Synthesis, Characterization and Property of Amphiphilic Copolymer

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Abstract. Atom transfer radical polymerization (ATRP) has been employed for the synthesis of an amphiphilic diblock copolymer MeOPEO-b-PBMA. The macroinitiator was prepared by poly(ethylene oxide) monomethyl ether with 2-Bromoisobutyryl bromide. The amphiphilic diblock copolymer was obtained by the macroinitiator and monomer n-Butyl methacrylate (BMA). The block copolymer was characterized by means of proton nuclear magnetic resonance (1H NMR). The honeycomb-patterned polymer films was obtained by the breath figure method. Water contact angle measurements revealed that a hydrophobic surface is obtained. The amphiphilic polymers expected to the application as the hydrophobic materials.

1. Introduction

Marine biofouling is caused by the adhesion of macroalgae, barnacles and microbial slimes. The ships navigating in the sea would be fouled by the marine life. In order to prevent the marine life attaching, it is the most effective that the surface of hull is coated by antifouling coatings. Traditional antifouling paints have relied upon the inclusion of biocides. Some of the virulent antifouling coatings which are difficult to degrade can accumulate in marine life, which not only causes adverse effects in the environment, but also threatens the health of humans. Consequently, research and development of environment benign antifouling coatings have already launched over the world. Honeycomb films constructed by the breath figure method have attracted scientists attention greatly[1-5]. They not only researched the formation mechanisms of the films, but also applied these films to various potential applications, such as superhydrophobic materials[6]. Amphiphilic systems have been widely used in antifouling coatings. Kim and coworkers found that an amphiphilic polymer network of polystyrene and polyurethane produced the microphase separated structures on the surfaces. Freij-Larsson and coworkers prepared amphiphilic graft copolymers and observed a reduction in the adsorption of blood proteins. The amphiphilic graft copolymers were PEG as hydrophilic blocks and styrene as hydrophobic blocks[7].

Herein, the breath-figure method was extended to an amphiphilic copolymer. In this work, the MeOPEO-Br as the macroinitiator was prepared firstly by the reaction of poly(ethylene oxide) monomethyl ether with 2-bromoisobutyryl bromide, secondly the amphiphilic copolymer was synthesized via the atom transfer radical polymerization (ATRP) of MeOPEO-Br and n-Butyl methacrylate respectively, and then the honeycomb-patterned polymer films was obtained by the breath figure method. The synthesis route was shown in Figure 1.
2. Experimental

2.1. Materials
Poly(ethylene oxide) monomethyl ether was purchased from Shanghai Chemical Reagent Co. n-Butyl methacrylate was purchased from Tianjin Guangcheng Chemical Reagent Factory of China. Azodisobutyronitrile was purchased from Shanghai Chemical Reagent Co. Petroleum benzene was purchased from Tianjin Fuchen Reagent Factory. 2-Bromoisobutyryl bromide was purchased from Creator Chemical Co., Ltd of China. N,N,N',N",N"-pentamethyldiethylenetriamine (PMDETA) and CuBr (99.99%) were purchased from Adrich and used as received. All other reagents were used as received without purification.

2.2. Measurements
\(^1\)H NMR spectra were taken on a Bruker ARX 400 MHz spectrometer with CDCl\(_3\) as solvent. The wetting behaviors of the polymeric coatings were investigated using a contact angle system (OCA20, Dataphysics, Germany) equipped with video capture at ambient temperature.

2.3. Synthesis of the macroinitiator MeOPEO-Br
MPEG (6.0 g, 5.0 mmol), CH\(_2\)Cl\(_2\) (40 ml), and triethylamine (TEA) (1.4 ml, 10 mmol) were added into 100 mL of dried round-bottomed flask. The solution was magnetically stirred until the MPEG completely dissolved. The flask was immersed in an ice bath under stirring. 2-Bromoisobutyryl bromide (1.85 mL, 15 mmol) was added dropwise to the flask. The mixture was stirred at 0 °C for 40 min and then at room temperature for 12 h. The resulting solution was filtered and washed three times with 10% sodium carbonate aqueous solution and 10% hydrochloric acid respectively. The organic solution was dried over anhydrous magnesium sulfate for 24 h. The product was precipitated by cool ether. The product was dried under vacuum for 48 h. The product was oily and viscous liquid. The yield was 72%.

