



Porous film fabricated by a thermoresponsive polymer poly(*N*-isopropylacrylamide-co-butylmethacrylate) with enhanced hydrophobicity

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ABSTRACT

Fabrication of porous polymer films is important for its potential applications in industry and everyday life. In this study, a thermoresponsive polymer poly(*N*-isopropylacrylamide-co-butylmethacrylate) (PNIBMA) was introduced to fabricate porous films on the glass surface. PNIBMA can alter its structure with temperature and has a lower critical solution temperature (LCST) of about 20 °C. The porous film of PNIBMA was prepared by drying a drop of PNIBMA solution (in CHCl₃) on a glass surface under a moist air flow. Atomic force microscope (AFM) images showed that the porous polymer film contained many layers of vacant spheres with diameters of about 1 μm. This unique surface characteristic endowed the porous film with higher hydrophobicity than a flat PNIBMA film made by direct coating. This study expanded the materials for porous films fabrication in the field of thermoresponsive polymers and should be of great potential in scientific researches and industry applications.

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1. Introduction

Porous polymer films have been extensively studied due to their applications in catalysts [1], as the template for inorganic growth masks [2,3], as the cell culture media [4–6], in making micro-lenses [7,8] and in surface hydrophobicity improvement [9,10]. These porous films showed many admirable optical, electronic, magnetic and chemical properties [11–13], which strongly attracted scientists' interest. A series of synthetic polymers were reported to be capable of forming such porous micro- or nano-structures, such as star polymers [14], linear polymers [15], semiconductor polymers [16], amphiphilic copolymers [17], dendronized block copolymers [18] and hairy nanoparticles [19]. However, up till now the materials that can be used to make the porous film are still limited. It is very interesting and also challenging to develop new materials to fabricate porous films.

In recent years, thermoresponsive polymers have been promoted as useful materials in diverse applications, such as drug delivery [20], protein modification and separation [21], immunoassay [22], etc. These polymers usually have *N*-isopropylacrylamide (NIPAAm) as the thermoresponsive groups, which can change their structures in water solution with temperature. The mechanism is

supposed to be relevant to the reversible volume phase transition caused by the coil-to-globule transition [23]. Recently, a great number of researches have copolymerized functional moieties onto NIPAAm to alter the properties of the polymers [24,25]. For example, butylmethacrylate (BMA) can be copolymerized onto NIPAAm to change the LCST of the copolymer. We determined that fabricating porous film with such thermoresponsive polymers should be of great interest because of the marvellous functions of these polymers.

In this study, we introduced a thermoresponsive polymer PNIBMA into porous film fabrication. PNIBMA was synthesized by copolymerizing BMA to NIPAAm. Porous film of PNIBMA was prepared by drying a drop of PNIBMA solution (in CHCl₃) on a glass surface under a moist air flow. Then a polymer surface with many vacant half-spheres was prepared by peeling off the top layer using an adhesive tape. AFM images revealed that there are not only many vacant half-spheres on the surface of the polymer film but also many spheres in the inner part of the polymer film. We supposed that the porous polymer film contained many layers of vacant spheres and the vacant half-spheres were resulted from peeling off the top part of the vacant spheres located on the surface of the polymer film. We also compared the water contact angle (WCA) of the porous PNIBMA film with that of a flat PNIBMA film made by direct coating. Data showed that the porous film had larger hydrophobicity than the flat film. The air bubbles trapped between the water and the polymer by the porous surface were believed

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to play an important role in the enhanced hydrophobicity of the porous film.

2. Experimental

2.1. Materials

N-Isopropylacrylamide was purchased from Aldrich Chemical Corp. It was purified by recrystallization in hexane and dried in vacuum at 25 °C. Butylmethacrylate was purchased from Aldrich Chemical Corp. and was distilled under reduced pressure before use. β -Mercaptoethanol was purchased from Genview Corp. The initiator, 2,2'-azobisisobutyronitrile (AIBN) was recrystallized from ethanol. All the reagents were of analytical grade.

2.2. Synthesis of PNIBMA

PNIBMA was synthesized by free radical polymerization in THF. Briefly, NIPAAm (2.829 g), butylmethacrylate (0.711 g), β -mercaptoethanol (50 μ g) and AIBN (20 mg) were dissolved in THF (30 mL). The mixture was incubated at 65 °C for 10 h in a thermostated oil bath under nitrogen-atmosphere. Then the mixture was cooled to room temperature. The cooled mixture was added to excess amount of petroleum ether to precipitate copolymer. The resultant precipitate was dried in vacuum overnight.

