

Supporting Information Available

**Improving hemocompatibility of polypropylene via
surface-initiated atom transfer radical polymerization for
covalently coupling BSA**

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1. ATR-FTIR of BSA modified films

Fig. S1 shows the ATR-FTIR of neat PP, PP-g-P(PEGMA-co-GMA) and BSA-modified films. Compared with neat PP and PP-g-P(PEGMA-co-GMA), there was another new weak peak at 1656 cm^{-1} for BSA-modified PP film, which was corresponding to the O=C-N-H stretch vibrations. This result also indicated that the BSA was immobilized on the PP surface successfully.

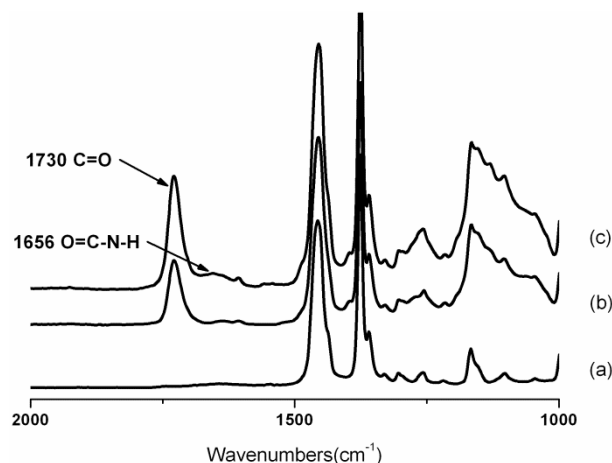


Fig. S1. ATR-FTIR spectra of (a) neat PP films (b) PP-g-P(PEGMA-co-GMA) (c) the BSA modified PP film surface

2. FT-IR microscopy analysis

Conventional FT-IR spectroscopy only provides information about chemical composition. FT-IR microscopy (FT-IRM) imaging further allows for the possibility to visualize the distribution of polymer on the surface^{2, 3}. In addition, FT-IRM has high resolution due to the Rayleigh criterion without essentially sample preparation. To visualize the surface functionalization of PP, high-resolution FT-IR microscopy was applied using FT-IR Imaging system of PE (American) (Fig. S2). The mapping area displayed in Fig. S2 corresponds to a surface of $100 \times 100\ \mu\text{m}$. As shown in Fig. S2a, b and c, the IR signal between 1700 and 1760 cm^{-1} was corresponded to the carbonyl (C=O) stretching vibrations. The false colorcode represented the signal intensity and, thus, the amount of the GMA and PEGMA repeating units localized on the PP surface (the intensity scales ranging from dark blue (low intensity) to pink (high intensity)).

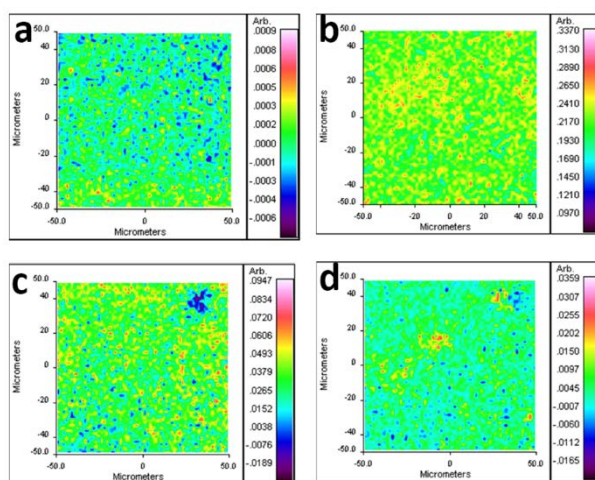


Fig S2. FTIR image (a) PP (C=O) (b) PP-g-P(PEGMA-co-GMA) (C=O) (c) BSA modified films (C=O) (d) BSA modified films (O=C-N-H)

As can be seen, Fig. S2a shows the FT-IR image of PP. The low intensity of PP indicated that there was nearly no carbonyl group on PP surface. The PP-g-P(PEGMA-co-GMA) films (Fig. S2b) showed a relatively uniform grafting density within the imaged area and almost all the surface was functional with the grafting brushes. The intensity of the grafted films was higher. After immobilized of BSA, the intensity of carbonyl (C=O) decreased and displayed small inhomogeneities (Fig. S2c). This result showed that the GMA in the grafting brushes may not homogeneities completely. Fig. S2d shows the IR signal between 1635 and 1660 cm^{-1} which corresponding to the amide group (O=C-N-H) stretching vibrations. Evidently, the amide group (O=C-N-H) existed on the surface. This result also demonstrated that the BSA was immobilized on the PP surface. The FT-IR microscopy image results are consistent with the ATR-FTIR. Besides, the image showed the distribution of grafting polymer and BSA on the surface.

