Electronic Supplementary Material (ESI) for Polymer Chemistry.
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Supporting information

Mussel-Inspired Catecholic ABA Triblock Copolymer Exhibits Better Antifouling Property Compared to Diblock Copolymer

Yadan Zhai[a], Xueqian Chen[b], Zhaobin Yuan[a], Xia Han[a,*], Honglai Liu[a,*]

[a]Key Laboratory for Advanced Materials and School of Chemistry and Molecular Engineering and [b]School of Science, East China University of Science and Technology, Shanghai 200237, PR China

*** Corresponding Author:**

Tel: +86 21 642 51942; fax: +86 21 642 51942

E-mail address: xhan@ecust.edu.cn (X.H.) hlliu@ecust.edu.cn (H.L.)

Scanning Electron Microscopy (SEM)

Surface morphologies of uncoated and coated silicon wafers were characterized using SEM (S-3400N, HITACHI, Japan). In order to obtain the surface thickness, the cross section of modified silicon was measured.

Proton Nuclear Magnetic Resonance Spectroscopy (^{1}H NMR)

^{1}H NMR spectra were recorded by using a Bruker Avance III 400 MHz spectrometer at room temperature and using $CDCl_3$, CD_3OD, or D_2O as solvents.

Transmission electron microscopy (TEM)

TEM images were obtained under JEOL JEM-1400 instrument operated at an accelerating voltage of 100 kV. The images were recorded by a digital camera. The TEM samples were prepared by following procedures: A drop of block copolymer aqueous solution (2 mg/mL) was dropped onto a copper grid with carbon film, and the solvent was absorbed by filter paper. Then, the TEM analysis was performed without staining.

Dynamic light scattering (DLS)

DLS was performed using a Zetasizer (Nano Series, Malvern Instruments, UK) at room temperature. Block copolymer aqueous solutions (2 mg/mL) were filtered through a membrane with a pore size of 0.45 mm prior to the measurements.

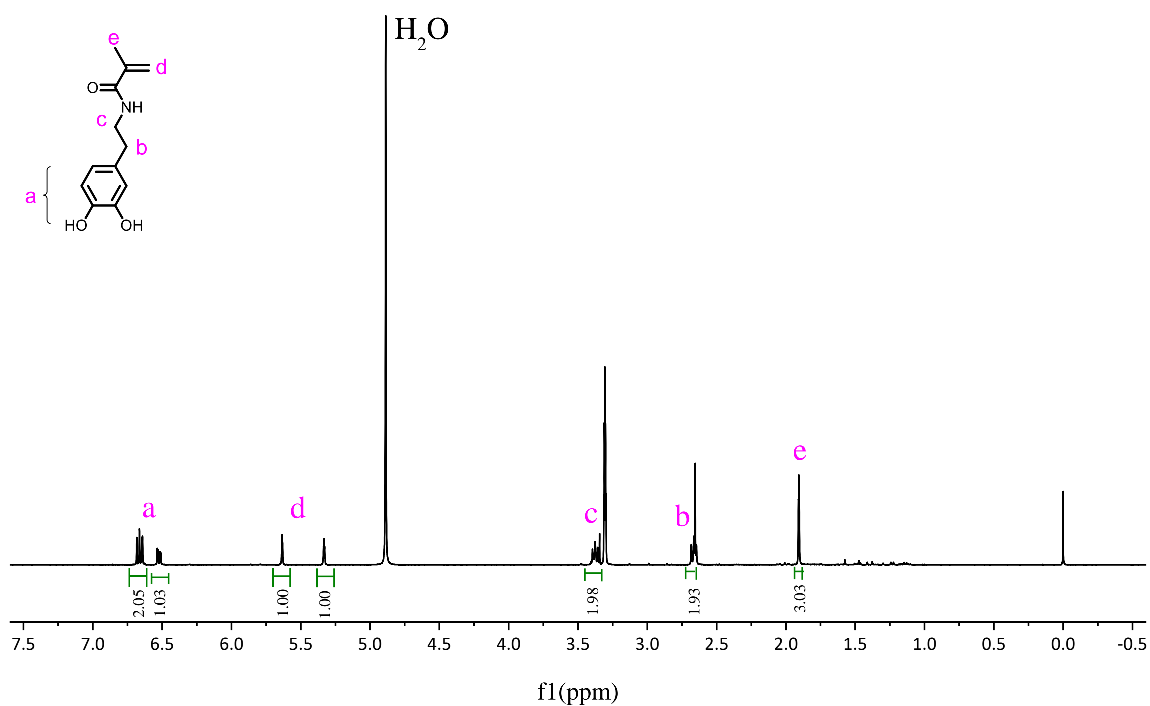

Figure S1. ^{1}H NMR spectrum of DMA monomer using D_2O as solvent.

