



## Dual pH-responsive smart gating membranes

Xiao-Xing Fan<sup>a</sup>, Rui Xie<sup>a,b,\*</sup>, Qian Zhao<sup>a</sup>, Xiao-Ying Li<sup>a</sup>, Xiao-Jie Ju<sup>a,b</sup>, Wei Wang<sup>a,b</sup>,  
Zhuang Liu<sup>a,b</sup>, Liang-Yin Chu<sup>a,b,\*</sup>

<sup>a</sup> School of Chemical Engineering, Sichuan University, Chengdu, Sichuan 610065, PR China

<sup>b</sup> State Key Laboratory of Polymer Materials Engineering, Sichuan University, Chengdu, Sichuan 610065, PR China

### ARTICLE INFO

#### Keywords:

Dual pH-responsive membranes  
Composite membranes  
Gating membranes  
Smart materials  
Responsive microgels

### ABSTRACT

A novel dual pH-responsive smart gating membrane is proposed for the first time by skillfully blending poly (*N,N'*-dimethylamino-2-ethyl methacrylate) (PDMAEMA) microgels into poly(ether sulfone) membrane as functional gates via liquid-induced phase separation method. The as-prepared membrane exhibits dual pH-responsive characteristics, i.e., this novel membrane is featured with both positively pH-responsive characteristics in acidic environment and negatively pH-responsive characteristics in basic environment. The mechanism of the positively pH-responsive performance is attributed to the pH-responsive volume change of PDMAEMA microgels embedded in the membrane, while that of the negatively pH-responsive performance is originated from the pH-responsive hydrophobicity and stiffness of the microgels. As a result, the permeability of this novel membrane is increased at first and then decreased with increasing the environmental pH value. The dual pH-responsive property of the prepared membrane is reversible and repeatable. The dual pH-responsive membrane proposed in this study provides a novel gating mode for design and development of pH-responsive smart membranes, which is highly potential for myriad applications, such as sewage treatments, sensors, controlled release of drugs and so on.

### 1. Introduction

The pH-responsive smart gating membranes can self-regulate their permeability and separation characteristics in response to the changes in environmental pH [1–3]. Such pH-responsive smart membranes are highly attractive for potential applications in various fields, including sensors [4,5], biological/chemical separations [6–8], controlled-release systems [9–11], and so on. There are two types of pH-responsive smart membranes according to the gating models, which are positively pH-responsive membranes [12–22] and negatively pH-responsive membranes [23–35]. With the increase of the environmental pH value, the pH-responsive membranes exhibiting increased permeability are defined as positively pH-responsive membranes, while those showing decreased permeability are called as negatively pH-responsive membrane [3].

Recently, either positively or negatively pH-responsive membranes have been extensively studied and reported. For the positively pH-responsive membranes, the gates shrink when the environmental pH value increases, which results in the opened membrane pores and increased permeability. Typically, cationic polymers containing weak alkaline groups, such as poly(*N,N'*-dimethylamino-2-ethyl methacrylate) (PDMAEMA), are used as the positively pH-responsive gates. In the

acidic environment, the tertiary amine groups are protonated and quaternary ammonium groups form, giving rise to internal charge repulsions among neighboring groups and extension of the PDMAEMA polymer chains. By contrast, the PDMAEMA polymer chains shrink in the basic environment due to the deprotonation of amine groups [36]. Usually, both chemical grafting [12,13,15,17,21,22] and physical blending [16,18–20] were employed to fabricate the positively pH-responsive membranes. Kang et al. took the advantage of surface-initiated atom transfer radical polymerization (ATRP) to prepare the positively pH-responsive nylon membranes [15]. The permeability of membranes was dramatically improved when the pH value of aqueous solution increased from 6 to 8, and the pH-responsive factor was approximately 5. Ulbricht et al. grafted the PDMAEMA polymers to the poly(ethylene terephthalate) track-etched membranes by ATRP and investigated the effect of grafting density and chain length on the stimuli-responsive properties of the membrane [17]. Moreover, Zhu groups prepared a series of positively pH-responsive membranes by blending PDMAEMA-based amphiphilic copolymers as additives during the membrane formation [16,19,20]. The effects of the sequence structures of amphiphilic copolymers, as well as the pH value and the ion strength of the coagulant baths on the pH-responsive performance of resultant membrane were investigated.

