Studies of the self-assembled monolayer prepared with lipid-like zwitterionic phosphorylethanolamine functionality

Yu-Ting Sun, Chun-Yen Yu, Jui-Che Lin
Department of Chemical Engineering, National Cheng Kung University, Tainan, TAIWAN

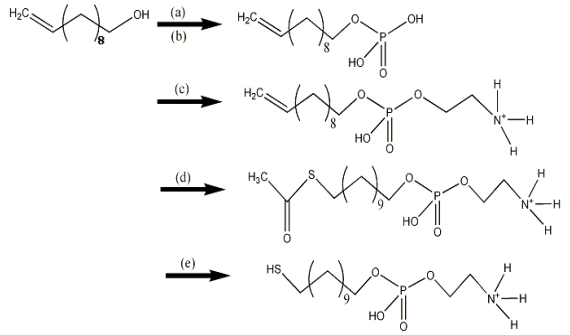
Introduction

Self-assembled monolayers (SAMs) prepared by organosulfur compounds on metal surfaces have been extensively studied because of the wide varieties of potential applications. In particular, alkanethiol SAMs on gold have been thoroughly studied due to their highly reproducibility, well-defined and highly stable structure, as well as ease of preparation. The surface properties of the SAMs can be tuned by varying the terminal functionalities of the monolayers. Generally, the solvent used in preparation of SAMs was ethanol, because it is cheap, low toxicity, high purity, and doesn't act with SAMs[1]. There were studies with different solvents[2-3], and it was found that solvents did affect the structure of SAMs. In the present study, we have established a novel synthetic method for the alkanethiol with a phospholipid-like functionality, 11-mercapto-undecane-phosphorylethanolamine (PE) $-P(=O)(OH)OCH_2CH_2NH_3^+$. In addition, different solvent was used in order to explore its likely effects on the surface properties and blood-contacting characteristics of the SAMs prepared.

Materials and Methods

Synthesis of 11-mercaptoundecanephosphoryl ethanolamine:

Alkanethiol with phospholipid-like terminal group, 11-mercaptoundecanephosphorylethanolamine (PE) was synthesized by the novel scheme as shown in Scheme 1. The purity of this alkanethiols was ensured by NMR and MS spectrometry.



(a) $POCl_3$, triethylamine in THF. (b) $NaHCO_3$(aq). (C) DMAP, TPS, ethanolamine hydrochloride in yridine. (d) thioacetic acid, AIBN in methanol (e) HCl(aq) in methanol reflux.

Scheme 1. Synthesis procedure for PE terminated thiol

Surface characterization and *in vitro* blood compatibility:

A similar gold deposition procedure as our past study[4] was used for Si (111) strip and cover glass slip. The sessile-drop contact angle technique and XPS analysis were utilized to characterize the "solvent" and "concentration" effects of thiol solutions on the SAM formation. The PE SAMs formation was carried out by immersing gold substrates into methanol (MeOH), ethanol (EtOH), deionized water (H_2O), and PBS at the concentration of 1mM and 0.1mM thiol solution for 24hrs. The SAMs prepared from CH_3-terminated thiol dissolved in ethanol solution at concentration of 1mM and 0.1mM (named as $1CH_3$ and 0.1 CH_3, respectively) were used for comparison. The nomenclature for the PE SAMs prepared was as follow: xxYY, where xx is the thiol concentration while YY is the solvent used. Human platelet–rich plasma (PRP, 3.5×10^{10} platelets/mL) was used for *in vitro* platelet adhesion assay.

Results/Discussion

It was clearly noted that the SAMs prepared from PBS at 0.1mM (0.1PBS) and 1mM (1PBS) concentration were the most hydrophilic ones (<10°, Figure 1). However, for other PE SAMs prepared, the contact angle values were all greater than the reported value for $-PO_3H_2$ terminated SAM, 37°[5], except those prepared by ethanol. The small contact angle values noted on the SAMs prepared from PBS are very likely resulted from the adsorption of salt ions, as indicated by the existence of salt ions on the ESCA spectra. As for the high contact angle values for other PE SAMs, this can be attributed to the less-ordered structure resulting from the steric hindrance effect caused by the bulky PE terminal ends.

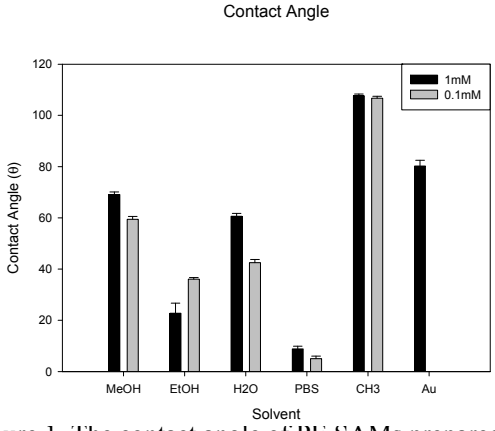


Figure 1. The contact angle of PE SAMs prepared from different solvent and concentration

Unbound thiols were noted in ESCA analyses. These unbound thiols should be resulted from the steric hindrance as well as the hydrogen bonding and ionic interactions associated with the phosphorylethanolamine functionalities. In combine of platelet activation and adhesion density evaluations, these PE SAMs exhibited better platelet-contacting property as compared to the $-CH_3$ terminated SAM and non-treated gold control, in which significant platelet activation was noted.

References:

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