

Study on aggregation states and physical properties of bioinert poly(2-oxazoline)-based alloy interfaces

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論 文 名 : Study on aggregation states and physical properties of bioinert poly(2-oxazoline)-based alloy interfaces (ポリ(2-オキサゾリン)を基盤とする生体不活性アロイ界面の凝集状態と物性に関する研究)

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論 文 内 容 の 要 旨

Due to the growing demand for polymer materials for biomedical devices, many polymer materials have recently been well applied to aqueous environments. However, it remains difficult to articulate what the aggregated state and physical properties of polymer chains are at the water interface. Therefore, it is of pivotal importance to obtain a better understanding of polymer behaviors at the water interface for the designing of the surface functions of biomedical devices in water.

Poly(2-oxazoline) (POx), which is a pseudopeptide polymer, has been recently paid a great deal of attention as a main ingredient for the bioinert surface. Unlike conventional bioinert polymers like poly(ethylene oxide), POx is known as a stable material for antibody production and oxidative degradation *in vivo* because of its protein like structure and relatively non polar backbone structure. Especially, poly(2-ethyl-2-oxazoline) (PEtOx) having ethyl side chains shows the high water solubility and outstanding bioinert properties. However, it is unclear why and how PEtOx exhibits such excellent bioinert properties.

In this study, at first, the stable and homogeneous PEtOx/water interface is tried to be constructed. Then, the surface aggregation states and physical properties of PEtOx at the water interface and their effects on the bioinert properties are examined.

In chapter 1, the background and purpose of this study were described.

In chapter 2, water stable and well-defined PEtOx derivatives, poly(methyl methacrylate)-*block*-poly[oligo(2-ethyl-2-oxazoline) methacrylate] (PMMA-*b*-P[O(Ox)_nMA])_s, were successfully prepared by combination of living cationic ring opening polymerization and atom transfer radical polymerization. In a similar manner, bottlebrush type homo P[O(Ox)_nMA]_s were synthesized.

In chapter 3, to construct the stable PEtOx/water interface, thin films of amphiphilic PMMA-*b*-P[O(Ox)MA] were prepared by a spin-coating method and following a thermal annealing method. The surface aggregation states of the thin films in air and water were examined by using atomic force microscope (AFM), static contact angle, angular dependent X-ray photoelectron spectroscopy (AD-XPS), and neutron reflectivity (NR) measurements. Under the ambient condition, the surface of the block copolymer film was covered with PMMA with a thickness of approximately 5 nm. However, once the film was soaked in water, the

structure reorganization occurred in the surface region, resulting in the formation of the relatively-hydrophilic surface in comparison with PMMA. By AD-XPS with the aid of a freeze-drying method, the chemical composition at the reorganized-surface was examined. This experiment revealed that the P[O(Ox)MA] block was segregated at the surface once the film contacted with water. In addition, NR measurement revealed that water molecules induced the formation of the diffused layer in the outermost region of the block copolymer film and penetrated into the interior bulk region as well. As a result, the cell adhesion and protein absorption on the block copolymer film were drastically suppressed comparing with those on the PMMA film.

In chapter 4, as another effective method to construct the stable P[O(Ox)_nMA]/water interface, the mixture film composed of PMMA and P[O(Ox)_nMA] was prepared by a spin-coating method. An effect of the length of the oxazoline main chain on the surface aggregation states, especially in water, was examined by AD-XPS, NR and a new type of spectroscopy, near ambient pressure X-ray photoelectron spectroscopy (NAP-XPS). The segregation layer at the water interface was thicker for P[O(Ox)₇MA] with the degree of polymerization of 7 than for P[O(Ox)₁₉MA]. This result made it clear that the extent of the segregation was dependent on the oxazoline unit length. Also, the diffuseness of the segregation layer at the water interface became more remarkable for P[O(Ox)₇MA] than for P[O(Ox)₁₉MA]. This difference leads to the difference of the bioinert properties between the two samples.

In chapter 5, an effect of annealing on the surface segregation in the PMMA-*b*-P[O(Ox)_nMA] films was examined. Since the P[O(Ox)_nMA] can migrate toward the surface in contact with water as previously describe, the PMMA-*b*-P[O(Ox)_nMA] thin films were annealed under a water vapor condition. In addition, the typical thermal annealing method was also conducted a under vacuum condition. Furthermore, the combination of the thermal and water vapor annealing methods was applied to the films. Subsequently, AD-XPS revealed that while P[O(Ox)_nMA] block was well segregated at the surface in the films annealed under water vapor, the PMMA wetting layer was formed at the surface after the thermal annealing. Also, it was found that the P[O(Ox)_nMA] block could be hardly segregated at the surface if the perfection of the PMMA wetting layer was improved, even though the film was annealed under a water vapor condition in the same manner. This was the case even after immersing the film in water. The results indicate that the extent of the surface aggregation states including the formation of the diffused layer could be regulated on the basis of the annealing methodology in conjunction with the presence of water vapor.

In chapter 6, the summary of the all chapters were described.