Supporting Information

Polymer brush growth by oxygen-initiated RAFT polymerization on various substrates

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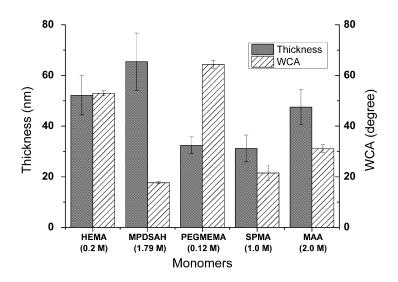


Figure S1. Film thicknesses (determined by ellipsometry) and water contact angles for various polymer brushes (4-hour polymerization under diffusion setup conditions) grown on Si/SiO₂ substrates.

	C 1s	N 1s	O 1s	S 2p	Ti 2p	K 2p
Ti/TiO ₂ bare	20.48	1.03	51.38	0.41	26.70	-
DOPA-DDMAT	45.86	3.65	34.50	1.99	14.00	-
PHEMA	67.42	0.50	31.80	0.13	0.15	-
PMPDSAH	45.02	15.92	30.41	8.36	0.29	-
PPEGMEMA	69.44	0.15	29.80	0.49	0.12	-
PSPMA	61.98	0.62	25.93	5.92	0.13	5.42
PMAA	72.00	0.63	26.94	0.23	0.20	-
PHEMA-b-PSPMA	52.98	0.49	33.80	6.33	0.17	6.23

Table S1. Atomic composition (%) of bare, DOPA-DDMAT-coated, and the polymer-grafted Ti/TiO₂ substrates.

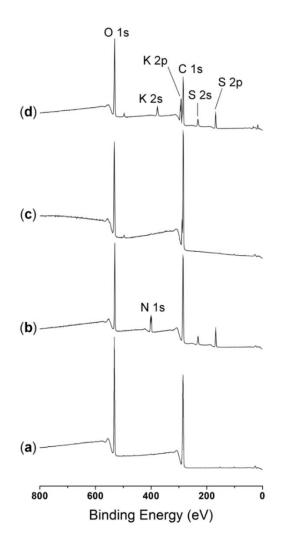


Figure S2. Survey XPS spectra of (a) PPEGMEMA, (b) PMPDSAH, (c) PMAA, and (d) PSPMA-grafted Ti/TiO₂ substrates.

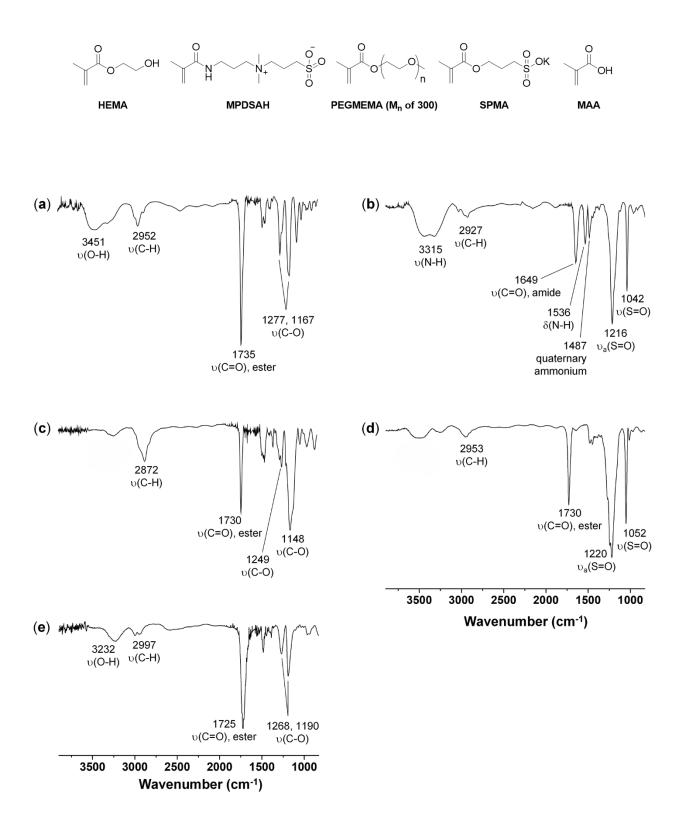


Figure S3. FTIR spectra of (a) PHEMA, (b) PMPDSAH, (c) PPEGMEMA, (d) PSPMA, and (e) PMAAgrafted Ti/TiO₂ substrates.

Chemical Stability Tests. The chemical stability of the PHEMA brushes was evaluated by immersing the polymer-coated substrates into physiological (10 mM PBS, pH 7.4), alkaline (50 mM NaOH, pH 12.72), and acidic (80 mM HCl, pH 1.19) solutions. At a specific time, the substrates were taken out from the solutions, rinsed with DI water, and dried under a stream of N_2 gas.

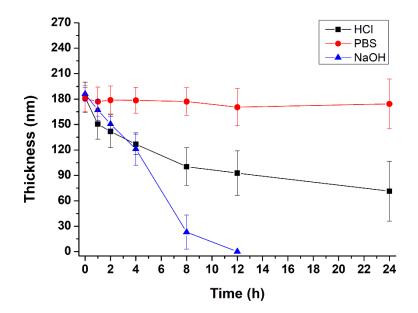


Figure S4. Thickness changes of the PHEMA films on Ti/TiO_2 substrates upon exposure to different pH environments over time. 0 h indicates the as-prepared film.

