We report the formation of three-dimensionally interconnected nanoporosities with \emph{in situ} PEGylated pore walls simply by swelling the block copolymers of polysulfone and poly(ethylene glycol) in paired solvents. The produced nanoporous polymers are expected to find important applications in membranes, batteries, chromatography, and haemodialysis.

Nanoporous polymers with interconnected porosities and controllable surface functionalities, either in the form of thin films or monoliths, are finding extensive applications owing to their easy accessibility and size selectivity in diverse fields ranging from separation and catalysis to optoelectronics and biomedicine. Among the various strategies for producing nanoporous polymers, microphase separation of block copolymers (BCPs) is a distinguished method because it leads to ordered nanopores with a rich variety of pore geometries and tunable uniform pore sizes. Typically, nanoporosities are generated in microphase-separated BCPs by selectively degrading the minority phases composed of labile blocks. The selective degradation method is advantageous in reliably producing the exact geometry of the minority phases, although it might be tedious and frequently requires harsh etching conditions. Alternatively, we developed a selective swelling-induced pore generation strategy to produce uniform nanoporous polymers simply by soaking BCPs in selective solvents.\textsuperscript{3,6}

Considering that (1) polysulfone (PSF), as one of the most extensively used engineering plastics with a $T_g$ of nearly 190 °C, exhibits excellent mechanical, thermal, and chemical stabilities\textsuperscript{7} (2) poly(ethylene glycol) (PEG) is known for its strong hydration ability and biocompatibility,\textsuperscript{8} which are highly desired in biotechnology and liquid separation applications, and (3) PSF and PEG can be easily bonded to form BCPs with adjustable block ratios by various synthesis techniques,\textsuperscript{9,10} we propose to use block copolymers of PSF and PEG (PSF-b-PEG) with PSF as the majority block that would serve as the precursor for nanoporous polymers by a swelling-based strategy. PSF-based block copolymers have been used to prepare porous membranes by different methods including nonsolvent-induced phase separation (NIPS) and selective degradation;\textsuperscript{11–13} however, obtaining well-defined nanoporosities remains a challenging task. Our previous strategy of directly soaking PSF-b-PEG in a PEG-selective solvent such as water or ethanol produced very limited porosities because of the constraint of the PSF matrix on the PEG microdomains. Here, we discover that by simply soaking PSF-b-PEG in solvent pairs containing both PS-selective and PEG-selective solvents for hours followed by air-drying well-developed, three-dimensionally (3D) interconnected nanoporosities with pore sizes tunable in the range of $\sim$10–100 nm could be obtained. Interestingly, the produced porous PSF materials were simultaneously \emph{in situ} PEGylated during the pore-forming process as the PEG blocks were enriched on the pore walls, thus maintaining excellent mechanical properties.

According to the mechanism of selective swelling-induced pore generation, the minority blocks in BCPs should have cylindrical morphology to form 3D interconnected porosities.\textsuperscript{6} Therefore, PSF-b-PEG with a total molecular weight ($M_w$) of 79.1 kDa and a PEG weight ratio of 21% was used in this study. We first discussed the nanoporous PSF thin films, which were prepared by spincoating the PSF-b-PEG solutions on silicon substrates. The dense and nonporous as-coated film (Fig. S1, ESI) was soaked in an ethanol/acetone solvent pair with 20% (v/v) acetone ($\phi_{\text{acetone}}$) at 70 °C for 5 h, and subsequently removed from the solvent pair and dried at room temperature. After treatment in the solvent pair and subsequent drying, the film showed a highly porous morphology with interconnected nanopores uniformly present on the surface (Fig. 1a). The pores can be roughly divided into two types: circular pores $\sim$30–50 nm in diameter and elongated channel-like pores with a width of $\sim$50 nm and a length of $\sim$100–300 nm, which correspond to the perpendicular and in-plane orientations of the PEG microdomains before soaking, respectively. The cross-sectional
SEM micrograph shown in Fig. 1b reveals that the pores are distributed throughout the entire thickness of the film and are 3D interconnected. The interconnected nanoporosity was further confirmed by TEM examination (Fig. 1c). The pore interconnectivity allows easy accessibility of the pore system to foreign substances, which is essential for many applications such as separation and catalysis.

