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Full Length Article

Protein valves prepared by click reaction grafting of poly(N-isopropylacrylamide) to electrospun poly(vinyl chloride) fibrous membranes

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ABSTRACT

In this study, poly(vinyl chloride) (PVC) was electrospun into fibrous membranes and then reacted with NaN_3 to generate azido-terminated PVC fibrous membranes. A propargyl-terminated poly(*N*-isopropylacrylamide) (PNIPAAm) was also synthesized and then grafted, through click reactions, onto the azido-terminated PVC fiber surface. Protrusion-, scale-, and joint-like structures of the PNIPAAm grafts on the PVC fibers were formed upon increasing the molecular weight of the PNIPAAm grafts. The PNIPAAm-grafted PVC fibrous mats exhibited completely wetted surfaces at 25 °C because of their high roughness. The static water contact angle of the PNIPAAm-grafted PVC fibrous mats reached 140° when the temperature was increased to 45 °C. This thermoresponsive behavior was significantly greater than that of the PNIPAAm grafted on a flat surface. Temperature-responsive membranes were constructed having a pore size of 1.38 μm and applied as protein valves to block and release an antibody (fluorescein-conjugated AffiniPure goat anti-rabbit IgG). At 25 °C, the collection efficiency remained at 94% for antibody concentrations up to 60 ng/L. As the temperature increased to 45 °C, the collection efficiency decreased abruptly, to 4%, when the antibody concentration was greater than 20 ng/L. Accordingly, this system of PNIPAAm-grafted PVC fibers functioned as a protein valve allowing the capture and concentration of proteins.

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1. Introduction

Smart polymers made of responsive polymer grafts attracted much interests due to their sensitive changes to surrounding environment, such as pH, temperature and ionic strength. Based on the response to various physical and chemical factors, related materials were widely studied for biomedical and biosensing applications. Among, them, a thermoresponsive polymer may perform a characteristic temperature, upper or lower critical solution temperature (U- or L-CST), which vary with entropic changes and phase behavior corresponding to their structural characteristics. Poly(*N*-isopropylacrylamide) (PNIPAAm), one well-studied thermoresponsive polymer, shows the LCST between 30 and 35 °C in aqueous solution, which would be influenced by the destruction of hydrogen bonds between water molecules and the N—H or C═O of PNIPAAm [1–5]. According to this property, membranes could be fabrication with a variable pore size around its LCST, but their mechanical strength is generally low and thus cannot bear pressures during filtration. It has been reported that the membrane surfaces grafted with PNIPAAm showed an improvement on its mechanical strength, and were decorated with its unique property of variable pore sizes. Many kinds of processes, such as corona discharge, UV- and plasma-assisted polymerization have been reported to graft PNIPAAm on membrane structure [6–9]. Such modifications commonly contain two steps: the first is to form a free radical or an active site on target surface by using one of above-mentioned methods. Then, through immersing the treated surfaces in an aqueous solution of NIPAAm, the functional polymers can be grafted onto its porous structure. The exposure time

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of the samples, the power of irradiation as well as the reaction time and temperature of the reaction vessel are the most effective factors during the modification process. Such surface modification can be achieved through physical treatment (e.g., plasma) or through direct chemical modification (e.g., chemical grafting) with activation of the chloro-terminated groups. Wet-chemical surface treatment through common organic reactions is one of the best approaches for controlling the chemical and physical properties of a surface, especially when active polymers are grafted onto it. Indeed, polymer grafting has many advantages over grafting with small molecules, including greater surface stability, higher surface coating, and higher bioactivity.

Polyvinyl chloride (PVC) is the third most widely produced polymer in the word, and has been widely utilized in many applications, owing to its excellent mechanical strength, thermal stability, flame retardancy and insulation characteristics [10,11]. Polymer fibers could commonly be fabricated with a diameter of 10–500 μm by conventional methods such as melt, dry, and wet spinning; however, studies now show a tendency to concentrate on preparing polymer fibers in nano-diameters and with excellent mechanical properties. Electrospinning process is generally used to continuously produce polymer fibers with diameters of the submicron scale, in which a spinneret connected to an external electric field is equipped to transfer the polymer solution into solid fibers. Additionally, this process also has the advantages of being simple, convenient, and inexpensive as compared with conventional methods [12]. Electrospun polymer fibers were further made into membranes because of their attractive features including high porosity and specific surface area, and interconnected porous structure [13]. Therefore, the electrospun membranes can directly be used to improve the flux efficiency, keeping the same contaminant rejection ratio [14], and to filter water as well as chemical separations in liquids [15–19].