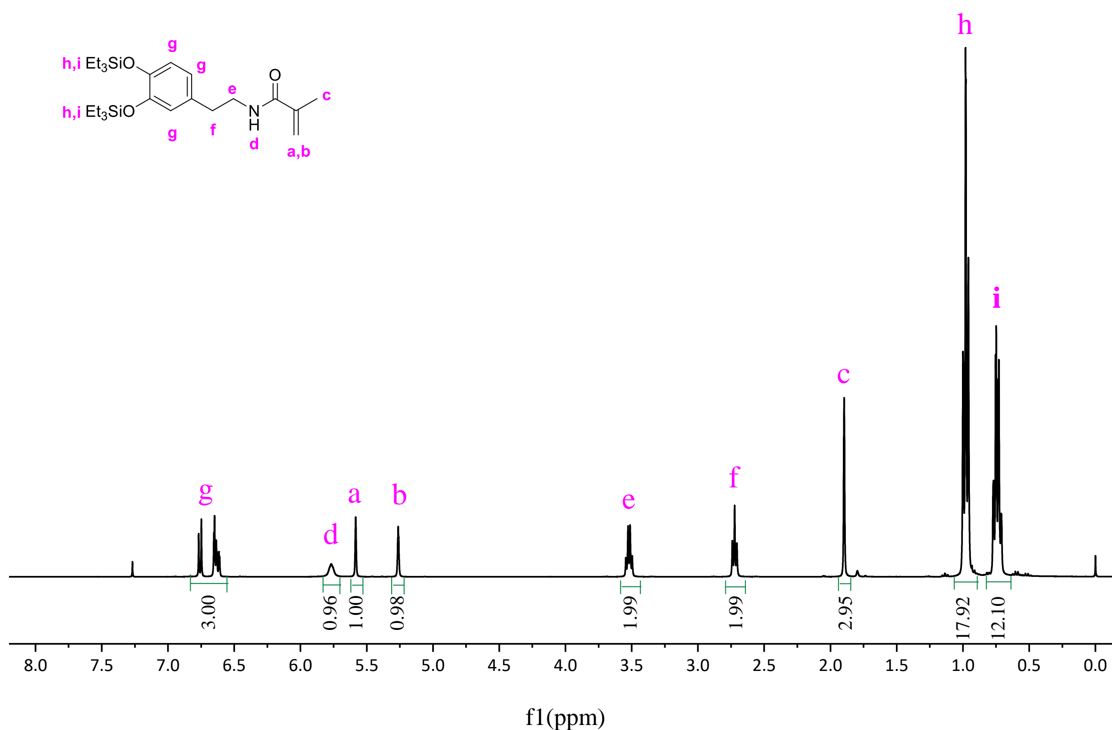

Figure S2. ^{1}H NMR spectrum of triethylsilane-protected TES-DMA monomer using CD_3Cl as solvent.

