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Supramolecular interaction facilitated block copolymer assembly and preparation of self-organized scaffold for chiral selective transport

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HIGHLIGHTS

- Supramolecular interaction facilitated BCP assembly was described.
- Symmetric membranes consisted of elongated aggregates were prepared.
- These self-organized membranes were used as scaffolds for chiral selective transport.
- Chiral filters derived from organized membranes delivered superior permselectivity.

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ABSTRACT

Self-assembly of block copolymers (BCPs) is strongly dependent on molecular compositions. However, there are many BCPs having compositions less than the lower limit that is required to induce the self-assembly, and self-organized membranes can be hardly prepared from them. To solve this problem, we described a method to fabricate self-organized membranes consisted of worm-like aggregates through the supramolecular interaction facilitated assembly. The polystyrene-*block*-poly(4-vinylpyridine) (PS4VP) with a P4VP fraction of 8.8 wt% was used as the material, and membranes were prepared through the SNIPS process. Sulfonated polyethylene glycol (SPEG) interacting with P4VP was developed as the supramolecular additive for the PS4VP, and effects of the ratio of SPEG to 4VP on membrane formation were systematically studied. It was found that SPEG not only facilitated the assembly of PS4VP into worm-like aggregates, but also increased the porosity and permeability of the membranes. The self-organized membranes were then transformed into chiral filters through metal deposition and cysteine immobilization. It was determined that the transport rates and transport coefficient ($\alpha_{L/D}$) of resultant chiral membranes for bovine serum albumin molecules reached 6.53 nmol/cm^2.h and 1.73, respectively, both of which were obviously higher than that of plain membranes prepared from the same BCP with inferior assembly. Our results demonstrated that the additive facilitated assembly was crucial to the performace improvement of those BCPs that were unable to self-assemble into organized membranes.

1. Introduction

Block copolymers (BCPs) are excellent candidates for preparing the membranes that are in urgent needs for challenging applications such as precise separation and molecular recognition [1–5]. Among the strategies adopted to fabricate self-organized membranes from BCPs [6,7], the process combining the self-assembly with non-solvent induced phase separation (SNIPS) attracts increasing attention [8,9]. Although it is applicable to BCPs of diverse properties, the successful fabrication of self-organized membranes through the SNIPS is closely dependent on preparation conditions. The factors, such as polymer concentrations, the solvents and the evaporation time all show great impact on polymer assembly and membranes formation [10]. Under certain conditions, a slight modification of preparation condition will lead to obviously different structures. For instance, we found that free-standing, symmetric membranes consisted of worm-like aggregates were readily prepared from the SNIPS using polystyrene-*block*-poly(4-vinylpyridine) (PS4VP) copolymers [11]. With the aid of small angle x-ray scattering (SAXS) analysis [12], we observed that membranes consisted of worm-like aggregated were actually generated from solutions with concentrations

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lower than the critical micelle concentration (CMC), which is usually used to descibed the aggregation of BCPs in solutions. Recently, membranes consisted of worm-like aggregates were also prepared from the thermo-responsive BCPs, implying that self-organized membranes other than isoporous structure could be fabricated from the SNIPS process [13].

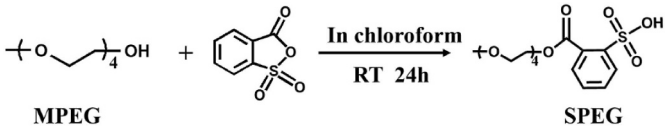
Besides the effects of preparation conditions on membrane formation, the properties of BCPs also show great impact on membranes structures. It is well-accepted that polymer assembly are usually determined by the molecular compositions and molecular weights [9,14,15]. For BCPs with the compositions that cannot effectively trigger self-assembly, the facilitated assembly is usually adopted [16]. It is observed that the complexation of additives to BCPs will not only enhance the microphase separation but also induce morphological transitions [17,18]. Selective loading of additives to specific domains is usually interpreted as the reason for these phenomena. Typically, fractions of BCPs will be changed by the additives loaded to the specific phase. Besides its effectiveness in thin films, additives facilitated polymer assembly was also observed in well-defined SNIPS process. For instance, Nunes and Gallei reported that the complexation of ions (Fe^{3+}, Ni^{2+}, Mg^{2+}) with P4VP led to better isoporous structures [19,20]. This complexation induced isopores formation has been also found for organic molecules such as acids [21] and carbohydrate [22]. However, additives facilitated assembly of BCPs into membranes consisted of worm-like aggregates has not been reported so far, although the facilitated isopores generation has been extensively studied before.

