

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

ARTICLE INFO

Article history:

Received 13 May 2014

Received in revised form 28 June 2014

Accepted 8 July 2014

Available online 16 July 2014

Keywords:

Methyl methacrylate

Butyl acrylate

Polymerization

Gradient wetting

Hydrolysis

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.

© 2014 Elsevier B.V. All rights reserved.

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.

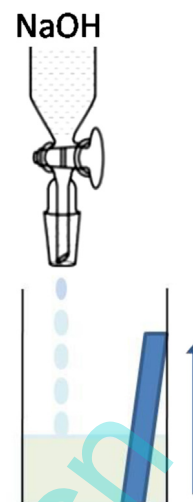
2.2. Preparation of copolymer solution

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].

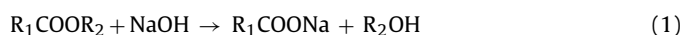
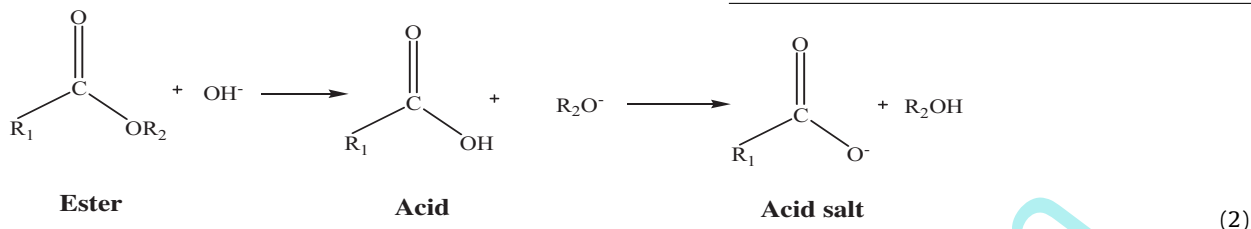




Fig. 1. Photographs of the water contact angles along the gradient surface. Images of the liquid droplets of 3 μ L water droplet in contact with the surface were recorded immediately after droplet stabilization. The photograph was combined with seven continuous photographs along the substrate because the view angle of the contact angle measurement system is not wide enough. 1 M NaOH was used for preparation.



where R_1 and R_2 represent different alkyl groups, respectively. Eq. (1) presents an irreversible hydrolysis reaction in basic solution which is called saponification. While Eq. (2) demonstrates that ester hydrolysis occurs through a typical nucleophilic acyl substitution pathway in which the tetrahedral intermediate goes through a nucleophilic attack process followed by OH^- group. A carboxylic acid is given, which is changed the acid salt.

It is well known that the wetting of a solid surface depends on both the surface chemical properties and the surface morphology [26–29]. To determine the effect of the surface morphology on the wettability of film, FESEM was used to examine the copper substrate with and without copolymer film as well as the one after hydrolysis. As depicted in Fig. 2, the FESEM images show a surface morphology evolution of the copolymer film on flat copper surface.

We can see that the copper substrate with copolymer film (Fig. 2(a)) is smoother than that one without copolymer (Fig. 2(b)). After hydrolysis, the morphology (Fig. 2(c)) remains almost the same with before hydrolysis, indicating insignificant change of physical properties after hydrolysis. The brighter part in Fig. 2(c) might be attributed to dissolution of the copolymer chain with lower molecular weight by NaOH solution. The effect of a varying concentration along the copolymer film surface length will be the only consequence of the chemical modifications introduced and we can deduce the surface morphology variations along the slide distance are negligible. Furthermore, AFM measurements showed negligible roughness variation along the film surface after hydrolysis, as summarized in Table 1, which also indicated negligible change of physical properties, consistent with the FESEM results.