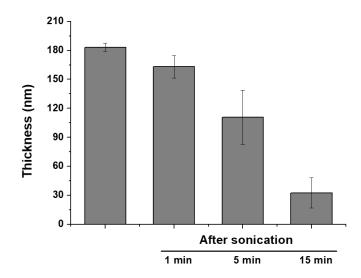


Figure S5. Thickness changes of the PHEMA-films on Ti/TiO_2 substrates after sequential sonication treatment.

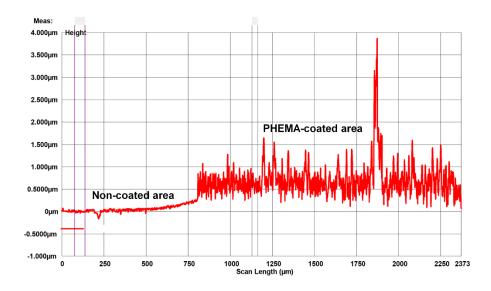


Figure S6. Thickness profile of the PHMEA brushes prepared with 1.5 M HEMA on Ti/TiO₂ substrates. It was measured by a contact surface profiler, Alpha-Step.

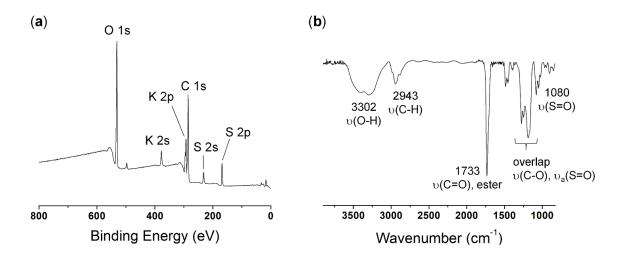


Figure S7. (a) XPS and (b) FTIR spectra of PHEMA-*b*-PSPMA-grafted Ti/TiO₂ substrate.

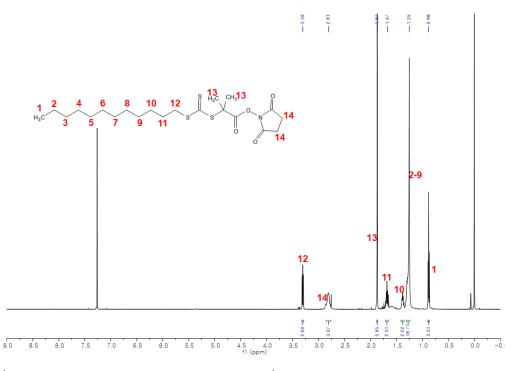


Figure S8. ¹H NMR spectrum of suc-DDMAT in CDCl₃.¹

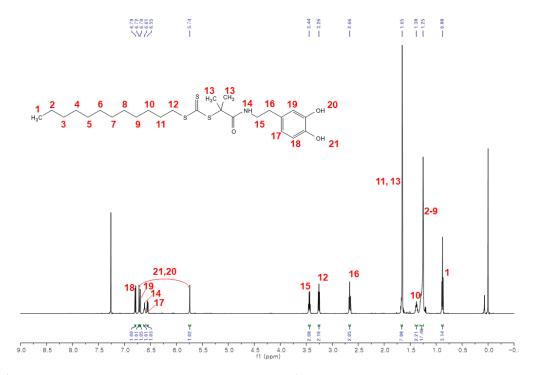


Figure S9. ¹H NMR spectrum of DOPA-DDMAT in CDCl₃.¹

Sample Preparation for GPC Analysis (polymer detachment from a substrate).^{2, 3} Titanium substrate coated with PMAA containing a CTA moiety at the chain end was placed in 325-mL dishes, and 0.1 M NaOH solution was added. The dishes were then placed in a fume hood for 100 minutes. The liquid was combined and transferred to a dialysis membrane (12.0-14.0 kDa MWCO), and dialyzed against water for at least 3 days. The water was changed three times per day and freeze-dried. Gel permeation chromatography (GPC) measurements were performed (Waters e2695; Waters Corporation, MA, USA) with deionized (DI) water as the eluent (flow rate 1 mL/min).

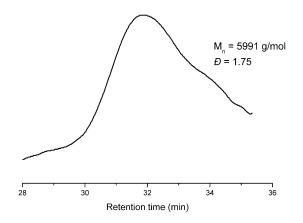


Figure S10. GPC chromatogram of PMAA brushes (30.3 nm) grown and detached from a large Ti/TiO₂ substrate ^{2, 3}

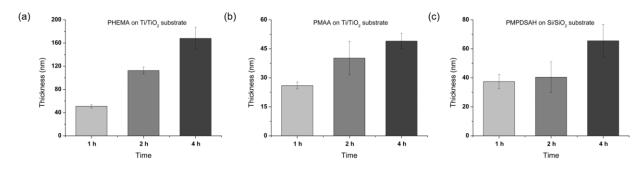


Figure S11. Evolution of polymer brush thickness of (a) PHEMA, (b) PMAA, (c) PMPDSAH grown *via* O₂-SI-RAFT polymerization

References

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