In our former work, we found that PS4VP with the P4VP fractions higher than 12 wt% easily self-assembled into worm-like aggregates. However, it was difficult for PS4VP copolymers with the P4VP fraction lower than 12 wt% to self-assemble into micellar structures with worm-like aggregates [11]. To demonstrate that membranes consisted of worm-like aggregates can be prepared from additive facilitate assembly, we used the PS4VP copolymers with the P4VP fraction lower than 12 wt% as starting materials, and membranes were fabricated following a well-defined SNIPS process. Sulfonated polyethylene glycol (SPEG), a water soluble agent was used as additive to regulate the polymer assembly. We observed that SPEG added to the casting solution not only facilitated the formation of worm-like structures but also improved the porosity and flux of prepared membranes. This obviously improved porosity and pore interconnectivity paved the ways for their applications that replied on surface functionality and specific surface area [23,24]. When these self-organized membranes consisted of worm-like aggregates were used as scaffold for chiral membranes, we found that transport rate and transport coefficient ($\alpha_{L/D}$) of BSA molecules through the chiral membranes were both higher than that of plain membranes prepared from the same BCP with inferior assembly, demonstrating that the facilitated assembly was critical to the improvement of molecular transport through the membranes based on PS4VP. As far as we know, there were rare reports on applying the micellar membranes derived from BCPs as substrates for chiral membranes before. Our results demonstrate that self-organized membranes consisted of worm-like aggregates can be used as excellent and novel scaffolds for chiral recognition.

2. Experimental section

2.1. Materials and reagents

Tetrahydrofuran (THF), dimethylformamide (DMF) and other solvents were purchased from Sinopharm Chemical Reagent Co., Ltd. Bovine serum albumin (BSA), L/D-cysteine and buffer solution (PBS, pH = 7.4) were commercially available and used directly. $PS_{91.2}$-*b*-$P4VP_{8.8}^{53.8k}$ was synthesized from the reversible addition-fragmentation chain transfer (RAFT) polymerization [25]. Details for polymer synthesis and characterization were showed in Fig. S1. The subscript and superscript in $PS_{91.2}$-*b*-$P4VP_{8.8}^{53.8k}$ denoted the weight fractions and molecular weight, respectively. Sulfonated polyethylene glycol (SPEG, Mn = 384.2 g/mol) was obtained following the process described in the previous publication [26]. The synthetic route and NMR spectrum of SPEG were showed in Scheme 1 and Fig. S2, respectively.



Scheme 1. Synthesis of SPEG from methoxy polyethylene glycols (MPEG-OH).

2.2. Membrane preparation

Membranes were fabricated following the process showed in Scheme 2. In general, $PS_{91.2}$-*b*-$P4VP_{8.8}^{53.8k}$ was dissolved into mixed solvent consisted of DMF and THF (60/40, wt%/ wt%). The polymer concentrations were ranged from 24 to 33 wt %, and molar ratios of SPEG to 4VP were changed from 1/16, 1/4, 1/2, 3/4 to 1/1. After stirring for 12 h at room temperature, the homogenous solution was cast onto glass plates using a doctor blade with a gap height of 150 μm. These films were evaporated in the air for 0, 60 and 180 s prior to immersing into water bath. Temperature (~25 °C) and humidity (40%) remained constant during the fabrication. The compositions of casting solutions were showed in Table 1.

2.3. Determination of the porosity

Porosity of wet membranes was determined following the method slightly modified from the literature [27]. Excess water on wet membranes was wiped off and the weights (m_W) of wet membranes were recorded. Sample were then dried in air to a constant weight (m_d). Porosity (ε) was calculated following the equation as shown below:

$$\varepsilon(\%) = \frac{\frac{m_w - m_d}{\rho_1}}{\frac{m_w - m_d}{\rho_1} + \frac{m_d}{\rho_2}} \times 100\% \quad (1)$$

Where m_w and m_d were the weights of wet and dried membranes, respectively. ρ_1 and ρ_2 were the density of water (0.998 g/cm^3, 20 °C) and PS-*b*-P4VP copolymer (1.05 g/cm^3), respectively.

2.4. Immobilization of L/D-cysteine on membranes

Prior to cysteine immobilization, the membranes were firstly coated by an ultrathin gold layer via electroless deposition. The deposition was conducted by immersing pieces of wet membranes into aqueous solution containing chloroauric acid ($HAuCl_4$, 0.5 mg/ml). After the predetermined time (3, 6 and 12 h), membranes were taken out and rinsed roughly with de-ionized water. Au^{3+} adsorbed on surface were then reduced by a sodium borohydride solution ($NaBH_4$, 0.1 mg/ml). The reduced, wine colored membranes were immersed in L- or D-cysteine solution (5 mg/ml) for 24 h to bind the cysteine. The resultant membranes were taken out, rinsed with PBS solution and used for protein transport without drying.

2.5. Protein transport

A diffusion cell with two compartments was used to study the transport of proteins through the cysteine immobilized membranes. Typically, the modified membranes with an effective area of 0.79 cm^2 were placed between two compartments. The left chamber was BSA solution with the concentration of 8 mg/ml. The right chamber was protein-free buffer solution and served as the receiver to collect the BSA transported from the left chamber. The volumes of both chambers were 20 ml. To eliminate concentration polarization, the solution was stirred

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