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Electrostatic and hydrophobic controlled self-assembly of PDMS-E grafted gelatin for self-cleaning application

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ABSTRACT

Understanding the assembly mechanisms of supramolecular architectures in nature is essential for the design and synthesis of novel biomaterials. In the work, self-assembly of gelatin-mono epoxy terminated polydimethylsiloxane polymer (PGG) controlled by electrostatic and hydrophobic interactions between gelatin and sodium dodecyl sulfate (SDS) was investigated in suit. Confocal laser scanning microscopy, circular dichroism spectroscopy, high-resolution transmission electron microscopy and X-ray photoelectron spectroscopy were conducted to reveal the structure evolution of PGG at a molecular level with the increment of SDS concentration, including micro-sized sphere, core-shell and multi-layer structure. Notably, the multi-layer structure was formed from the large contribution of antiparallel β-sheets on the boundary and new hydrophobic aggregation driven by higher monomer conversions. The delicate supramolecular architectures preliminarily present excellent anti-water, anti-contamination and anti-radiation properties in the surface of skin. The excellent self-cleaning function of PGG indicates potential application in biomaterials.

1. Introduction

Self-assembling processes are commonly throughout nature and technology to fabric well-defined materials. Understanding the assembly mechanisms of supramolecular architectures in nature is essential for the design and synthesis of novel biomaterials [1]. Over the past few decades, hybrid block copolymers [2,3], composed of synthetic and polypeptide segments, exhibit interesting supermolecular structures through hierarchical self-assembly in bulk [2] or in solution [4]. Hybrid block copolymers are known to form α-helical secondary structures in solution or solid states. In nature, the formation of α-helical secondary structures is mainly controlled by the sequence of monomer units. The secondary structure can be combined with coiled conformation of the synthetic segments, such as polystyrene, polybutadiene, poly (ethylene glycol), which have shown assembly capacity to form vesicular nanoaggregates [5,6], vesicles, bilayer filaments, superhelices [7] or nanoribbons [8,9]. The presence of the peptide segment gives them properties such as biocompatibility, bioactivity and self-assembly [10–12].

Recently, the main advantage of using macromolecules of natural origin is related to their chemical complexity and self-assembly properties, for which no synthetic equivalent is usually available, together with their sustainable character namely their large abundance and non-fossil origin, two key aspects for the development of “green” materials [13,14]. Among biopolymers, gelatin, a proteinaceous material obtained by the hydrolytic degradation of naturally occurring collagen [15], has been widely used due to its high biocompatibility and good biodegradability [16,17]. However, the complicated intermolecular interaction results in the diversified secondary structure of gelatin. Instead of focusing on controlling the primary and secondary structure, researchers now have interest in non-covalent bond interactions among gelatin molecules. Still, it always is a challenge work to explain the fabrication structure of modified gelatin at a molecular level. As far as we know, only few papers about the controlled self-assembly of modified gelatin *via* non-covalent bonds are reported [18].

Electrostatic and hydrophobic interactions between gelatin and sodium dodecyl sulfate (SDS) would be utilized to control the aggregation of gelatin. SDS interacts with gelatin through the electrostatic attraction between surfactant head-groups and lysine (Lys) and arginine (Arg) residues in gelatin molecules, as well as the hydrophobic interaction among hydrophobic chains [19]. Critical aggregation concentration (CAC) is a vital parameter to control electrostatic and hydrophobic

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interactions between gelatin and SDS. At low surfactant concentrations, interactions between gelatin and SDS are mainly the electrostatic interactions [20]. The effect of hydrophobic interactions become manifest as SDS concentration is near to CAC. Further, hydrophobic interactions become dominant with gradually increasing SDS concentration.

For another, the effect of complex behavior of gelatin-anionic surfactant on the reaction of mono epoxy terminated polydimethylsiloxane grafted gelatin (PGG) was studied in our previous paper [21]. The results indicated the extension of the gelatin chains at interface could be caused by the electrostatic repulsion or hydrophobic interaction between gelatin and anionic surfactant, which was an important role in determining reaction rate of mono epoxy terminated polydimethylsiloxane polymer (PDMS-E) grafting onto gelatin. Electrostatic and hydrophobic interactions between gelatin and anionic surfactant in a nondilute solution can cause dispersed particles to accumulate preferentially at a fluid interface [22,23]. In brief, it can be naturally deduced that gelatin-SDS complexes with various SDS concentration play a crucial role in determining the monomer conversion in the two-phase system. Indeed, in solutions, the factors including monomer conversions, monomer or copolymer dispersity, play important roles in determining the self-assembly of resulting copolymers [24,25]. Above all, tuning the SDS concentration can be a success approach to control the self-assembly of PGG.

Gelatin is produced by the acid or alkali denaturation of collagen. The special compatibility between gelatin and collagen makes it be used in tissue engineering [26,27]. It can be expected that the self-assembly of modified gelatin is utilized to design self-cleaning coating on the surface of skin for those self-defensive processes naturally occur when the mimicking tissue is exposed to the real environment [28]. Self-cleaning materials have been developed by introducing certain physical properties for desired performance, such as creating hydrophobic surfaces mimicking natively occurring systems or rendering the materials low surface energies to prevent adhesion of stains to initiate desired self-cleaning functionality [29,30]. Polydimethylsiloxane exhibits special low surface free energy, super-hydrophobicity, low glass transition temperature, biocompatibility, excellent gas permeability and exceptional elasticity when lightly cross-linked [31,32]. Undoubtedly, PGG can be a good candidate for self-cleaning coating on the surface of skin. In this work, the structure evolution of PGG at a molecular level is explored by confocal laser scanning microscopy, circular dichroism spectroscopy, high-resolution transmission electron microscopy and X-ray photoelectron spectroscopy. Furthermore, we demonstrate that the delicate supramolecular architectures present excellent anti-water, anti-contamination and anti-radiation properties on the surface of skin, as shown in Scheme 1 .