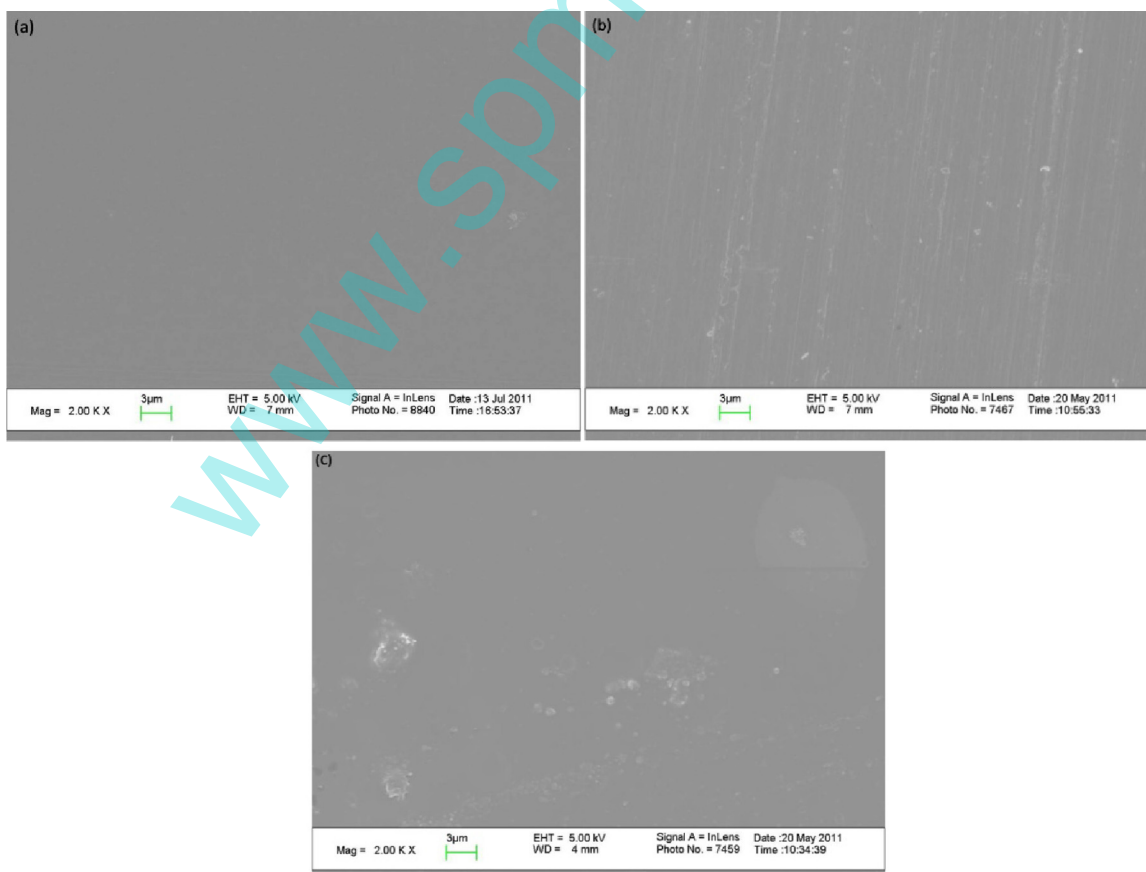


Fig. 2. FESEM images (a)–(c) of corresponding copolymer films on copper substrate: (a) with copolymer film, (b) without copolymer film and (c) hydrolysis 30 min with copolymer film.

Table 1
Statistical data of roughness parameters.^a

Water contact angle (°)	86.6	81.1	76.4	72.4	66.0	57.3	50.7
Ra/nm	0.531	0.496	0.539	0.502	0.592	0.665	0.718

^a The WCA of gradient wettability surface decreases with the hydrolysis reaction time; Ra is roughness average. The functional films were prepared on the copper substrates.