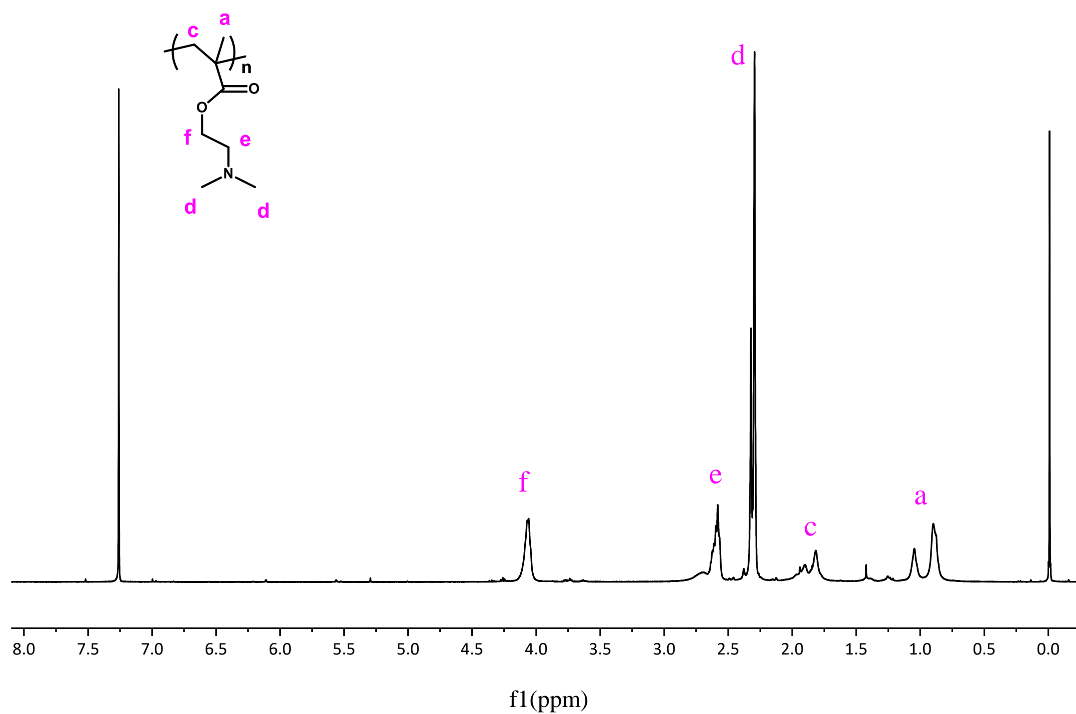

Figure S3. ^{1}H NMR spectrum of macroinitiator (Br-PDMAEMA-Br) using CD_3Cl as solvent.

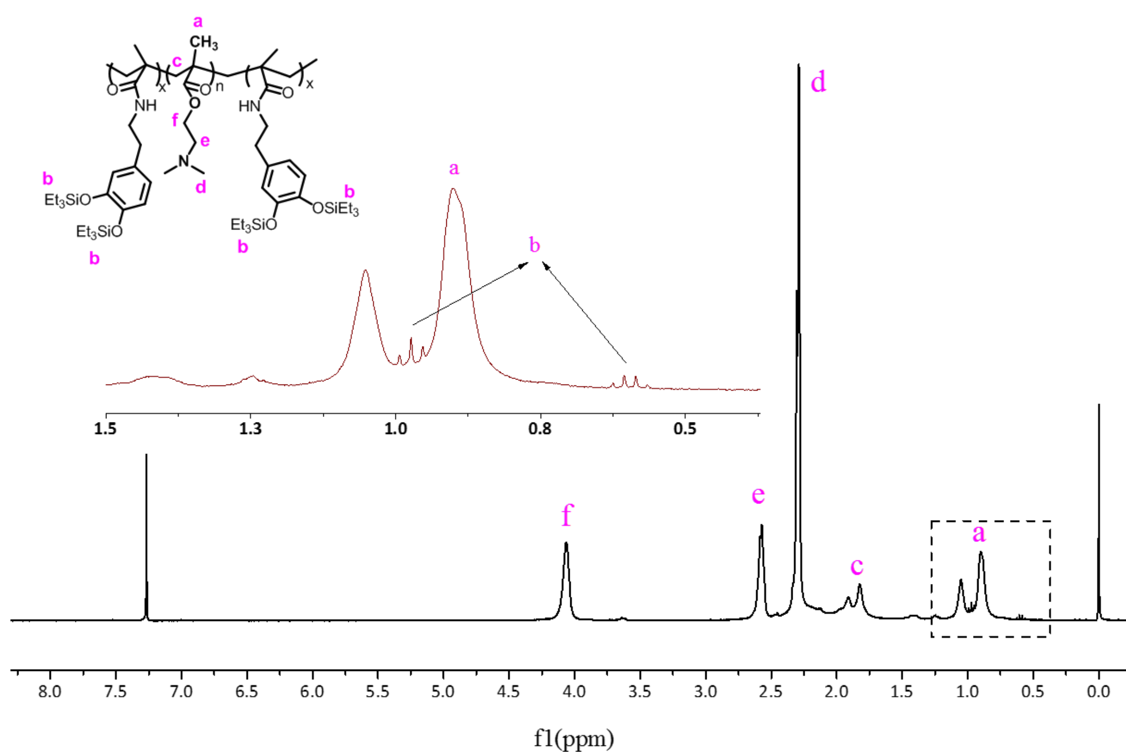

Figure S4. ^{1}H NMR spectrum of triethylsilane-protected triblock copolymer (TES-protected PDMA-PDMAEMA-PDMA) using CD_3Cl as solvent. The inset is the peaks (b) of protected group on catechol ring.