2. Experimental

2.1. Materials

Type A gelatin from pigskin was purchased from China National Medicines Corporation Ltd., and used after dialysis. The isoelectric point (IP, 8.5) of the dialyzed gelatin after complete deionizing was determined by fluorescent spectroscopy. Weight-average molecular weight (M_w, 1.48×10^5 g mol^{-1}) and molecular weight distribution (M_w/M_n, 1.43) of the gelatin were determined by Gel Permeation Chromatography (GPC, Supporting Information (SI)). Protein concentration in the gelatin was measured by Kjeldahl method (SI) and was 83.38%. The content of primary amino groups in the gelatin was 4.95×10^{-4} g mol^{-1}, which was determined by the Van Slyke method (SI) at 50 °C. Conductivity of the gelatin aqueous solution (5 wt%) was 5.98 μS cm^{-1} and that of deionized water was 2.06 μS cm^{-1}. The results indicate that small molecules and tiny salt in original gelatin were cleaned *via* dialysis. Protein content (CP), amino group content (CA, SI), M_w and IP of gelatin were compared before and after dialysis, and the results are shown in Table 1. It was illustrated that the structure of gelatin molecule had no obvious change after dialysis. Amino acid contents are given in Table S1 (SI).

SDS and sodium 1-tetradecanesulphonate (STSo) were purchased from Alfa Aesar and recrystallized from ethanol before use. Ally glycidyl ether (AGE) and chloroplatinic acid hexahydrate ($H_2Pt_6Cl_6{\cdot}6H_2O$) were obtained from Alfa Aesar. Hexamethylcyclotrisiloxane (D3, > 95%), *n*-butyllithium (C_4H_9Li, 99 + %), chlorodimethylsilane (C_2H_7ClSi, 99 + %) were purchased from Sigma-Aldrich. Benzene, tetrahydrofuran (THF), ethanol and acetone solvents (China National Medicine Co.) were all AR grade and dehydrated strictly before use.

2.2. Synthesis of α-[3-(2,3-epoxy-propoxy) propyl]-ω-butyl-polydimethysiloxanes (PDMS-E)

D3, C_4H_9Li and C_2H_7ClSi were used to synthesize polydimethylsiloxanes with Si—H group at one end (PDMS-H) through anionic addition polymerization. First, 10 mL benzene was added to the flask, and then 24 mL C_4H_9Li was added. After reducing pressure and ventilation with argon gas, 45.99 g D3, which were resolved in 40 mL benzene, were added to the flask. After reaction for 30 min, 50 mL THF was added into the system to react for 8 h. Then, 11 mL C_2H_7ClSi was injected into the flask to stop the reaction. The solution was firstly filtered by sand-core filtration to remove the lithium chloride precipitation. Then, the filtrate was distilled under reduced pressure at 50 °C (−0.01 Mpa) to remove the low-boiling-point solvent. Subsequently, the temperature was increased to 90 °C to remove the unreacted D3 to obtain the purified PDMS-H. PDMS-E was prepared by hydrosilylation of PDMS-H and AGE under Pt-catalyst. ($M_w = 1.14 \times 10^3$ g mol^{-1}, $M_w/M_n = 1.16$, Table S2 (SI)).

2.3. Synthesis of PGG

All the samples were prepared from a stock solution of dialyzed gelatin in order to minimize the experimental errors. The 100 mL stock solution was prepared by dissolving gelatin in distilled water (5 *wt* %), and stirred for 3 h at 50 °C. Subsequently, the pH of the stock solution was adjusted to 10.0 using NaOH solution (2.0 mol L^{-1}, about 200 μL). The 100 mL stock solution was divided to ten equal parts. SDS was added to eight parts with SDS concentration (X) setting at 0, 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, and 3.5 g L^{-1}. STSo was added to the remaining parts with STSo concentration setting at 1.5 and 3.0 g L^{-1}. All the solutions were stirred for 6 h. Then, PDMS-E was added to the above solutions at 50 °C at an interval of 20 drops min^{-1} with stirring until the epoxy groups/primary amino groups ratio reached 0.8:1.0 (mol:mol). These reactions were allowed to continue for another 24 h. Finally, the pH of the stock solution was then adjusted to 7.0 using HCl solution (2.0 mol L^{-1}, about 150 μL) to obtain the solution samples, which were used for zeta potential measurement (model: ZC-2000, Microtec, Japan) at 50 °C. Ten samples were obtained: one is PGG without SDS solution, seven are PGG-SDS solutions with different SDS concentration, and two are PGG-STSo solutions. About 8 g of each solution was taken out to measure the content of primary amino groups for calculating the monomer conversion. The remaining solutions were used to evaluate self-assembly behavior of PGG. The details of coating and abrasion experiments for PGG are described in SI. Cytotoxicity tests of PGG films were carried out according to the method reported previously, see SI [33].

2.4. Characterization

High-resolution solid-state NMR experiments were capable of providing structural information of protein at a molecular level [34]. In the experiment, high-resolution solid-state NMR experiments were conducted at room temperature using a JNM-ECZ600R spectrometer at resonance frequencies of 150 MHz for ^{13}C. ^{13}C NMR spectra were observed either using cross-polarization (CP) magic-angle spinning (MAS)