

Construction of wettability gradient surface on copper substrate by controlled hydrolysis of poly(methyl methacrylate–butyl acrylate) films



Yong Zhang^{a,*}, Jiang Cheng^b, Zhuo-ru Yang^b

^a Guangzhou Panyu Polytechnic, Guangzhou 511483, China

^b School of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou 510640, China

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ABSTRACT

We report a gradient wettability surface on copper slide prepared by a simple controlled ester group hydrolysis procedure of poly(methyl methacrylate–butyl acrylate) [P (MMA–BA)] films coated on the copper substrate. In the method, sodium hydroxide solutions are selected to prepare surface gradient wettability on P (MMA–BA) films. The P (MMA–BA) copolymers with different MMA contents are first synthesized by a conventional free atom radical solution polymerization method. The transfer of surface chemical composition from the ester group to acid salt is achieved by hydrolysis in NaOH solution. The effects of different concentrations of NaOH solution and reaction times on the physicochemical properties of the resulting surfaces are studied. The field-emission scanning electron microscopy (FESEM), atomic force microscopy (AFM) and X-ray photoelectron spectroscopy (XPS) results show that the varying concentration along the substrate length is only attributed to the hydrolysis reaction of ester groups. The hydrolysis causes insignificant change on the morphology of the original film on the copper substrate. In addition, it is found that the MMA copolymer content has a significant influence on the concentration of ester groups on the outermost surface and thus important for forming the slope gradients.

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1. Introduction

Wettability gradient surfaces, a kind of functional gradient material (FGM), are surfaces with water contact angles (CAs) that gradually change over a given distance. This surface usually displays a gradual change in its surface tension along its length. Intensive research interest has focused on wettability gradient surfaces because of their various applications including droplet moving [1–4], micro-fluid flow [5,6], protein adsorption [7,8] and cell adhesion [9–12]. Generally, wettability gradient surfaces can be fabricated mainly via two mechanisms. One involves the surface-chemical gradients by SAM-based techniques (self-assembled monolayer) and polymer-based techniques. The other one focuses on morphological gradients which generated by electrochemical etching, erosion/chemical polishing-replica methods, lithography and polymers-temperature gradient [13]. Due to both fundamental and practical interests, many different methods generating a wettability gradient along a solid surface have been developed.

These includes vapor phase polymerization [14], polymers-heat treatment [15,16], electron beam treatment [17], photolithography [18], plasma treatment [19], counterion exchange [20] and corona discharge treatments [11,12,21]. However, most of the reported approaches induce both chemical and physicochemical changes on surface properties. Therefore, it is difficult to decouple such effects caused by physical modifications and attribute protein adsorption and cell adhesion to the surface chemical composition. To overcome such a problem, novel approaches have been proposed. For example, Ueda-Yukoshi and Matsuda [22] reported that a chemical gradient surface was selectively produced by continuous immersion of a poly(vinylene carbonate) (PVCa) film into an aqueous solution of sodium hydroxide, in which molar fractions of cyclic carbonate and hydroxyl groups were inversely varied. The advancing water angle values on the untreated PVCa surface rapidly decreased on the surface regions with shorter periods of hydrolysis and followed by a slower decrease on surface regions with long periods of hydrolysis with increasing distance from the untreated end. Chilkoti et al. [23] demonstrated that the ester group along the main chain of the polymer could be used to introduce a reactive COOH group on their surface. Besides, Laugnas et al. [24] described a simple method for the construction of a wettability gradient surface based on the poly(methyl methacrylate) by a controlled hydrolysis

* Corresponding author at: Guangzhou Panyu Polytechnic, Guangzhou, Guangdong 511483, China. Tel.: +86 20 84740240; fax: +86 20 84740240.

E-mail address: Yong.Z@mail.scut.edu.cn (Y. Zhang).

procedure. The chemical gradient surface was fabricated and the results showed that the formation of a smooth, highly controllable carboxylic acid gradient with increasing concentration along the sample surface. The chemical modification of the polymer surface barely affects its physical properties along the sample length. However, there is a slight decrease from $78 \pm 1^\circ$ to $71 \pm 2^\circ$ for the CAs measurements, in the case from the least hydrolyzed part of the slide to the most hydrolyzed one. The formation of gradual hydrolysis process may be due to the insufficient ester group to be used as reactive points for surface modification on the outermost surface.

In this work, a smooth copper slide was chosen as a substrate, which is widely used as an engineering material. The functional gradient film on the slide was prepared by continuous immersion in a sodium hydroxide aqueous solution. The hydrolysis of ester groups can be tuned by controlling the addition speed of NaOH solution, immersion time, and concentration of NaOH. The effects of chemical composition and surface roughness on the wettability of the copolymer film were studied by field-emission scanning electron microscopy (FESEM), atomic force microscopy (AFM) and X-ray photoelectron spectroscopy (XPS). Contact angles (CAs) of water were measured by an optical contact angle system.

