

Full Length Article

Engineering repairable nanoporous functional coatings on arbitrary substrates by manipulating phase behaviors of block copolymers

Jiemei Zhou^{1, #}, Xiang Ying^{1, #}, Daiwen Li¹, Mingjie Wei¹, Xiangyue Ye¹, Yong Wang^{1, 2, *}¹ State Key Laboratory of Materials-Oriented Chemical Engineering, College of Chemical Engineering, Nanjing Tech University, Nanjing 211816, China² School of Energy and Environment, Southeast University, Nanjing 210096, China

ARTICLE INFO

Article history:

Received 23 June 2025

Received in revised form

21 August 2025

Accepted 21 August 2025

Available online 2 September 2025

Keywords:

Nanoporous coating

Block copolymers

Selective swelling

Polymer–solvent interactions

Antireflection

ABSTRACT

Nanoporous polymers are extensively coated on various substrates to deliver optical, permselective, or other functions. However, it remains desired to fast produce uniform nanoporous polymer coatings on substrates with complex surfaces. Herein, by manipulating the interactions between block copolymers and selective solvents, we prepare repairable nanoporous polymers on arbitrary substrates. This is realized by an extremely simple sequential coating process: sequential coating of block copolymers and their swelling agents on substrate surfaces. The swelling agents are comprised of two solvents that swell the constituent blocks of the copolymers to different degrees, rapidly producing polymer coatings with uniform, interconnected, sub-50 nm pores. This sequential coating process is able to conformally build nanoporous polymers on nonplanar substrates with large lateral sizes and complex surface features, and also to *in situ* repair defects arising during usages. We further demonstrate that the nanoporous coatings show excellent antireflective and membrane separation performances. This sequential coating process is dictated by polymer–solvent interactions, and is expected to find applications in diverse fields for its simplicity, adaptability, and the capability to produce well-defined nanoporosities.

© 2025 The Chemical Industry and Engineering Society of China, and Chemical Industry Press Co., Ltd. All rights are reserved, including those for text and data mining, AI training, and similar technologies.

1. Introduction

Nanoporous coatings are functional layers hosting nanoscale porosities, providing new functions to the substrates, and have been extensively used in an array of arenas such as optoelectronics [1–4], biomedicines [5–7], catalysis [8–10], and separations [11–13]. In the coatings, the pores regulate the entry and exit of matter (photons, molecules, particles, etc.), thus determining the performances of the composite structures composed of the coatings and the substrates [14]. Consequently, the pore parameters, including pore size and size distribution, pore interconnection and accessibility, are essential for the coatings to maximize their performances. Also, the coating process to efficiently and controllably produce uniform nanoporous layers on various substrates is of critical importance.

Continuous efforts have been made to improve the pore structure as well as the manufacturing processes of nanoporous polymer coatings. However, it remains challenging for current processes to meet the demands from both sides. Macrophase separation of polymeric solutions, as the most extensively used process to develop porous coatings, allows the formation of highly porous coatings from a large number of polymers [15,16]. Frustratingly, the produced pores have poor uniformity and the pore sizes are scattered in a wide range from the nanometer to micrometer scale [17]. Consequently, such coatings are inferior in applications such as optical coatings and size-based separation where selectivity of pores dictates the performances. In contrast, chemical removal of one component of the coating materials is advantageous in producing uniform pores with designed sizes and shapes [18–20]. Unfortunately, the pore formation is relying on chemical reactions, and typically requires a long time, tedious reaction and purification operations. Moreover, both processes also face the same challenge, that is, it is practically difficult for them to build uniform coatings on large-area or nonplanar substrates. This severely hinders their applications in some very

* Corresponding author.

E-mail address: yongwang@seu.edu.cn (Y. Wang).

These authors contributed equally to this work.

important area. Therefore, it remains highly desired for efficient yet facile processes to produce surface coatings with uniform nanoscale porosities.

In this work, we manipulate the interactions between block copolymers (BCPs) and selective solvents, and develop such a long-desired process to coat nanoporous polymers with highly uniform and interconnected porosities on almost arbitrary substrates. In this process, BCPs are first coated on substrates, and then a small amount of swelling solvents is coated on the surface of the previously coated BCP layers (Fig. 1). The swelling solvent evaporates at room temperature within a few minutes, and simultaneously converts the initially dense BCP layers to highly porous coatings. This process proceeds very fast, relies on no chemical reactions, and produces well-defined, three-dimensionally interconnected, sub-50-nm pores. This process is exceptionally well-suited for the fabrication of nanoporous coatings on large-area, nonplanar substrates characterized by intricate surface geometries. Remarkably, any defects that may emerge during application within the porous structure can be efficiently repaired *in situ* through the reapplication of the swelling solvent—a process that can be conveniently executed for a second time. The nanoporous layers resulting from this sequential coating process demonstrate excellent antireflective and separation performance when applied to dense and porous substrates, respectively. We anticipate that this sequential coating strategy will also find interesting applications in the preparation of large-scale coatings having anti-fouling and anti-freezing functions.

2. Materials and Method

2.1. Materials

Polystyrene-*block*-poly(2-vinylpyridine) (PS-*b*-P2VP, abbreviated as S2VP, $M_n^{PS} = 53.0$ kDa, $M_n^{P2VP} = 21.0$ kDa, polydispersity index (PDI) = 1.17) was obtained from Tubang Polymer Materials Co., Ltd., China. Polystyrene-*block*-poly(2-dimethylaminoethyl methacrylate) (PS-*b*-PDMAEMA, $M_n^{PS} = 70.1$ kDa, $M_n^{PDMAEMA} = 21.5$ kDa, PDI = 1.16) was synthesized according to our previous work [21]. Polysulfone-*block*-poly(ethylene glycol) (PSF-*b*-PEG, $M_n^{PSF} = 62.5$ kDa, $M_n^{PEG} = 16.6$ kDa, PDI = 2.00) was obtained from Nanjing Bangding, China. Nylon microfiltration membranes with a

nominal pore size of ~ 0.8 μm were provided by Haining Shenghua Filtration Equipment Co., Ltd. (China) and used as the supports to prepare composite membranes. Monodispersed gold colloids with a diameter of 15 nm were obtained from British Biocell International. Acid orange 7 (>85%) was purchased from Aladdin, China. All other reagents including ethanol, chloroform, dichloromethane (DCM), tetrahydrofuran (THF), 1,4-dioxane (DOX) and toluene (TL) were of analytical grade and purchased from Shanghai Lingfeng Chemical Reagent Co., Ltd, China. Deionized water (conductivity: 8–20 $\mu\text{S}\cdot\text{cm}^{-1}$) was used in all tests.

2.2. Preparation of the nanoporous coatings

Typically, BCP was dissolved in chloroform with a mass concentration of 2%. Prior to usage, the solution was filtrated through a 0.22 μm polytetrafluoroethylene (PTFE) filter three times to remove any possibly present particulate impurities. For the investigation of swelling behavior, the BCP solution was spin-coated on cleaned silicon wafers (1.5 cm $\times$ 1.5 cm) at 2000 $\text{r}\cdot\text{min}^{-1}$ for 30 s to produce dense films. As-coated films were dried at 60 $^{\circ}\text{C}$ for 20 min to evaporate the residual solvent. The solvent pairs of ethanol mixed with another desired solvent (DCM, THF, DOX or TL) were used as the swelling agents. The selective swelling process was performed at room temperature (20 $^{\circ}\text{C}$) with a relative humidity of 20% and the swelling agents were coated on the substrate surfaces by dropping or spraying. For dropping coating, 20–50 μL of the swelling agent was dropped and spread evenly on the BCP film surface. The solvent-spread film was kept at ambience for a few minutes to evaporate the solvent naturally, thus producing the nanoporous coating. For spray coating, the swelling agent was sprayed on the film surface using a sprayer with the distance between the spraying nozzle and the film being maintained at ~ 2 cm. After spraying, the film was also waited for a few minutes to make sure the solvent was fully evaporated, and the nanoporous coating was obtained.