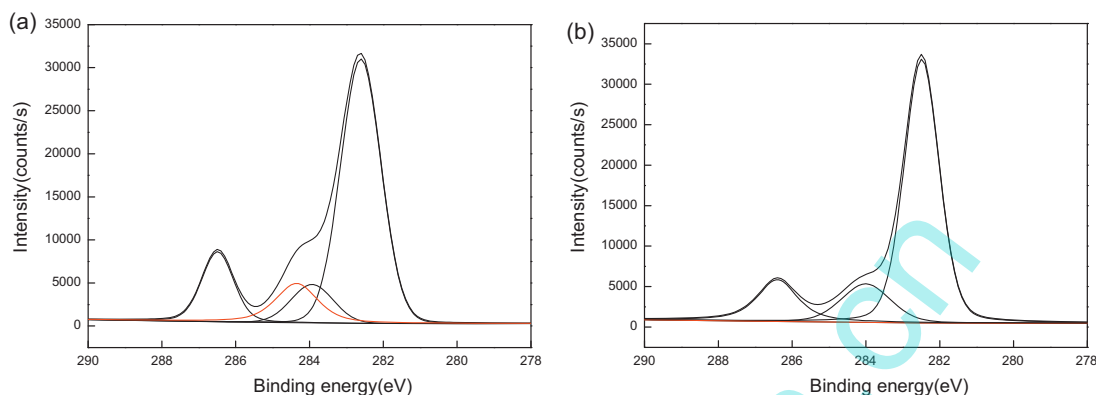


Fig. 3. C 1s core-level XPS spectra for (a) the least hydrolyzed part of the film and (b) the most hydrolyzed region, showing the red relative area decrease, which can be assigned to the methoxy group carbon (MMA) or ethoxy group carbon (BA). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

To determine the surface chemical compositions along the wettability film, XPS was performed. Fig. 3 shows the curve-fitted C 1s XPS spectra of hydrolyzed film, the spectral region with a broad peak that can be deconvoluted into four carbon 1s core signals which is attributed to the different carbon types of the polymer [30], and the red relative area signal should be attributed to the methoxy group carbon [24]. Figs. 3 and 4 show the relative area decrease for the component 3, which has been assigned to the methoxy group carbon (MMA) or the ethoxy group carbon (BA). Comparing the least hydrolyzed part (Fig. 3(a)) with the most hydrolyzed part (Fig. 3(b)), where the peak centered at 284.4 eV is assigned to methoxy group carbon (MMA) or the ethoxy group carbon (BA), one can see the extent of the carboxylic acid salt along the sample length increases obviously for the red relative area against the total polymer C 1s area permits us to calculate the extent of the component 3 along the sample length, which varies from 9.9 to 0.0%. Additionally, in the XPS C1s deconvolution spectrum, there is also a decrease of the intensity of the peak attributed to the carbonyl carbon in the spectrum of the most hydrolyzed part of the slide. This is because of the dispersion of the copolymer.

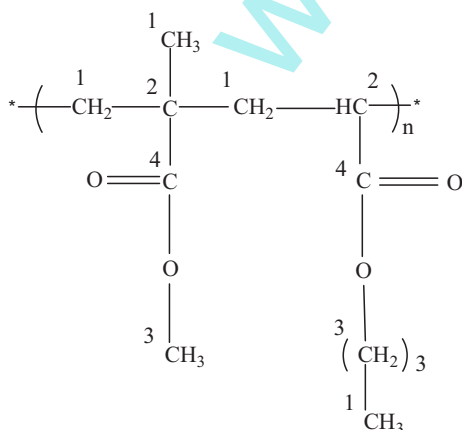


Fig. 4. Chemical structure of P (MMA-BA).

Lagunas et al. [24] obtained a low slope wettability gradients by hydrolysis procedure and their water contact angle results showed a gradual decrease from $78 \pm 1^\circ$ to $71 \pm 2^\circ$, indicating that the hydrolysis method has the unique characteristic of barely changed the surface physical properties along the substrate length. The same method was used here to enlarge the slope gradients, and water contact angle decreased from $86.6 \pm 0.7^\circ$ to $50.7 \pm 0.8^\circ$. As compared with the PMMA hydrolysis, the enhancement of P (MMA-BA) slope gradients is more significant, when a content of 60% was used for MMA. Besides, the slope gradients of P (MMA-BA) is smaller than the copolymer of P (MMA-BA), when the MMA content was 40%, compared with the one of a content of 60%. Because the acrylate units are more active during reaction [31], side ester groups could be hydrolyzed by NaOH, the ester group on the outermost surface will introduce more reactive COOH groups and acid salt by controlling hydrolysis process and using alkaline solutions of various concentrations, resulting in a larger slope gradients.