2.3. FTIR analysis of PNIBMA

The PNIBMA was poured into plastic dishes and maintained in vacuum at 50 °C overnight to form a film. FTIR spectra were measured over 4000–800 cm^{-1} on a Bio-Rad FTS 135 spectrophotometer.

2.4. ^1H NMR spectroscopy of PNIBMA

To estimate the composition of PNIBMA, ^1H NMR spectra of PNIBMA were measured at ambient temperature on a Varian UNITY plus-400 NMR spectrometer using dimethyl sulfoxide- d_6 as the solvent.

2.5. Gel permeation chromatography (GPC)

The molecular weight and molecular weight distribution of PNIBMA were determined by gel permeation chromatography (GPC waters 1525) using THF as a mobile phase. Monodisperse polystyrene was used for calibration. GPC analysis showed $M_n = 4695$, $PDI = 2.02$.

2.6. Determination of polymer solution LCST

Optical transmittance of 1.0 wt% aqueous PNIBMA solution at various temperatures was measured at 500 nm with a UV-vis spectrometer equipped with a circulating water bath. The temperature was continuously increased at a rate of 0.2 °C/min. The absorbance of the solution was recorded every 5 min. The LCST was chosen at the inflection point in the curves of the absorbance versus temperature.

2.7. Preparation of porous structure

The glass was rinsed with alcohol and water for several times and was dried before use. The moist air flow was generated by boiling a bottle of water. PNIBMA was solved in CHCl_3 solution to the concentration of 10 mg/mL. 100 μ L of PNIBMA solution was dispersed on the glass substrate and was incubated at room temperature under the moist air flow [26] for 5 min. Then the substrate was dried using

a hair drier. The top layer was peeled off using an adhesive tape to expose the porous structure to the outside. The experiment was repeated for three times. The size of the pores did not vary obviously. That means the method did not require strict conditions and was easy to repeat.

2.8. AFM observation

A CSPM4000 AFM instrument was employed (Being Nano-Instruments Ltd., China), of which the nonlinear behavior of the piezotube was compensated to increase the accuracy and resolution of the topography image. This measurement was carried out in contact mode under ambient conditions and the commercial tips were used in all the experiments. Spring constant was 0.12 N/m and the scan speed was 1–3 Hz. All images were flattened after recording using CPM software.

2.9. WCA measurement

The wettability of the surface was investigated by WCA measurement. 2 μ L of water was dripped on the surfaces under ambient conditions with an optical contact angle meter (HARKE-SPCA). The WCA values were averaged from triple individual measurements at different locations of the same surface. All measurements were within 3.0° off the average value.

3. Result and discussion

3.1. PNIBMA characterization

PNIBMA was synthesized by free radical polymerization of NIPAAm and BMA as shown in Fig. 1a. The structure of PNIBMA was well confirmed by ^1H NMR, GPC and FTIR measurements. The ^1H NMR spectrum of PNIBMA is depicted in Fig. 1b as PNIBMA (400 MHz, dimethyl sulfoxide- d_6 , TMS): 3.97–3.74(s, $30 \times 1\text{H} + 10 \times 2\text{H}$), 1.04(s, 6H), 0.90(s, 3H). The NIPAAm/BMA ratio of the polymer is 3:1 by comparing the areas of peak b and peak a in ^1H NMR spectrum, which represents the proton of the isopropyl CH_3 in the NIPAAm and the CH_3 of BMA, respectively. GPC result shows that the M_n of PNIBMA is 4695. Combining the results of ^1H NMR with GPC, we calculated that one PNIBMA molecule contained 30 monomers of NIPAAm and 10 monomers of BMA.

The FTIR spectra were further used to characterize the structure of PNIBMA. In Fig. 1c the amide peaks of NIPAAm units appear at 1640–1650 cm^{-1} (C=O stretching), 1510–1540 cm^{-1} (N–H bending) and 3300–3330 cm^{-1} (N–H stretching). The bands at 1366 cm^{-1} and 1388 cm^{-1} are attributed to the deformation of the two methyl groups in isopropyl groups. The C=O stretching peak of BMA appears at 1720–1730 cm^{-1} . The result indicates that the structure of PNIBMA is well consist with the design.