The nanoporous coatings were built on various substrates. Different objects with different materials and different shapes including a glass plate, a seal with a protruding symbol of “V”, a metal icon, a ceramic ornament, an egg and a glass tube were used as the substrates, respectively. For these substrates, the BCP solution with a mass concentration of 0.5% was spraying-coated on

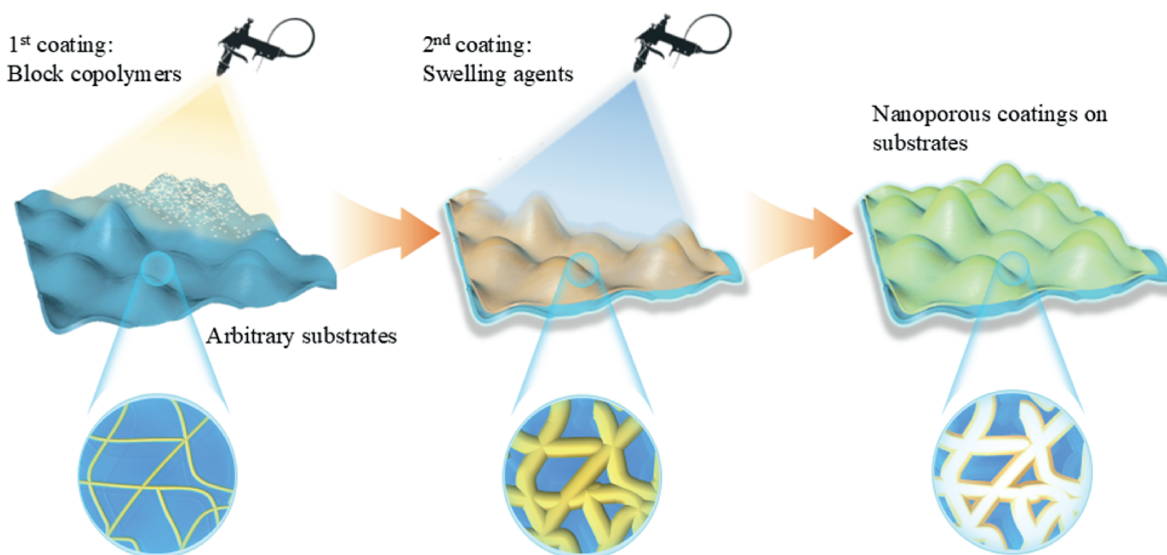


Fig. 1. Schematic illustration of the double-coating process to establish nanoporous coatings on substrate surfaces.

the surfaces producing thin layers, then the swelling agent was sprayed on the BCP-coated substrates to conduct the selective swelling and convert the dense layers to nanoporous coatings.

2.3. Applications of the nanoporous coatings as antireflection coatings and ultrafiltration membranes

For the application as antireflection coatings, the S2VP solution with a mass concentration of 0.8% was spin-coated on cleaned glass slides (7.6 cm × 2.5 cm), then the swelling agent was sprayed on the S2VP-coated slides to cavitate the S2VP layers.

For the application as separation membranes, macroporous nylon membranes were used as supports, and the S2VP solution with a mass concentration of 2% was first spray-coated on the supports using the spray apparatus (SEV-300EDN, Suzhou Second Automatic Equipment Co., Ltd, China) with a deposition volume of 13.5 μl·cm⁻². Then, the swelling agent was sprayed on the S2VP-coated nylon supports, and the S2VP layers were converted to nanoporous selective layers compositing on the nylon supports with the evaporation of the swelling agent.

2.4. Coarse-grained molecular dynamics simulations

Coarse-grained models constructed from all-atom simulations. All-atom molecular dynamics simulations were performed with OPLS-AA force-field and coarse-grained molecular dynamics simulations with Martini_v2.2 force field [22,23], they were both calculated in Gromacs 2022.2 [24]. Three-dimensional periodic boundaries and Verlet truncation scheme were used. The reaction-field method was used to calculate the electrostatic interaction, van der Waals interactions were calculated using the cut-off scheme with a truncation radius of 1.1 nm. Velocity-rescale method was used for temperature coupling with a time constant of 1.0 [25], and Parrinello–Rahman [26] method for pressure coupling in production phase with a time constant of 12.0.

2.5. General characterizations

The surface and cross-sectional morphologies of the samples were examined on a field emission scanning electron microscope (FESEM, Hitachi S-4800, Japan) at the accelerating voltage of 5 kV. The thicknesses and refractive indices of S2VP films before and after swelling were measured using a spectroscopic ellipsometer (Complete EASE M – 2000U, J. A. Woollam, USA) with an incidence angle of 70°.

The antireflection performances were evaluated using an ultraviolet–visible–near infrared spectrophotometer (UV-vis-NIR, Lambda 950, PerkinElmer, USA) to record the transmittance in the wavelength range of 400–2000 nm of the pristine and BCP-coated glass substrates. The separation performances of prepared composite membranes were characterized using a dead-end filtration module (Amicon 8010, Millipore, USA). For the permeability test, the membrane was subjected to pre-compacting for 10 min under the pressure of 20 kPa, making sure of a stable permeance. Then the test was carried out at the same pressure. The water permeance (L·m⁻²·h⁻¹·MPa⁻¹) was determined by calculating the volume of water passing through a unit area in unit time under unit transmembrane pressure. The monodispersed gold colloids with a diameter of 15 nm served as the feed solution to evaluate the rejection property. To avoid any adsorption of gold nanoparticles on the membrane surface, the composite membranes were pretreated with the acid orange 7 solution (5 mg·L⁻¹) for 20 min to neutralize the surface before rejection testing [27]. The concentrations of the feed and filtrate solutions were measured by a UV-vis absorption spectrophotometer (NanoDrop 2000c,

Thermo, USA) at the wavelength of 520 nm to determine the rejections.

3. Results and Discussion

3.1. Molecular simulation

We previously reported that the dispersed phases in block copolymers can be converted to interconnected nanoporosity based on the mechanism of selective swelling-induced pore generation [28–31]. Typically, selective swelling-induced pore generation requires to be performed at elevated temperatures, *e.g.* 50–70 °C, as rising temperature enhances segmental mobility of the blocks. However, heating solvents to a temperature close to their boiling points not only consumes much energy, but also poses serious environment and safety risks to the process, which is highly unfavorable for practical applications [32]. Especially, heating and using of large volumes of solvents are strongly not applicable to the coating of large-area substrates. We understand that elevating temperature in selective swelling-induced pore generation is to sufficiently enhance the chain mobility of the block copolymer. Considering that chain mobility can also be efficiently enhanced by exposing the polymer to its good solvent, that is, the plasticization effect [33], we anticipate that selective swelling-induced pore generation may also take place at room temperature if an additional component, a good solvent to the majority block, is incorporated into the swelling agent.

To verify our anticipation, we first perform molecular simulation on the process of selective swelling of S2VP, the most extensively used block copolymers in the studies of selective swelling-induced pore generation. With regard to the selection of swelling agents, the affinity between solvents and the constituent blocks of S2VP is the key factor that needs to be considered. The Flory–Huggins interaction parameter, χ_{sp} , is usually used to evaluate the affinity [34]:

$$\chi_{sp} = \frac{V}{RT} (\delta_s - \delta_p) + 0.34 \quad (1)$$

where V , R , T , δ_s , and δ_p are the molar volume of solvent, the gas constant and Kelvin temperature, the solubility parameters of the solvent and the polymer, respectively. When $\chi_{sp} < 0.5$, the solvent is considered to have a strong affinity for the polymer (*i.e.* a good solvent for the polymer), otherwise, the solvent has a weak affinity for the polymer. According to Eq. (1), ethanol is a good solvent for P2VP as $\chi_{ethanol/P2VP} = 0.38$ but a poor solvent for PS as $\chi_{ethanol/PS} = 1.65$. DCM has a strong affinity for both P2VP and PS blocks as $\chi_{DCM/P2VP}$ and $\chi_{DCM/PS}$ are 0.34 and 0.41, respectively. A binary mixture of ethanol, a good solvent for P2VP, and DCM, a good solvent for PS, was used as the swelling agent to perform the simulation. We constructed a model of S2VP coarsely granulated with 27% volume fraction of the P2VP block based on the Martini force field, which contains 153 PS repeat units and 60 P2VP repeat units. Coarse-grained molecular dynamics simulations were performed to compare the microscopic process course of swelling of the S2VP film in pure ethanol and in the 30% (volume ratio) DCM/ethanol mixture at room temperature. In the system with 100 chains of PS₁₅₃–P2VP₆₀ of the same configuration as the starting point, the addition of solvents in the x -direction simulates the process of solvent entry into the S2VP film. A comparison of the morphological snapshots before and after the simulation shows that the solvent penetrating into the film would cause swelling of the film (Fig. 2(a), (b)). By recording the mean square displacement of PS and P2VP blocks with the solvent penetration time (Fig. S1, in Supplementary Material), we could evaluate the swelling degrees