There are three kinds of functional groups on the film surface, including methyl, ethyl and ester group, and the surface energy of ester group is greater than the others. More ester groups on the surface will result in the lower contact angle. The P (MMA-BA) copolymers with different mass percentage of MMA, which were synthesized by the method of solution polymerization, have been characterized by Xu et al. [32]. Besides, the effect of copolymerization on pendant group and chain segment motions was investigated by Zhou et al. [33]. Fig. 5 shows the water contact angle variation of P (MMA-BA) with different MMA contents. The smallest average value of water contact angle can be found when the MMA content was 60%, indicating the ester group was the most on the outermost surface when the contact angle was the lowest. This may be due to the fact that the average value m of the side chain reduces (the side chain length of the BA is greater than that of MMA), resulting in a weak effect of covering the ester group. However, if the MMA content exceeds 60%, the contact angle increased significantly with the increase of the MMA content, probably due to the increase of glass temperature T_g of the copolymer P (MMA-BA), which made the side chain hard to move [33]. The smallest contact angle with 60% (wt%) MMA is a result of the balance between the side chain length and T_g of the copolymer. In addition, the film mechanical properties of the P (MMA-BA) increase more favorably, compared with

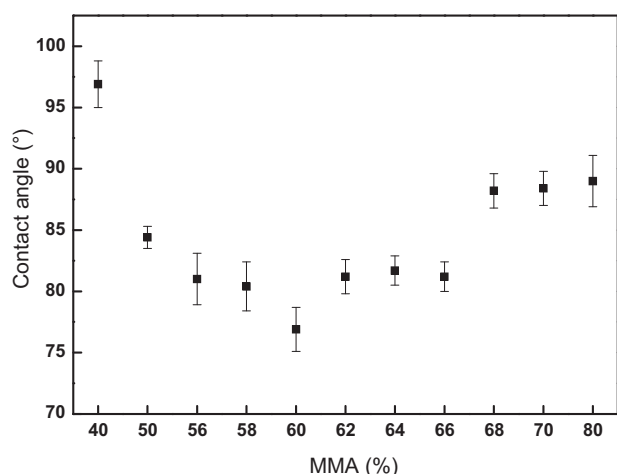


Fig. 5. Contact angle of copolymers P (MMA-BA). The coating procedure was recycled for 1 time.

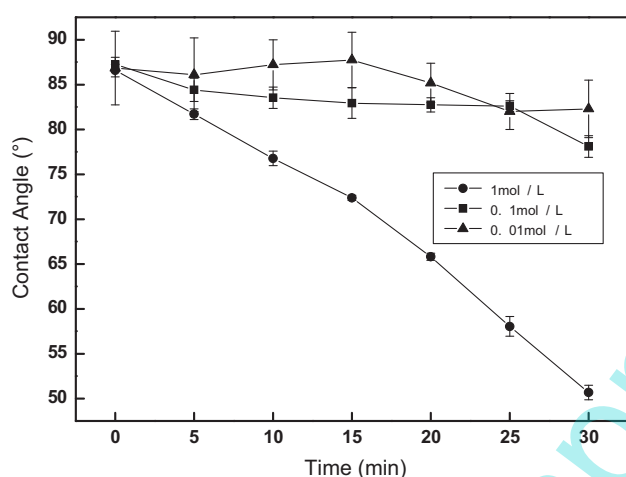


Fig. 6. Water contact angle of the film surface after being modified with an alkaline solution at different concentrations and different reaction time. All measurements were measured after the rinse of the films with distilled water for three times. The measurement was measured on copolymer film coated on the copper surface with different places.

the PMMA. However, the effect of the MMA content on the water contact angle after hydrolysis of the ester group is more related to steric hindrance effects than to mechanical properties.

Fig. 6 shows the relationship between the contact angles of the surface and immersion time and concentration of NaOH solution. The contact angle has a dramatical decrease with the reaction time for the one using 1 M NaOH, which is significantly different from using 0.01 or 0.1 M NaOH. It was observed that the film was dissolved when the concentration of alkaline solution increased further and the contact angle could reveal the superhydrophilic (CAs 10°) occasionally, and subsequently one can find that the content of ester group on the outermost surface is quite important to the slope gradients via the hydrolysis procedure.

4. Conclusion

A wettability gradient film on copper slide was prepared via a controlled hydrolysis process. The gradient wettability surfaces were achieved owing to the gradual change of the chemical composition from the ester group to acid salt by changing the reaction time and the concentration of the sodium hydroxide solutions. The hydrolysis gradients have the unique characteristic of

negligibly changing the surface physical properties along the substrate length. One can find that MMA component has a great influence on the content of ester groups on the outermost surface. Because of the polymers polydispersity, the wettability of the P (MMA-BA) coating film needs to be further validated by research. The more ester groups on the surface would introduce more reactive COOH groups and acid salt by the controlled hydrolysis procedure using relatively alkaline solutions, which will result in the larger slope gradients. To the best of our knowledge, this is the first report of the fabrication of gradient wetting surface on copper slide by a simple controlled ester group hydrolysis procedure of P (MMA-BA) films coated on the copper surface. More importantly, as compared with other more complex processes, a surface with WCAs can be achieved by a more simple and feasible way here with gradual changing for various practical applications such as heat transfer, micro-fluid flow and biomaterials analysis.