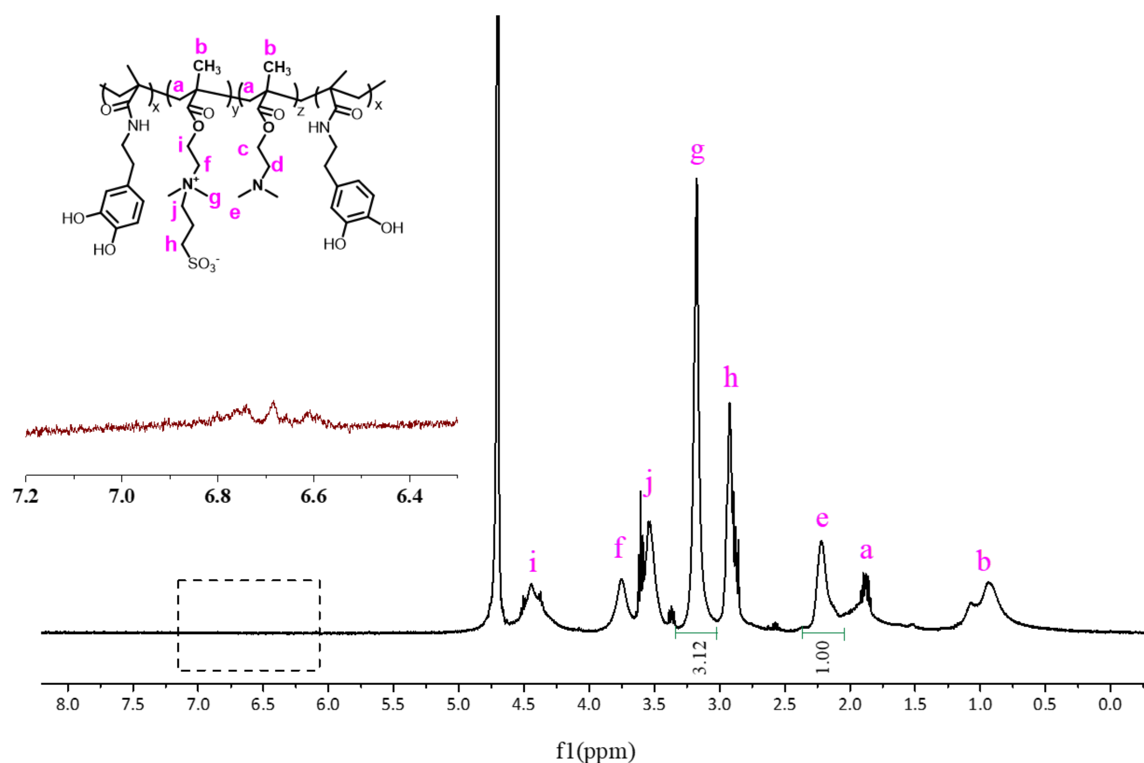

Figure S5. ^{1}H NMR spectrum of the de-protected triblock copolymer (PDMA-P(SBMA-*co*-DMAEMA)-PDMA) using D_2O as solvent. The inset is the peak of catechol group in DMA.

From the ^{1}H NMR spectrum of triethylsilane-protected triblock copolymer (TES-protedcted PDMA-PDMAEMA-PDMA) using CD_3Cl as solvent (inset in Figure S4), the signals from the triethylsilane on catechol ring were clearly observed. Additionally, in a partially enlarged curve (inset in Figure S5), the signal from catechol group in DMA can be seen at 6.5-6.9 ppm. Although the DMA signals is weak in the NMR spectroscopy, all data indicate successful grafting of DMA end groups to the block copolymers.