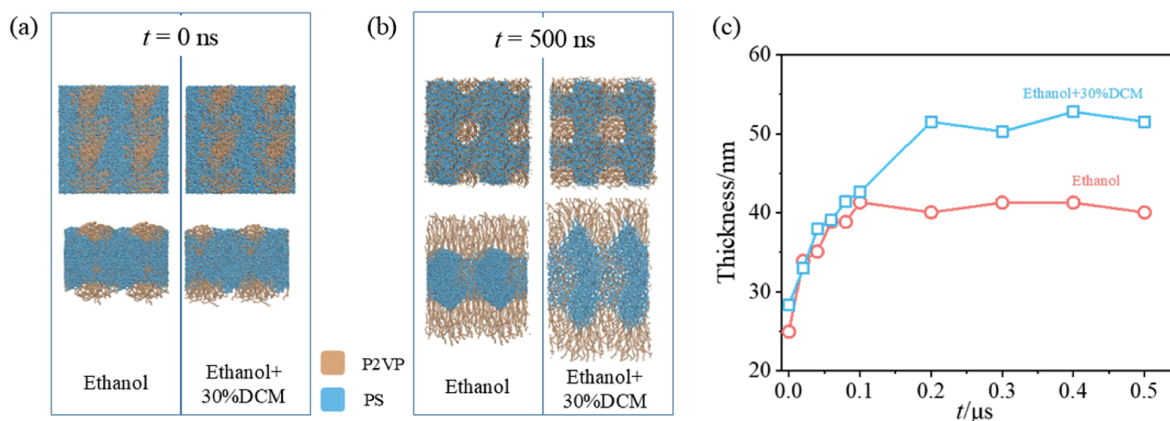


Fig. 2. Simulation snapshots of solvent entry into the S2VP film during solvation corresponding to (a) the initial configuration and (b) the results at the moment of 500 ns. (c) Changes in thickness of the S2VP film during swelling as a function of simulation time.

of PS and P2VP blocks in solvents. It was found that ethanol could hardly swell PS blocks, while the addition of DCM caused a small degree of swelling. Both pure ethanol and the 30% DCM/ethanol mixture enabled the swelling of P2VP blocks, and the latter led to a higher swelling degree. Accordingly, there was a more significant increase in the film thickness of the S2VP film in the 30% DCM/ethanol mixture (Fig. 2(c)). The simulated results imply that the DCM/ethanol mixture is capable of selectively swelling S2VP films enabling the formation of pores at room temperature.

3.2. Effects of the volume and composition of the swelling agents

We then experimentally swelling treated S2VP to generate nanoporosity. The experimentally used S2VP has a 27% P2VP volume fraction, the same with that in simulation. According to the phase diagram of diblock copolymers [35], the P2VP phase will form a cylindrical morphology dispersed in the PS matrix. The S2VP solution was spin-coated on a silicon wafer ($1.5\text{ cm} \times 1.5\text{ cm}$) to produce the dense film (Fig. S2). Unlike the conventional process of selective swelling where the films are completely soaked in swelling baths with large volumes (typically 10–1000 times of the volume of the films together with the substrates), herein instead of bath swelling, we spread very little volume of swelling agents down to a few tens of μl directly on the film surface to perform selective swelling-induced pore generation at room temperature as shown in Fig. 3(a). The swelling agent of ethanol mixed with 30% DCM (volume ratio, 40 μl) was evenly spread on the S2VP film surface by drop coating. Diffusion of the swelling agent downward into the bulk interior of the film and evaporation of the swelling agent upward to the atmosphere took place simultaneously. The thickness of the film investigated in the present work was in the scale of several hundreds of nm, and the diffusion of the solvent into the polymer film occurred very fast, which finishes within a few seconds or even shorter [36]. In contrast, the evaporation of the swelling agent from the surface took a few minutes. That is, the diffusion of the swelling agent into the S2VP film would soon reach equilibrium, and maintained in this equilibrated state until the complete evaporation of the swelling agent on the film surface. After the diffusion of the swelling agent into the film, ethanol selectively permeated into the P2VP minority phase and strongly swollen them, leading to the volume expansion of P2VP domains. DCM could diffuse into the PS majority blocks because of their strong affinity and the increased segmental mobility of PS chains, allowing the plastic deformation of the PS matrix. Swollen P2VP cylinders squeezed the PS matrix and merged with neighboring ones, forming a continuous P2VP phase. After the swelling agent

on the film surface was fully evaporated, the swelling agent diffused in the film interior began to evaporate. With the loss of the swelling agent in the film, the PS matrix was frozen and remained in a moderately deformed state, while the strongly swollen P2VP chains were collapsed and condensed, thus turning the spaces initially occupied by the swollen P2VP phases into pores with pore wall lined with condensed P2VP chains. The formation of abundant pores would result in an increase in film thickness, as indicated by the change in the apparent color of the S2VP film coated on the silicon wafer (Fig. S3). A bi-continuous porous morphology throughout the surface and entire thickness of the film was evidenced as shown in the surface and cross-sectional SEM images (Fig. 3(b)). Such a porous morphology is similar to the morphology of BCP films subjected to conventional selective swelling in a swelling bath at elevated temperatures [29]. Significantly, this process of coating swelling agents on the BCP film surface requires only μl -scale volume of the swelling agent, and it takes only a few minutes, which is much faster than the conventional selective swelling typically taking hours.

We then investigated the influence of the volume of the swelling agent (20–50 μl) on the swelling behavior. We tracked the mass changes of the swelling agents consisting of ethanol mixed with 20% (volume ratio) DCM until they were evaporated completely (Fig. 3(c)). The evaporation processes lasted for ~110, 190, 270 and 350 s when the used swelling agents were 20, 30, 40 and 50 μl , respectively. That is, the total swelling durations were increased with the rising volume of the swelling agents. As a result, the average porosities were consequently increased with the volume of the swelling agents (Fig. S4). However, this increment in porosity was relatively small, implying that the effect of the volume of the swelling agent on the swelling degree was weak and a minimum supply of swelling agent was enough for producing a high porosity. Nevertheless, the used volumes of the swelling agent affect the swelling evenness. With the usages of 20 μl and 30 μl , the swelling agent was more difficult to spread evenly on the film surface. The colors in the marginal areas of the films after swelling were observed to be different from the central areas (insets in Fig. S4), intuitively reflecting the uneven swelling of the film. Increasing the volume of the swelling agent to 40 μl and 50 μl , the appearance of the films showed uniform colors after swelling. Therefore, bearing the principle of consuming the swelling agent as little as possible while guaranteeing the uniformity of swelling in mind, 40 μl swelling agent was preferred for the S2VP film with a size of $1.5\text{ cm} \times 1.5\text{ cm}$.

We further investigated the swelling behavior of the S2VP film under different swelling agent compositions. We used a fixed

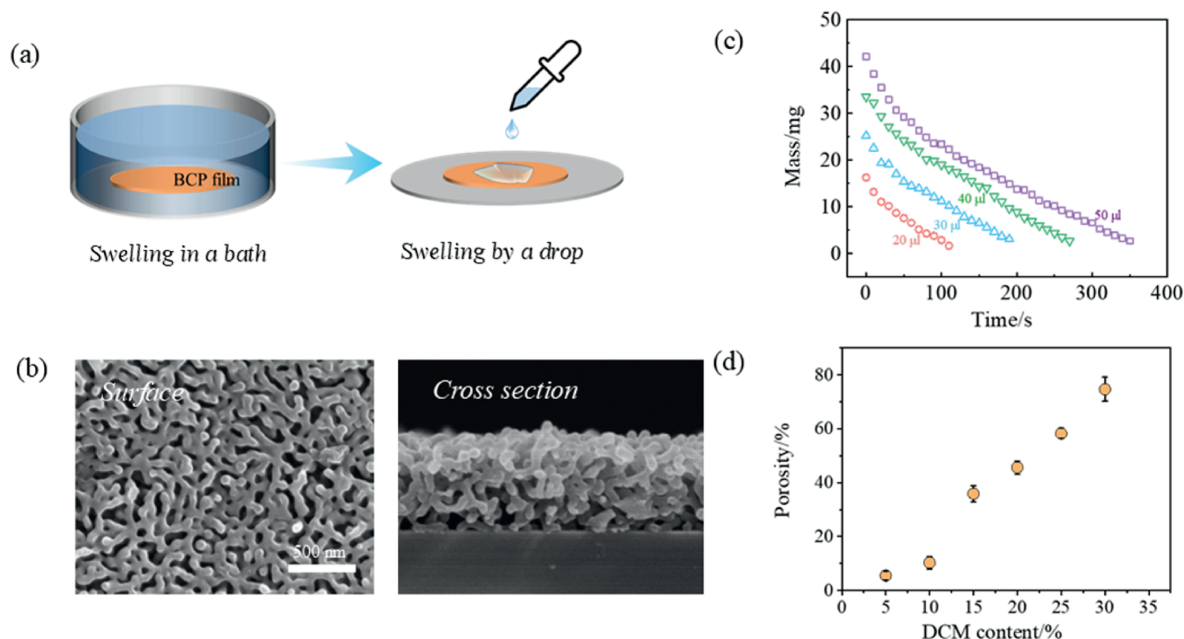


Fig. 3. (a) Schematic illustration for the different swelling strategies. (b) The surface and cross-sectional SEM images of the S2VP film prepared with 40 μl of the swelling agent of ethanol mixed 30% (volume ratio) DCM. The scale bar applies to both images. (c) Mass changes of different volumes of ethanol mixed with 20% (volume ratio) DCM during natural evaporation after being coated on the S2VP film. (d) The porosities of S2VP films prepared with swelling agents containing various contents of DCM.

