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Two-dimensional (2D) infrared correlation study of the structural characterization of a surface immobilized polypeptide film stimulated by pH

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ABSTRACT

The pH-induced structural changes to surface immobilized poly (L-glutamic acid) (PLGA) films were examined by Fourier transform infrared (FTIR) spectroscopy and two-dimensional (2D) correlation analysis. Significant spectral changes were observed in the FTIR spectra of the surface immobilized PLGA film between pH 6 and 7. The 2D correlation spectra constructed from the pH-dependent FTIR spectra of the surface immobilized PLGA films revealed the spectral changes induced by the alternations of the protonation state of the carboxylic acid group in the PLGA side chain. When the pH was increased from 6 to 8, weak spectral changes in the secondary structure of the PLGA main chain were induced by deprotonation of the carboxylic acid side group.

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1. Introduction

Stimuli responsive polymers exhibit rapid and reversible conformational changes or phase transitions caused by the variations of local environment, such as temperature, pH, light, and concentration [1–9]. Recently, stimuli-response polymers have attracted considerable attention in both academia and industry for their potential applications, such as controlled drug delivery and release systems, biomedical sensing, biomimetic actuators, and electronic devices [10–15]. Among the many types of external environment-responsive polymers, pH responsive stimuli response polymers have been studied extensively for potential applications in the biomedical field [1–3,10–16]. In general, pH response polymers have weak acid or base moieties, such as carboxylic acids and amines, respectively, and show conformational changes induced by the ionization state upon the variation of pH [16]. Moreover, pH response polymers can be categorized into three types according to their physical conformation, i.e., (i) linear free polymer chain, (ii) covalently cross-linked gel, and (iii) surface grafted polymer brush [15]. Among these approaches, the surface grafted polymer brush is the most widely used material type because a surface grafted polymer brush can alter its conformation or phase easily within a short time. In addition, surface grafted polymer brushes have attracted considerable research attention because of their unique surface properties, such as friction, biocompatibility, wettability, and corrosion resistance [17–22].

Surface grafted polymer brushes can be prepared by the adsorption of pre-formed polymer chains on a surface (grafting to) or by growing polymer chains via surface initiated polymerization on various initiator pre-treated surfaces (grafting from) [1,10,15]. Commonly, the “grafting from” method provides high density polymer brushes with a well-controlled thickness and composition on a range of surfaces. Indeed, pH-responsive surface grafted polymer brushes have been prepared by many research groups. For example, vinyl monomer-based polyacids and polybases polymer brushes have been prepared using various surface initiated

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polymerization methods, such as atom transfer radical polymerization (ATRP), reversible addition fragmentation chain transfer (RAFT) polymerization and ring opening metathesis polymerization (ROMP), and the behaviors of the polymer brushes have been investigated by varying the pH or ionic strength variation [22–24]. In addition, polypeptides with acid or base moieties as the side groups were prepared by the ring opening polymerization (ROP) of N-carboxy anhydride (NCA) monomers and characterized [25–27]. The behaviors according to the change in pH of the almost-surface grafted brushes have been investigated by ellipsometry, atomic force microscopy (AFM) and fluorescence microscopy. On the other hand, surface grafted polymer brushes by external stimulation are not completely understood. Therefore, it is important to understand the pH-induced chemical behaviors, such as conformational changes, as an external stimulation for surface grafted polymer brushes.

In this study, a surface grafted polymer brush composed of poly(L-glutamic acid) (PLGA), which has a peptide main chain and glutamic acid side chains, was fabricated using a ring opening surface initiated polymerization method with a NCA of γ-benzyl L-glutamate (BLG) (Fig. 1) [25,28]. This study examined the pH-induced structural changes in the surface immobilized PLGA film by Fourier transform infrared (FTIR) spectroscopy. The pH-induced PLGA FTIR spectra were used to examine the pH-induced spectral changes closely by analyzing the changes in the characteristic bands of the peptide unit in the main chain and the alkyl and glutamic acid groups in the side chain of the surface immobilized PLGA film after different pH treatments. 2D correlation spectroscopy and principal component analysis (PCA) were also conducted to closely examine the pH-induced structural changes in the surface immobilized PLGA film.

2. Experimental

2.1. Materials and synthesis

2.1.1. Materials and preparation of substrate

L-Glutamic acid γ-benzyl ester (GBL, Aldrich), triphosgene (Aldrich), *n*-hexane (Samchun), toluene (Aldrich), and 3-(aminopropyl)trimethoxysilane (APTMS, Aldrich) were used as received. The solvents for synthesis, i.e., dimethylformamide (DMF) and ethyl acetate (EA), were purchased from Aldrich, purified by distillation over calcium hydride and stored over 4 Å molecular sieves. All buffer solutions were purchased from Duksan Chemicals.

