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Communication

Block copolymer assisted topochemical polymerization: A facile and efficient route to robust polymeric nanoporous membranes decorated with versatile amino acids

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ABSTRACT

Based on block copolymer assisted topochemical polymerization, a new strategy for facilely producing robust nanoporous membranes with controlled incorporation of functional groups onto nanopores is developed. As exemplified by preparing nanoporous polypyrrole decorated with amino acids, this strategy exhibits a high degree of freedom for tailoring the surface functionality in the created pores.

Nanoporous polymeric membranes have shown great potential for numerous applications, including separation/purification, nanoobject templates, (bio)chemical sensors, catalysis supports, energy storage and conversion, and biomedical engineering [1–2]. Among a variety of strategies for fabricating well-defined nanoporous polymers, assembly of block copolymers (BCPs) stands out for their remarkable control over pore geometry and size as well as distinct processability in large-scale fabrication [3–5]. In this approach the incompatibility of the segments in the copolymer tends to phase-separation at the nanometer scale to provide a nanostructured precursor, and subsequent removal of the minority phase by chemical etching, UV irradiation, or thermal treatment to generate the desired porosity [6]. Over the past decades, a large number of BCPs have been synthesized, and a diverse set of nanoporous membranes was reported [7]. In this respect, besides the efficient control over the geometry and orientation of nanochannels as well as the size of nanopores, the ability to precisely tailor the pore surface properties plays a pivotal role in dictating the final performance of the resulting nanoporous materials in most cases, and specially is critical for the utilization of these materials in a wide range of applications, such as selective transport, biomolecule separation, supported catalysis, and seeded templating [8].

Currently, three main approaches have been exploited to produce nanoporous polymeric materials with controlled pore-wall functionality [9]. The first approach is based on a functional group incorporated into the junction between the segment blocks in BCPs. The synthesized copolymers self-assemble into nanostructured thin films. The removal of the dispersed minor phase (sacrificial block) embedded in the matrix by breaking the junction then affords the chemically reactive functionality left out in the pore surface of the resulting nanoporous membranes [10]. The second one deals with the introduction of a functionalized mid-block between the matrix and the sacrificial block, leading to a functional polymer brush in the created pores [11]. Compared to the first one, this strategy provides high density of functional groups at the pore wall. The last one exploits the use of the blending of AB and AC diblock copolymers in which the common A block serves as the matrix, the B and C blocks are miscible, and only one of the two blocks is selectively cleaved and a desired functional block is left out along the pore wall [12]. Although these strategies provide the successful incorporation of functional groups into the pores, they are overwhelmingly dependent on the preparation of synthetically more elaborate BCPs, and still the controlled introduction of sophisticated functions such as biomolecules or multiple functional groups, is challenging. On the other hand, in most cases, the functional porous membranes made by using the