Acknowledgment

The financial support of the National Natural Science Foundation of China (NSFC) with the project No. 20976055 is gratefully acknowledged.

References

- [1] M.K. Chaudhury, G.M. Whitesides, How to make water run uphill, *Science* 256 (1992) 1539–1541.
- [2] S.I. Yeh, W.F. Fang, H.J. Sheen, J.T. Yang, Droplets coalescence and mixing with identical and distinct surface tension on a wettability gradient surface, *Microfluid. Nanofluid.* 14 (2013) 785–795.
- [3] S. Daniel, M.K. Chaudhury, J.C. Chen, Fast drop movements resulting from the phase change on a gradient surface, *Science* 291 (2001) 633–636.
- [4] J. Ju, K. Xiao, X. Yao, H. Bai, L. Jiang, Bioinspired conical copper wire with gradient wettability for continuous and efficient fog collection, *Adv. Mater.* 25 (2013) 5937–5942.
- [5] M. Mayur, D. Chakraborty, J. Chakraborty, S. Chakraborty, Surface-charge-induced alteration of nanovortex patterning in nanoscale confinements with patterned wettability gradients, *Phys. Rev. E* 85 (2012) 15.
- [6] B. Suman, Effects of a surface-tension gradient on the performance of a micro-grooved heat pipe: an analytical study, *Microfluid. Nanofluid.* 5 (2008) 655–667.
- [7] H. Elwing, A. Askendal, I. Lundström, Desorption of fibrinogen and [gamma]-globulin from solid surfaces induced by a nonionic detergent, *J. Colloid Interface Sci.* 128 (1989) 296–300.
- [8] S. Glassford, K.L.A. Chan, B. Byrne, S.G. Kazarian, Chemical imaging of protein adsorption and crystallization on a wettability gradient surface, *Langmuir* 28 (2012) 3174–3179.
- [9] H.T. Spijker, R. Bos, H.J. Busscher, T.G. van Kooten, W. van Oeveren, Platelet adhesion and activation on a shielded plasma gradient prepared on polyethylene, *Biomaterials* 23 (2002) 757–766.
- [10] C.C. Barrias, M.C.L. Martins, G. Almeida-Porada, M.A. Barbosa, P.L. Granja, The correlation between the adsorption of adhesive proteins and cell behaviour on hydroxyl-methyl mixed self-assembled monolayers, *Biomaterials* 30 (2009) 307–316.
- [11] M. Cantini, M. Sousa, D. Moratal, J.F. Mano, M. Salmeron-Sanchez, Non-monotonic cell differentiation pattern on extreme wettability gradients, *Biomater. Sci.* 1 (2013) 202–212.
- [12] J.H. Park, C.E. Wasilewski, N. Almodovar, R. Olivares-Navarrete, B.D. Boyan, R. Tannenbaum, Z. Schwartz, The responses to surface wettability gradients induced by chitosan nanofilms on microtextured titanium mediated by specific integrin receptors, *Biomaterials* 33 (2012) 7386–7393.
- [13] S. Morgenthaler, C. Zink, N.D. Spencer, Surface-chemical and -morphological gradients, *Soft Matter* 4 (2008) 419–434.
- [14] X.F. Li, H.J. Dai, S.X. Tan, X.Y. Zhang, H.Y. Liu, Y.X. Wang, N. Zhao, J. Xu, Facile preparation of poly(ethyl alpha-cyanoacrylate) superhydrophobic and gradient wetting surfaces, *J. Colloid Interface Sci.* 340 (2009) 93–97.
- [15] X. Fan, L.F. Zheng, J. Cheng, S.P. Xu, X.F. Wen, Z.Q. Cai, P.H. Pi, Z.R. Yang, Template synthesis of raspberry-like polystyrene/SiO₂ composite microspheres and their application in wettability gradient surfaces, *Surf. Coat. Technol.* 213 (2012) 90–97.
- [16] X.Y. Lu, J.L. Zhang, C.C. Zhang, Y.C. Han, Low-density polyethylene (LDPE) surface with a wettability gradient by tuning its microstructures, *Macromol. Rapid Commun.* 26 (2005) 637–642.
- [17] S. Burkert, M. Kuntzsch, C. Bellmann, P. Uhlmann, M. Stamm, Tuning of surface properties of thin polymer films by electron beam treatment, *Appl. Surf. Sci.* 255 (2009) 6256–6261.

