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Studies on Stimuli-Responsive Nano-Structured Materials: Fabrication of Functional Surfaces with Ultrathin Hydrogel Films

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1. Introduction

Recently, stimuli responsive polymers can provide a variety of applications for the scientific, technological and biomedical fields. The interest in these polymers has exponentially increased due to their promising potential. Among them, temperature and pH responsive mechanisms have been considerably investigated because they are relatively convenient and effective stimuli in many applications. One of the most intensively studied polymers is poly(N-isopropylacrylamide) (PNIPAAm). PNIPAAm exhibits a sharp phase transition in water at 32 °C. It reversible changes collapse from an extended coil to a globular structure, around the lower critical solution temperature (LCST).

In the present study, we investigated the molecular design, preparation and characterization of the stimuli-responsive ultrathin hydrogel film by photo-cross-linking. To develop the films on a solid substrate, a novel photo-cross-linkable polymer with both temperature- and pH-responsive properties was prepared. The photo-reactive 4-aminobenzophenone (BP) was introduced onto the side groups of poly(N-isopropylaclylamide-*co*-2-carboxyisopropylaclylamide)[poly(NIPAAm-*co*-CIPAAm)].Photo-cross-linkable polymers [poly(NIPAAm-*co*-CIPAAm)-BP] were obtained by the condensation reaction of the carboxyl groups of poly(NIPAAm-*co*-CIPAAm) and the amino groups of 4-aminobenzophonone. First, the spin-coated films using poly(NIPAAm-*co*-CIPAAm)-BP were prepared and then the photo-cross-linking reaction was performed by UV light irradiation.

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2. Results and Discussions

A photo-cross-linkable polymer [poly(NIPAAm-*co*-CIPAAm)-BP] was prepared by the condensation reaction between the DCC-activated carboxyl groups in the side chains and the amino groups of BP. We investigated the polymer layer formation onto the solid surfaces by the QCM method. The QCM frequency shifts were accompanied by the poly(NIPAAm-*co*-CIPAAm)-BP adsorption. The spin-coating of the DMF solution of poly(NIPAAm-*co*-CIPAAm)-BP successfully formed ultrathin and smooth polymer layers, and the thickness depended on the polymer concentration. The photo-cross-linking reaction occurred very quickly, and the obtained film demonstrated a high stability.

Next we checked temperature or pH-response of the prepared films. The cyclic voltammetries using potassium ferricyanide revealed that ions could permeate through the photo-cross-linked polymer film, producing ultrathin hydrogel films. Furthermore, the permeability of the ultrathin hydrogel films changed as the pH and temperature varied.

3. Conclusions

Based on these results, we can conclude that the photo-cross-linkable poly(NIPAAm-*co*-CIPAAm)-BP is very useful for the functionalization of the solid material surfaces and could be utilized for a controlled delivery device.