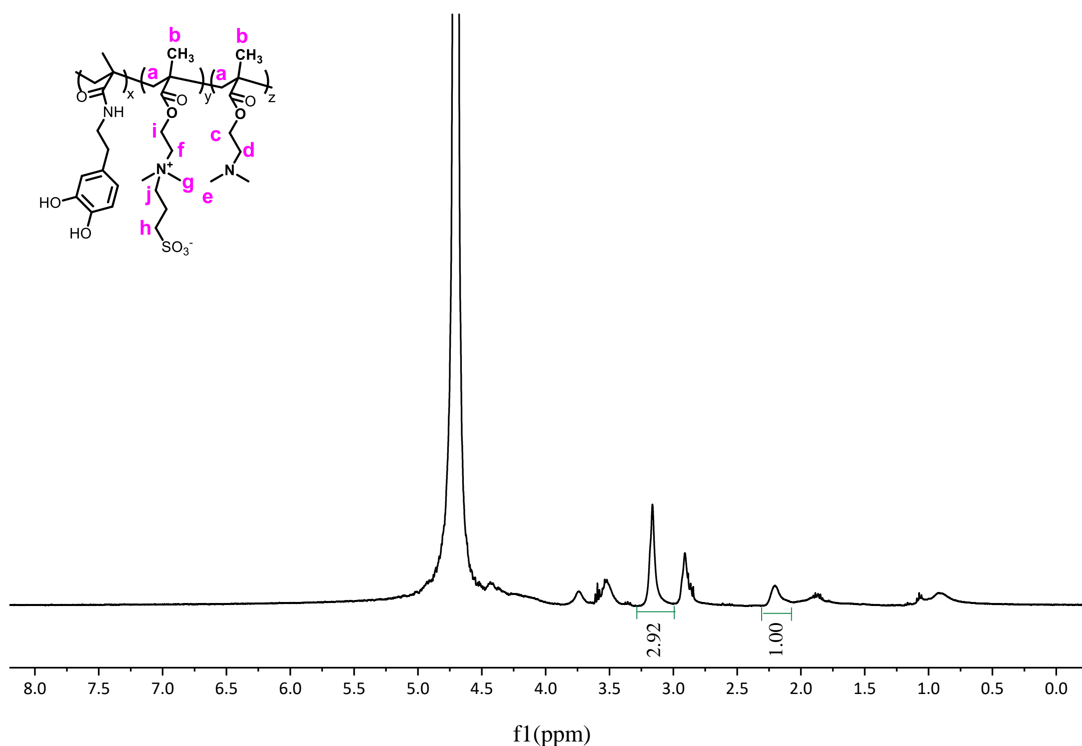

Figure S6. ^{1}H NMR spectrum of the de-protected diblock copolymer (PDMA-P(SBMA-*co*-DMAEMA)) using D_2O as solvent.

The conversion of DMAEMA can be calculated by taking the ratio of representative proton peak areas, i.e., the ratio between methyl protons (6H, –$N(CH_3)_2$) of PDMAEMA and one of the vinyl protons (2H, CH_2=$C(CH_3)C$=O–) of the DMAEMA monomer. The calculation equation is shown in eq 1, and the conversions of Br-PDMAEMA-Br and PDMAEMA-Br are 90% and 47%, respectively. Thus, the degrees of polymerization of PDMAEMA segment are 90 and 47 for triblock copolymer and diblock copolymer, respectively. The results are summarized in Table S1:

$$X_{DMAEMA} = \frac{(S_b-6)/6}{1+(S_b-6)/6} \times 100\% \quad (1)$$

Table S1. Molecular weight data for macroinitiators

Sample	Degree of polymerization^a	Degree of polymerization^b	M_{NMR}^{a}	Mn^b
Br-PDMAEMA-Br	90	88	14148	13955
Br-PDMAEMA	47	57	7388	9065

^{a} From NMR analysis. ^{b}From GPC analysis.

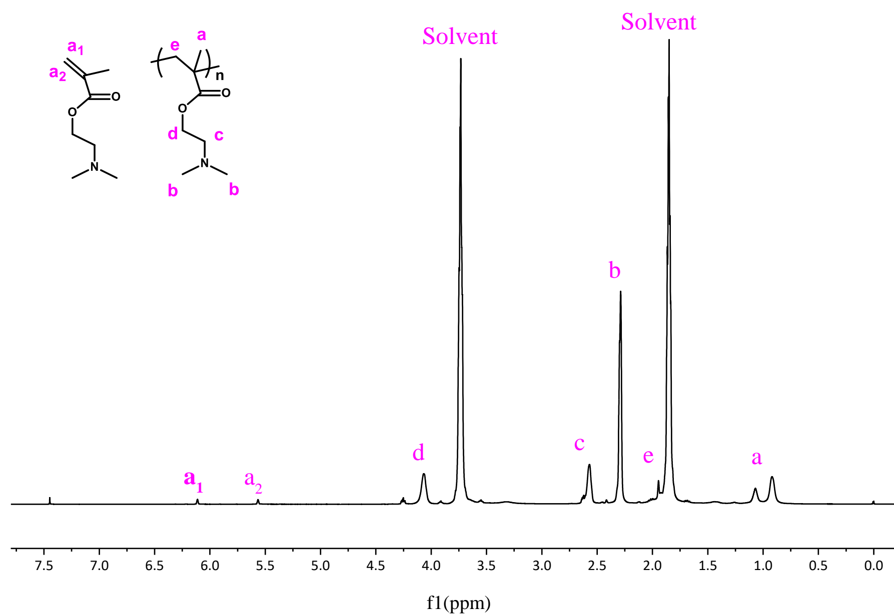

Figure S7. The ^{1}H NMR spectrum of unpurified PDMAEMA macroinitiators in $CDCl_3$.