volume of the swelling agent of 40 μl while changed the DCM content (5% to 35%) to swell the S2VP film. The film porosity had a significant increase with the DCM content changed from 5% to 30%

until a steep drop at the 35% DCM content as shown in Fig. 3(d). The morphological evolution of the film was observed by SEM (Fig. S5). At the DCM content of 5% and 10%, only shallow circular pores

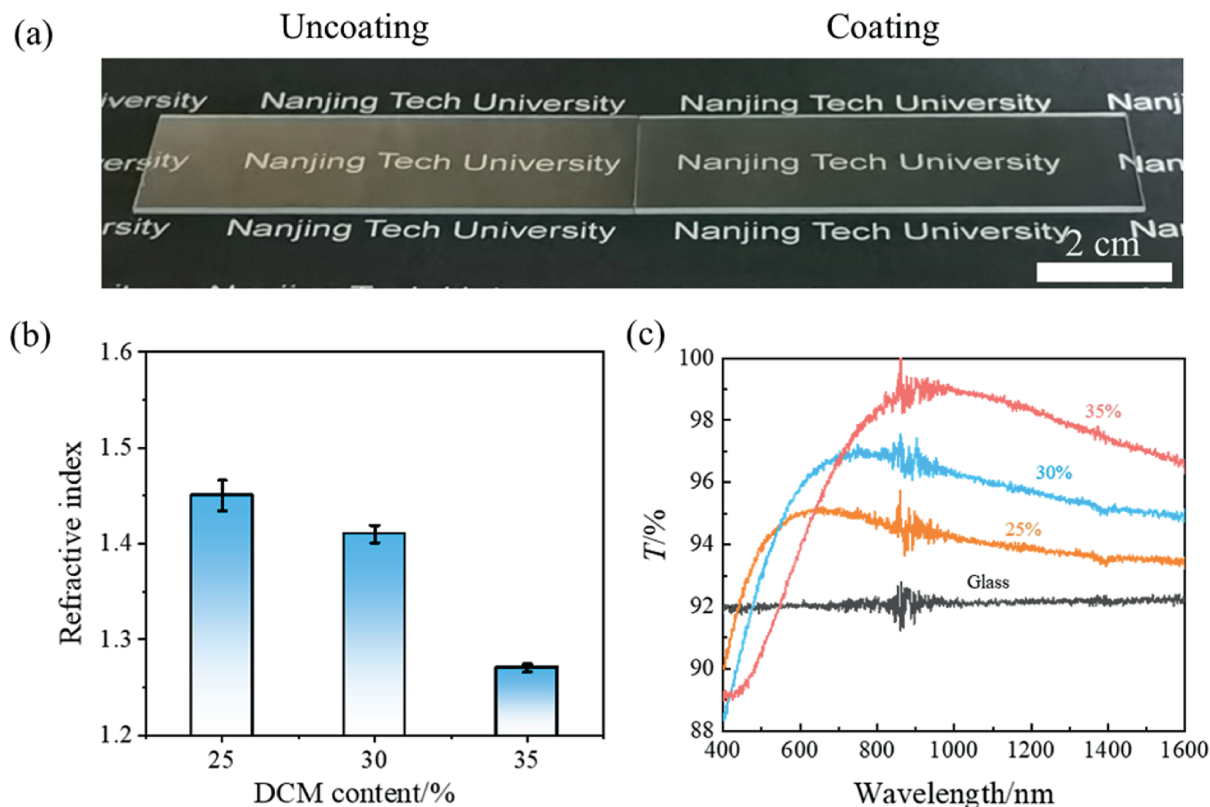


Fig. 4. Nanoporous S2VP films prepared by spray swelling as antireflection coatings. (a) The photograph of a bare glass slide (left) and a glass coated with the nanoporous S2VP film prepared with 35% DCM (right). (b) The refractive indexes of nanoporous S2VP coatings prepared with different DCM contents. (c) The transmittance spectra of glass slides coated with nanoporous S2VP films prepared with different DCM contents.

appeared on the film surfaces and failed to pierce the film thickness to form continuous channels, and the films exhibited a low porosity of 5.5% and 10.3%, respectively. As the DCM content increased to 15% and 20%, the channel-like pores were gradually formed and interconnected both in the surface and cross section of the films, thus the porosity was rapidly increased to 35.9% and 45.7%, respectively. When the DCM content was 25%, the porosity reached 58.3%. Further increasing the DCM content to 30%, the film presented a typical bi-continuous morphology, giving a fairly high porosity value of 74.7%. 35% DCM content caused the dissolution of the S2VP film by micellization and destroyed the structural integrity of the film, leading to sharply decreased thickness and nearly zero porosity. Micellar structures could be clearly observed on the film surface as shown in Fig. S5. Apparently, the DCM content has a much greater effect on the film morphology compared to the effect of the volume of the swelling agent. This is because the strong affinity of DCM to the PS blocks could significantly change the segmental mobility of the film matrix during selective swelling. The higher DCM content in the swelling agent would result in more DCM diffused into the PS matrix, leading to the higher mobility of PS chains. As a consequence, the PS matrix experiences plastic deformation to a larger degree, eventually resulting in larger pores and higher porosity.

In addition to DCM, other solvents having favorable interactions with PS were chosen and mixed with ethanol to be used as the swelling agent to compare their swelling effects. Three solvents including THF, DOX and TL were investigated, and their contents in swelling agents were fixed at 20% (volume ratio). The porosities of S2VP films after swelling with 40 μ l swelling agent were measured to be 45.7%, 48.3%, 51.4% and 55.1% for DCM, THF, DOX and TL, respectively (Fig. S6). We know that the affinity between solvents and the blocks of BCP determines the swelling degree of BCP films. Compared with DCM, THF has a stronger affinity for PS as $\chi_{\text{THF/PS}}$ is calculated to be 0.36 according to Eq. (1), lower than $\chi_{\text{DCM/PS}}$. Therefore, THF produced a slightly higher porosity than DCM. Furthermore, the volatility of these solvents is also a key factor determining the final porosity of S2VP films. The solvents with low volatility take more time to dry under the ambient condition, which means the swelling durations for them are longer. For example, DOX has a weaker affinity for PS than DCM and THF as $\chi_{\text{DOX/PS}}$ is calculated to be 0.47. However, it produced a higher porosity because DOX is less volatile and leads to a longer swelling duration and consequently a higher swelling degree. In the case of TL, it has both a strong affinity for PS and a less volatile nature, reasonably producing the highest porosity among the four solvents. As shown in Fig. S7, the surface all exhibited a bi-continuously porous morphology for the S2VP films prepared with these four solvents, however, from the surface SEM images, it is obvious that the films were cavitated to increasing degrees in the order of DCM < THF < DOX < TL, which is consistent with their porosities.

3.3. Nanoporous coatings by spray swelling

The above results demonstrate that coating a very small volume of swelling agents on BCP films to conduct selective swelling is highly efficient and solvent-saving to produce porous BCP films at room temperature. However, it may not work well for the film with a large area because of the difficulty in operation to coat the swelling agents evenly on the film surface by solvent dropping. From the standing point of large-scale manufacturing and practical applications, processes with wider applicability are needed. Therefore, we improved the process by spraying the swelling agents on BCP films instead of dropping, that is, spray swelling. Similarly, we used the mixture of ethanol and DCM as the swelling

agents and investigated the swelling effect under different DCM contents. With the DCM contents changed from 15%, 20%, 25%, 30% to 35%, the porosity was correspondingly raised from 12.3%, 18.1%, 42.8%, 56.3% to 74.9%, respectively (Fig. S8). Nevertheless, the film thickness was significantly decreased when further increasing the DCM content to 40% because of the dissolution of the S2VP film. Clearly, the changes in thickness and porosity along with the DCM content in the spraying coating follow exactly the same trend as the case of the dropping coating. The difference lies in that the S2VP film treated by the spraying coating presented a lower porosity than the one treated by dropping coating when the swelling agent with the same composition was used. This should be ascribed to the faster evaporation of DCM than ethanol during spraying, which results in lower DCM content spread on the film surface. Consequently, the actual content of DCM to swell the film was below than the content we set in the sprayer, leading to the reduced swelling degree. In addition, the spraying durations were tuned, which would change the volume of the swelling agent sprayed on the film surface, so as to investigate their effect on the selective swelling. The porosities of S2VP films remained nearly unchanged with the spraying duration increased from 2, 4 to 6 s (Fig. S9).