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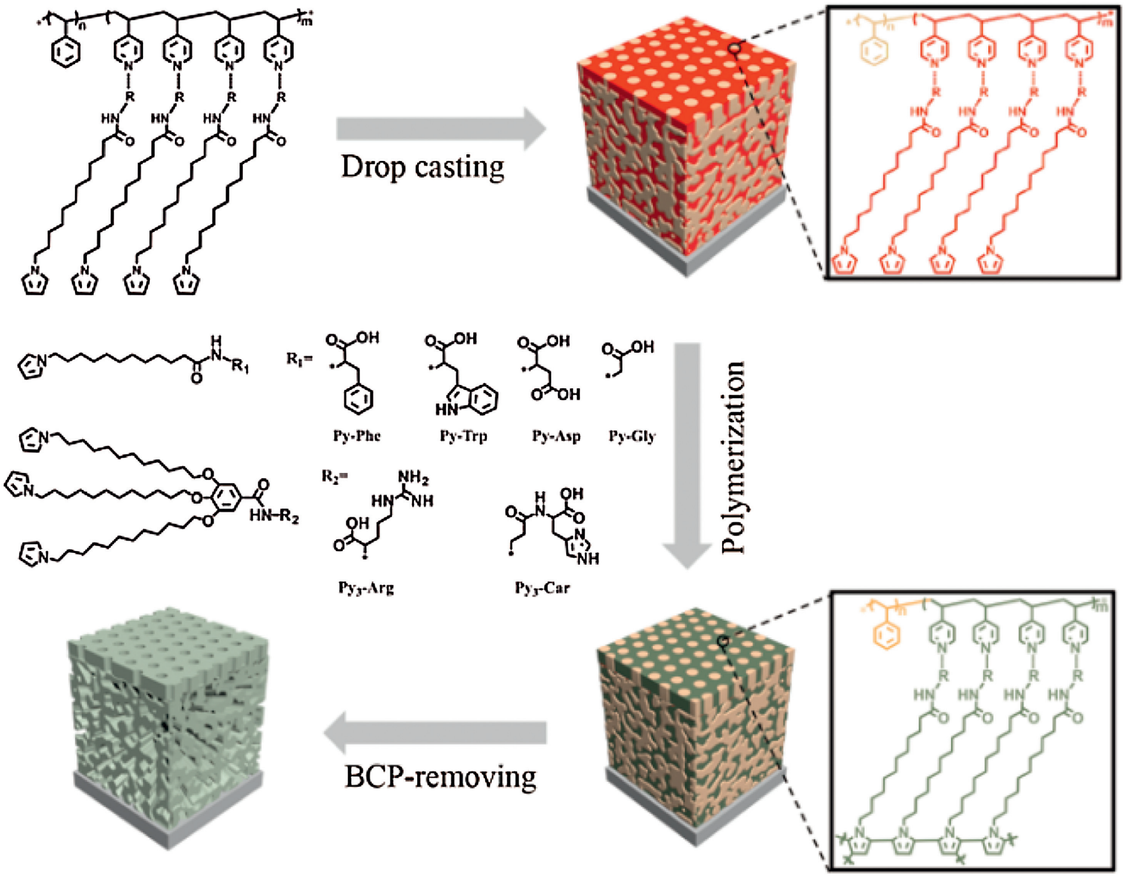
above-described approaches generally show poor resistance toward a wide range of solvents and lower thermal stability since no structural stabilization by cross-linking is performed, limiting their practical applications [13]. Thereby, developing a new strategy to facilely access robust nanoporous polymer membranes with a high degree of freedom for tailoring the surface functionality in the created pores is highly desired.

In this communication, based on block copolymer assisted topochemical polymerization, a strategy for facilely producing robust nanoporous membranes with controlled incorporation of functional groups onto nanopores is developed. The essence of this strategy is to first preorganize the functional monomers into a well-ordered nanostructured film with the assistance of block copolymer assembly, which is followed by topochemical polymerization of the preorganized monomers in solid state. Upon the extraction of the used BCP template, the ordered nanoporous polymer film with the concomitant exposure of the functional groups in the created pores is achieved. In this approach, by the selection of proper BCPs, in principle, a wide range of functional monomers can be supramolecularly grafted to one of the blocks of a copolymer by noncovalent interactions, finally leading to the controlled incorporation of diverse functional groups in the resultant porous materials after the assembly of the copolymer-based supermolecules and the subsequent polymerization as well as the extraction. In this process, the polymerization performed in solid state, especially for the case of forming a polymer network, will endow the obtained polymers with good physicochemical stability.

As a proof of our concept, the easily available polystyrene-block-poly(4-vinylpyridine) (PS-*b*-P4VP) was employed as template in our work, and phenylalanine derivative bearing a terminal pyrrole moiety (Py-Phe) was first synthesized as a functional monomer to demonstrate the fabrication of nanoporous material with the correct incorporation of phenylalanine units in the nanopores. Scheme 1 illustrates the preparation procedure. PS-*b*-P4VP and Py-Phe in the desired ratio were dissolved in a common solvent $CHCl_3$ for several hours to form supramolecular complex PS-*b*-P4VP(Py-Phe)$_n$ through hydrogen bonding Py-Phe molecules to the pyridine rings (the subscript n denotes the ratio between Py-Phe molecules and pyridine repeat units). Then, the obtained supramolecular complex was drop-coated onto a silicon substrate to give nanostructured film with further improved alignment of Py-Phe molecules by slowly evaporating the solvent in a dried chamber. The polymerization of the preorganized pyrrole units was accomplished by exposing the formed solid film to oxidative agents ($HAuCl_4$ or I_2). Finally, removal of PS-*b*-P4VP template by extraction using THF and $CHCl_3$ afforded the nanoporous polypyrrole scaffold, and concomitantly released the functional groups (phenylalanine) from the hydrogen bonds with P4VP segment.

The ^{1}H NMR titration confirmed the formation of hydrogen bonding between Py-Phe molecules and the pyridine units of PS-*b*-P4VP (Fig. S1 in Supporting information). The SEM image of the as-casting film from the PS-*b*-P4VP(Py-Phe)$_1$ supramolecular complex shows smooth and featureless morphology (Fig. S2 in Supporting information). However, upon the immersion of the film into ethanol for several hours for the removal of the incorporated Py-Phe molecules, an embedded ordered perpendicular cylinder array was observed (Fig. 1a), clearly indicating that the microphase separation of the PS-*b*-P4VP(Py-Phe)$_1$ supramolecular complex through simple solvent evaporation led to a morphology with



Scheme 1. Schematic illustration of the fabrication of nanoporous polymer membranes decorated with amino acid groups *via* BCP assisted topochemical polymerization.