2. Experimental

2.1. Materials

Copper Slides 10 mm × 100 mm were purchased from Tianjin Kermel Chemical Reagents Company (Tianjin, China). BA (99%, A.R.) and xylene (99%, A.R.) were obtained from Chengdu Kelong Chemical Reagents Company (Chengdu, China). Sodium hydroxide (96%, A.R.) and absolute ethanol (99.7%, A.R.) were purchased from Guangdong Guanghua Tech Co., Ltd. (Guangdong, China). MMA (98%, A.R.) was obtained from Shanghai Lingfeng Chemical Reagents Co., Ltd. (Shanghai, China). Acetone (99.5%, A.R.) was purchased from Hengyang Kaixin Chemical Reagents Company (Hengyang, China). BPO (99%, A.R.) was obtained from Guangzhou Huaxue Chemical Reagents Company (Guangzhou, China).

Stock solutions of sodium hydroxide (three concentrations, 0.01, 0.1 and 1 M) were prepared by dissolving NaOH in distilled water respectively.

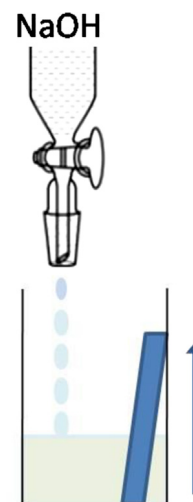
2.2. Preparation of copolymer solution

A series of P (MMA-BA) random copolymer can be obtained by the conventional free radical solution polymerization method. A 25 g absolute xylene, 25 g comonomers (MMA: BA = 3:2, wt%) and 0.125 g BPO were introduced in a 150-mL, three neck, round-bottom flask equipped with a heat exchange system. Firstly BPO was added to the mixture of MMA and BA. The mixture was allowed to stir for 10 min to dissolve the BPO. Then the mixture was added slowly to the xylene solutions for 30 min with 300 rpm agitation at 120 °C. The polymerization reaction occurred at the chosen temperature and constant stirring for 2.5 h.

2.3. Fabrication of wettability gradient surfaces on copper slides

All copper slides (10 mm × 100 mm) were cleaned in acetone and ethanol for 5 min, respectively, then washed thoroughly with distilled water and hence dried at 50 °C for 30 min before use. The cleaned copper slides were dipped into the copolymer solutions for about 1 min, and dried at 120 °C for 30 min. This coating procedure was recycled for 3 times to get enough thickness of the polymer film.

To generate a gradient surface, the polymer-coated-copper slide was placed in a glass container (150 mL) with its back standing against the wall of the container as showed in Scheme 1. And then



Scheme 1. Schematic illustration of the preparation process of the gradient wettability surface on a copper slide.

NaOH solution was gradually added into the container at room temperature. In this way, the time of the hydrolysis reactions between NaOH and polymer varied gradually along the slide. Namely, the content of the product of the reaction, a carboxylate, decreased gradually from the lower part of the slide to the upper part and thus a gradient surface was generated.

At the same time, the addition was controlled at such a speed that it took 30 min for the surface of the NaOH solution in the container to reach the upper edge of the slide. Then the slide was rinsed with distilled water and absolute ethanol, and dried at 50 °C for 1 h.

The preparation process of wettability gradient film is shown in Scheme 1.

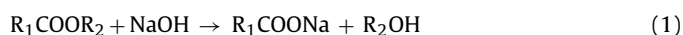
2.4. Characterization

The surface chemical compositions of the film on copper slide were measured on an Axis Ultra X-ray photoelectron spectroscopy system (XPS, Kratos Axis Ultra DLD, UK) equipped with a monochromator source (Aluminum K α line of 1486.6 eV energy and 150 W). The surface roughness of the film was analyzed by atomic force microscopy (AFM, CSPM5000, Benyuan, China). The polymer film surface morphology was observed by field-emission scanning electron microscopy (FESEM, LEO 1530 VP, Germany). Water contact angles measurement was performed with an optical contact angle system (CAs, JC2000C1, China). The volume of the water droplet used for the static CA measurements was 3 μ L. WCA values were obtained by averaging three measurements made on same district of the different sample. All experiments were carried out at room temperature.

3. Results and discussion

The photographs of the water contact angles along the gradient surface for the one using 1 M NaOH are shown in Fig. 1. It can be seen that the substrate exhibits a novel gradient wettability property. The contact angles change continuously along the surface from $86.6 \pm 0.7^\circ$ to $50.7 \pm 0.8^\circ$ in 10 cm for the least hydrolyzed part to the most hydrolyzed one.

In this work, the surface chemical gradients were generated by a controlled hydrolysis process which contains two reactions as depicted below [25].



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