

Supporting Information

S1. Surface Morphology.

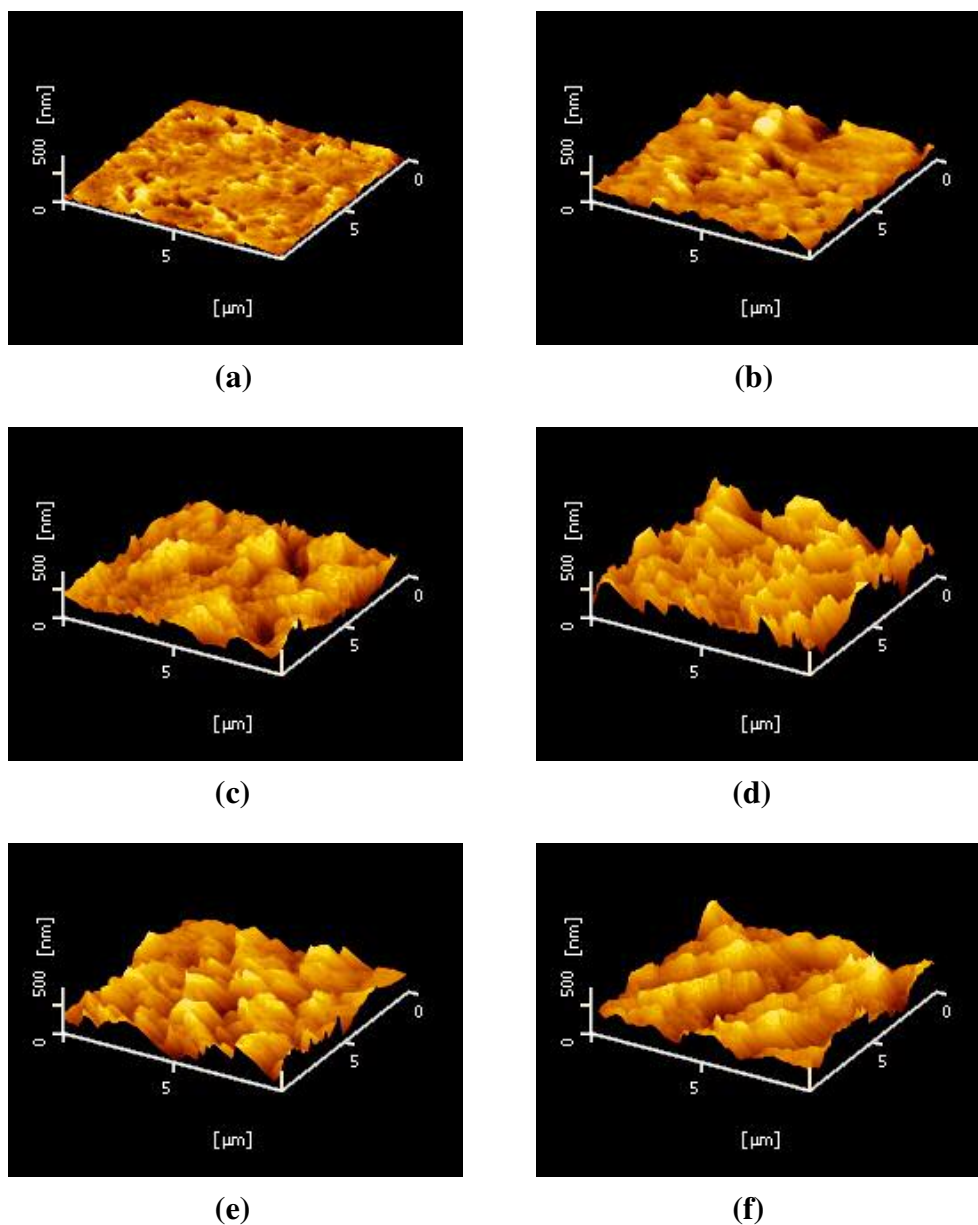
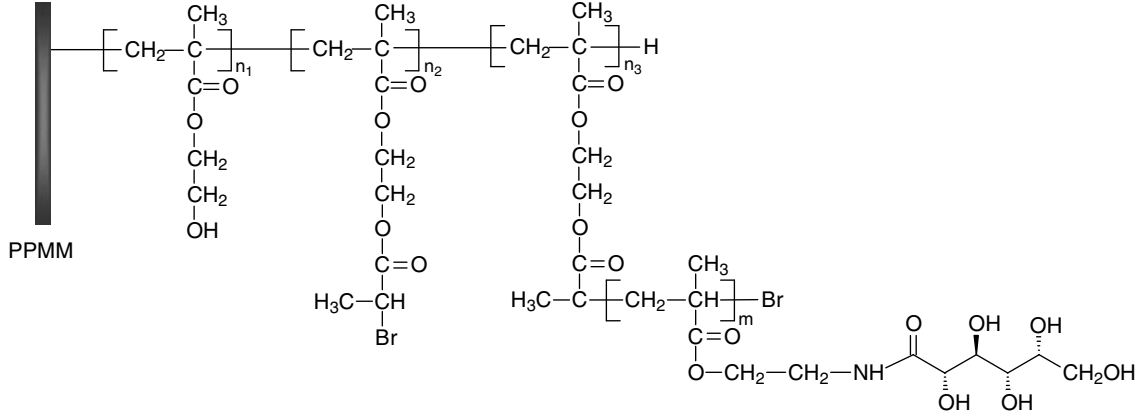


