Study of Thiol-Ene Chemistry on Polymer Brushes and Application to Surface Patterning and Protein Adsorption

Supplementary Information

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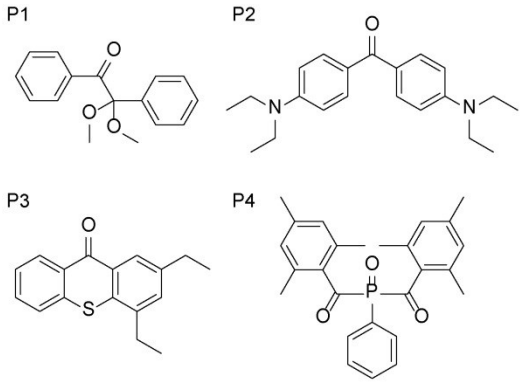


Scheme S1. Structure of photoinitiators used.

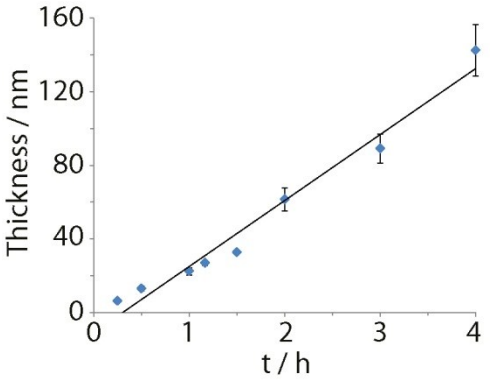


Figure S1. Controlled growth of PGMA brushes. Change in ellipsometric thickness (dry) as a function of time.

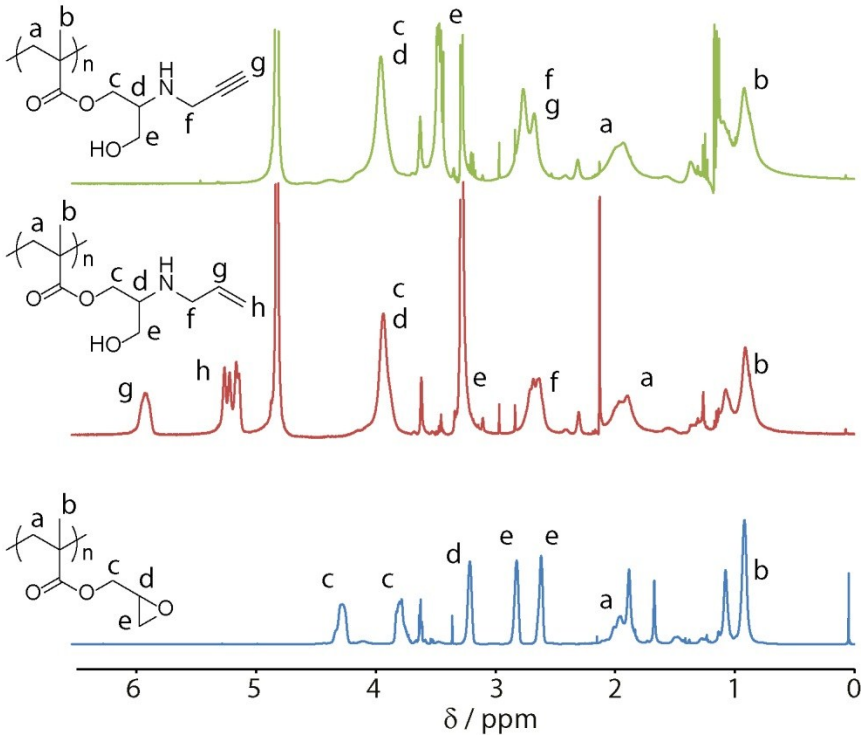


Figure S2. NMR characterisation of free PGMA and brushes reacted with allylamine and propargylamine.

