Protein resistant silicones by graft polymerization of 2-methacryloyloxyethyl phosphorylcholine (MPC) via surface-initiated atom transfer radical polymerization (ATRP)

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Introduction: Polymethylsiloxane elastomers (PDMS) have many attributes leading to their use as ophthalmic and blood contacting biomaterials. However, their use in these applications is somewhat constrained by their extremely high surface hydrophobicity, which results in the adsorption of significant quantities of protein from the surrounding environment [1]. We hypothesize that a hydrophilic, protein repellant and highly oxygen permeable PDMS surface might be obtained by surface modification of PDMS with 2-methacryloyl-oxyethyl phosphorylcholine (MPC) polymers. In this study, poly (MPC) modified PDMS surfaces were prepared by grafting from the surfaces at room temperature using surface-initiated atom transfer radical polymerization (ATRP) as shown in Figure 1.

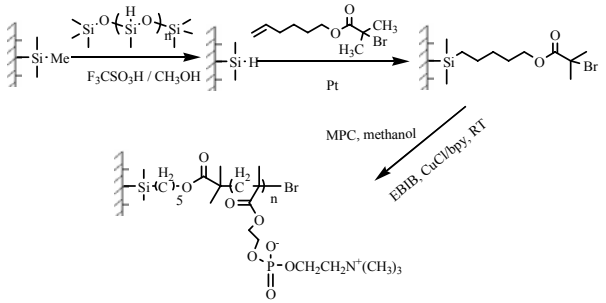

Figure 1 Preparation of poly (MPC) modified PDMS surfaces

Methods: MPC was synthesized as described by Ishihara et al [2]. Si-H functionalized PDMS surfaces were obtained by acid-catalyzed equilibration reaction with DC1107 ($(MeHSiO)_n$). The 2-bromoisobutyryl terminated ATRP initiator was then grafted onto these surfaces using the Pt catalyzed hydrosilylation reaction between the Si-H and allyl groups. Poly (MPC) was subsequently grown from this surface by ATRP [3]. Free initiator was added to the reaction system to control the grafting process (Figure 1). The surfaces were analyzed by ATR-FTIR, NMR, GPC, XPS and AFM. Water contact angles were used to characterize the hydrophilicity of the poly (MPC) modified PDMS surfaces. Protein resistance was assessed by measuring adsorption of fibrinogen from TBS (pH 7.4) using radioiodination methods.

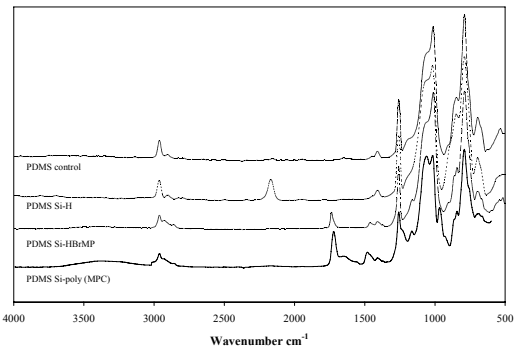

Figure 2 ATR-FTIR of modified PDMS surfaces

Results and Discussion: The poly (MPC) chain length on the grafted surfaces was varied from 5 to 200. This is indicated by "polyMPC-5", "polyMPC-200" etc. ATR-FTIR spectroscopy was used to trace the entire process of surface modification. The spectra showed in Figure 2 confirm the grafting of poly (MPC) on the surfaces. The advancing water contact angle of the PDMS was significantly reduced by modification from greater than 100° to ~25° (Figure 3). In vitro fibrinogen adsorption experiments from buffer, summarized in Figure 4 show reductions of more than 90% with modification.

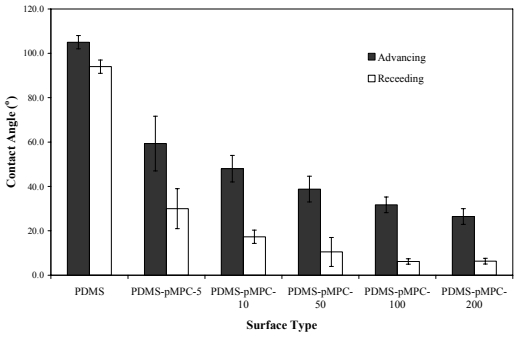

Figure 3 Water contact angle of modified surfaces

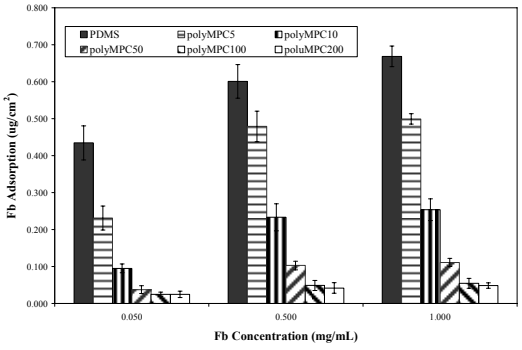

Figure 4 Fibrinogen adsorption on modified surfaces

Conclusions: PDMS surfaces were successfully modified by grafting with poly (MPC) via surface initiated ATRP, resulting in a hydrophilic PDMS surface that shows minimal protein adsorption.

References:

[1] H. Chen et al., Biomaterials 2004, 25:2273-2281
[2] K. Ishihara et al., Polym J 1990; 22:355-360
[3] W. Feng et al., J Polym Sci, Part A 2004; 42: 2931-2942

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