\* Corresponding authors at: School of Chemical Engineering, Sichuan University, Chengdu, Sichuan 610065, PR China.  
E-mail addresses: [xierui@scu.edu.cn](mailto:xierui@scu.edu.cn) (R. Xie), [chuly@scu.edu.cn](mailto:chuly@scu.edu.cn) (L.-Y. Chu).

As far as negatively pH-responsive membranes are concerned, the gates swell with the increase of environmental pH value, resulting in the decrease of membrane pore sizes and the decrease of membrane permeability. The negatively pH-responsive gates are usually anionic polymers possessing weak acidic groups, e.g., poly(acrylic acid) (PAA). At low pH value, the PAA polymer chains shrink due to the formation of intermolecular hydrogen bonding between the carboxylic groups. At high pH value, however, the carboxyl groups on the PAA polymer chains lose protons, and PAA polymer chains significantly swell due to the electrostatic repulsion between the deprotonated carboxylic groups. In general, the negatively pH-responsive membranes were also prepared by chemical grafting [24–26,28,30] and physical blending [29,31–33,35]. Yang et al. grafted PAA onto porous nylon membranes via surface-initiated ATRP, and the prepared membranes showed satisfactory negatively pH-responsive property in the range of pH = 3 to pH = 6 [28]. Galia et al. fabricated the negatively pH-responsive membranes by the grafting of PAA onto the porous poly(vinylidene fluoride) (PVDF) membranes via supercritical carbon dioxide assisted thermal-induced grafting polymerization [30]. Chu et al. prepared poly(ether sulfone) (PES) membranes with negatively pH-responsive performance by blending PAA based amphiphilic diblock copolymers [33]. The effects of both copolymer content and polymerization degrees of PAA block on the membrane morphology and pH-responsive characteristics were investigated systematically. Jewrajka et al. prepared the negatively pH-responsive membranes with good reversibility and stability by blending PAA based amphiphilic copolymers with PVDF [35]. Up to now, various positively/negatively pH-responsive membranes with linear copolymers as functional gates provided with excellent pH-responsive performance have been successfully prepared by chemical grafting or physical blending. The effects of parameters such as preparation conditions and the microstructure of polymeric functional gates on the stimuli-responsive performance of membranes have been studied systematically.

However, the previously reported positively or negatively pH-responsive membranes are featured with single gating model, i.e., they merely respond to acid or base. Thus, it is hard for these membranes with single responsive gating model to meet the practical needs in certain fields. For example, during the process of biological degradation of sewage, too low or too high pH values in the environment leads to the decreased enzyme activity of microbe, resulting in lowered degradation efficiency of pollutants [37,38]. Hence, dual pH-responsive membranes, which could respond to both acid and base, are highly desired. Such membranes could exhibit decreases in the membrane pore sizes after recognizing either acid or base, as a result the trans-membrane flux of solution containing undegraded toxic substance could be decreased and the emission of pollutants could be reduced. Therefore, the development of dual pH-responsive membranes is of great significance to expanding the application fields of pH-responsive smart membranes. However, it is still a great challenge to design and prepare smart membranes with dual pH-responsive performance till now.

In this study, we report on a novel pH-responsive smart gating membrane with dual pH-responsive gating characteristics for the first time. The trans-membrane flux of the proposed membrane decreases in either acidic or basic environmental condition, while increases in neutral condition. The dual pH-responsive membrane is designed and developed by blending PDMAEMA microgels into the PES membrane as functional gates via liquid-induced phase separation (LIPS) method. Compared with PDMAEMA linear polymers, the PDMAEMA microgels have cross-linked gel network structures. Therefore, there is an additional change in stiffness of PDMAEMA microgels in different pH values except for the pH-responsive change of microgel size, which makes the proposed composite membranes blended with PDMAEMA microgels possess dual pH-responsive performances. With increasing the environmental pH value, the flux of solution across the proposed membrane increases at first and then decreases, due to the protonation and deprotonation of amine groups of PDMAEMA microgels. Thus, the

proposed membrane exhibits both positively pH-responsive performance and negatively pH-responsive performance as the environmental pH value increases, with satisfactory reversibility as well as repeatability. The proposed membranes are highly potential to be materials candidates for myriad applications, such as sewage treatments, sensors and controlled release of drugs.

