# Surface Conjugation of Anti-fouling Polymers via Pyrogallol-based Chemistry

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**Statement of Purpose:** Surface modification for anti-fouling purpose is important for some biomedical devices. However, many methods for conjugation of anti-fouling materials are substrate-dependent. We developed a simple one-step coating method for surface immobilization of sulfobetaine methacrylate (SBMA) or poly-(ethylene glycol) (PEG) via deposition of self-polymerized pyrogallol (PG). The anti-fouling polymers were successfully anchored on various substrates when the SBMA conjugation of monomers containing amine groups or PEG tailing with aldehyde groups. The modified surfaces exhibited excellent resistance to fibroblast cells and proteins. Controlling the coating for an array of incubation time, we investigated through the surface properties corresponding to anti-fouling behaviors of biomolecules. The high transparency of the coating allow this strategy applied on the development of new generation medical devices.

**Methods:**

***Synthesis of pSBMA-co-AEMA (pSBAE)***

SBMA and aminoethyl methacrylate (AE) were dissolved in deionized water to the desired concentrations, and then 0.03 mmol Azobisisobutyronitrile in DMSO was added. After the monomer solution was purged with nitrogen, the polymerization was initiated by raise of temperature to 70°C. After 20-hr reaction, the products were dialyzed against deionized water in order to remove monomers or oligomers, followed by lyophilization. The addition of AE at a molar ratio of 10%, 20% and 50% of SBMA, as formed copolymers are referred as pSBAE0.1, pSBAE0.2 and pSBAE0.5.

***Surface Conjugation of anti-fouling materials***

For the surface deposition of SBMA or PEG, PG in phosphate buffered saline (PBS, pH7.4) was mixed with the same volume of pSBAE or PEG-aldehyde in PBS to the desired concentrations. The mixtures were added onto several types of substrates and then incubated at 45°C with constant agitation. After incubation, the substrates were rinsed with deionized water and then air-dried.

**Results:**

***Antifouling efficacy of PG/pSBAE coatings***

A series of PG/pSBAE coatings were fabricated with different AE compositions. The cell adhesion was almost inhibited on the substrate coated with pSBAE0.1. However, approximately 15% and 25% of cells were still attached on the surface after deposition of pSBAE0.2 and pSBAE0.5 respectively (Figure 1A). Our results suggest that AE is critical for the anchorage of the zwitterionic polymer onto the substrates. In this study, the PG/pSBAE0.1 coating has been successfully applied on various substrates. We demonstrated that pSBAE could be immobilized on PDMS, silicon, PET, polystyrene, glass, polyurethane and PVDF and then resisted cell adhesion(Figure1B).

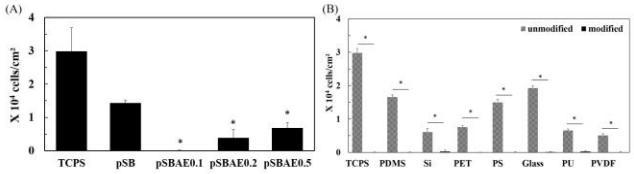


**Figure 1.** The evaluation of the anti-fouling efficacy with (A) different AE molar ratio (B) Cell adhesion on PG/pSBAE0.1 modified surface (* $p < 0.001$, n=4)

***Coating time-dependence on surface properties and anti-fouling abilities of PG/PEG-aldehyde deposition***

The water contact angle (WCA) decrease from 93 to 27 degree while the film thickness increase from 8.57 nm to 68.45 nm with the increase of the coating time from 2hr to 12hr. (Table 1) The results suggest that the increase in film thickness reflects the enrichment of anti-fouling polymers, and thus the enhancement of surface wettability, in accordance with the cell or fibrinogen repellent property. For coating longer than 12hr, some anti-fouling layer would be covered by PG deposition so the anti-fouling effect would decrease. (Figure 2)

**Table 1.** Surface properties on PG/PEG-aldehyde modified PDMS controlled for different coating time

| Coating time (hr) | Nor. cell conc. | Fibrinogen attachment conc. (μg/cm²) | Film thickness (nm) | WCA (deg.) |
|---|---|---|---|---|
| 0 | 1 | 8.143 | 0 | 101.7 |
| 2 | 0.749 | 6.853 | 8.59 | 92.9 |
| 4 | 0.560 | 5.079 | 26.6 | 80.3 |
| 6 | 0.191 | 3.755 | 32.94 | 69.4 |
| 8 | 0.027 | 1.349 | 47.34 | 43.8 |
| 10 | 0.001 | 0.228 | 50.54 | 27.0 |
| 12 | 0.002 | 0.026 | 68.44 | 35.6 |
| 24 | 0.103 | 2.262 | 77.5 | 54.0 |

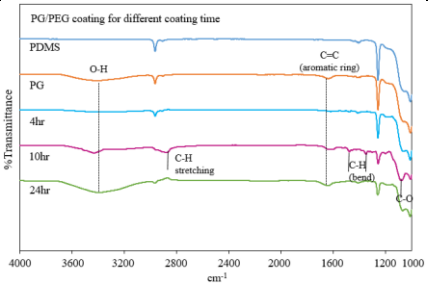


**Figure 2.** ATR-FTIR spectra of PG/PEG-aldehyde modified surface with different coating time

**Conclusions:** This work developed a simple one-step coating method for surface immobilization of anti-fouling materials on various substrates. PG anchors SBMA to substrates via the assistance of AE moiety of pSBAE or anchors PEG via the assistance of aldehyde group. The anti-fouling efficacy of the coating is positively correlated with surface wettability and film thickness. We expect that the strategy for anti-fouling coatings is suitable for medical devices.