- [18] D.J. Huang, T.S. Leu, Fabrication of high wettability gradient on copper substrate, *Appl. Surf. Sci.* 280 (2013) 25–32.
- [19] H.T. Spijker, R. Bos, W. van Oeveren, J. de Vries, H.J. Busscher, Protein adsorption on gradient surfaces on polyethylene prepared in a shielded gas plasma, *Colloids Surf. B: Biointerfaces* 15 (1999) 89–97.
- [20] G.Y. Zhang, X. Zhang, M. Li, Z.H. Su, A surface with superoleophilic-to-superoleophobic wettability gradient, *ACS Appl. Mater. Interfaces* 6 (2014) 1729–1733.
- [21] Y.N. Shin, B.S. Kim, H.H. Ahn, J.H. Lee, K.S. Kim, J.Y. Lee, M.S. Kim, G. Khang, H.B. Lee, Adhesion comparison of human bone marrow stem cells on a gradient wettable surface prepared by corona treatment, *Appl. Surf. Sci.* 255 (2008) 293–296.
- [22] T. Ueda-Yukoshi, T. Matsuda, Cellular responses on a wettability gradient surface with continuous variations in surface compositions of carbonate and hydroxyl groups, *Langmuir* 11 (1995) 4135–4140.
- [23] J. Hyun, Y.J. Zhu, A. Liebmann-Vinson, T.P. Beebe, A. Chilkoti, Microstamping on an activated polymer surface: patterning biotin and streptavidin onto common polymeric biomaterials, *Langmuir* 17 (2001) 6358–6367.
- [24] A. Lagunas, J. Comelles, E. Martinez, J. Samitier, Universal chemical gradient platforms using poly(methyl methacrylate) based on the biotin streptavidin interaction for biological applications, *Langmuir* 26 (2010) 14154–14161.
- [25] J. McMurry, *Fundamentals of organic chemistry*, seventh ed., Graphic World Inc, 2011.
- [26] Y.L. Zhang, H. Xia, E. Kim, H.B. Sun, Recent developments in superhydrophobic surfaces with unique structural and functional properties, *Soft Matter* 8 (2012) 11217–11231.
- [27] S. Herminghaus, M. Brinkmann, R. Seemann, Wetting and dewetting of complex surface geometries, *Annu. Rev. Mater. Res.* 38 (2008) 101–121.
- [28] B. Bhushan, Y.C. Jung, Natural and biomimetic artificial surfaces for superhydrophobicity, self-cleaning, low adhesion, and drag reduction, *Prog. Mater. Sci.* 56 (2011) 1–108.
- [29] A. Marmur, Solid-surface characterization by wetting, *Annu. Rev. Mater. Res.* 39 (2009) 473–489.
- [30] P. Louette, F. Bodino, J.J. Pireaux, Poly(methyl methacrylate) (PMMA) XPS reference core level and energy loss spectra, *Surf. Sci. Spectra* 12 (2005) 69–73.
- [31] M. Lazzari, D. Scalarone, G. Malucelli, O. Chiantore, Durability of acrylic films from commercial aqueous dispersion: glass transition temperature and tensile behavior as indexes of photooxidative degradation, *Prog. Org. Coat.* 70 (2011) 116–121.
- [32] P. Xu, X.Y. Zhang, H.B. Lu, Liquid–liquid transition and detrapping of trapped carriers of P(MMA/BA) copolymers by thermally stimulated depolarization current, *J. Macromol. Sci. B: Phys.* 45 (2006) 849–858.
- [33] Z.L. Zhou, X.Y. Zhang, P. Xu, H.B. Lu, Investigation of pendant group and chain segment motions in P(MMA/BA) copolymers by thermally stimulated depolarization current, *J. Macromol. Sci. B: Phys.* 46 (2007) 1013–1021.