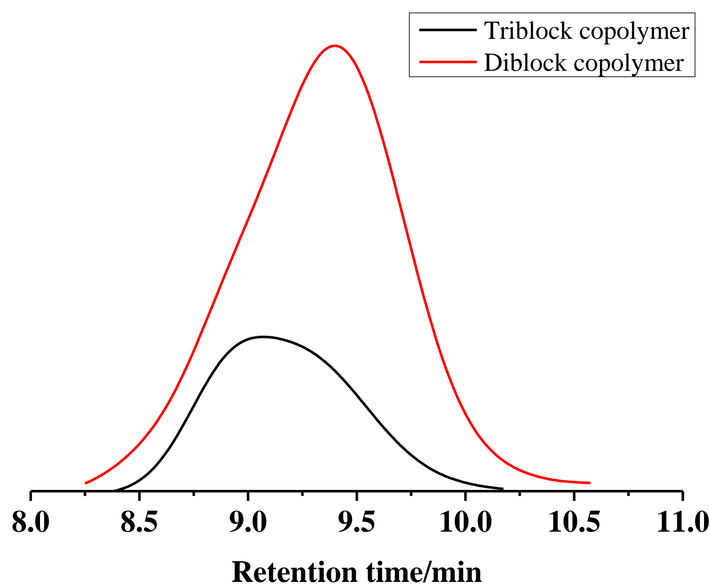

Figure S8. GPC traces of PDMA-P(SBMA-*co*-DMAEMA)-PDMA triblock copolymer and PDMA-P(SBMA-*co*-DMAEMA) diblock copolymer.

In order to calculate the degree of betainization of PDMAEMA in the (PDMA-P(SBMA-*co*-DMAEMA)-PDMA) triblock copolymer and in the (PDMA-P(SBMA-*co*-DMAEMA)) diblock copolymer, ^{1}H NMR measurement was conducted using D_2O as solvent. As shown in **Figure S5** and **Figure S6**, the proton signals of the CH_3 group linked to the quaternary amine ($=N^+(CH_3)_2$) was located at 3.16 ppm. The peak ascribed to the CH_3 group linked to the tertiary amine ($-N(CH_3)_2$) was located at 2.23 ppm. Using the integrations of the signals at 3.16 and 2.23 ppm, respectively, ascribed

to SBMA and DMAEMA, the degree of betainization of PDMAEMA for triblock and diblock copolymer can be estimated to be 75.7% and 74.5%, respectively. The results calculated from ^1H NMR data basically accorded with the value calculated from XPS results.

Table S2. Molecular weight data for triblock and diblock copolymers

Sample	degree of betainization[a]	M_{NMR}[a]	Mn[b]	PDI[b]
$PDMA_5$-P(SBMA-*co*-DMAEMA)-$PDMA_5$	75.7%	24605	22275	1.43
$PDMA_5$-P(SBMA-*co*-DMAEMA)	74.5%	12453	16458	1.59

[a] From NMR analysis. [b] From GPC analysis.

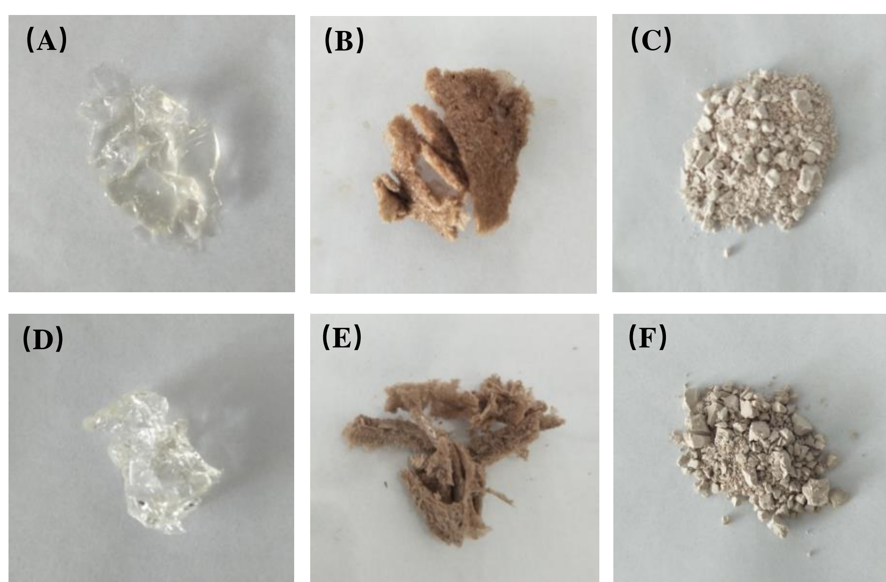

Figure S9. Photographs of each product: (A) Br-PDMAEMA-Br, (B) PDMA-PDMAEMA-PDMA, (C) PDMA-P(SBMA-*co*-DMAEMA)-PDMA, (D) Br-PDMAEMA, (E) PDMA-PDMAEMA, (F) PDMA-P(SBMA-*co*-DMAEMA).