3.4. Application as antireflective coatings

The nanoporous coatings prepared by spray swelling of BCP films are expected to find important applications in diverse fields. Herein, we first explored their use as antireflection coatings. We

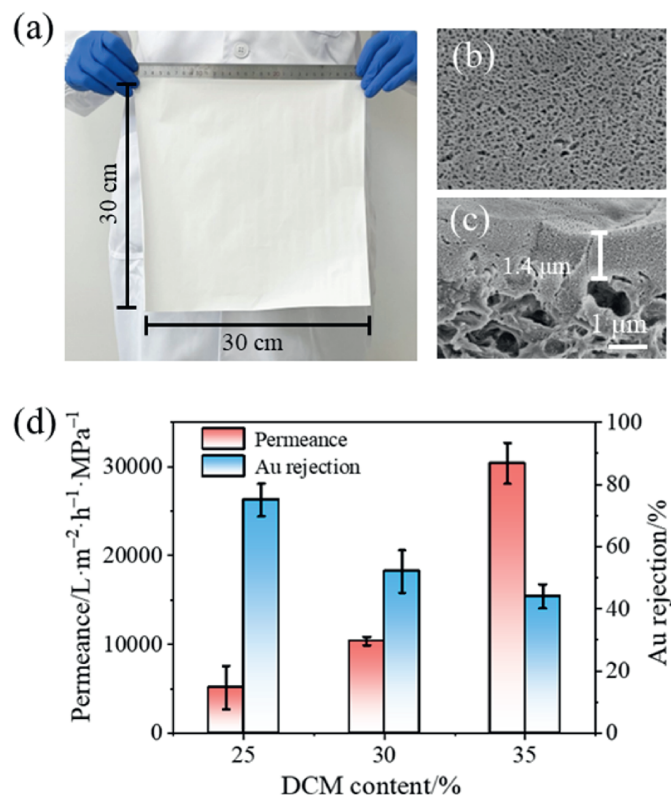


Fig. 5. Nanoporous S2VP films prepared by spray swelling as separation membranes. (a) The photograph of a 30 cm $\times$ 30 cm composite membrane with the nanoporous S2VP coated on the surface of the nylon substrate. The (b) surface and (c) cross-sectional SEM images of the nanoporous S2VP coatings after spraying the swelling agent of ethanol mixed with 30% DCM. (d) The separation performances of the S2VP composite membranes prepared with different DCM contents. The scale bar given in (c) applies to all SEM images.

spin-coated the S2VP solution with a mass concentration of 0.8% on a glass slide and obtained a dense S2VP layer. The coated slide was then treated by spraying the swelling agent of ethanol mixed with different contents of DCM on the surface to convert the S2VP layer into the porous structure. The photographs of the bare slide and the porous S2VP layer-coated slide are shown in Fig. 4(a). We can clearly notice that the bare glass exhibited a slight tint of yellow, while the coated glass became clear and showed a higher transparency than the bare one. For the glass slide with a refractive index of 1.52 we used, the index of an antireflective layer coated on the glass substrate should be 1.23 to have zero reflectance in air [37]. The closer to 1.23 the refractive index of the coated S2VP layer, the higher the transmittance of the glass. Fig. 4(b) displays the refractive index of the S2VP layer after swelling. When the DCM content of 25% was used, the refractive index of the S2VP layer was measured to be 1.45 by ellipsometry. Increasing the DCM content to 30% and 35% led to the refractive index decreased to 1.41 and 1.27, respectively. We then recorded the transmittance spectra of the glass slides coated with the porous S2VP layers prepared with different DCM contents by UV-vis-NIR spectrophotometry. As shown in Fig. 4(c), the bare glass slide exhibited a transmittance of ~92%. All the glass slides coated by nanoporous S2VP layers demonstrated enhanced transmittance. The nanoporous S2VP layer prepared with 25% DCM content yielded a maximum transmittance ($T_{\max}$) of 95%. The $T_{\max}$ was enhanced to 97% for the case of swelling with 30% DCM content. Increasing the DCM content to

35% further improved the $T_{\max}$ to 99% because of the decreased refractive index of the porous S2VP layer. The spray swelling process to produce porous BCP layers not only provides a practical way to prepare antireflection coatings but also enables the easy control of the transmittance of the glass slide by adjusting the composition of the swelling agents thus changing the obtained refractive index of the BCP layer.

3.5. Application as ultrafiltration membranes

To explore the potential of this spray swelling process in producing nanoporous separation membranes for ultrafiltration, a piece of composite membrane (30 cm × 30 cm) with an S2VP layer atop the porous nylon support was prepared and subjected to spray swelling (Fig. 5(a)). The pristine composite membrane presented a smooth appearance, and the surface and cross-sectional SEM image demonstrated the dense nature of the S2VP layer (Fig. S10(a), (b)) with a thickness of 0.8 μm. The spray swelling was performed as shown in the attached Movie S1. After spray swelling, the S2VP layer turned to be nanoporous both on the surface and the cross section (Fig. 5(b), (c)). As the DCM content in the swelling agent was changed from 25% to 30% and 35%, the thickness of the porous S2VP layer was increased from 1.0 μm to 1.4 and 1.8 μm, respectively (Fig. 5(c) and Fig. S10). The permeance and rejection to 15 nm gold nanoparticles were then tested to examine the separation performances of the prepared membranes

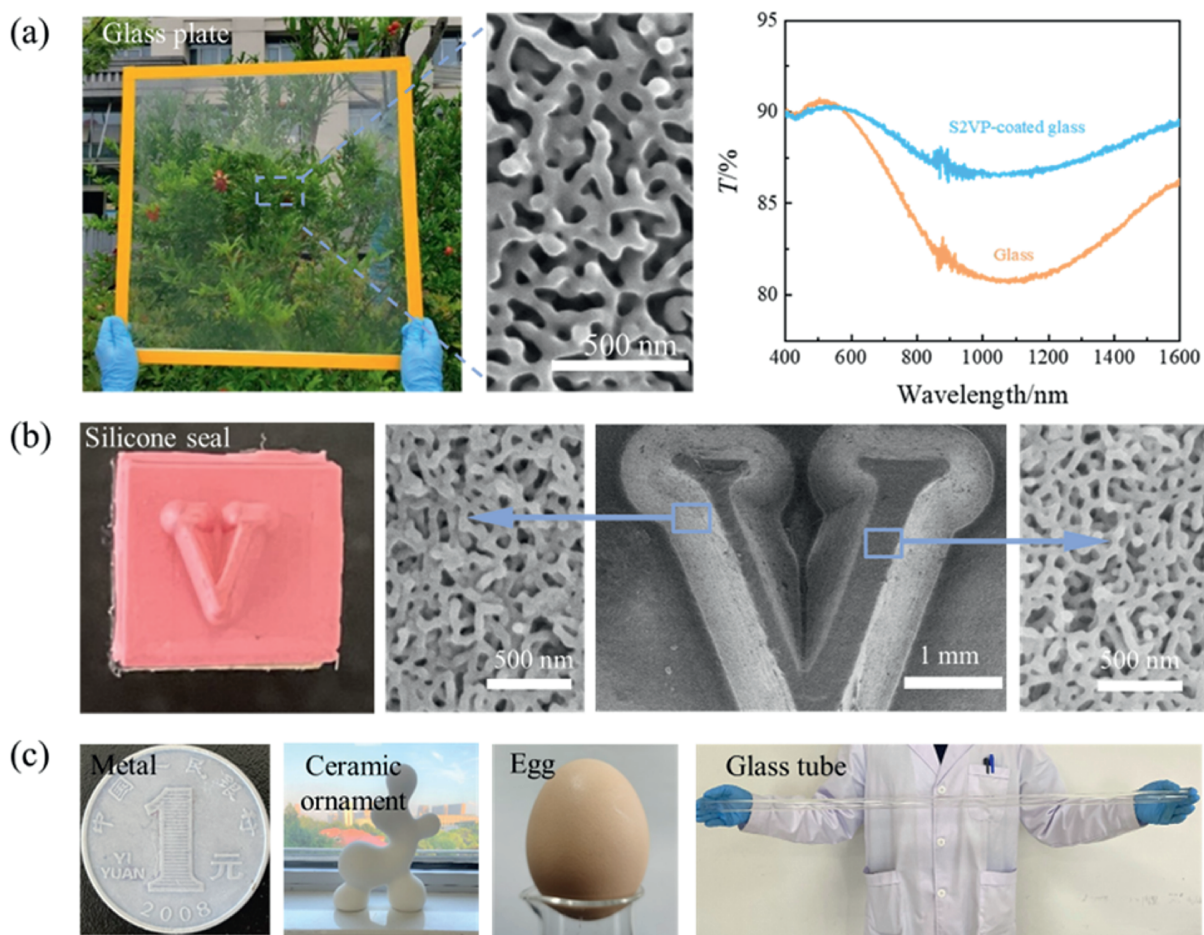


Fig. 6. The photographs and surface morphologies of nanoporous S2VP films coated on different substrates: (a) a glass plate, (b) a silicone seal, (c) a metal coin, a ceramic ornament, an egg and a glass tube. The transmittance spectra of the glass plate coated with and without nanoporous S2VP films are given in (a).