Figure S1. AFM images of PPMMs. a: nascent PPMM; b: PPMM-g-PHEMA; c: PPMM-g-PHEMA Br; d-f: PPMM-g-PHEMA-co-GAMA with glycopolymer chain lengths of 5, 12 and 20 respectively.

Figure S1 shows the AFM images of PPMMs. All the images were taken on a SEIKO SPI3800N AFM system by tapping mode at 300 KHz. The nascent PPMM exhibits a relatively flat surface and some membrane pores can be seen. After the graft polymerization of HEMA and the immobilization of ATRP initiator, the PPMM surfaces have been covered by grafted layers. However, membrane pores can still be seen on these

surfaces. After the surface-initiated ATRP of GAMA, a dense layer has been created on the PPMM. The whole surfaces, including the membrane pores, have been covered by the grafted layers. Moreover, with the increase of glycopolymer chain lengths, the grafted layers become denser and the chains huddle.

S2. Calculation of DP by XPS Data.



For the PPMM-*g*-HEMA-*co*-GAMA chain, three kinds of component are involved. They are unreacted HEMA moieties, uninitiated HEMA-Br moieties and HEMA-*co*-GAMA moieties. The chain lengths of these components are n_1 , n_2 and n_3 respectively. The polymerization degree of GAMA is m .

We can define:

$$\frac{[Br]}{[N]} = a, \quad \frac{[C]}{[N]} = b, \quad \text{and} \quad \frac{[C]}{[O]} = c$$

Thus, we can get:

$$\frac{n_2 + n_3}{m \cdot n_3} = a \quad (1)$$

$$\frac{6n_1 + 9n_2 + (12m + 9)n_3}{mn_3} = b \quad (2)$$

$$\frac{6n_1 + 9n_2 + (12m + 9)n_3}{3n_1 + 4n_2 + (8m + 5)n_3} = c \quad (3)$$

Also, the bromination ratio can be expressed as:

$$\frac{n_2 + n_3}{n_1 + n_2 + n_3} = d \quad (4)$$

from formula (1) we can get:

$$n_2 = amn_3 \quad (5)$$

from formulas (5) and (2) we can get:

$$n_1 = \frac{bm - 9am - 12m - 9}{6} n_3 \quad (6)$$

then, we can get:

$$m = \frac{6 + 3d}{d \cdot b - 6a - 12d - 3ad}$$

The values of a and d can be obtained by XPS core-level spectral area ratio. The value of d can be calculated from mass weighting data. Therefore, we can get the value of m . The formula (5) is obtained by assuming the contribution of Br in the XPS data all came from n_2 . It is reasonable because the relative concentrations of the low initiation efficiency and the element Br after ATRP processes decreased significantly (see Figure 2 (c) and (d)) which means the end Br groups were lost in the ATRP. When we used the XPS data for calculations, we ignored the enhancement of the carbon signal, which was brought by the PPMM substrate. The XPS has an examining depth about 10 nm and may penetrate the grafting layer. As can be seen in Table 1, the [C]/[O] ratio is appreciably larger than the theoretical one for the PPMM-g-HEMA surface. However, this error is negligible. The XPS data used for calculations were listed in Table S1.

Table S1. Chemical composition of GAMA-g-HEMA-co-GAMA surface obtained in different ATRP conditions.

Samples ^a	Solvents (V/V) Methanol:H ₂ O	GAMA:Bpy:CuBr:CuBr ₂ (molar ratio)	ATRP time (h)	Chemical composition (mol %)			
				C	N	O	Br
GAMA-g-HEMA-co -GAMA	3 : 2	100 : 2 : 1 : 0	1	65.33	3.97	29.68	1.02
			5	62.19	4.25	32.91	0.65
	4 : 1	100 : 2 : 1 : 0	1	75.62	3.88	19.40	1.10
			5	68.20	4.70	26.41	0.69
		100 : 2 : 1 : 0.25	2	63.38	4.43	31.72	0.47
			5	68.50	4.64	26.22	0.64
		100 : 2 : 1 : 0.5	2	76.80	3.78	18.71	0.71
			4	76.54	4.53	17.54	1.39