To understand the kinetics of the pore-forming process, we tracked the change in film thickness with soaking durations. As shown in Fig. 2, the film thickness rapidly increased to 362 nm from 253 nm for the as-coated film after a very short soaking time of 10 s. The thickness increased but at a much lower rate with prolonged soaking, and levelled off at a soaking duration of 1 h at which the thickness was 415 nm. Further soaking did not noticeably increase the film thickness. The increase in thickness is a consequence of pore formation in the film without the consumption of any component in the BCP. In addition, the porosity of the film changed with soaking duration. The porosities of the soaked films can be estimated from their refractive indices according to the following equation:\n\begin{equation}
n_1^2 = n_0^2(1 - \varphi_{\text{pore}}) + n_{\text{air}}^2 \varphi_{\text{pore}}
\end{equation}
where \(n_1\), \(n_0\), and \(n_{\text{air}}\) represent the refractive indices of the soaked film, the as-coated dense film, and air, respectively. \(n_{\text{air}}\) is known to be 1, and \(n_0\) (measured as 1.61) and \(n_1\) can be obtained by ellipsometry. Furthermore, as shown in Fig. 2, a short soaking time of 10 s resulted in a remarkably high porosity of 37.5%, which further increased with prolonged soaking duration, reaching a saturated value of 53.6% after 5 h of soaking.

SEM was used to monitor the morphology evolution of the films with increasing soaking time (insets in Fig. 2 and Fig. S2, ESI\(^\ddagger\)). A short exposure to the solvent pair (10 s) produced nanopores in the films. Extending the soaking duration up to 20 min continuously increased both pore size and pore interconnectivity. Further prolongation of the soaking duration to 1 h or 5 h did not noticeably enlarge the pores. The trend of morphological evolution is the same as that of the change in film thicknesses and porosities with soaking durations. Clearly, this is a very fast pore-forming process as about two-thirds of the total porosity could be achieved within the initial 10 s. This is ascribed to (1) the very strong affinity between ethanol and the PEG blocks, (2) the enhanced segmental mobility of the PSF matrix in the solvent pair at elevated temperature, and (3) a strong concentration gradient of ethanol in the PEG microdomains compared to the bulk reservoir of ethanol in the initial stage of soaking. The concentration gradient soon diminishes, and therefore, the porosity increases slightly in the later stage.

Pore formation in the PSF-b-PEG films eventuates from the difference in the swelling of the PSF and PEG blocks in the solvent pair. PSF is a highly hydrophobic polymer, whereas PEG is a watersoluble, polar polymer. When they are covalently bonded as block copolymers, the strong repulsion between them leads to microphase separation, as is expected due to the difference in their solubility parameters (22.9 MPa\(^{1/2}\) for PSF vs. 27.4 MPa\(^{1/2}\) for PEG; Table S1, ESI\(^\ddagger\)).\(^{15}\) Swelling tests indicate that at a temperature of 70 °C ethanol completely dissolves PEG homopolymers while it only negligibly swells PSF homopolymers (swelling ratio: ~0.2%), and acetone moderately swells PSF homopolymers with a swelling ratio of ~34%. The observations reveal that ethanol has a very stronger affinity to PEG but almost no swelling effect on PSF, while acetone has a moderate swelling effect on PSF. The PEG block accounts for 21 wt% of the BCP used in our work; hence, the morphology of the BCP can be considered as cylindrical PEG microdomains embedded in the PSF matrix (Scheme 1a), according to the phase diagram of the BCPs.\(^3\) As we did not perform any

![Scheme 1](image_url)

**Scheme 1.** Schematic illustration for the preparation of nanoporous PSF-b-PEG by swelling in solvent pairs. (a) The PSF-b-PEG block copolymer has an asymmetric structure with PSF as the majority block. (b) The PEG blocks form cylinders embedded in the PSF matrix. (c) In the solvent pair, the PEG cylinders are strongly swollen by ethanol and the PSF matrix is moderately swollen (plasticized) by acetone. (d) Upon drying, the PEG chains collapse and produce nanopores with PEG lined along the pore walls.
alignment process, the PEG cylinders were randomly distributed in the PSF matrix in both perpendicular and in-plane orientations (Scheme 1b and Fig. S3, ESI†). In the solvent pair containing both PSF-selective and PEG-selective solvents, the swelling degree of both the PSF and PEG blocks can be separately tuned by changing the solvent type as well as the relative ratios between the two constituent solvents. Upon soaking in the solvent pair, ethanol is preferentially enriched in the PEG cylinders as it has a much stronger affinity to PEG than to PSF, leading to strong swelling of the PEG cylinders. In addition, the segmental mobility of the PSF chains is enhanced because of the plasticization effect of acetone and the elevated temperature (70 °C). Therefore, owing to the expanding PEG cylinders, the PSF matrix is subjected to local deformation mainly along the Z direction as the film is laterally confined on the substrate (Scheme 1c). After air-drying, with the evaporation of both ethanol and acetone, the deformed PSF chains are frozen and cannot recover to their original positions because of their reduced mobility and the lack of a driving force to deform back. Simultaneously, the swollen PEG chains collapse, leaving voids along the original positions of PEG cylinders, that is, forming pores with the collapsed PEG chains lined along the pore wall as well as the film surface (Scheme 1d). Longer soaking allows the PEG cylinders to uptake more ethanol until saturation, leading to greater swelling of the PEG chains, and consequently stronger deformation of the PSF matrix. As a result, larger pores and greater porosity are obtained at longer soaking durations.