2.4. Synthesis of diblock copolymer MeOPEO-b-PBMA
Macroninitiator MeOPEO42 -Br (203.5 mg, 0.1 mmol), butyl methacrylate BMA (4.7 ml, 30 mmol), CuBr (14.50 mg, 0.10 mmol), and PMDETA (21 µL, 0.1 mmol) were charged to a clean, dry Schlenk tube. After three freeze-pump-thaw cycles to remove oxygen, the tube was sealed and placed in preheated oil bath at 85 °C for 8 h. The polymerization was then quenched by merging the tube in liquid nitrogen. The product was diluted with THF and was passed through an Al\(_2\)O\(_3\) column, and was dropped into petroleum ether for precipitation of the product. This purification procedure was repeated three times, and the collected samples were dried in a vacuum oven for 48 h at room temperature.
2.5. Preparation of Honeycomb Films

Organic solutions of with 5mg/ml were prepared. Typically, the honeycomb films were prepared by casting 10 μL of a carbon disulfide solution of the copolymer with 75% relative humidity.

3. Results and Discussion

3.1. Chemical structure identification of the polymers

The synthesis of copolymers was shown in Figure 1. Figure 2 and Figure 3 show the 1 H NMR spectra of the macroinitiator MeOPEO-Br and the diblock copolymer MeOPEO-b- PBMA respectively. Figure 2 shows the 1 H NMR spectra of the MeOPEO-Br. In Figure 2, three important resonance signals can been found at 1.93 ppm for -C(CH3)2Br, at 4.42 ppm for -COOCH2CH2O-, at 3.69-3.58 ppm for -CH2- and at 3.33ppm for-CH3. Figure 3 show the 1H NMR spectra of the diblock copolymer MeOPEO-b- PBMA. In the 1H NMR spectrum of the copolymer, the peak integral of the methylene protons at 3.6 ppm is in the PEO block. New peaks appeared at 1.0ppm for methylene protons and 1.6 ppm for methyl protons of PBMA block.

![Figure 2. 1 H NMR spectra of the MeOPEO-Br](image-url)
Figure 3. \(^{1}\)H NMR spectra of the MeOPEO-b- PBMA

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3.2. Hydrophobicity and Wetting Characteristics of the Polymeric Coatings

The condensation of water vapor and the growth of water droplets are dependent on the evaporation rate of the organic solvent, which controls the cooling degree and the growth time[8]. The solvent is a key factor during the formation of honeycomb patterns. The CH\(_2\)Cl\(_2\) and THF were selected to study the influence of the solvents on the pattern formation. The solubility was determined with 5mg of the copolymer dissolved in 1ml of the solvent at room temperature with 75% relative humidity. Figure 4 and Figure 5 show the water contact angle on the films prepared from copolymer/CH\(_2\)Cl\(_2\) and copolymer/THF solution respectively on a cover glass. The contact angle of copolymer/CH\(_2\)Cl\(_2\) solution was 116\(^\circ\) and the contact angle of copolymer/THF solution was 108\(^\circ\). The contact-angle with the CH\(_2\)Cl\(_2\) was higher than that of the THF. The major reason is the polymer in the CH\(_2\)Cl\(_2\) solution formed the honeycomb-patterned film.
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Figure 4. Water contact angle on honeycomb-patterned films prepared from copolymer / CH₂Cl₂ solution on a cover glass with 75% relative humidity

Figure 5. Water contact angle on honeycomb-patterned films prepared from copolymer / THF solution on a cover glass with 75% relative humidity

4. Conclusion
A honeycomb-patterned film was prepared by the copolymer in methylene chloride with the 75% relative humidity. The amphiphilic copolymer has the potential application as excellent hydrophobicity. Further research is undergoing.

Acknowledgments
This work was supported by Shandong Provincial Key Research and Development Plan (2015GGX102028); Shandong Provincial Higher Educational Science and Technology Program (J12LD12); Shandong Provincial Natural Science Foundation (ZR201702230080); Shandong Provincial Higher Educational Science and Technology Program (J14LA57).

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