The thermoresponsive property of PNIBMA was well characterized by LCST measurement. The LCST of PNIBMA solution was determined by UV-vis spectrometer. As shown in Fig. 2, the absorbance of the polymer solution increased with temperature increasing, because the polymer was precipitated from the solution. The absorbance of the PDMNIB solution changed sharply at about 20 °C. That means the LCST of PDMNIB is about 20 °C. As is known, the LCST of PNIPAAm is 32 °C [24]. In this study, PNIBMA was synthesized by copolymerization of the hydrophobic monomer BMA to NIPAAm. This procedure caused a decrease in LCST of the thermoresponsive polymer.

3.2. Preparation of the porous film of PNIBMA

Varieties of solutions can be used for fabricating porous structure with polymers, such as CS_2 , CHCl_3 , THF, etc. [23]. Especially CS_2

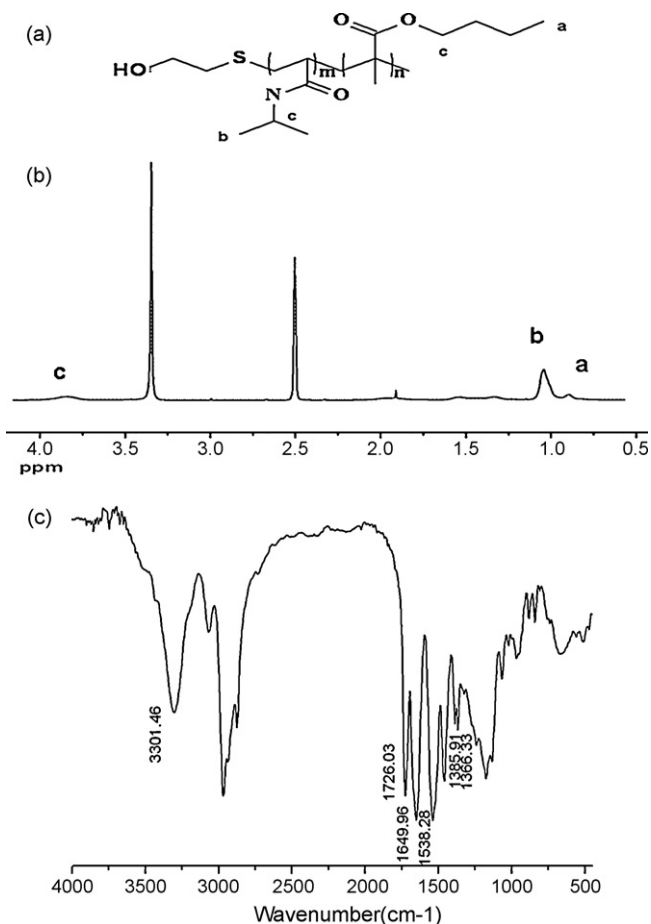


Fig. 1. (a) Structure of PNIBMA. (b) The ^1H NMR spectra of PNIBMA. (c) The FTIR spectra of PNIBMA.

is a suggested solution by Billon when testing the feasibility of using new polymers to form porous structures [27]. However, PNIBMA cannot be solved in CS_2 , but can be solved in CHCl_3 . So we used the water-immiscible solvent CHCl_3 as the solution for PNIBMA to probe the feasibility of forming porous film. A standard technique was employed to fabricate porous structure with PNIBMA on glass surface [28]. As shown in Fig. 3, PNIBMA solution in CHCl_3 was dispersed on the glass substrate and was then dried under a moist air flow. After drying, a porous PNIBMA film with many vacant spheres was obtained. Finally, we peeled off the top layer of the film by an

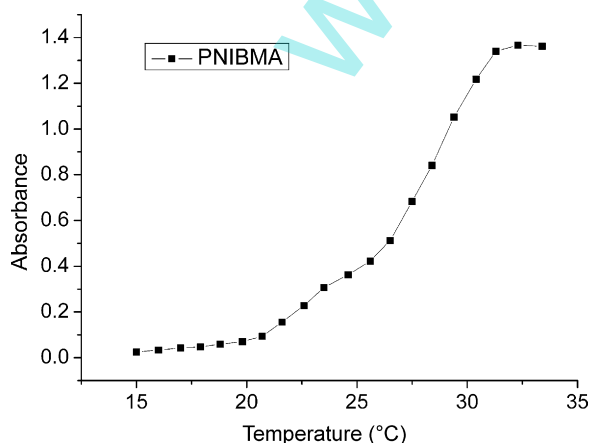


Fig. 2. LCST measurement of PNIBMA.

