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Thermo-responsive polysulfone membranes with good anti-fouling property modified by grafting random copolymers *via* surface-initiated eATRP

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ABSTRACT

We graft thermo-responsive polymer chains of PNIPAm, random polymer chains of P(NIPAm-*co*-Am), and P(NIPAm-*co*-GMA) on the surface of polyethersophone membrane via SI-eATRP method. The polymer chains of PNIPAm are thermo-responsive segment, and PAm and PGMA are hydrophilic and hydrophobic segment, respectively, which endow the modified membrane thermo-responsive property and adjust the lower critical solution temperature (LCST) of the modified membrane. The influence of temperature on membrane permeation and fouling process are investigated. The LCST is determined by filtration experiment at different temperature. The results show that all modified membranes have thermo-responsive behavior, and LCST of M-PNIPAm-*co*-PAm increased to 38 °C compared with M-PNIPAm; but M-PNIPAm-*co*-PGMA has the same LCST with M-PNIPAm. The modified membranes have higher flux than that of pristine polyethersulphone membrane whether feeding with pure water or BSA solution, which mainly owing to the hydrophilic surface and rich porosity of modified membranes.

1. Introduction

Polymeric membrane plays a crucial role in separation fields, such as water treatment, protein separation, and biomedical field [1–3]. Recently, stimuli-responsive behavior including light irradiation [4,5], temperature, pH [6], and electric fields have attracted more attention and have been introduced on polymeric membrane to design environment-responsive membrane for further applications [7–11]. Among these environmental sensitivities, temperature sensitive is the most commonly used in biotechnology industry. Poly (N-isopropylacrylamide) (PNIPAm) is a widely known temperature responsive polymer [12–14], which showed a lower critical solution temperature (LCST) in aqueous solution [15–17]. Fujishige et al. reported a change in conformation of individual PNIPAm chains from random coil to globular particles when heated to a critical temperature (about 32 °C) [18]. Wu et al. prepared temperature-responsive polymeric composite membranes by blending nanoparticles of poly (N-isopropylacrylamide-*co*-methacrylic acid) with hydrophobic polymer, and then they investigated the permeability of membranes to protein in response to environmental stimuli. They found that the membranes containing more nanoparticles of PNIPAm units exhibited higher thermal sensitivity [19]. Some papers have demonstrated that incorporating with hydrophilic or hydrophobic monomer in polymer composition is one of the useful methods to modulate the phase transition behavior of PNIPAm. LCST can be increased after the introduction of hydrophilic monomer, whereas decreased by incorporating with hydrophobic monomer [20–23]. Yu et al. reported that the copolymers P(NIPAm-*co*-Am) had higher LCST than that of PNIPAm; and they prepared copolymers with different weight ratios of Am and NIPAm, then they found that the copolymer synthesized from higher Am weight ratio had a relatively higher LCST due to the hydrophilic nature of Am [24].

There are varieties of polymeric membranes have been reported [25–31]. Among them, polyethersulfone (PES) exhibits many good properties and performance, such as good thermal stability, chemical stability, and outstanding mechanical property. These materials have been widely used as manufacturing asymmetric membranes in separation fields [32–35]. For applications, membrane fouling should be considered in aqueous filtration due to its relatively hydrophobic character [36,37]. Membrane fouling will bring a series of problems, such as decline of flux, increase of cleaning cost, and reduction of service life, which ultimately causes a limitation of the extensive