3. Hemolysis rate of modified PP with different ratio of PEGMA and GMA

Fig. S3 showed the hemolysis rate of different molar ration of monomer modified PP at ATRP time of 6 h. The PEGMA modified PP showed lower hemolysis rate of 0.8% due to the hydrophilicity of PEGMA. But the hemolysis of PEGMA modified PP is higher than BSA modified PP. The hemolysis rate increased with the increasing of GMA in the reaction system. The GMA modified PP film had hemolysis rate of 1.5 % which was a little higher than neat PP film. The hemolysis rate of different

ration of PEGMA and GMA indicates that PEGMA can decrease hemolysis of the film due to the hydrophilicity. Besides, the anti-hemolysis of BSA modified film is better than PEGMA modified film.

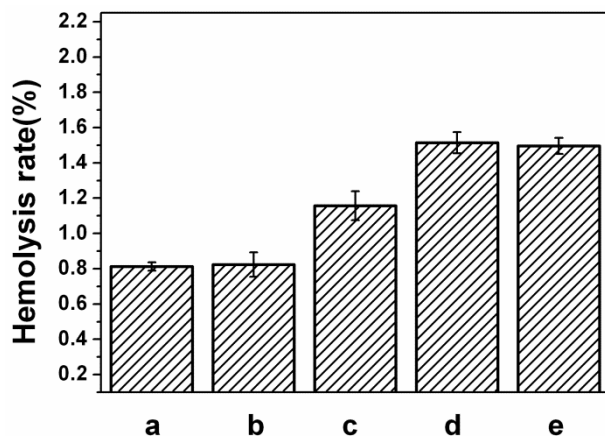


Fig. S3. Hemolysis test results of (a) PEGMA modified PP film, (b, c and d) PEGMA and GMA modified PP films at molar ratio of 8:1, 4:1 and 1:1, (e) GMA modified PP film (ATRP time: 6 h).

4. Fibrinogen (Fib) adsorption test

Fib was used as model protein to determine protein adsorption of films. Neat and modified PP films in square shape (1 cm×1 cm) were immersed into PBS solution for 12 h. Then the films were transferred into PBS solution of Fib (1 mg/mL) at 37°C for 120 min. After rinsing with fresh PBS three times by gentle shaking, the samples were immersed into an aqueous solution of 1.0 wt. % SDS and the protein adsorbed on the surface was completely desorbed by sonication for 20 min. A micro BCATM protein assay reagent kit based on the bicinchoninic acid (BCA) method was used to determine the concentration of the protein in the SDS solution. The concentrations were determined on the basis of the absorptiometer at 570 nm using a microplate (TECAN GENIOS, Austria). The reported data were the mean values of three samples for each film.

Plasma protein absorption plays a significant role in hemocompatibility of biomaterials, which is the first step when biomaterial surface in contact with blood, subsequently induced platelet and cell adhesion^{4,5}. Many factors such as surface free energy, surface charge character, surface morphologies, and solution environment affect protein adsorption. From Fig. S4, it can be seen that neat PP film has the

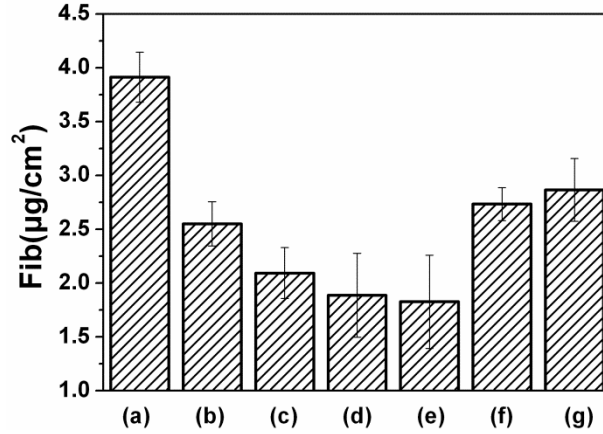


Fig S4. Fib adsorbed mass on PP and modified PP surfaces. (a) Neat PP film; (b, c, d and e) the PP-g-P(PEGMA-co-GMA) surface obtained at the graft density of 7.5, 13.8, 22.5 and 40.0 $\mu\text{g}/\text{cm}^2$, respectively; (f and g) BSA immobilization on the PP-g-P(PEGMA-co-GMA) obtained at the graft density of 22.5 and 40.0 $\mu\text{g}/\text{cm}^2$.