(Fig. 5(d)). The composite membrane showed the gradually rising water permeance of 5320, 9980 and 28370 L·m⁻²·h⁻¹·MPa⁻¹ with the DCM content increased from 25%, 30% to 35%, respectively. Correspondingly, the rejection was 77%, 54%, and 44%. Clearly, the nanopores in thus-produced porous S2VP layers were interconnected and penetrated the entire layer, capable of serving as sieving channels for membrane separations. This spray swelling process is highly efficient in building nanoporous selective layers on macroporous substrates, enabling the preparation of composite membranes with tunable ultrafiltration performances.

3.6. Nanoporous coatings on complex or large substrates

In addition to producing nanoporous coatings on substrates with a flat surface, we further investigated the capability of this double-coating process to build nanoporous layers on various substrates with different materials and different shapes. Different objects were used as the substrate as shown in Fig. 6. The BCP solution and the swelling agent of ethanol mixed with 30% DCM were sequentially coated on substrate surfaces. A glass plate with a larger size of 50 cm × 50 cm was used as the substrate. Similarly, the S2VP film was coated on the surface by spray coating and then subjected to spray swelling. As expected, the porous morphology was observed on the surface. We examined the antireflection performance of the porous coating by transmittance spectra, and the result showed that the transmittance of the glass was improved by ~5% (Fig. 6(a)). Further, a seal with a protruding symbol of “V” was used as the substrate. After sequential coating of the S2VP solution and the swelling agent, both the front and side of the “V” symbol presented a bi-continuous porous structure (Fig. 6(b)). Moreover, we built S2VP coatings on the surfaces of a metal coin, a ceramic ornament, a biological substrate (an egg), and a glass tube with a length of 1 m and a diameter of 24 mm (Fig. 6(c)).

The successful formation of the porous structure was also demonstrated (Fig. S11). Clearly, this spraying swelling method is capable of facile preparation of nanoporous coatings on various materials of substrates with planar or nonplanar surfaces. It should be noted that the uniformity of coatings on different substrates was significantly influenced by the spraying technique employed. Coatings fabricated through automated spraying processes, which enable precise parameter control, exhibited superior uniformity in comparison to those produced through manual spraying. Therefore, an appropriate spraying method can be carefully selected in accordance with specific application requirements.

3.7. Universality of the double-coating process

The universality of the double-coating process was explored by using another two BCPs, PS-*b*-PDMAEMA and PSF-*b*-PEG, to prepare nanoporous coatings (Fig. 7(a)). The dense films were prepared by spin-coating BCP solutions on silicon wafers. Then ethanol mixed with different DCM contents were spray-coated on the surfaces to swell PS-*b*-PDMAEMA films, while the PSF-*b*-PEG films were swelled with ethanol mixed with different TL contents as swelling agents. The porosities of PS-*b*-PDMAEMA films were increased with the DCM contents changed from 10%, 15%, 20% to 25%, and reached a highest porosity of 42.9% (Fig. 7(b)). The bi-continuous porous structure was formed in surface and cross section as shown in Fig. 7(c). Then, the porosity was decreased because of the micellization of PS-*b*-PDMAEMA when the DCM contents were 30% and 35%. At 40% DCM content, the PS-*b*-PDMAEMA film was dissolved, resulting in zero porosity. For PSF-*b*-PEG films, the porosity reached the highest value of 48.9% (Fig. 7(d)) when the TL content was 35%, and the porous structure also spanned through the entire film thickness (Fig. 7(e)). It turns out this double-coating process works for various BCPs, including not

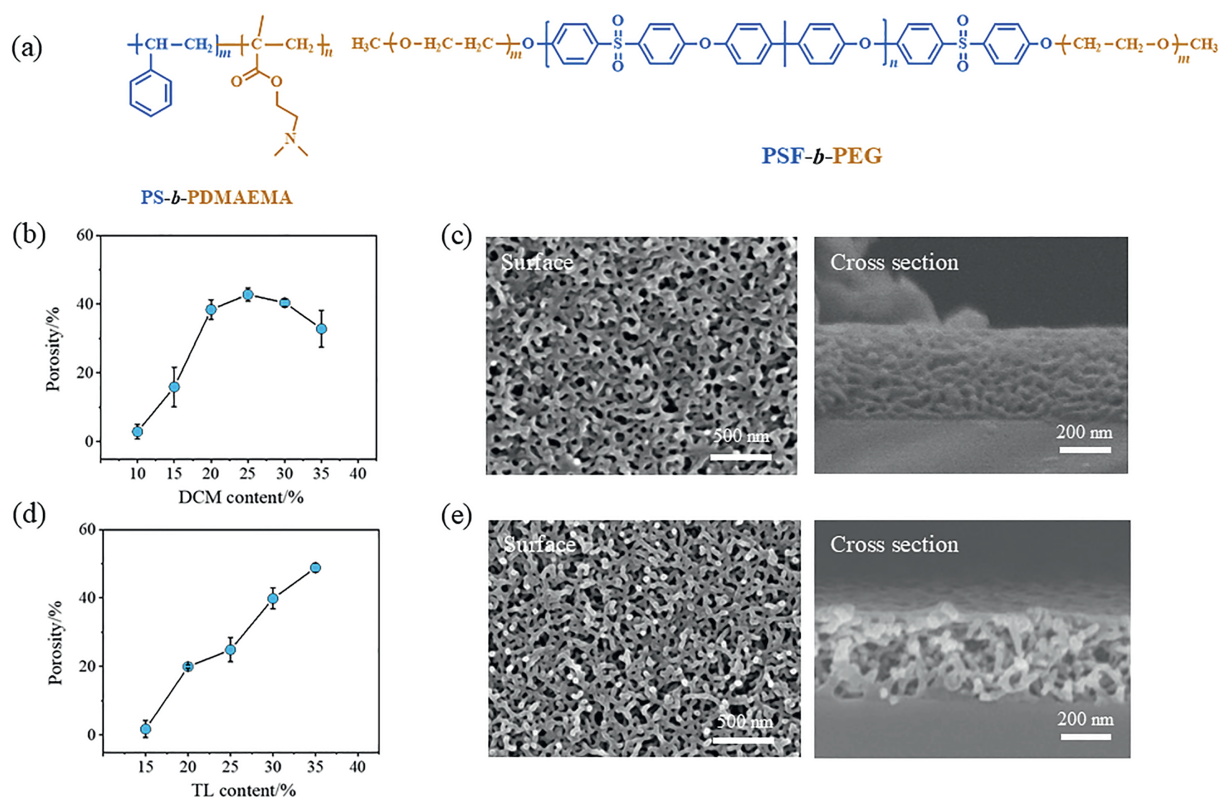


Fig. 7. (a) The chemical structures of BCPs of PS-*b*-PDMAEMA and PSF-*b*-PEG. Porosities of (b) PS-*b*-PDMAEMA films and (d) PSF-*b*-PEG films prepared by spraying the swelling agent of ethanol mixed with different contents of DCM and TL on the film surfaces. The surface and cross-sectional SEM images of (c) the PS-*b*-PDMAEMA film and (e) the PSF-*b*-PEG film prepared with 25% DCM and 35% TL, respectively.

only the PS-based BCPs with different minority blocks but also PSF-based BCPs with high glass transition temperature (T_g) polymers as the majority block.

3.8. In situ repairing defects in nanoporous coatings

Given the nondestructive nature of selective swelling-induced pore generation as well as the extreme ease of the double-coating process to produce nanoporous coatings on substrates, it can be anticipated that any damage on the porous structure during usage could be repaired by re-applying the swelling agent onto the films, thus re-constructing the porous structure (Fig. 8(a)). We prepared a nanoporous PSF-*b*-PEG layer on a glass slide as an antireflection coating, then exposed the glass to daylight irradiation (approximately $100 \text{ mW} \cdot \text{cm}^{-2}$) for 100 days. The pristine glass slide coated with the PSF-*b*-PEG layer exhibited a T_{max} of 99%, whereas, after daylight irradiation, the T_{max} was decreased to 97% as a result of the degradation in the porous structure. Then we spray-coated ethanol mixed with 35% TL on the surface to re-swell the PSF-*b*-PEG layer. Interestingly, the PSF-*b*-PEG layer was recovered to the highly porous morphology, and the T_{max} correspondingly went back up to 99% (Fig. 8(b), (c)). Furthermore, we simulated another situation of external damage by abrasion with sandpaper on the nanoporous PSF-*b*-PEG layer (Fig. 8(d)). Obvious cracks and closed pores appeared on the surface of the PSF-*b*-PEG layer after abrasion. Surprisingly, spray-coating the swelling agent

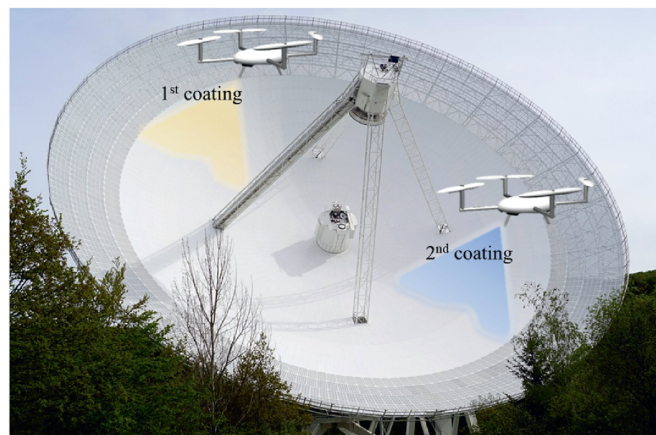


Fig. 9. The schematic of building antireflection coatings on large astronomical lenses by the double-coating process.

onto the surface enabled the reformation of nanopores and largely remedied the cracks (Fig. 8(e)). That is, the double-coating process is not only effective in constructing nanoporous layers but also in repairing defects. It has the potential to significantly prolong the service life of nanoporous coatings, which is highly desired in real-world applications.