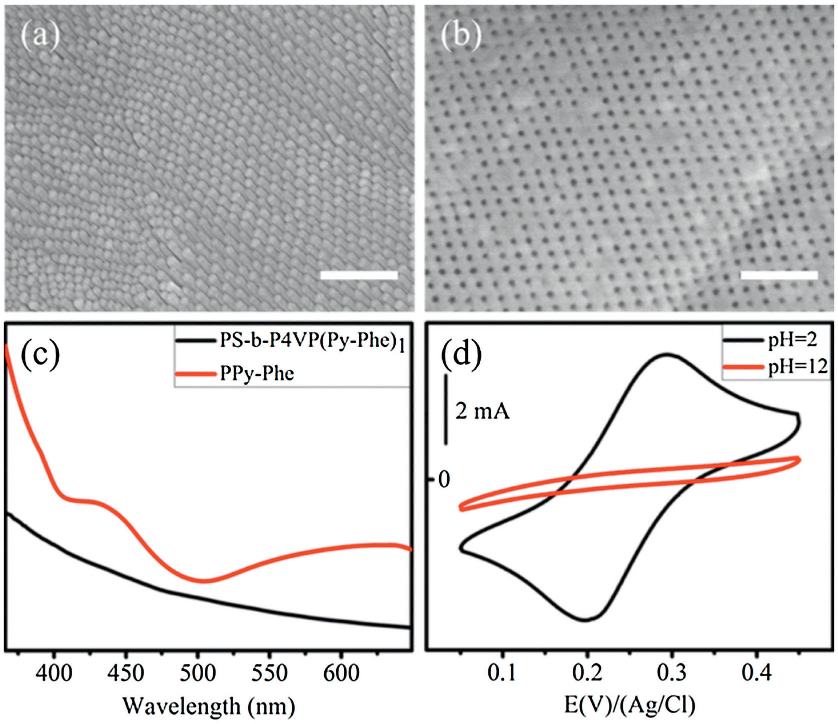


Fig. 1. SEM images of (a) the as-casting membrane of PS-*b*-P4VP(Py-Phe)$_1$ after the removal of the incorporated Py-Phe molecules and (b) the resulting membrane after polymerization followed by the removal of PS-*b*-P4VP template; (c) Comparison of UV-vis spectra of the as-casting membrane of PS-*b*-P4VP(Py-Phe)$_1$ before and after polymerization; (d) Gating property of the obtained nanoporous membrane using $K_3[Fe(CN)_6]$ as electrochemical probes. Scale bars are 500 nm in (a), 200 nm in (b).

cylinder PS microdomains distributed in the matrix of P4VP(PDP)$_1$. Relative to the PS-*b*-P4VP(Py-Phe)$_1$ complex in solution, the arrangement of Py-Phe molecules in the nanostructured film undoubtedly was further enhanced, which would be favorable for the transformation of the preorganized pyrrole units into polymer network. Indeed, upon the exposure of the self-assembled film to $HAuCl_4$ or I_2 oxidative agent, the appearance of this film is gradually changed from colorless to dark brown, indicative of the occurrence of the polymerization of pyrrole monomers. The SEM images in Fig. 1b and Fig. S3 (Supporting information) show the surface and cross-sectional structure of the resultant nanoporous membrane after the removal of PS-*b*-P4VP template, a typical nanoporous structure with ordered pores on surface layer and disordered pores inside because of the insufficient assembly of the whole film.

Compared to that of the as-casting film, the UV/vis spectrum of the obtained porous film shows a broad absorption around 440 nm, confirming the formation of the conjugated polypyrrole (Fig. 1c) [14]. FTIR studies reveal that the characteristic C-H in-plane deformation bands of the pyrrole ring at 1282 cm^{-1} and 1061 cm^{-1} disappeared after polymerization process (Fig. S4 in Supporting information), further indicating the occurrence of the C-C coupling between pyrrole units [15]. Importantly, we found that the characteristic bands of phenylalanine moiety at 1722 cm^{-1} (carboxyl), 1640 cm^{-1} (amide I), 1610 cm^{-1} (C = C stretching), 1535 cm^{-1} (amide II), 1350 cm^{-1} (C-N stretching) and 1250 cm^{-1} (amide III) maintain, and withstood the used oxidative polymerization process [16]. Also, the comparison of the N 1s XPS spectrum of the as-casting film with that of the obtained porous film verifies the successful formation of polypyrrole and the correct incorporation