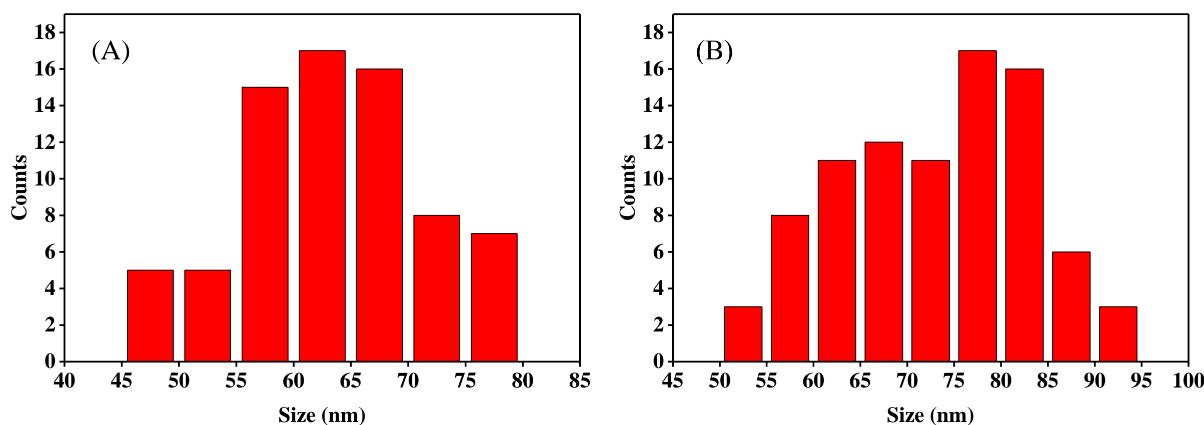

Figure S10. Size distribution histograms of the triblock copolymer (A) and diblock copolymer (B) micelles.

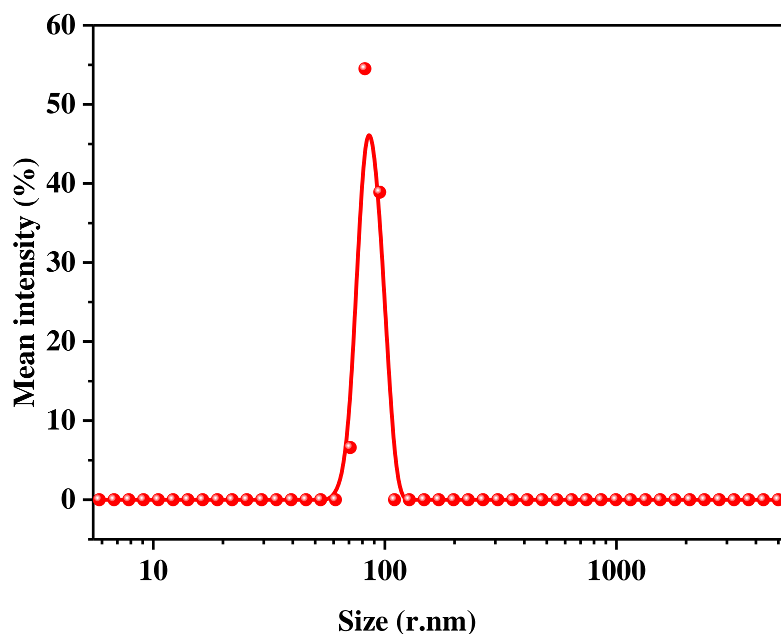

Figure S11. Hydrodynamic radius distributions of the micelles for the triblock copolymers in aqueous solution (2 mg/mL) at 25 °C.