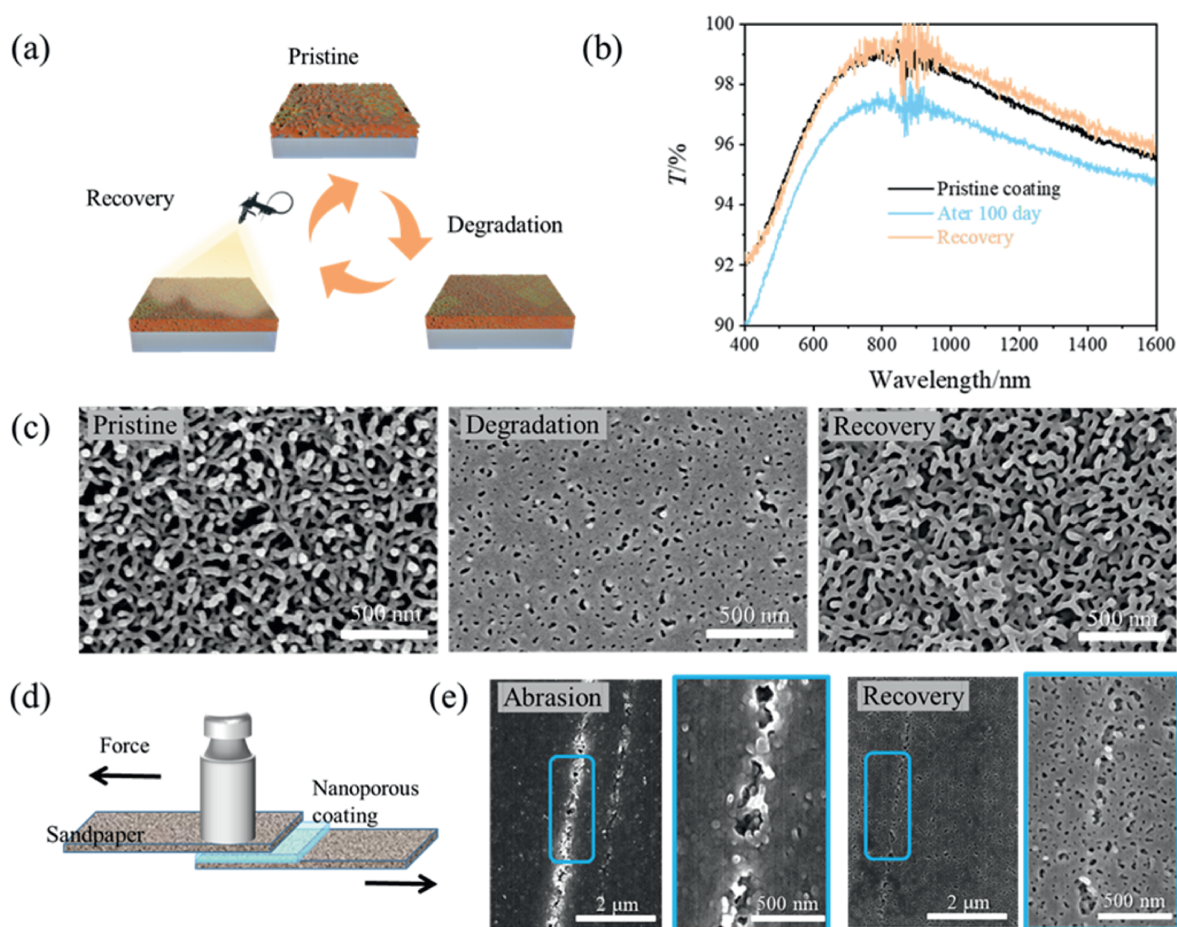


Fig. 8. (a) The schematic of repairing defects in nanoporous coatings. (b) The transmittance spectra and (c) surface SEM images of the glass slide coated with the nanoporous PSF-*b*-PEG film before and after degradation and subsequent recovery. (d) The schematic of abrasion treatment on the glass slide coated with the nanoporous PSF-*b*-PEG film, and (e) the SEM images of the film after abrasion and recovery.

Considering the two unique advantages of this double-coating process: (1) it is able to rapidly produce nanoporous coatings on large, nonplanar substrates, and (2) defects in the coatings can be *in situ* repaired by another spraying of the swelling agents, we image that we can adopt this process to *on-site* build antireflection coatings on large astronomical lenses by sequentially spraying the block copolymer solutions and the swelling agents by drones. Moreover, defects that appear due to long-time exposure to ambience may be on-demand repaired by flying the drone carrying the swelling agents to the defective places and spraying the swelling agents for another time (Fig. 9, Movie S2).

4. Conclusions

In summary, we develop a facile and fast process to produce nanoporous polymer coatings feasible for arbitrary substrates. This process relies on the delicate manipulation of interactions between block copolymers and selective solvents, and simply contains sequential coating of block copolymers and swelling agents on the substrates, and interconnected nanopores are produced by the mechanism of selective swelling-induced pore generation. For the preparation of S2VP coatings on the substrates with relatively small areas and flat surfaces, S2VP solutions were spin-coated on substrates, then μ -scale swelling agents were drop-coated on the surfaces. Leaving the swelling agent volatilized naturally in few minutes could simply realize pores formation in S2VP films. The component of swelling agents plays a great role in the swelling degree. Higher DCM contents lead to higher swelling degrees and consequently larger porosities. The amount of swelling agent used for swelling has a weak effect on the swelling degree, while determines the uniformity of swelling. For the substrates with large lateral sizes and complex surface features, sequentially spray coating of S2VP and swelling agents on the surfaces of substrates allow the preparation of nanoporous coatings easily. We manifested the applications of this process in producing antireflection coatings and separation membranes with tunable performances. Interestingly, the defects in nanoporous coatings that may occur during usage can be repaired by simply spraying the swelling agent again. Considering the fast, facile, and scalable inheritance of this sequential coating process, we believe it would be very much desired for the large-scale manufacturing of nanoporous coatings for practical applications in various fields.

CRedit Authorship Contribution Statement

Jiemei Zhou: Writing – original draft, Investigation, Data curation. Xiang Ying: Writing – original draft, Investigation, Data curation. Daiwen Li: Investigation. Mingjie Wei: Investigation. Xiangyue Ye: Investigation. Yong Wang: Writing – review & editing, Supervision, Methodology, Funding acquisition, Conceptualization.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

Financial support from National Science Foundation of China (22438005) and the Natural Science Foundation of Jiangsu Province (BE2022056-3) is gratefully acknowledged.

Supplementary Material

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.cjche.2025.08.007>.