An oxidized silicon (Si) wafer was cut into 2 × 2 cm squares. After sonication with ethanol for 10 min and rinsing with deionized water, the Si substrates were immersed in a “piranha solution” (H_2SO_4/30% H_2O_2 = 7/3 (v/v)), (Caution: Piranha solutions are extremely dangerous and should be used with extreme care) at 80 °C for 10 min. The cleaned substrates were rinsed with deionized water and dried with N_2. Immobilization of the amine terminated molecules on the Si wafer was conducted by immersing the Si substrates into a 2 wt. % APTMS solution in toluene. The amine functional group pre-treated substrates were rinsed sequentially with ethanol and distilled water, and dried with N_2.

2.1.2. Synthesis of γ-benzyl-L-glutamate-N-carboxyanhydride

γ-Benzyl-L-glutamate-*N*-carboxyanhydride (BLGNCA) was synthesized from a reaction of GBL and triphosgene. A mixture of GBL and triphosgene in EA was heated under reflux for 12 h under a N_2 atmosphere. The resulting pale yellow solution was cooled to room temperature, and washed with cold deionized water. The organic layer was dried with $MgSO_4$ and concentrated. The crude product was recrystallized from *n*-hexane to obtain the white crystals. The product was identified by proton nuclear magnetic resonance (^{1}H NMR, model AM300, Bruker) spectroscopy from a solution in chloroform-d_1 ($CDCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.3 (m, 5H, Ph-*H*), 6.3 (s, 1H, N*H*-), 5.1 (s, 2H, C*H*$_2$- benzylic), 4.3 (t, 1H, NH—C*H*), 2.6 (m, 2H, C*H*$_2$—C=O), 2.1–2.3 (d, 2H, CH—C*H*$_2$—CH$_2$).

2.1.3. Preparation of surface immobilized poly(L-glutamic acid)

The surface immobilization of poly(γ-benzyl-L-glutamate) (PBLG) was conducted using BLGNCA and an APTMS immobilized Si wafer in anhydrous DMF. The APTMS-modified Si wafer was immersed in a 100 mM solution of BLGNCA in anhydrous DMF at ambient temperature under a N_2 atmosphere for 12 h. After polymerization, the substrates were rinsed with copious amounts of DMF. The substrates were sonicated several times in DMF to

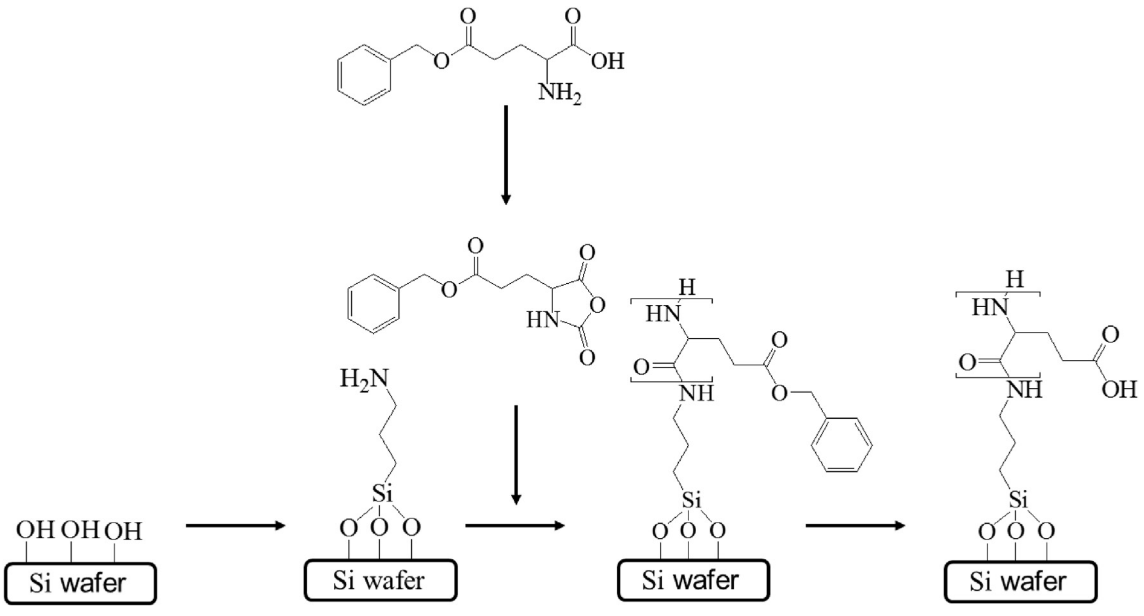

Fig. 1. Synthetic scheme of the surface immobilized poly(L-glutamic acid) (PLGA).

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