Protein Resistance of Polyurethane Film Grafted with Poly(oligo(ethylene glycol) methacrylate) via Atom Transfer Radical Polymerization

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Introduction

The objective of this work was to investigate the possibility of generating protein resistant surfaces by graft polymerizing the PEO macromonomer oligo(ethylene glycol) methacrylate (OEGMA, Fig. 1) on polyurethane (PU) films. Poly(OEGMA) chains have a carbon backbone with a PEO side chain on every second carbon. Thus although the PEO is of short chain length (in this case 4 to 5 monomer units), the density of ethylene oxide units is high. Grafting was carried out using surface-initiated atom transfer radical polymerization (ATRP), a living free radical process. This method controls the process such that the chains are of predictable and uniform length. The effect of chain length of the grafted poly(OEGMA) on fibrinogen (Fib) adsorption from TBS (pH 7.4) and from human plasma was investigated.

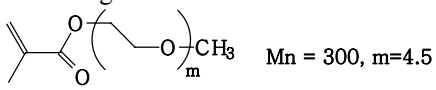

Fig. 1. Chemical structure of OEGMA

Methods

Polyurethane films were exposed to an oxygen plasma etcher (RF power, 100W; flow rate, 8 mL/min) for 30 min. These films (PU-OH) were then treated with the initiator 2-bromoisobutyryl bromide to produce initiator-coated films (PU-Br). Graft polymerization was carried out using CuBr-bipyridine (bpy) as catalyst. ATRP was initiated simultaneously in the solution (using ethyl 2-bromoisobutyrate, EBiB, as sacrificial initiator) to provide data on the properties of the poly(OEGMA).[1] The chain length of the poly(OEGMA) was controlled via the ratio of OEGMA/EBiB. Grafted surfaces are referred to as PU-x, where x is the chain length (5 to 200 monomer units).

Surfaces were characterized by water contact angle and X-ray photoelectron spectroscopy (XPS). Fibrinogen adsorption from TBS and human plasma was measured using ^{125}I-radiolabelling methods.

Results and Discussion

Advancing water contact angles of the PU-OH films were ~ 30°, compared to ~ 100° for the unmodified PU. Following initiator treatment, the contact angles increased to 65°, which is comparable to data reported previously for isobutyrate bromide-terminated monolayers.[2] OEGMA grafting led to decreases in contact angle, and the angle decreased with increasing chain length. The PU-200 surface was strongly hydrophilic with an advancing contact angle less than 20º. The XPS spectra of initiator-treated surfaces showed the presence of bromine. On the grafted PU films the XPS data showed an increase in oxygen content with increasing chain length. The water contact angle and XPS data thus confirmed the surface modifications.

Fibrinogen adsorption on the PU-Br surfaces from TBS (2 h incubation) was ~ 0.53 and 0.79 μg/cm^2, respectively, at concentrations of 0.05 and 1.0 mg/mL. Adsorption on the poly(OEGMA)-grafted surfaces decreased with increasing chain length (Fig. 2). For the PU-200 surface fibrinogen adsorption was ~40 ng/cm^2, i.e. less than 5% of the value on the unmodified surface.

Fibrinogen adsorption from plasma (Fig. 3) on the PU-Br surface was high and showed a strong Vroman effect. All of the poly(OEGMA)-grafted surfaces showed reduced adsorption and weak Vroman effects. No Vroman effect was evident on surfaces having chain length ≥ 100 and adsorption decreased with increasing chain length.

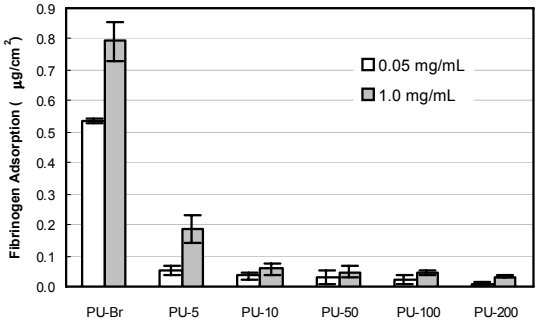

Fig. 2. Fibrinogen adsorption to PU films from TBS.

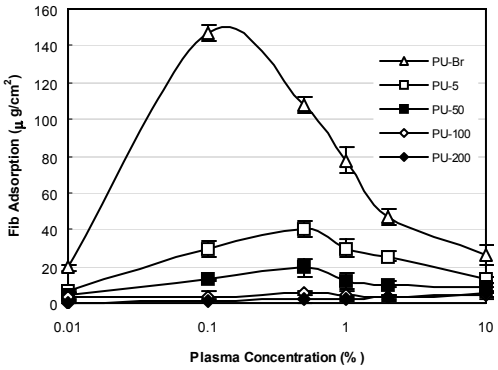

Fig.3. Fibrinogen adsorption to PU films from plasma

It is concluded that poly(OEGMA) grafting using ATRP methods gives surfaces that are protein resistant. The mechanism of resistance is probably different than on surfaces based on grafting of PEO itself, since the structure of the grafted layer is undoubtedly very different. In particular the PEO chain length is very short. Given the strong dependence on poly(OEGMA) chain length it is possible that the surface density of EO residues may be the determining factor.

References

1. W. Feng, J.L. Brash, S.P. Zhu, 2005, Macromolecular Rapid Communications, 26:1383.
2. W. Feng, J.L. Brash, S.P. Zhu, 2004, J. Poly. Sci. A: Polym. Chem., 42:2931

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