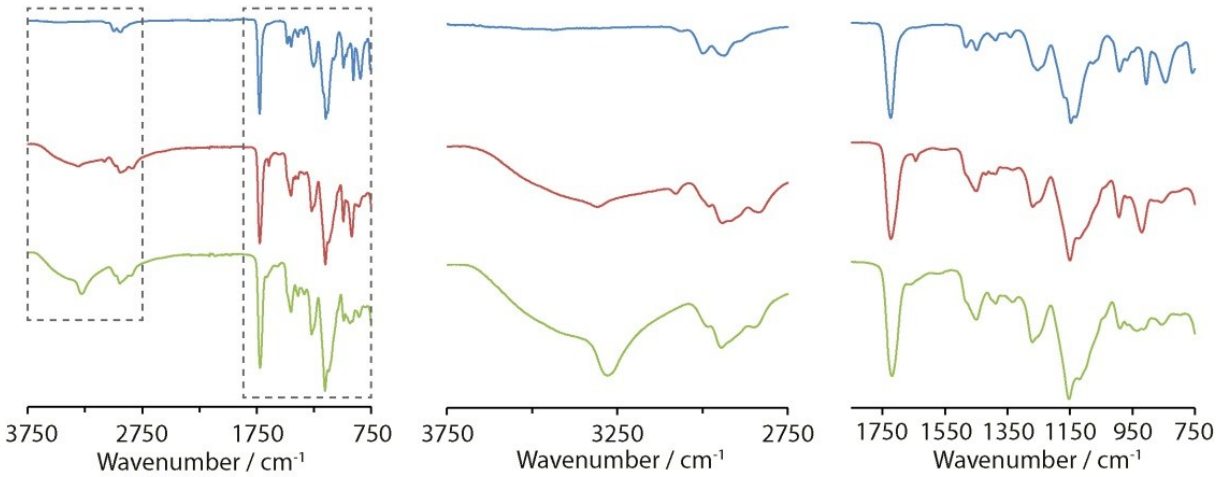


Figure S3. FTIR characterisation of free PGMA before and after aminolysis. From top to bottom, spectra corresponding to free PGMA, PGMA-aa and PGMA-pa.

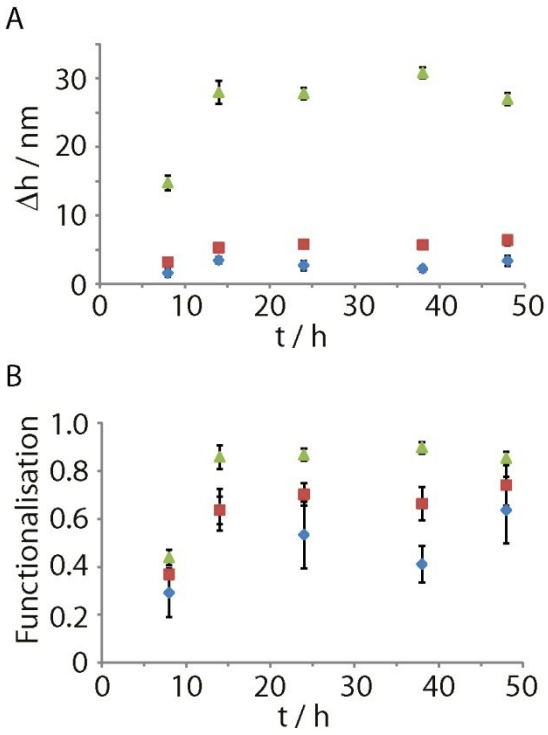


Figure S4. Functionalisation of PGMA brushes with propargylamine. A, changes in dry brush thickness measured by ellipsometry. B, corresponding functionalisation levels. Starting PGMA brush thicknesses were: 14 nm, blue diamonds, 22 nm, red squares, 85 nm, green triangles.