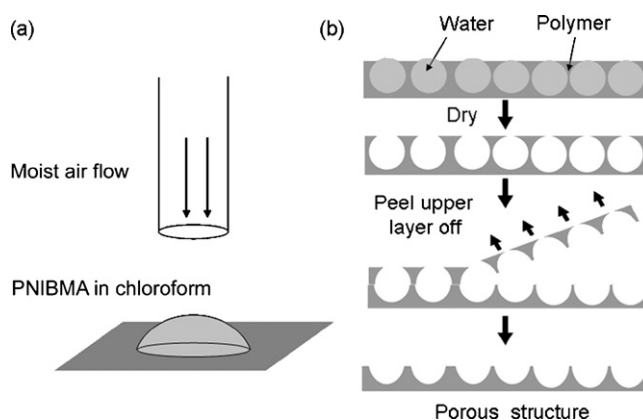


Fig. 3. Fabrication of porous structure of PNIBMA: (a) instrument for porous structure fabrication and (b) fabrication process for porous structure.

adhesive tape to expose the pores to the outside and got a porous surface.

Typical formation of porous films usually involves exposing a drop of polymer solution to a flow of moist air flow. When the solution is dried, the imprint of the water droplets remains and the polymer is immobilized in the matrix. Although the detailed mechanism of porous structure formation is unknown, there lies an attractive explanation: the formation of the porous structure is caused by the arranged arrays of air bubbles in the polymer film [26]. That means, when the moist air is blown over a surface of the polymer solution, water droplets will nucleate on the surface and subsequently grow [29,30]. After some time, the rafts of the droplets will form and organize on the surface, which do not coalesce. Then a second layer of droplets can be deposited on top of the first one. Finally an imprint of the water droplets (finally as an air bubble array) is left in the polymer matrix.

Because the structure of PNIBMA film could be destroyed during scanning electronic microscope (SEM) observation, we used AFM to observe the surface morphology of the PNIBMA film. As shown in Fig. 4a, many vacant pores were generated on the surface of the PNIBMA film. These pores covered most of the film surface area and made the film porous. From Fig. 4b, we could notice that the pores in the film of PNIBMA were almost half-spheres, of which the depth was about 500 nm and the calibre was about $1\ \mu\text{m}$. This indicates that PNIBMA solution can effectively condense water droplets on the glass surface without coalescence during preparation process. Consequently, the air bubbles (originally as water bubbles) were remained in the polymer film and were exposed to the outsides after peeling off the top layer.

From the image of a cleaved slice on the porous film in Fig. 4c and d, it is confirmed that there are multiple layers of pores in the film. The dimensions of these pores were similar but not exactly the same. We supposed that the variance in the size of the pores was caused by two reasons. First, the sizes of air bubbles in the polymer film were different. Consequently, the pores, which were resulted from peeling off the top layer of the bubbles, were of different sizes. Second, the cleaving locations of the air bubbles were different. When the bubbles were cut near the equator, the pores would be larger.

Commonly, the associated functional group, amphiphilic moiety and star-shaped molecular architecture are believed to be essential requirements for generating porous structure for homopolymers [4,26,31,32]. At room temperature, the NIPAAm groups could be deemed as the hydrophilic moieties and the BMA groups could be deemed as the hydrophobic moieties. However, the hydrophobic moieties and hydrophilic moieties were randomly copolymerized in the PNIBMA molecule. Consequently, the PNIBMA molecule was

