same protocol applied for b-120 (poly(MPC-*b*-MPTSSi-*r*-MPTMSi)). The thicknesses of the coating films were measured with ellipsometry. The sample uniformity was examined under fluorescent microscopy by Rhodamine 6G staining. The wettability of the diblock copolymers was evaluated by static and dynamic contact angle (DCA) measurement. The characteristics of the diblock copolymers are summarized in Table S1.

Table S1. Characteristics of diblock copolymers.

Abbr.	In feed (monomer contents)	In copolymer ^{a)} (monomer contents)	M_w ^{b)}	M_w/M_n ^{b)}	SCA (deg)	DCA (deg)
	MPC/MPTSSi/MPTMSi	MPC/MPTSSi/MPTMSi				
p-120	120/80/0	117/74/0	1.5×10^4	1.4	60.0	51.2
c-100	120/0/80	117/0/82	1.5×10^4	1.1	38.5	44.2

a) Determined by ¹H NMR measurement. b) Determined by GPC measurement using polymethyl methacrylate (PMMA) as a standard

Coating thickness and uniformity

The thickness of the p-120 coating was 12.1 ± 3.6 nm, whereas that of the c-120 coating was approximately 8.4 ± 2.7 nm. The rhodamine 6G stained surfaces of p-120, c-120, and b-120 were observed by a fluorescence microscope. The images are shown in Figure S1. The uniformity of the fluorescence intensity of b-120 is the best compared to that of p-120 and c-120; the c-120 coating contains brighter regions indicative of aggregates, probably caused by intramolecular condensation between c-120 chains.^{S1}

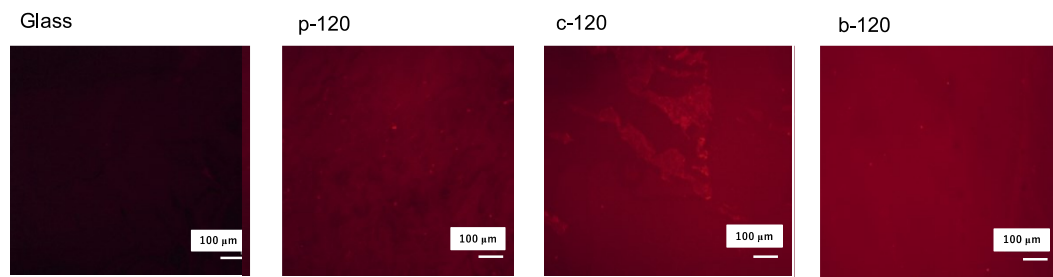


Figure S1. Film uniformity evaluated by Rhodamine 6G staining after coating of each polymer.

Durability tests of b-120 and b-160 coated glasses after treatment at various pH

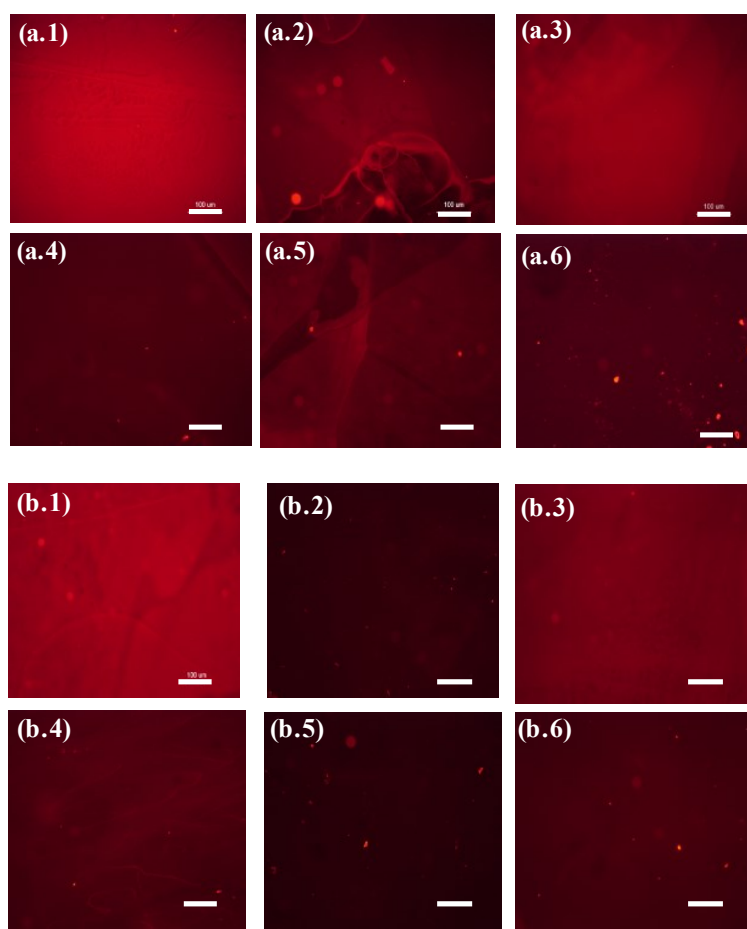


Figure S2. Fluorescence image after pH treatment. b-120 (a) and b-160 (b) were coated on glass. (1) shows non-pH treatment, (2) is treated at pH 1, (3) is pH 9, (4) is pH 10, (5) is pH 11, and (6) is pH 12.

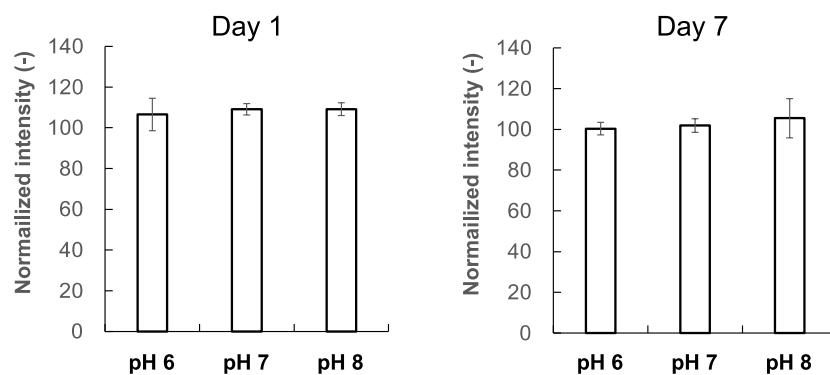


Figure S3. Long term durability test of the b-120 coated surface in pH 6, 7, or 8, which was investigated by rhodamine 6G staining test. The fluorescence intensity of each sample was normalized by that of the b-120 coated surface without pH treatment. Compared with the surface without pH treatment, the fluorescence intensity unchanged after immersing the polymer-coated surface in aqueous solutions at pH 6 – 8 for 1 day and 7 days.

References

(S1) Y. Xie, C. A. S. Hill, Z. Xiao, H. Miltz, C. Mai, *Compos. Part A*, 2010, **41**, 806.