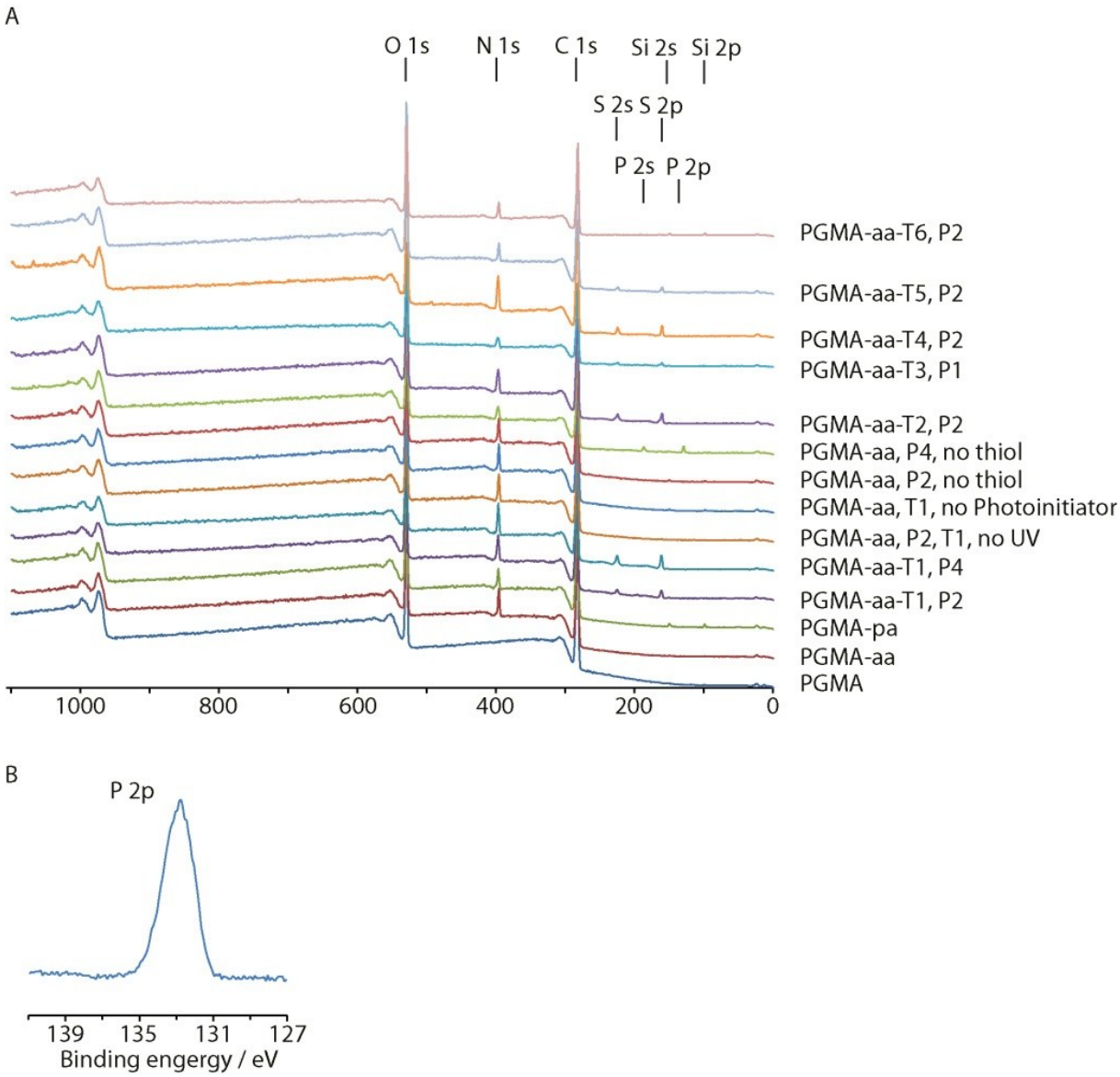


Figure S5. A. Full XPS spectra for functionalised PGMA brushes. B. XPS spectrum (P 2p) obtained for PGMA-aa brushes reacted with **P4** but no thiol.

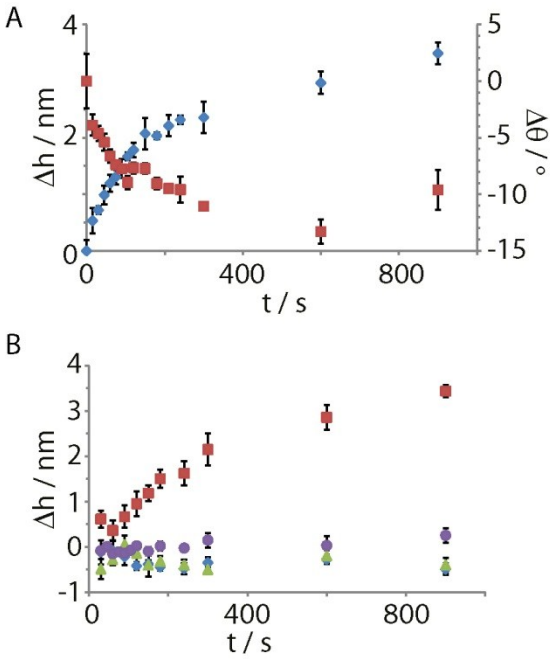


Figure S6. Thiol-yne functionalisation of PGMA-pa brushes. A. Increase in brush thickness (blue diamonds) and change in contact angle (red squares) during the reaction of PGMA-pa with **T1** and **P1**. B, reaction of PGMA-pa without **T1** (red squares), **P1** (blue diamonds), UV (green triangles) or with a dark photomask (purple circles). Δh are the changes in ellipsometric thickness measured with respect to the starting PGMA-pa brushes.