References

- [1] S.Y. Leo, Y.F. Zhang, J. Jiang, N.Q. Lin, P. Jiang, C. Taylor, Reconfigurable anti-reflection coatings enabled by PDMS oligomer infusion in templated nanoporous polymer films, *ACS Appl. Mater. Interfaces* 16 (42) (2024) 57792–57803.
- [2] L. Zhang, A.N. Zhang, S.M. He, G.Q. Zheng, F.R. Zeng, Y.Z. Wang, B.W. Liu, H.B. Zhao, Biomimetic nanoporous transparent universal fire-resistant coatings, *ACS Appl. Mater. Interfaces* 16 (15) (2024) 19519–19528.
- [3] B.H. Yu, Z.J. Huang, D. Fang, S.D. Yu, T. Fu, Y. Tang, Z.T. Li, Biomimetic porous fluoropolymer films with brilliant whiteness by using polymerization-induced phase separation, *Adv. Mater. Interfaces* 9 (1) (2022) 2270001.
- [4] X.M. Zhu, C.C. Zhao, W.W. Zhang, B. Zhang, M.T. Sun, X.H. Chen, V.I. Belotelov, Y.J. Song, Structural color control of CoFeB-coated nanoporous thin films, *Coatings* 11 (9) (2021) 1123.
- [5] T. Walsh, Z. Hadisi, S.M.H. Dabiri, S. Hasanpour, S. Samimi, M. Azimzadeh, M. Akbari, Facile roll-to-roll production of nanoporous fiber coatings for advanced wound care sutures, *Nanoscale* 16 (33) (2024) 15615–15628.
- [6] T.X. Zheng, N.Y. Yang, J.P. Deng, W. Dong, L.F. Feng, J.P. Yang, X.J. Cai, Y. Liu, M. C. Qi, Multifunctional Sr/Zn-doped TiO₂ micro/nanoporous coating enhances osseointegration by modulating signaling crosstalk of bone-related cells, *Chem. Eng. J.* 511 (2025) 161734.
- [7] L. Yu, Z.Y. Guo, Y.C. Yin, H.S. Sun, Y.X. Yu, X.H. Ni, H.H. Ji, Y.M. Yang, J.Z. Hu, Preparation of cerium-containing nanoporous titanium coatings for osseointegration and their promotion of osteogenic differentiation and anti-inflammatory properties, *Mater. Today Chem.* 34 (2023) 101821.
- [8] J.D. Calangi, T. Tago, K. Kimura, Calcined hydrotalcite-coated ZSM-5 with acidic and basic bifunctionalities for 5-hydroxymethylfurfural production from glucose, *Chem. Eng. J.* 519 (2025) 165013.
- [9] M. Motay, D. Martel, B. Vilen, C. Soraru, L. Ploux, M.G. Méndez-Medrano, C. Colbeau-Justin, G. Decher, N. Keller, Virtually transparent TiO₂/polyelectrolyte thin multilayer films as high-efficiency nanoporous photocatalytic coatings for breaking down formic acid and for escherichia coli removal, *ACS Appl. Mater. Interfaces* 12 (50) (2020) 55766–55781.
- [10] P. Srivastava, C. González, J. Palma, E. Garcia-Quismondo, Nanoporous oxide coating on carbon paper electrodes to enable bio-hydrogen production in microbial electrolysis cells, *Catal. Today* 422 (2023) 114246.
- [11] X.S. Shi, L. Wang, N.N. Yan, Z.G. Wang, L.M. Guo, M. Steinhart, Y. Wang, Fast evaporation enabled ultrathin polymer coatings on nanoporous substrates for highly permeable membranes, *Innovation* 2 (1) (2021) 100088.
- [12] Z.Z. Zhang, M.M. Rahman, C. Abetz, A.L. Höhne, E. Sperling, V. Abetz, Chemically tailored multifunctional asymmetric isoporous triblock terpolymer membranes for selective transport, *Adv. Mater.* 32 (8) (2020) e1907014.
- [13] S.L. Lin, Y.Q. Zhang, L. Shao, C.H. Lau, Spray-assisted assembly of thin-film composite membranes in one process, *Adv. Membr.* 4 (2024) 100080.
- [14] U. Hwang, J.D. Nam, D. Lee, Dual porosity-enhanced antireflection coatings with continuous gradient, *ACS Appl. Mater. Interfaces* 15 (34) (2023) 40913–40922.
- [15] M.K. Hadi, L.R. Su, Y. Li, A. Ismail, S. Sangaraju, F. Ran, Tethering hydrophilic macromolecules onto inorganic nanoparticles via RAFT toward biocompatible polyethersulfone membrane, *Adv. Membr.* 3 (2023) 100074.
- [16] J.X. Lu, S.L. Wu, Z.H. Liang, H.C. Yang, W.H. Li, Brushable lubricant-infused porous coating with enhanced stability by one-step phase separation, *ACS Appl. Mater. Interfaces* 13 (19) (2021) 23134–23141.
- [17] C.Y. Yang, G.D. Zhu, Z. Yi, Y. Zhou, C.J. Gao, Critical contributions of additives on the fabrication of asymmetric isoporous membranes from block copolymers: a review, *Chem. Eng. J.* 424 (2021) 128912.
- [18] G. Cossio, E.T. Yu, Zeta potential dependent self-assembly for very large area nanosphere lithography, *Nano Lett.* 20 (7) (2020) 5090–5096.
- [19] K. Omotosho, J. Tran, E.V. Shevchenko, D. Berman, Polymer infiltration synthesis of inorganic nanoporous coatings: does polymer template affect their properties? *Surf. Coat. Technol.* 452 (2023) 129107.
- [20] P. Mokarian-Tabari, R. Sentharamaikkannan, C. Glynn, T.W. Collins, C. Cummins, D. Nugent, C. O'Dwyer, M.A. Morris, Large block copolymer self-assembly for fabrication of subwavelength nanostructures for applications in optics, *Nano Lett.* 17 (5) (2017) 2973–2978.
- [21] J.M. Zhou, C.X. Zhang, Y. Wang, Nanoporous block copolymer membranes immobilized with gold nanoparticles for continuous flow catalysis, *Polym. Chem.* 10 (13) (2019) 1642–1649.
- [22] W.L. Jorgensen, J. Tirado-Rives, Potential energy functions for atomic-level simulations of water and organic and biomolecular systems, *Proc. Natl. Acad. Sci. USA* 102 (19) (2005) 6665–6670.
- [23] S.J. Marrink, H.J. Risselada, S. Yefimov, D.P. Tieleman, A.H. de Vries, The MARTINI force field: coarse grained model for biomolecular simulations, *J. Phys. Chem. B* 111 (27) (2007) 7812–7824.
- [24] M.J. Abraham, T. Murtola, R. Schulz, S. Páll, J.C. Smith, B. Hess, E. Lindahl, GROMACS: high performance molecular simulations through multi-level parallelism from laptops to supercomputers, *SoftwareX* 1–2 (2015) 19–25.

- [25] G. Bussi, D. Donadio, M. Parrinello, Canonical sampling through velocity rescaling, *J. Chem. Phys.* 126 (1) (2007) 014101.
- [26] M. Parrinello, A. Rahman, Polymorphic transitions in single crystals: a new molecular dynamics method, *J. Appl. Phys.* 52 (12) (1981) 7182–7190.
- [27] L.M. Guo, L. Wang, Y. Wang, Stretched homoporous composite membranes with elliptic nanopores for external-energy-free ultrafiltration, *Chem. Commun.* 52 (42) (2016) 6899–6902.
- [28] J.M. Zhou, Y. Wang, Selective swelling of block copolymers: an upscalable greener process to ultrafiltration membranes? *Macromolecules* 53 (1) (2020) 5–17.
- [29] Y. Wang, Nondestructive creation of ordered nanopores by selective swelling of block copolymers: toward homoporous membranes, *Acc. Chem. Res.* 49 (7) (2016) 1401–1408.
- [30] M.J. Wei, W. Sun, X.S. Shi, Z.G. Wang, Y. Wang, Homoporous membranes with tailored pores by soaking block copolymer/homopolymer blends in selective solvents: dissolution versus swelling, *Macromolecules* 49 (1) (2016) 215–223.
- [31] L.M. Guo, Y. Wang, Monolithic membranes with designable pore geometries and sizes via retarded evaporation of block copolymer supramolecules, *Macromolecules* 48 (23) (2015) 8471–8479.
- [32] Y.J. Wang, C.X. Zhang, J.M. Zhou, Y. Wang, Room-temperature swelling of block copolymers for nanoporous membranes with well-defined porosities, *J. Membr. Sci.* 608 (2020) 118186.
- [33] K. Tashiro, A. Yoshioka, Molecular mechanism of solvent-induced crystallization of syndiotactic polystyrene glass. 2. Detection of enhanced motion of the amorphous chains in the induction period of crystallization, *Macromolecules* 35 (2) (2002) 410–414.
- [34] E. Wang, J.H. Zhu, D. Zhao, S.Y. Xie, F.S. Bates, T.P. Lodge, Effect of solvent selectivity on chain exchange kinetics in block copolymer micelles, *Macromolecules* 53 (1) (2020) 417–426.
- [35] H.Y. Hsueh, C.T. Yao, R.M. Ho, Well-ordered nanohybrids and nanoporous materials from gyroid block copolymer templates, *Chem. Soc. Rev.* 44 (7) (2015) 1974–2018.
- [36] D. Tan, Q. Li, B.S. Yang, X. Wang, S.Q. Hu, Z.Z. Wang, Y.F. Lei, L.J. Xue, Continuous gradient nanoporous film enabled by delayed directional diffusion of solvent and selective swelling, *Langmuir* 35 (17) (2019) 5864–5870.
- [37] J. Yang, L. Tong, Y. Yang, X.Q. Chen, J. Huang, R.Z. Chen, Y. Wang, Selective-swelling-induced porous block copolymers and their robust TiO₂ replicas via atomic layer deposition for antireflective applications, *J. Mater. Chem. C* 1 (33) (2013) 5133–5141.