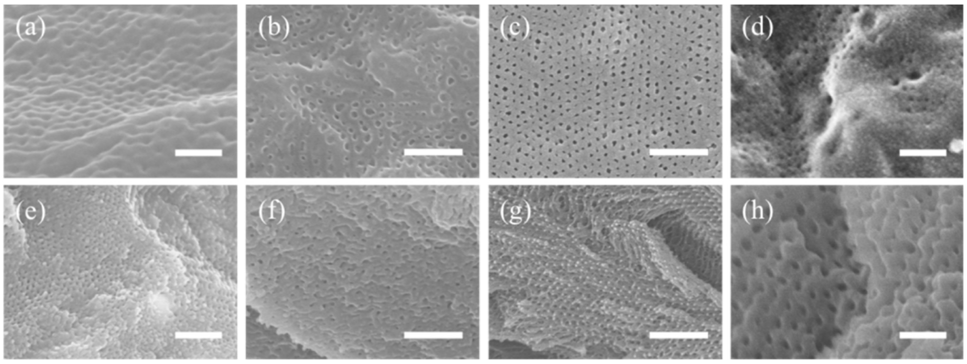


Fig. 2. Top-view SEM images of the porous membranes functionalized with Gly (a), Trp (b), Asp (c) and Arg (d), respectively. Cross-sectional SEM images of the porous membranes functionalized with Gly (e), Trp (f), Asp (g) and Arg (h), respectively. Scale bars are 500 nm except 200 nm in (a, d).

of the phenylalanine functional group in the resultant porous film. As shown in Fig. S5 (Supporting information), the performed polymerization led to the shift of N 1s position of pyrrole unit from 400 eV to 399.7 eV, and in contrast the N 1s position of phenylalanine moiety is unchanged at 400.5 eV. Additionally, the presence and accessibility of phenylalanine moieties decorated on the created pore wall is electrochemically evidenced as a gating membrane using $K_3[Fe(CN)_6]$ as a redox probe (Fig. 1d). When the phenylalanine moieties are altered from neutral (COOH) to deprotonated state (COO^-), correspondingly the change of the pore state from opening to closed was detected toward $[Fe(CN)_6]^{3-}$ because of a strong electrostatic repulsion for the negative probe.

To demonstrate the general applicability of our strategy to introduce diverse functional groups into nanoporous films, a series of amino acid functionalized pyrrole monomers was synthesized (Scheme 1). To improve the solubility of some monomers synthesized in $CHCl_3$ to form desired supramolecular complex with PS-*b*-P4VP, more than one alkyl chain with terminal pyrrole were also used in monomer structure. We found that all the synthesized monomers could be grafted onto the pyridine rings of PS-*b*-P4VP by noncovalent interactions, and by properly adjusting the stoichiometry between the monomer molecules and PS-*b*-P4VP the formed supramolecular complexes could lead to the desired perpendicular cylinder morphologies in all cases in the as-casting films without further treatment (Fig. S6 in Supporting information). After the polymerization of the preorganized pyrrole monomers followed by removal of PS-*b*-P4VP all the as-casting films were converted into well-defined nanoporous films (Fig. 2 and Fig. S7 in Supporting information). FTIR studies confirmed the correct incorporation of the amino acid functional groups used in all cases (Fig. S8 in Supporting information), and various functionalized nanoporous films were successfully fabricated. In general, the oxidative polymerization of pyrrole or pyrrole derivates produce a polymer network, since both α and β positions of pyrrole ring are active for polymerization. As a result, the films described above are very robust materials, and exhibit excellent resistance to common organic solvents as well as good mechanical toughness, as shown in Figs. S9 and S3 (Supporting information). It should be noted that all preparations of the nanoporous films in our work only involve the use of the as-casting films without further optimization.

In our strategy, the supramolecular nature of non-covalent grafting of functional monomer to a single BCP provides great flexibility to modulate the types of the incorporated functional groups and to turn the morphologies in the as-casting films by varying the functional monomers as well as the loading ratio of the small monomer molecule to PS-*b*-P4VP. This approach also offers the opportunity to introduce multiply functional groups in the created pores by using mixed functional monomers in the same preparation process. As a demonstration, equal molar functional monomers of bicomponent (Py-Phe and Py-Asp) and tricomponent (Py-Phe, Py-Asp, and Py-Trp) were grafted onto PS-*b*-P4VP, respectively, and the corresponding nanoporous films were created. Fig. 3 displays the top and cross-section SEM images of the obtained materials, showing the formation of well-defined pore structures. The characteristic bands in FTIR studies confirmed the incorporation of the multiply function groups in the resultant materials (Fig. S10 in Supporting information). Unfortunately, at present quantitative determination of the amount and ratios of different functional groups is still difficult.