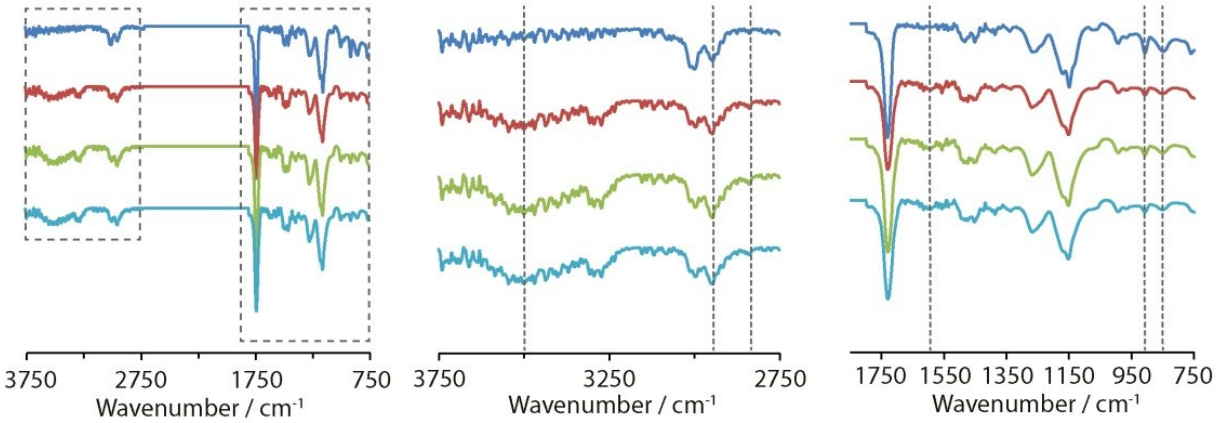


Figure S7. FTIR of functionalised PGMA brushes. From top to bottom: PGMA brush, before (dark blue) and after (red) propargylamine functionalisation, and PGMA-pa-**T2** (green) and PGMA-pa-**T4** (light blue) using the photoinitiator **P1**.

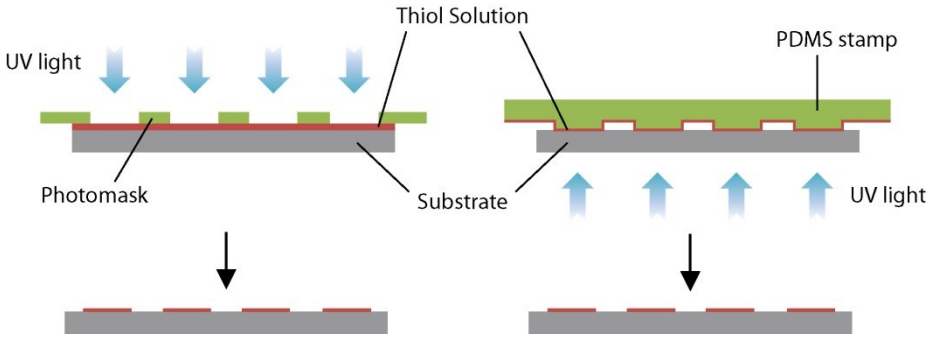


Figure S8. A schematic representation of the patterning configurations for photo-patterning (left) and reactive micro-contact printing (right).

Calculation of functionalisation ratios f1 and f2 based on the dry polymer thickness (ellipsometry)

All calculations based on dry ellipsometric thickness assume that the level of hydration of the brush remains unchanged after functionalisation.

First reaction (aminolysis)

The following equation provides a relationship between the initial brush thickness h_{d0}, the grafting density σ, the molecular weight M_n (or degree of polymerisation X_n and molar mass of the repeating units M_0), the density ρ and the Avogadro number N_A.

$$h_{d_0} = \frac{\sigma M_n}{\rho N_A} = \frac{\sigma X_n M_0}{\rho N_A} \qquad \text{(Equation S1)}$$

The change in ellipsometric thickness upon aminolysis is:

$$\Delta h_d = \frac{\sigma X_n M_1}{\rho N_A} - \frac{\sigma X_n M_0}{\rho N_A} = \frac{\sigma X_n (M_1 - M_0)}{\rho N_A} \qquad \text{(Equation S2)}$$

Where M_1 is the molar mass of the repeat units after functionalisation.

This can be simplified as:

$$\Delta h_d = \frac{h_{d_0}(M_1 - M_0)}{M_0} \qquad \text{(Equation S3)}$$

M_1 depends on the functionalisation level f_1 and the molar mass of the fragment added (M_x), according to the following equation.

$$M_1 = M_0 + f_1 M_x \qquad \text{(Equation S4)}$$

From equations S3 and S4, the functionalisation f_1 can be determined as:

$$f_1 = \frac{\Delta h_d M_0}{h_{d_0} M_x} \qquad \text{(Equation S5)}$$

Second reaction (thiol-ene coupling)

The change in brush thickness during the second reaction (thiol-ene coupling) is:

$$\Delta h_{d_2} = \frac{h_{d_1}(M_2 - M_1)}{M_1} \qquad \text{(Equation S6)}$$

Where M_2 is the molar mass of the repeat units after the second functionalisation.