Several synthetic methods have been reported for the grafting of PVC through radical chain transfer reactions (e.g., grafting of PVC with butyl acrylate [20]), ionic polymerizations from labile chlorine in PVC (e.g., grafting with isobutylene [21]), and electrochemical polymerizations with aniline [22]. Various styrene and acrylates functional groups have been successfully grafted through atom transfer radical polymerization (ATRP) with chloroacetyl groups introduced to serve as initiating sites [23]. Since 2001, click chemistry was proposed to be an extraordinarily powerful tool; especially, thiol-ene reactions were successfully applied in preparing new functional polymer textiles due to its versatility, simplicity, and high efficiency [24,25]. The term "click" was highlighted that the chemistry can be used to efficiently link or click together two components, instead of focusing on the tedious construction of different bonds.[25] Three of the most popular specifications established for click reactions are thiolyne, thiolene, and azide–alkyne chemistry. The chemistry of thiols basically varies with its structures, whether radical or catalyst mediated [26]. However, the classic radical-based photo-polymerization presents several critical problems, including complex polymerization kinetics [27,28]. Normally, the -yne or -ene structure for both thiolyne and thiolene chemistry depends on whether the reaction is limited to chain-transfer or not [26]. Hence, the synthesis with thiolene chemistry has also been reported as a convenient way for functional polymeric materials [29–32]. In this study, PVC was electrospun to form fibrous membranes that were then reacted with NaN_3 to generate azido-terminated PVC fibrous membranes. In addition, propargyl-terminated PNIPAAm was synthesized and grafted onto the azido-terminated PVC fiber surface through click reactions. The wettability of the resulting PNIPAAm-grafted azido-modified PVC electrospun fibrous membranes was controllable merely by changing the temperature, the result of changes to the conformation of the PNIPAAm macromolecular structure. More importantly, this responsive material formed temperature-controlled membranes that blocked and released proteins in flow streams, thereby behaving as an inexpensive, tunable, and environmentally friendly protein valve.

2. Experimental section

2.1. Materials

Polyvinylchloride (PVC) was provided by Aldrich Chemical (Mn ~ 48,000, Mw/Mn = 1.85). *N*-isopropyl acrylamide (NIPAAm, Acros Organics) was the product of hexane and toluene (50% in vol. ratio) and then dried in a vacuum oven for the following procedures. The other chemicals used in atom-transfer radical-polymerization process, including triethylamine (TEA), propargylamine, copper(I) bromide, copper(II) bromide, sodium azide (NaN_3), 2-bromo-2-methylpropionyl bromide (BIBB), and 1,1,4,7,7 -pentamethyldiethylenetriamin (PMDETA) were provided by Acros Organics. As-obtained PMDETA, TEA, and BIBB were further purified through vacuum distillation before use. All unmentioned solvents and chemicals used in this experiment were of reagent grade and provided by Aldrich Chemical. Fluorescein-conjugated AffiniPure goat anti-rabbit lgG (H + L) (No:111-095-003; FGARI, ~14 nm, ~156 KDa) was provided by Jackson ImmunoResearch Lab.

2.2. Azido-terminated PVC electrospun fibrous membranes

Fig. 1 depicts the grafting, through click reactions, of PNIPAAm brushes onto the electrospun PVC fibers to form thermally responsive membranes. A homogeneous solution of PVC (concentrations: 15 wt%) in THF and DMF (30 mL; 1:1) was obtained after magnetic stirring for 1 h at 25 °C. For electrospinning of films, a syringe pump (KDS-100, KD Scientific) was utilized to provide a uniform injection of the PVC solution onto a cylinder substrate at an injection rate of 7 m/min. All needle tips of the syringes were connected to the positive electrode of a high-voltage power supply (YSTC Technology) with a feeding solution rate of 1 mL/h, the applied voltage of 20 kV, and the tip-to-collector distance of 15 cm. The fibrous membranes were deposited and collected on an Al sheet, and then dried under vacuum at 25 °C overnight for the following characterizations. Azido-terminated EPFMs were obtained after treating the chloro-terminated substrates overnight with a saturated solution of NaN_3 in DMSO in a sealed vessel; then, the samples were rinsed sequentially with DMSO, MeOH, and DI water before drying with N_2 stream [33]; he samples were moved to a Soxhlet apparatus to clear away any unreacted materials and dried with a stream of N_2.

2.3. N-Propargyl-PNIPAAm

A three-neck flask containing a solution of propargylamine (0.556 g) and TEA (1.02 g) in THF (10 ml) was cooled in an ice bath for 30 min, deoxygenated, and then filled with N_2. A solution of BIBB (2.36 g) in THF (20 mL) was added to the flask under N_2, resulting in a white deposit triethylammonium bromide. The mixture was stirred at 0 °C under N_2 for 24 h. The solids were filtered off; repeated extraction of the mixture gave *N*-propargyl-2-bromo-2-methylpropionamide [34].(Scheme 1) Copper(I) bromide (7 mg), PMDETA (21 mg), and the as-prepared *N*-propargyl-2-bromo-2-m ethylpropionamide (0.204 g) were mixed with isopropyl alcohol (10 mL) in a reaction vessel under a N_2 atmosphere. After deoxygenation, NIPAAm (1.5 g) was added into the vessel under a N_2 atmosphere at 25 °C. After polymerization times of 12, 24, and 36 h, the resulting solution was poured into MeOH (100 mL); the precipitate was placed in a Soxhlet apparatus and washed with