Peptide functionalized nanoporous membrane is of interest for many applications. In this work, a peptide functionalized monomer was also synthesized (Scheme 1), and successful formation of nanoporous membrane was realized, as show in Fig. S11 (Supporting information). Compared to amino acid functionalized monomers, probably due to multiply intra- and/or intermolecular interaction between PS-*b*-P4VP and peptide functionalized monomer, the control over the morphology in the casting film is a challenge. Notably, our results indicate this strategy could be devoted to develop such important functional nanomaterials. Collectively, the resultant amino acid/peptide-functionalized nanoporous polymeric membranes potentially have a broad scope of applications such as separation [17], absorption of heavy metal ions [18] and antifouling [19].

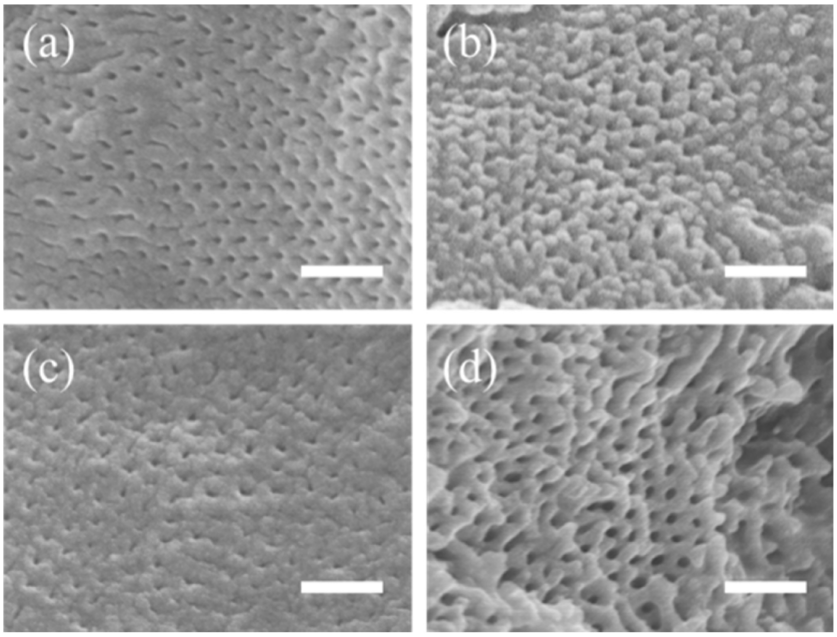


Fig. 3. Top-view (a) and cross-sectional (b) SEM images of Phe and Asp functionalized nanoporous membrane; Top-view (c) and cross-sectional (d) SEM images of Phe and Asp and Trp functionalized nanoporous membrane. Scale bars are 200 nm.

Over the past years, self-assembly of supramolecular complexes based on block copolymers, especially PS-*b*-P4VP, and small molecules or additives in thin films has been extensively studied [20–27]. The most of the reported works, however, are focused on the preparation of functional nanocomposites or on the topological polymerization of diacetylene-containing system. To the best of our knowledge, no work has been described for the development of functional nanoporous films by exploiting the block copolymer assisted topochemical polymerization of the functional monomers. Our preliminary results reported herein are quite encouraging. Although only pyrrole based functional monomers were tested in this work, in principle, the strategy described should be generally applicable for other monomers to achieve different nanoporous films with efficient incorporation of diverse functional groups as long as the block copolymer and functional monomer are appropriately selected.

In summary, a strategy based on block copolymer-assisted topochemical polymerization has been successfully developed to efficiently produce robust nanoporous films with controlled incorporation of functional groups onto the nanochannels. As a demonstration, a series of amino acid-functionalized pyrrole monomers was synthesized, and stepwise self-assembly by the aid of PS-*b*-P4VP and subsequent in-situ polymerization of the preordered monomers in a nanostructured monomer/PS-*b*-P4VP composite yielded the corresponding amino acid-functionalized nanoporous polymeric films after the removal of PS-*b*-P4VP template. The obtained results indicate that our strategy allows for facilely accessing various functional nanoporous materials using one single BCP, and exhibits a high degree of freedom for tailoring the surface functionality in the created pores.

Acknowledgments

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.cclet.2019.07.035.

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