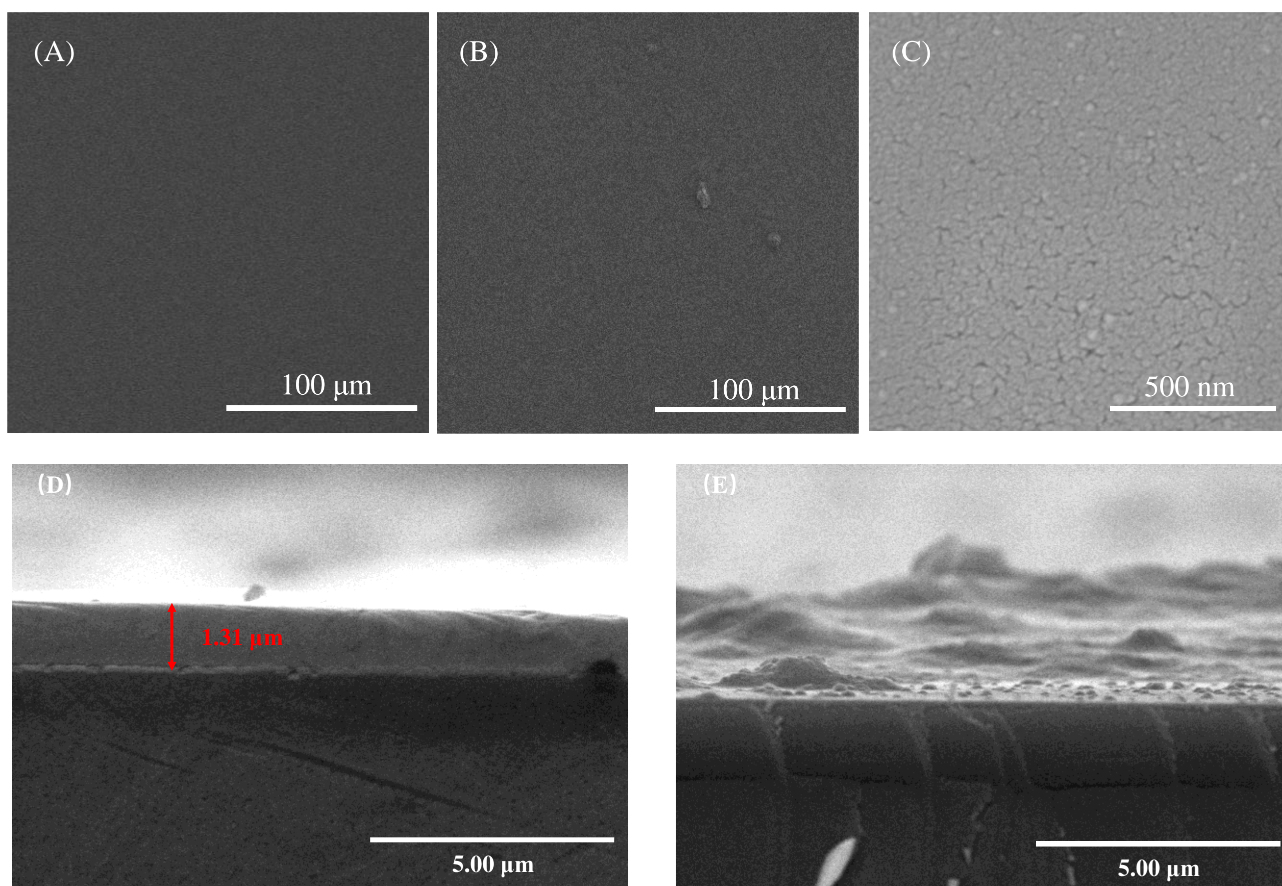

Figure S12. SEM images of (A) bare silicon surfaces, and triblock copolymer (B) and diblock copolymer (C) coated silicon wafers. Cross-section SEM images of triblock (D), diblock (E) copolymer coated silicon wafers.

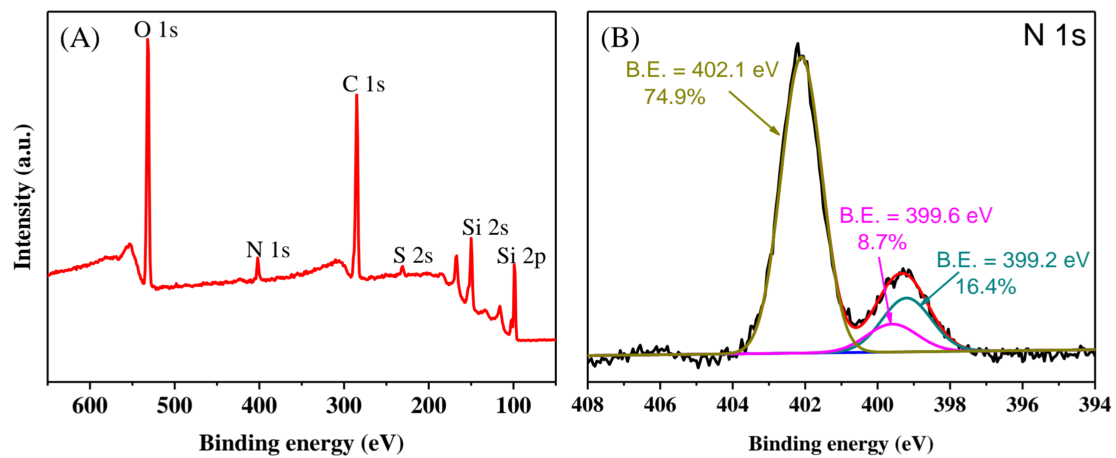

Figure S13. XPS spectrum of diblock copolymer (PDMA-P(SBMA-*co*-DMAEMA)) coated silicon wafer.