This can be rewritten as:

$$\Delta h_{d_2} = \frac{(h_{d_0} + \Delta h_{d_1})(M_2 - M_0 - f_1 M_x)}{M_0 + f_1 M_x} \qquad \text{(Equation S7)}$$

The relationship between M_2 and the second functionalisation level f_2 is (with M_y being the molar mass of the added fragment in the second step):

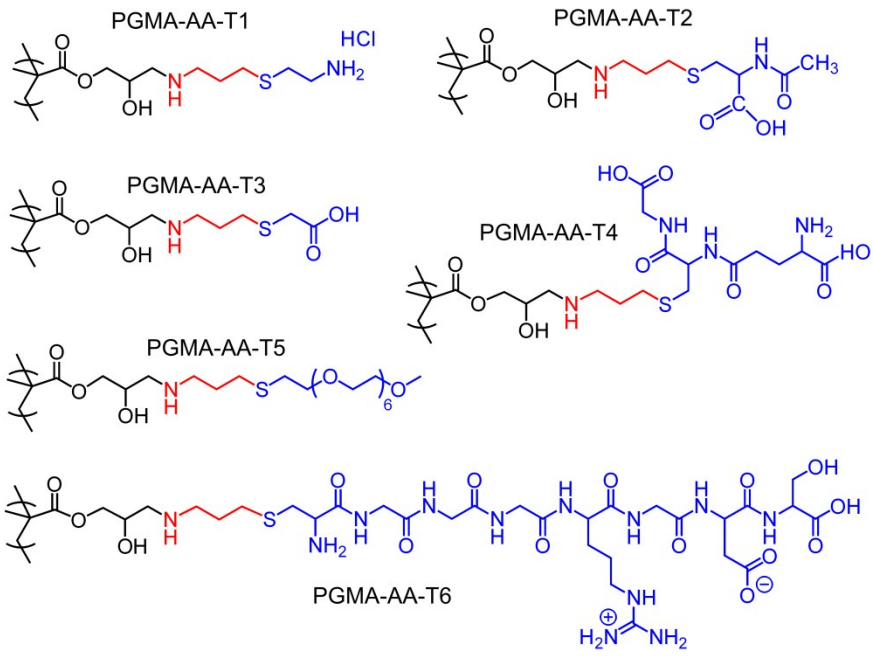
$$M_2 = M_1 + f_1 f_2 M_y = M_0 + f_1 M_x + f_1 f_2 M_y \qquad \text{(Equation S8)}$$

From equations S7 and S8, the functionalisation level f_2, during the second coupling is:

$$f_2 = \frac{\Delta h_{d_2}(M_0 + f_1 M_x)}{(h_{d_0} + \Delta h_{d_1})(f_1 M_y)}$$ (Equation S9)

Calculation of functionalisation ratio f3 based on the atomic % (XPS)

1. The sulphur/carbon ratio S/C_I corresponding to 100% functionalisation of PGMA-aa via the thiol-ene reaction is calculated first. The repeat unit of the resulting polymers is illustrated as below:



Polymers	C		O		N		S		S/C_I ratio
	Total atom†	Atomic %	Total atom†	Atomic %	Total atom†	Atomic %	Total atom†	Atomic %	
PGMA-aa-T1	12	66.67	3	16.67	2	11.11	1	5.56	0.083
PGMA-aa-T2	15	62.50	6	25.00	2	8.33	1	4.17	0.067
PGMA-aa-T3	12	63.16	5	26.32	1	5.26	1	5.26	0.083
PGMA-aa-T4	20	58.82	9	26.47	4	11.76	1	2.94	0.050
PGMA-aa-T5	25	67.57	10	27.03	1	2.70	1	2.70	0.040
PGMA-aa-T6	34	54.84	15	24.19	12	19.35	1	1.61	0.029

† Total of the respective atom in a repeat unit

2. The S/C_{II} ratio is calculated based on the atomic % obtained from XPS (Table 1). E.g., for PGMA-aa-**T1**, the atom % of S and C are 1.9% and 74.5% respectively. Therefore, S/C_{II} = 1.9/74.5 = 0.026.

3. For PGMA-aa-**T1**, the functionalisation level f3 is calculated as below:

$$f3 = \frac{S/C_{II}}{S/C_I} = \frac{0.026}{0.083} = 31\%$$

4. The functionalisation ratio f3 for the aminolysis of PGMA with allylamine and propargylamine was calculated using a similar approach, based on the N/C ratios.