## 2. Materials and methods

### 2.1. Materials

*N,N'*-Dimethylamino-2-ethyl methacrylate (DMAEMA) (99.5%) and polyvinylpyrrolidone (PVP 360,  $M_w = 360000$  Da) were purchased from Sigma-Aldrich and used as received. *N,N'*-Methylenebisacrylamide (MBA), *N,N'*-azobisisobutyronitrile (AIBN), ammonium persulfate (APS) and dimethyl sulfoxide (DMSO) were all purchased from Chengdu Kelong Chemical Reagents. Methacryloxy thiocarbonyl rhodamine B (Polyfluor 570, Polysciences) was used as fluorescence dye. PES (Ultrason E 6020 P,  $M_w = 66000$  Da) was purchased from BASF. All solvents and other chemicals were analytical grade and used as received. Deionized water (18.2 M $\Omega$  cm, 25 °C) used in all experiments was from Milli-Q Plus water purification system (Millipore).

### 2.2. Synthesis of PDMAEMA microgels

Monodisperse PDMAEMA microgels were synthesized by the dispersion polymerization method [39]. Typically, the monomer DMAEMA (0.5 mol L<sup>-1</sup>), cross-linker MBA (0.5 wt% of DMAEMA) and initiator AIBN (0.2 mol L<sup>-1</sup>) were directly dissolved in 2 mL of ethanol. After addition of 18 mL of water and stabilizer PVP360 (5 wt% of DMAEMA), the reaction solution was magnetically stirred. The reaction solution was bubbled with nitrogen gas for 20 min to remove the dissolved oxygen, and then was kept at 65 °C to initiate the dispersion polymerization. After reaction for 3 h, the dispersion solution of the PDMAEMA microgels was diluted with 200 mL of deionized water and purified by microfiltration under stirring, which was carried out by a porous nylon-6 membrane with an average pore size of 0.22  $\mu$ m under a trans-membrane pressure of 90 kPa at room temperature. This process was repeated twice and then the concentrated dispersion solution of PDMAEMA microgels was freeze-dried at -35 °C for 48 h.

### 2.3. Characterization of PDMAEMA microgels

The morphology and size of the air-dried PDMAEMA microgels were observed by Field-Emission Scanning Electron Microscope (FESEM) (JSM-7500F, JEOL). The pH-responsive performance of PDMAEMA microgels in aqueous solutions at pH values ranging from 2.5 to 11.0 was observed by Confocal Laser Scanning Microscope (CLSM) (SP5-II, Leica) with red fluorescent channel excited at 543 nm. The fluorescence-labeled PDMAEMA microgels were fabricated by adding the double-bonded rhodamine B with the concentration of 3.0 mmol L<sup>-1</sup> during the dispersion polymerization. The PDMAEMA microgels were allowed to equilibrate in each aqueous solution at predetermined pH for 30 min. The stiffness of air-dried PDMAEMA microgels at pH = 5.8 and pH = 11.0 was investigated by Atomic Force Microscope (AFM) (Nanoscope V controller, Bruker). The microgels suspensions at pH = 5.8 or pH = 11.0 were dropped onto the silicon wafer and air dried. The pH values of aqueous solutions were adjusted by 0.2 M HCl or 0.1 M NaOH using a Mettler-Toledo pH meter (SevenCompact, Switzerland) throughout the whole experiments. In addition, 0.005 M NaCl was used to remain the ion concentrations of all solutions.

### 2.4. Synthesis and characterization of PDMAEMA hydrogel

PDMAEMA hydrogel was synthesized by free radical polymerization according to the method described previously [40]. Briefly, the

Download English Version:

<https://daneshyari.com/en/article/7019894>

Download Persian Version:

<https://daneshyari.com/article/7019894>

[Daneshyari.com](https://daneshyari.com)