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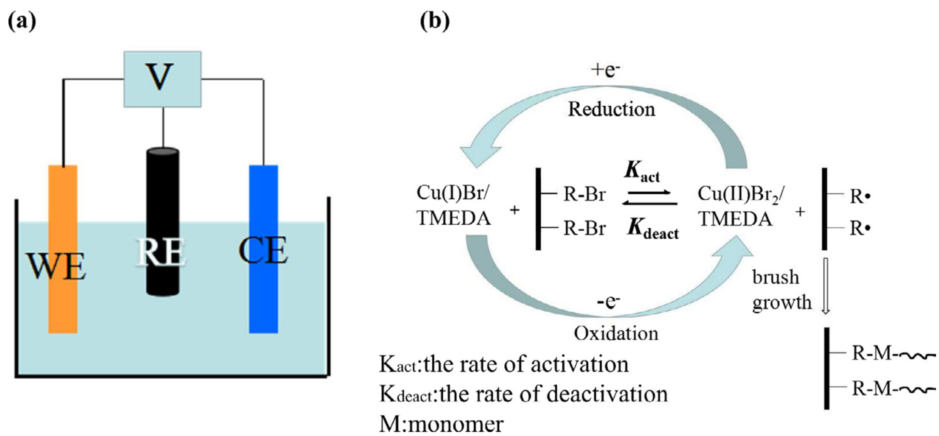
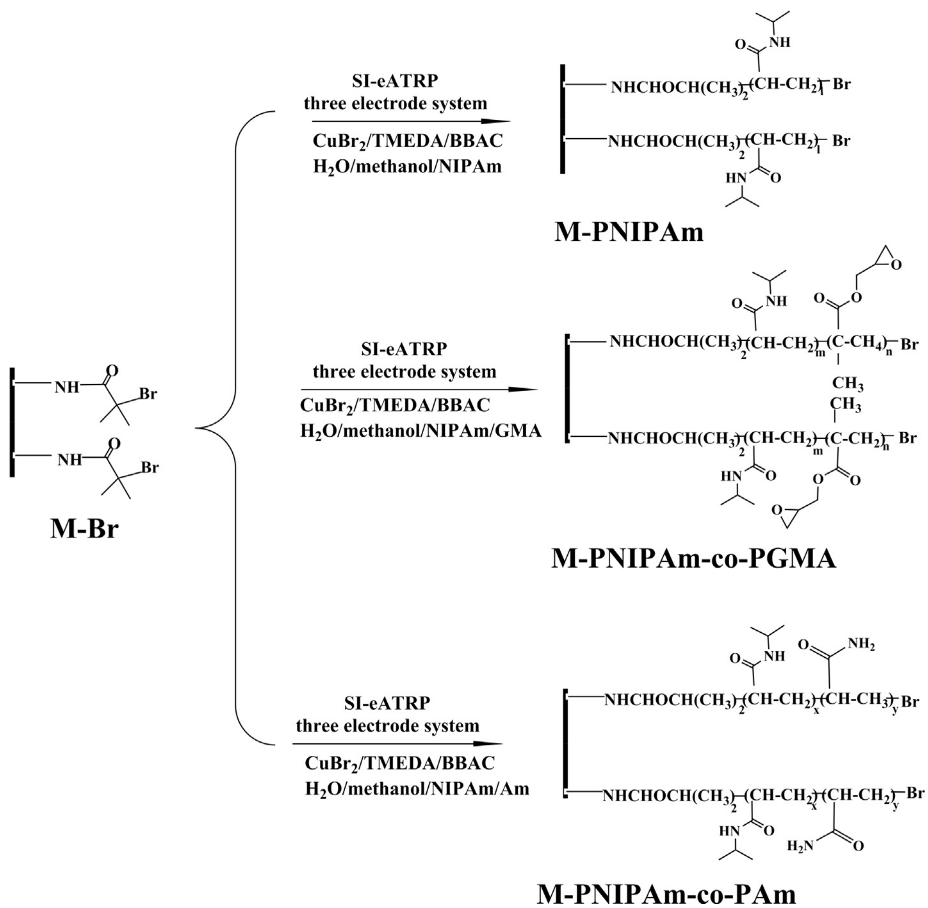


Fig. 1. (a) Schematic of three-electrode system; (b) theoretical scheme of SI-eATRP.



Scheme 1. Schematic illustration for strategy of grafting functional copolymers on membrane by SI-eATRP.

application of membrane [38–40].

As we have accepted, surface or interface wettability is mainly governed by surface structure and chemical composition [41–43]. An increase of membrane surface hydrophilicity can effectively reduce the adsorption of biomacromolecule and suppress membrane fouling. To overcome the fouling problem of membranes, a variety of modification methods such as coating, grafting, and blending have been applied to surface modification of PES membranes [44–46]. Grafting polymer chains with responsive function on the microporous membrane is the most common way to construct responsive membranes. The microporous membrane can be used as a mechanical support, and the permeability can be adjusted by the conformational change of the polymer chains due to the environmental stimulation. Among the different grafting methods, atom transfer radical polymerization (ATRP) method is widely used for the synthesis of homopolymer and copolymer on a wide range of monomers [47–50]. To control the balance of activators (Cu(I)/L)/deactivators (X-Cu(II)/L) and extend the reaction system to the condition under air atmosphere, Matyjaszewski and co-workers introduced electrochemistry to ATRP technology (eATRP) [51,52]. Furthermore, polymer brushes were grafted on the initiator-functionalized surface by surface-initiated eATRP (SI-eATRP) for surface modification [53–56].

We extend the SI-eATRP method to endow the PES membranes with thermo-responsive property and adjust the value of LCST by copolymerization with hydrophilic or hydrophobic monomer. Herein, thermo-sensitive PNIPAm chains, thermo-sensitive random polymer of P