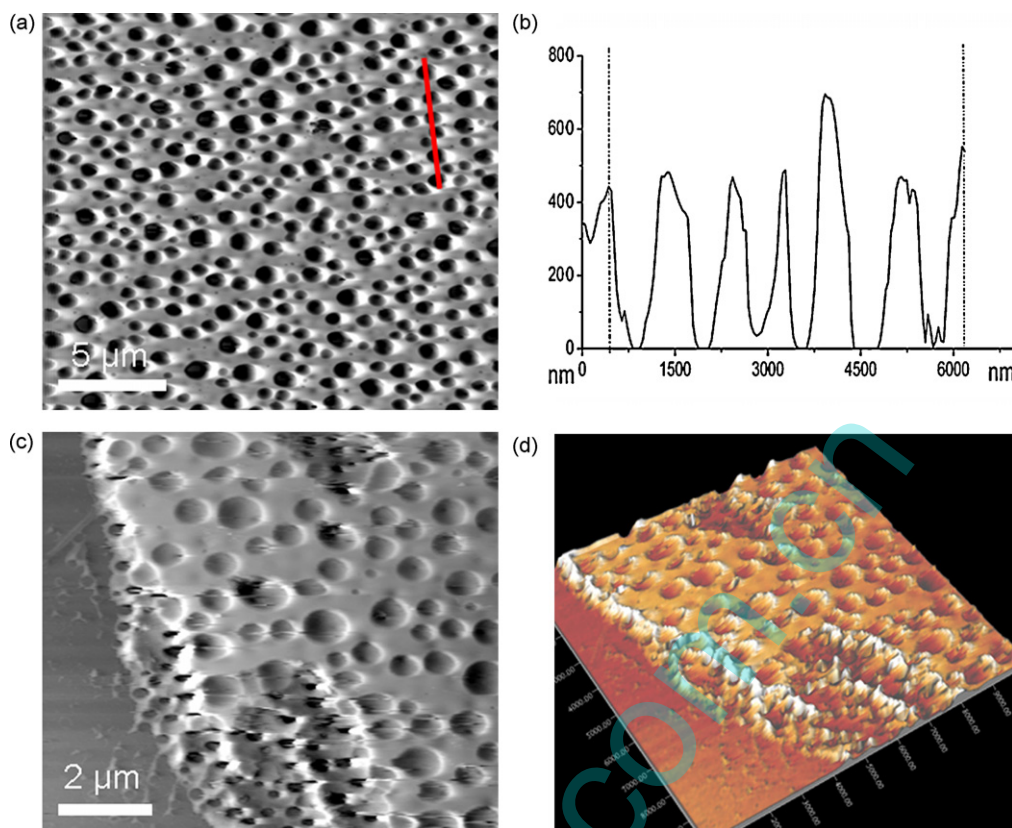


Fig. 4. Surface topology of porous structure of PNIBMA: (a) AFM image of porous structure of PNIBMA, (b) height measurement of the red line in (a), (c) AFM image of cleaved porous film of PNIBMA, and (d) 3D image of (c).

not an amphiphilic one. However, some researches also showed that certain molecules that did not meet any of the requirements could also form porous structures [33]. Thus it is hard to find a versatile rule to judge whether a material can form porous structure by its molecular structure.

This study expanded materials for porous structure preparation in the field of thermoresponsive polymers. Recently, the polymers with polystyrene component are the major materials reported to be capable of forming porous structure [34]. But polystyrene is not always a suitable component in every case. Sometimes the polystyrene component may cause some trouble in the application of the polymer, such as bad biocompatibility and bad degradability. In this study, the material we used is a thermoresponsive copolymer PNIBMA, which contains no polystyrene component. Although we do not mean that the polymers without polystyrene component are superior to the polymers with polystyrene component in each case, our polymer still offers an additional option for scientists when choosing the materials for porous structure preparation. This study also provides a possible insight to prepare porous films using polymers with similar structure with PNIBMA and should be of certain value for researchers engaged in surface modification and biodevice fabrication.

3.3. Enhanced hydrophobicity of the porous structure of PNIBMA

The PNIBMA films have many admirable properties, such as thermoresponsivity; however, in this study, we are only interested in the new properties that the porous surface of PNIBMA film brings. One of the most important properties is the enhanced surface hydrophobicity. As shown in Fig. 5, the flat PNIBMA film made by direct coating has a WCA of 26.94° on average. The result indicates that the PNIBMA film fabricated by direct coating method is very

hydrophilic. The porous PNIBMA film fabricated by our method has a WCA of 94.83°. Compared with the film obtained by direct coating method, the hydrophobicity of the porous film is greatly enhanced.