The ratio of the two components in the solvent pair significantly influences the swelling process, and consequently, the morphology of the films. As shown in Fig. S4 and S5 (ESI†), a $\phi_{\text{acetone}}$ as low as 5% is able to increase the thickness by 54% after swelling for 5 h, indicating the formation of pores. However, the pores are sparsely formed and mostly isolated from each other. Increasing the $\phi_{\text{acetone}}$ to 10% or 20% accelerates the swelling process and further increases the film thickness, and the thus-treated membranes exhibit an interconnected porous morphology. When $\phi_{\text{acetone}} = 30\%$, there is a sharp increase in thickness within 10 s followed by a fast and nearly linear decrease for a longer soaking duration; this is because the dissolution of the BCP by micellization started from the film surface, leading to progressive depletion of the BCP films. Micellar structures can be clearly observed on the film surface, and micellization becomes more pronounced at $\phi_{\text{acetone}} = 50\%$ (Fig. S5, ESI†). Higher $\phi_{\text{acetone}}$ in the solvent pair leads to higher segmental mobility of the PSF chains, thus allowing greater swelling of the PEG cylinders. Consequently, the pores are enlarged, resulting in larger porosities and thicker films after drying. We inferred that $\phi_{\text{acetone}}$ in the range of ~10–20% can sufficiently produce pores in the BCP films at a temperature of 70 °C while maintaining their structural integrity.

The swelling-based pore-forming mechanism was confirmed by the preferential segregation of PEG blocks along the pore walls, as revealed by TEM characterization. As shown in Fig. 1c, the pores exhibited a darker contour because of the selective adsorption of OsO4 in this region, evidencing the enrichment of PEG blocks along the pore walls. XPS was also employed to trace the migration of PEG blocks to the film surface after treatment in the solvent pair. Fig. 3a shows that the S 2p peaks diminish with soaking durations, indicating a progressive reduction in the S content on the film surface. This confirms the migration of PEG chains onto the film surface during the soaking process. The enrichment of PEG blocks on the film surface is actually an in situ PEGylation process, which is much more convenient and efficient than the typical PEGylation methods involving post-modification of the existing pores.26 The in situ PEGylation enhances the hydrophilicity of the nanoporous PSF films. As shown in Fig. 3b, the water contact angle (WCA) of the as-coated film is around 86°, which indicates that its surface is preferentially enriched with PSF blocks. Strikingly, after briefly soaking in the solvent pair for 10 s, the WCA significantly reduced to 55°, and further slowly decreased to 49° after 5 h of soaking. It is noteworthy that the change in WCAs with soaking durations follows an inverse trend to the change in film thicknesses and porosities (Fig. 2).

Pairing both the PSF-selective and PEG-selective solvents is essential to obtain well-developed nanoporosity in the PSF-b-PEG films. Soaking in a PSF-selective solvent alone, e.g. acetone, leads to the dissolution of the BCP by micellization (Fig. S6, ESI†), whereas soaking in a PEG-selective solvent alone, e.g. ethanol, hexanol, or acetic acid, produces few pores in the PSF-b-PEG films, as evidenced by the small increase (~10–20%) in the film thickness after soaking at 70 °C for 5 h compared to soaking in the ethanol/acetone pair with $\phi_{\text{acetone}} = 20\%$ (Fig. S7, ESI†). Therefore, appropriate selection of the solvent pair is critical to enable the selective-swelling-induced pore generation process. The basic principles for formulating the solvent pair are as follows: (1) the solvent pair includes a PEG-selective solvent and a PSF-selective solvent, which should be compatible with each other; (2) the PEG-selective solvent should have a very strong affinity to PEG and negligible or weak affinity to PSF; and (3) the PSF-selective solvent should have a moderate affinity to PSF. Following these principles, we identified a number of solvent pairs capable of producing pores in the PSF-b-PEG films such as ethanol/acetone and hexanol/acetone. The degree of pore formation or porosities can be tuned by adjusting the relative ratios and swelling temperatures/durations of the two components in the solvent pair according to their different selectivities.

