Supporting Information

Post-polymerization modification of styrene-maleic anhydride copolymer brushes

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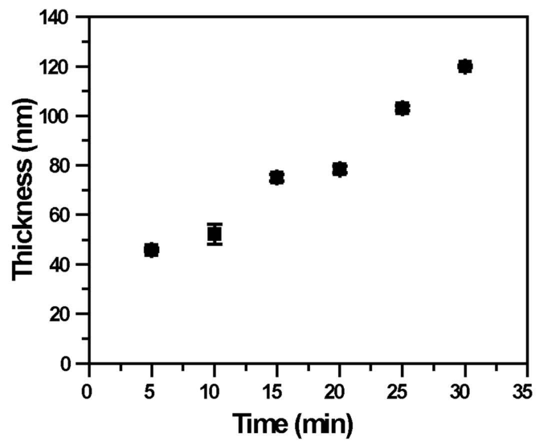

Fig. S1 Thickness of pSMA brush versus polymerization time.

The thickness values of pSMA brush samples before and after cystamine modification were measured using ellipsometry and the results are summarized in Table 1. The modification of the pSMA brush with cystamine increases the molecular mass of the repeat units and results in an increase in brush thickness. Note, the pSMA brush surfaces were thoroughly rinsed with DI water (pH < 6) prior to thickness measurements. We do not attempt to account for swelling that may arise from electrostatic repulsion of deprotonated carboxylic acid moieties. Anhydride conversions determined from ellipsometry are in good agreement with conversions determined by grazing angle FTIR. Equation S1 describes the relationship between polymer brush thickness, *T*, molecular weight of polymer repeat unit, *M*, and the mass density, ρ, of polymer brush before and after modification,[1]

$$\frac{T_2}{T_1} = \frac{M_2\rho_1}{M_1\rho_2} \qquad \textbf{Equation S1}$$

where the subscripts 1 and 2 denote the unmodified and cystamine-modified polymer brush, respectively. Assuming equivalent mass density of the polymer brush before and after postmodification, Equation 1 becomes Equation S2, where *k* represents conversion and M_{PPM} denotes the molecular weight of the modifier that reacts onto the polymer chain, respectively.

$$\frac{T_2}{T_1} = \frac{M_2}{M_1} = \frac{M_1+kM_{PPM}}{M_1} \qquad \textbf{Equation S2}$$

At full conversion, (k=100%), the molecular mass of modifier, M_{PPM}, was calculated to be 135.06 g/mol, based on Equation S2. The calculated M_{PPM} is less than the molecular weight of cystamine (152.28 g/mol) which can be attributed to the cystamine molecules that react with polymer brush by two amines. The percentage of cystamine as crosslinker, *x*, was calculated to be 12.7%, following Equation

S3 in which $M_{cystamine}$ is the MW of cystamine (152.28 g/mol). The result suggests that most cystamine molecules reacted with the pSMA brush by only one amine.

$$x = \frac{M_{cystamine} - M_{PPM}}{M_{PPM}} \qquad \textbf{Equation S3}$$

The anhydride conversion k can be calculated according to Equation S4 and the results are shown in Table 1.

$$k = \frac{M_1}{M_{PPM}}\left(\frac{T_2}{T_1} - 1\right) \qquad \textbf{Equation S4}$$

Table S1. Thickness and conversion of cystamine-modified pSMA brush.

Time (s)	Before PPM (nm)	After PPM (nm)	Conversion (%)
7	82.3±1.2	116.7±0.3	63±4
10	79.8±0.8	118.3±0.6	72±4
15	82.8±0.1	126.7±0.9	80±4
20	82.3±0.3	130.7±0.8	88±4
30	81.1±0.3	131.7±0.6	94±5
45	75.0±0.6	123.3±0.4	97±5
60	76.3±0.6	125.5±1.0	97±5
1200	76.9±0.7	128.1±3.0	>99

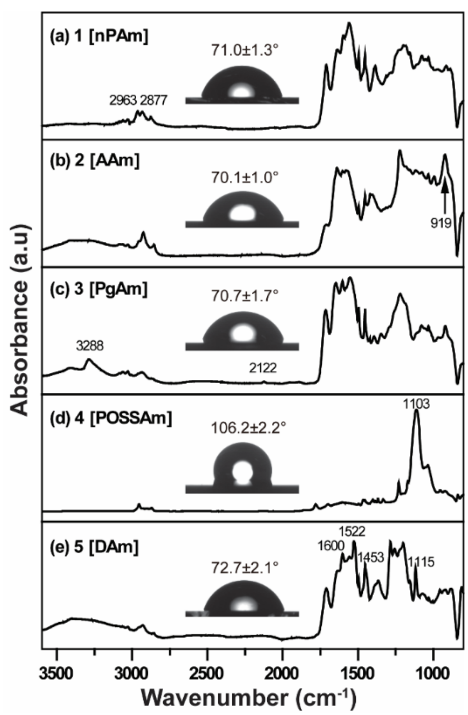

Fig. S2 Grazing angle ATR-FTIR of pSMA brushes postmodified with (a) propylamine (2963 cm^{-1} and 2877 cm^{-1} –C-H vibrations of methyl groups), (b) allylamine (919 cm^{-1} =C-H moiety), (c) propargyl amine (2122 cm^{-1} -C≡C- vibration, 3288 cm^{-1} ≡C-H), (d) aminopropylisobutyl POSS (1103 cm^{-1} –Si-O-), and (e) dopamine hydrochloride (1600 cm^{-1}, 1522 cm^{-1}, and 1453 cm^{-1} aromatic –C-H groups, 1115 cm^{-1} aromatic –OH group).

Table S2. Thickness and conversion of amine modified pSMA brush

	Thickness (nm)		Conversion (%)
	pSMA	After thiol-ene	
PAm	78.2±0.1	100.3±0.4	97±2
AAm	93.9±0.7	120.7±1.5	>99
PgAm	78.4±0.3	99.2±0.5	97±3
POSSAm	46.8±0.3	171.9±1.3	62±2
DAm	78.6±0.4	130.2±1.0	87±3

(1) Murata, H.; Prucker, O.; Ruhe, J. Synthesis of Functionalized Polymer Monolayers from Active Ester Brushes. *Macromolecules* **2007**, 5497-5503.