One reason that the porous film has a better hydrophobicity is supposed to be its surface three-dimensional structure. The film made by direct coating method has a very flat surface, which can be confirmed by the AFM image in Fig. 5d. While the porous film made by our method has a porous three-dimensional structure. It has been reported that the surface topology has an influence on the wettability of the surfaces. Especially it has been well documented that a high degree of surface roughness enhances the wetting properties of solid surface [34], which can be well explained by the modified Cassle's equation [35]:

$$\cos \theta' = f \cos \theta - (1 - f)$$

where θ' is the apparent water contact angle (WCA) on a rough surface, θ is the intrinsic WCA on a flat surface, f is the fraction of the solid/water interface and $(1 - f)$ is that of the air/water interface. This equation indicates that, when a rough surface comes into contact with water, air trapping in the trough area may occur and will contribute greatly to the increase of hydrophobicity. In this study, the porous PNIBMA film has many pores on the surfaces. When the water drop is placed on the film, there will be many air bubbles trapped in the pores. These bubbles are located between the polymer film and the water. Therefore, water drops can only contact with a small area of the micrometer scale polymer surface, which will greatly contribute to the enhanced hydrophobicity of the surface [36].

Polymer films with porous structure have very important applications. The porous PNIBMA film has larger surface area than a flat one, which can facilitate the absorption of molecules. The porous structure endows PNIBMA films with enhanced hydrophobicity.

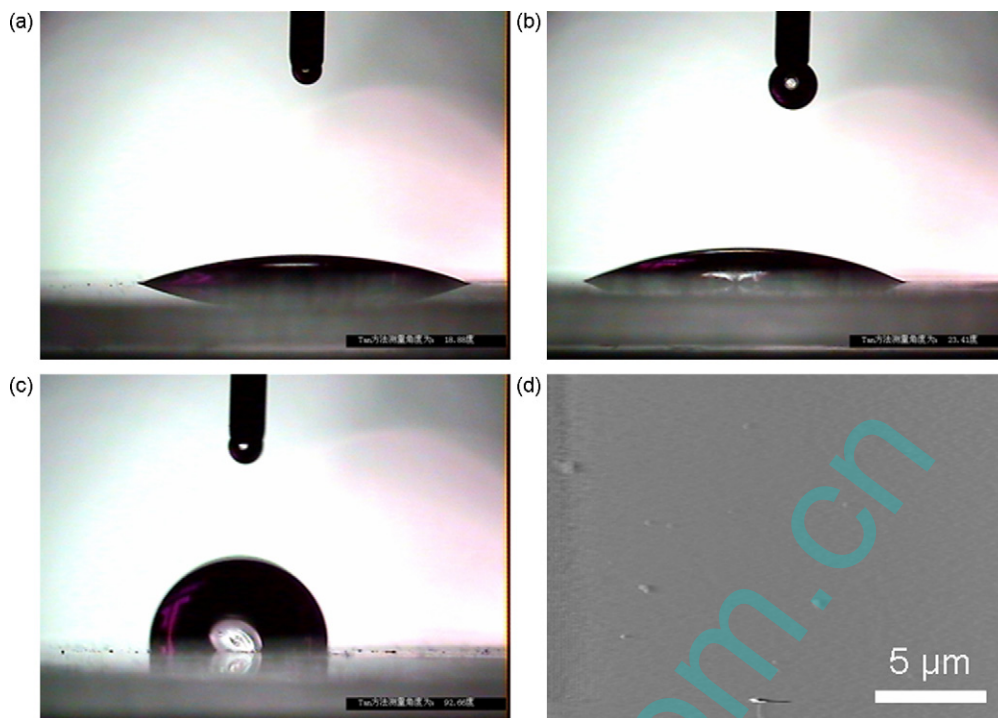


Fig. 5. WCAs of (a) a bare glass surface, (b) a glass surface coated with PNIBMA, (c) a glass surface with porous structure of PNIBMA and (d) AFM image of a glass surface coated with PNIBMA.

The hydrophobicity is of great importance, which is related to self-clean system and water repellent system [27]. In addition, the morphology of the films is of many applications in themselves. For example, the porous structure of the PNIBMA film can be used as the template for protein adsorption and cell growth. We believe that more applications can be found in the porous surface of the PNIBMA film.

4. Conclusions

We successfully introduced a thermoresponsive polymer PNIBMA into fabricating porous film on the glass surface, which expanded the materials for porous film fabrication to thermoresponsive polymers. Compared with the flat polymer film fabricated by direct coating method, this porous film has many superior properties, such as enlarged surface area and enhanced surface hydrophobicity. The porous film of thermoresponsive copolymer PNIBMA is anticipated to be of great potential in industry applications and scientific researches.

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