Pore formation via swelling in solvent pairs can be directly used to produce nanoporous PSF-b-PEG bulk materials including thick films and monoliths. Flat sheets of PSF-b-PEG with a thickness of ~60 μm were soaked in a hexanol/acetone solvent pair with $\phi_{\text{acetone}} = 20\%$ at 60 °C for 6 h. Fig. 4a shows the picture of a soaked
film with dimensions of ~10 cm × 10 cm. The initial clear and transparent film became opaque with a milky white colour, indicating the formation of pores in the film. The film is wrinkled due to the volume expansion of the bulk film in the pore-forming process; however, the structural integrity of the film is well maintained. Microscopic examinations show that interconnected nanopores are interwoven throughout the entire soaked film (Fig. 4b). It should be noted that pores appear on both sides of the film (Fig. S8, ESI†), and nonporous skin layers, which are frequently formed in many pore-forming processes such as foaming, are absent on both the sides. The nitrogen adsorption test reveals that the soaked PSF-b-PEG thick film has a moderate surface area of ~38 m² g⁻¹ and its pore size is centered around 26 nm (Fig. S9, ESI†), which is consistent with the SEM examination. Similarly, pores can be produced in a few-millimetre-thick monoliths by swelling in the hexanol/acetone solvent pair with 198 acetone = 20% at 60 °C for 12 h, which yields a nanoporous morphology homogeneously distributed throughout the entire monolith (Fig. 4c and Fig. S10, ESI†).

Although the nanoporosity induced by swelling is kinetically trapped, the nanoporous PSF materials are expected to maintain their structural integrity because the Tg (~190 °C) of PSF is much higher than room temperature. The ultimate stress and maximum strain of the nanoporous PSF-b-PEG film were determined to be 3.3 MPa and 16.2%, respectively. As shown in Fig. S11 (ESI†), the mechanical properties of the nanoporous PSF films are much better than the PS-based BCP membranes, which exhibit a stress of ~0.3 MPa and a strain at break of 4.2%. The high mechanical stability of the nanoporous PSF-b-PEG films is due to the coexistence of the rigid PSF phase and the flexible PEG phase, which allows the nanoporous films to be used as filtration membranes in the self-supporting form. The films exhibited a water permeability of ~30 L m⁻² h⁻¹ bar⁻¹ and a rejection rate of ~20% for the BSA protein with a diameter of ~6.7 nm and a rejection rate of ~90% for monodispersed silica nanoparticles with a diameter of 22 nm. The filtration tests indicate that the produced nanoporous films allow water penetration, confirming that their nanopores are interconnected and accessible by fluids on the one hand, and the film surface and pore walls are water-wettable on the other hand as hydrophobic pores do not allow water to permeate under low pressures. Moreover, a retention rate of ~90% for 22 nm silica nanoparticles implies the strong selectivity of the pores. It should be noted that the current permeability of the nanoporous films is modest because of their relatively large thickness and symmetric structures; however, these are expected to improve through optimization of the membrane structures, such as by compositing thin layers of the nanoporous PSF-b-PEG on macroporous substrates.

In conclusion, nanoporous polysulfones, either in the form of thin films or bulk materials, are prepared simply by soaking PSF-b-PEG in solvent pairs containing a PSF-selective solvent and a PEG-selective solvent. Accessible, interconnected porosities with pore sizes of several tens of nanometers were formed in the copolymer because of the different degrees of swelling of the two blocks in the solvent pair. The PEG blocks were progressively enriched on the pore walls, leading to in situ PEGylation of the surfaces of the nanoporous PSF. The interconnected nanoporosity and the strong surface wettability of the produced nanoporous PSF were confirmed via filtration tests. Thus the produced porous PSF materials with 3D interconnected nanoporosity and hydrophilic pore walls are expected to find important applications as separation membranes, battery separators, haemodialyzers, bioengineering scaffolds, etc. Moreover, the pore-forming strategy by swelling in solvent pairs is expected to create nanoporosities in other copolymers containing different polymer chains with sufficiently large differences in their swelling behaviour.

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Notes and references

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