highest protein adsorbed amount due to its high hydrophobic property. After grafting with PEGMA and GMA, the amount of Fib absorbed decreased significantly. It indicated that these modified surfaces exhibited resistance to protein adsorption (Fig S4b-e). The reason is the good protein resistance property of PEG. As shown in Fig. S5b, it also can be seen that nearly no protein was adsorbed on the PEGMA modified surface. Protein resistance mechanisms of PEG can be explained by the water layer barrier and the excluded volume⁶⁻⁸. A tightly-bonded water molecule interfacial layer existed on the PEGMA modified surface⁹. The bound water layer provided a force barrier against the approach of Fib. Besides, when Fib compressed the chain of PEG-covered surface, the available volume was reduced for each polymer segment. Consequently, the loss of conformation freedom of PEG chains on the modified PP surface formed a repulsive force¹⁰. The amounts of Fib adsorption on the modified surface decreased from 3.91 ± 0.23 to $1.82 \pm 0.43 \mu\text{g}/\text{cm}^2$ with increasing graft concentration density 0 to $40.0 \mu\text{g}/\text{cm}^2$. The main reason is that more PEGMA on the surface with increasing the graft density leads to much more water barrier and the excluded volume. Although the amount of adsorbed Fib increased after BSA immobilization compared with the PEGMA modified PP, the Fib adsorbed amount on BSA modified surface was lower than that of neat PP. The inertness of BSA could

inhibit the conformational changes of Fib which is the much greater determinant of the platelet response than the amount of Fib adsorbed. Therefore, the Fib adsorption was suppressed by the modification of PEGMA and BSA modified PP could inhibit transformation of Fib in plasma to fibronectin.

5. FITC-Fib adsorption test

To estimate the static protein adsorption of neat and modified PP films, the protein adsorption test was also performed using fluorescein isothiocyanate-conjugated Fibrinogen (FITC-Fib). The BCA method has showed that the amount of Fib absorbed decreased significantly of modified films than PP. The FITC-Fib adsorption test (Fig. S5) is corresponded to BCA method. Intense fluorescence intensity was observed across the PP surface due to its high hydrophobic property (Fig. S5a). After grafting with PEGMA and GMA, there was nearly no fluorescence on the surface (Fig. S5b and c). It indicated the excellent protein resistance of the grafted films. The fluorescence intensity of BSA-modified films (Fig. S5d and e) was a little higher than PP-g-P(PEGMA-*co*-GMA) but much lower than PP films.

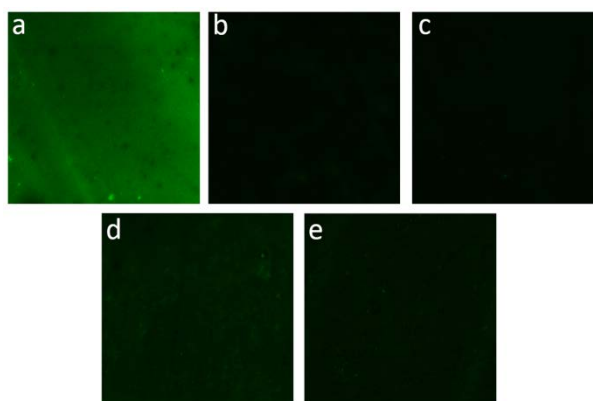


Fig. S5. Fluorescence images of FITC-Fib adsorption onto (a) PP (b and c) the PP-g-P(PEGMA-*co*-GMA) surface obtained at the graft density of 22.5 and 40.0 $\mu\text{g}/\text{cm}^2$, and (d and e) BSA immobilization on the PP-g-P(PEGMA-*co*-GMA) obtained at the graft density of 22.5 and 40.0 $\mu\text{g}/\text{cm}^2$.

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